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## PULSED LASER DEPOSITION OF ELECTRONIC CERAMICS AND ANALYSIS OF THE ABLATION PLUME

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A thesis submitted to the University of London in partial fulfilment for the degree of Doctor of Philosophy

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to Liz , Joe and Charley

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## Abstract

Thin film growth by pulsed laser deposition, (PLD) is a technique, which has been investigated for over thirty years but has come to prominence more recently in the growth of complex multicomponent materials. These materials include several technologically important perovskite structured compounds that display high temperature superconductivity or ferroelectricity and are difficult to process into high quality thin films.

Despite the enormous range of thin films and multilayers that have been deposited by PLD, many of the physical processes involved during the transfer of material from target to substrate are not well understood.

The aim of this project is twofold:

1. To study the energy and mass distribution of ions ablated from the target surface by the laser pulse under similar conditions to those found in PLD with a view to using this technique to better understand PLD and as an *in situ* diagnostic method during PLD.

2. To briefly investigate the ideal growth conditions of lead zirconate titanate, PZT. This allows the data from the plume to be examined in the context of thin film deposition rather than simply in the context of laser ablation or desorption.

The ion mass and energy spectra in the plume are obtained by placing an electrostatic cylindrical mirror analyser in tandem with a quadrupole mass spectrometer where the substrate would normally be in PLD. The former filters out all but a narrow "kinetic energy window" in the ions while the latter passes only a narrow range of masses. The method can give inconsistent and spurious results which are difficult to identify; the conditions under which these results occur are laid out and a procedure to avoid them is shown. The laser source used is mainly a Q-switched, frequency doubled Nd:YAG operating at a wavelength of 532nm although a frequency quadrupler (266nm) is used for some of the later deposition work.

The thesis concentrates on electroceramics as these materials are both interesting from a technical and scientific point of view and also because many of the materials most successfully deposited by PLD fall into this general category. Other materials such as carbon and iron are investigated mainly to contrast their behaviour with that of the principle group, that of electroceramics.

The ceramic compounds studied include PZT (lead zirconate titanate), cerium oxide and the high temperature superconductors  $Bi_2Sr_2Ca_2Cu_3O_{10}$  which has a critical temperature of 110K, and also  $YBa_2Cu_3O_{7-\delta}$  which has a critical temperature of 90K is briefly mentioned.

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## **1.0 INTRODUCTION**

The extraordinary developments in electronics manufacturing over the last twenty years have been brought about by the use of integrated circuitry on the surface of single crystal silicon wafers. This development was made possible by successfully bringing together several different technologies including crystal growth, photoresist processing, ion implantation and thin film deposition. Unfortunately however many potentially useful materials are difficult to produce and process in thin film form and have been left behind by the advances in silicon based manufacturing processes.

One technique which opens up the range of available materials is pulsed laser deposition or PLD. This is a thin film vapour deposition technique which has rapidly grown in importance in recent years partly due to the facility it allows in growing thin films of such materials as the perovskite structured ceramic oxides. This group encompasses high temperature superconductors, (e.g.  $YBa_2Cu_3O_{7-\delta}$  and  $Bi_2Sr_2Ca_2Cu_3O_{10}$ ), ferroelectric ceramics (e.g.  $PbZr_xTi_{(1-x)}O_3$ ) and some giant magnetoresistive materials (e.g LaCaMnO<sub>3</sub>). As such PLD is now an important technique for the growth of a variety of thin films of electronic materials (Beech and Boyd - 1992).

A major attraction of PLD is the ability to fabricate nanometer scale thin films in multilayer structures and in this context strict control of the growth parameters and most particularly of the plume constituents is vital.

Many characterisation techniques can be used to determine the nature of the ablation plume including optical spectroscopies, (Auciello *et al* - 1988, Saenger -1989, Geohegan and Mashburn - 1989, W. Marine *et al* - 1992 and Dreyfus - 1991), mass spectrometry, (Bykovskii *et al* - 1987, Wiedeman and Helvajian - 1991, Chrisey *et al* - 1991, Nishikawa *et al* - 1992, ), photographic methods, (Dyer et *al* - 1990), and electron probes, (Gutfeld and Dreyfus - 1989). Significant quantitative information may also be obtained from angular-resolved time-of-flight studies when combined with mass spectrometry (Kools, *et al* - 1992). Generally, these techniques give complementary information and thus two or more methods are often utilised in tandem to best understand the underlying kinetics.

The laser induced ablation plume contains a variety of species including atoms, ions, clusters etc., and its complexity causes problems in the simultaneous characterisation of both the mass composition of the ejecta and the kinetic energy (K.E.) distributions of the varied particles within the plume. The pronounced forward directionality of the expanding plasma makes this a still more challenging problem.

## 1.1 A Brief History Of Pulsed Laser Deposition

The idea of using a laser as a heating source to cause the vaporisation of a solid in a classical evaporation system is a fairly natural one. Not surprisingly the first attempts at laser evaporation quickly followed the development of high power lasers, (Smith and Turner - 1965), using a ruby laser.

Laser ablation first became a viable technology however with the development of the Q-switched laser which greatly improved the peak power levels to a point where even the most refractory materials could be deposited. However, the development of PLD continued slowly for many years as PLD appeared unable to offer outstanding advantages over existing and mature thin film deposition techniques, such as evaporation, sputtering, CVD etc.

This situation changed with the discovery of HTSCs towards the end of the 1980s, (Bednorz and Muller - 1986) as the ensuing interest in superconducting thin films gave the necessary impetus to the development of PLD primarily through the work of Venkatesan and co-workers at Bellcore (Dijkkamp *et al* - 1987). The advantages of PLD in the growth of thin film ceramics will be described in detail later but it was the early success in growing thin films of YBa<sub>2</sub>Cu<sub>3</sub> O<sub>7- $\delta$ </sub> which lead directly to interest in other structurally related materials, such as the perovskite ferroelectrics.

Nowadays PLD is a deposition technique of major importance being practised by groups all over the world for the deposition of an enormous variety of materials; in the appendix to a recent book (Chrisey and Hubler - 1994) on pulsed laser deposition, K.L.Saenger lists 181 materials and mixtures of materials that have been deposited by PLD.

Before PLD had come to prominence interest in ferroelectric materials had risen during the 1970s, based on their piezoelectric, pyroelectric, electrooptic behaviours and high dielectric constants. They were seen as possible materials for use in sensors, displays, actuators and memories but their development was partly held back by the difficulties of fabricating high quality thin films economically.

## 1.2 Pulsed Laser Deposition

The remainder of this introduction considers

1. PLD as a deposition technique outlining the main elements of the equipment needed for production of thin films.

2. PLD in relation to other deposition techniques.

3. The advantages and disadvantages of PLD in the context of other deposition processes.

4. Adaptations designed to overcome some of the difficulties of thin film fabrication with PLD.



Figure 1.0 Basic PLD system

Figure **1.0** is a diagram of the principle elements of the vacuum chamber system for making thin films by PLD.

A solid target material is placed in a vacuum chamber facing a suitable substrate which is normally held in a heated holder. The chamber is typically evacuated to below 10<sup>-6</sup> mbar and then may be back filled with a specific gas to a pressure of up to 0.5 mbar.

An energetic pulse of light from a laser is directed onto the target through a window in the vacuum chamber after passing through a converging lens which increases the local laser fluence on the target surface sufficiently to cause vaporisation.

The source of ablation can, in principle, be any pulsed laser capable of heating the target surface to a point where the vapour pressure is sufficient for deposition. In practice however only a few types of laser are capable of providing the high powers and repetition rates at wavelengths which are strongly absorbed by the target. The most commonly used lasers are the excimer, Nd:YAG, and occasionally pulsed carbon dioxide.

Laser-type	Laser medium	Wavelength {nm }	(energy), (eV)	pulse width(ns)
Excimer	XeCl	308	4	20 - 25
	KrF	248	5	20 - 25
	ArF	193	6.4	20 -25
Nd:YAG	Nd3+	1064	1.2	4, (Q-
		(fundamental)		switched)
	Nd <sup>3+</sup>	532 (λ/2)	2.3	4*
	Nd3+	355 (λ/3)	3.5	4*
	Nd <sup>3+</sup>	266 (λ/4)	4.7	4*
CO <sub>2</sub>	CO <sub>2</sub>	10600	0.12	150-7000

\*The pulse widths of the higher harmonics are slightly less than the fundamental.

Table 1.1 - The main lasers used for pulsed laser deposition

Typical parameters for the lasers commonly used in PLD are shown in table **1.1**.

Energy levels depend on laser size but a typical range is 0.1 to 3J per pulse with a repetition rate of 1 to 10 Hz.,  $CO_2$  lasers generally being used at higher energies to compensate for the greater pulse lengths.

# **1.2.1** Pulsed Laser Deposition in Relation to Other Deposition Processes

Pulsed laser deposition, (PLD), is a form of physical vapour deposition with many superficial similarities to other evaporative techniques such as electron beam evaporation. There are a number of features characteristic of PLD that, while not individually unique, together constitute a uniquely powerful and versatile method of thin film formation. The specific features of PLD that shall be contrasted with rival deposition methods are the following:

- 1. The energetic nature of the plume.
- 2. The directional nature of the plume.
- 3. The growth of films at high background gas pressures.
- 4. High deposition rates and high instantaneous deposition rates.
- 5. Congruent evaporation of multicomponent materials.

## **1.2.1.1** The energetic component of the plume.

PLD is distinguished from other evaporation techniques by virtue of the extreme instantaneous power levels that can be coupled to the target material. This is due to the combination of quite modest energy levels combined with the extremely short pulse duration achievable with Q-switched Nd:YAG and excimer lasers.

To illustrate this fact consider these typical PLD conditions:

Laser Pulse: 500mJ, 4nsec. FWHM

Spot size on target: 2mm diameter

Instantaneous power on target surface: 4×10<sup>9</sup> W/cm<sup>2</sup>

Time averaged power at the target surface, at 10Hz.: 160W/cm<sup>2</sup>

In consequence the surface of the target is vaporised in a time scale comparable with the duration of the pulse and the vapour is ejected into a volume above the target where it may interact with the extreme, high frequency electric and magnetic fields of the laser irradiation.

Typical target particle energies associated with PLD are 0.1eV to 1000eV, an energy normally associated with sputtering systems, compared to 0.1 eV for thermal evaporation. More details of the energy ranges of particles in PLD will be given in the chapters dealing specifically with energy analysis of the ablation plume.

Figure **1.1** illustrates a comparison of the energies of deposited particles involved in various thin film deposition techniques. The figure quoted for solgel indicates that essentially there is no energy during the deposition other than the ambient thermal energy.



**Figure 1.1 -** Comparison of deposition particle energies in competing thin film deposition techniques

- PLD Pulsed Laser Deposition
- MBE Molecular Beam Epitaxy
- IVD Ionised Vapour Deposition
- TE Thermal Evaporation (including e-beam evaporation )
- MOCVD Metal-Organic Chemical Vapour Deposition

IVD is a technique in which the vapour originating from thermal evaporation is ionised by electron bombardment and accelerated towards the substrate by a bias potential. However, due to the relative inefficiency of the ionisation system, the result is a two component flux, one ionised and arriving first with higher kinetic energy followed by a slow stream of neutral particles.

## 1.2.1.2 The Role of Energetic Particles in Thin Film Deposition

Energetic ions are known to have profound effects on thin film quality and can even influence the degree of crystallographic orientation, composition, density and grain size of polycrystalline films (Harper *et al* - 1984).

The role of highly energetic deposition particles is a complex one. High particle energies, like high substrate temperatures, increase the surface mobility of the atoms in the growing film and can assist in crystallisation at lower substrate temperatures as well as increasing film density, adhesion and stress, (Hirvonen - 1991; Smidt - 1990).

Note that there are three basic modes of film growth depending on the interaction energies associated with the cohesion of the film atoms and the adhesion between film and substrate atoms.

1. Layer growth or Frank - v.d. Merwe mode growth. In this mode the adhesive forces are higher than the cohesive forces and a film layer tends to cover the substrate before the next layers are formed.

2. Island growth or Volmer- Weber mode growth. This is the reverse of layer growth and cohesion dominates adhesion leading to small islands of film growth on the substrate which gradually coalesce with further deposition to form a complete film.

3. Stranski-Krastonov mode. This mode of growth can occur when the lattice constants of the film and substrates are sufficiently dissimilar to cause distortions in the growing film. Hence the deposition may proceed with several layers up to a certain thickness after which islands will grow on top of them. The real situation is in fact more complicated than this and the film growth mode can be predicted from calculation of the free energies associated with different cluster sizes and adatom mobilities etc., (Reichelt - 1988) One calculation (Gilmore and Sprague - 1992) based on the effect of

depositing three monolayers of silver on silver at 300K showed that between 0.1 and 1eV the nature of thin film growth changes from island to layer by layer growth. Increasing the energy of the ion flux in this analysis, which ignores long term diffusion effects, is equivalent in terms of film growth to increasing the substrate temperature. However, although there was negligible mixing of substrate and film atoms for particles up to 10eV; between 20 and 40eV mixing did occur with increasing effect at higher energies.

However, particles with excessive energies will displace atoms in the substrate and lead to the formation of a diffuse film/substrate interface with consequent negative implications for device fabrication, particularly for complex multilayers as in, for example, the fabrication of X-ray mirrors.

As indication of this effect; in sputtering technology there is generally considered to be a threshold below which no sputtering occurs, usually between 20 and 40eV, depending on the atomic mass of the sputtered material. At higher energies it is estimated that argon ions penetrate a silicon substrate at depths of 28, 52, and 83Å for energies of 200, 500 and 1000eV (Reese *et al* - 1991).

The sputtering coefficient reaches its maximum when the atomic masses of the particle flux and the sputtered material are most similar (Metev - 1986) indicating that resputtering of the growing film by the plume in PLD would be strongly favoured.

The negative consequences of film sputtering (i.e loss of the growing film) and film/ substrate mixing and the positive consequences of film atom mobility (i.e allowing crystal growth at lower substrate temperatures), suggest the existence of an ideal particle energy window for deposition. The deposition particle energy of choice depends on the nature of the growing film and the substrate as well as the practical difficulties associated with heating the substrate to within 40% of the film melting point ( an ideal value for film growth).

However as a rough guide the value for the ideal deposition energy would be somewhere in the region of 20-40eV.

It should also be noted that resputtering of the growing film can cause contamination of the target which is a particular problem when multiple targets are used in the growth of multilayers.

#### 1.2.1.3 The Directional Nature of the Plume.

The plume emitted from the target during PLD is highly directional (see section **1.3.5**). Estimates of the angular distribution in high vacuum vary, but a  $\cos^n \theta$  distribution is commonly quoted, where **n** may be 11 for the non-thermal component of the plume which coexists with a small thermal component for which **n** =1 (Venkatesan *et al* - 1988).

There is no clear consensus on the exact angular distribution of the plume with results depending on the experimental conditions, particularly spot size. Some authors have found a  $\cos\theta$  distribution (Balooch *et al* - 1989) with other authors finding **n**=46 in vacuum and **n**=336 in 0.133mbar O<sub>2</sub> (Chrisey *et al* - 1990) and the actual difference is quite small in effect.

The quoted angular distributions would be applicable for deposition depth profiles if the substrate were hemispherical and centred on the point where the laser strikes the target (neglecting sticking coefficients and resputtering) as shown in Figure **1.2**.



**Figure 1.2 -** The relationship between a cosθ distribution and a flat substrate

In reality, the substrate is more commonly flat and hence a  $\cos^n\theta$  angular distribution would translate to a  $\cos^{n+3}\theta$  deposition profile.

Although important from a theoretical point of view for modelling processes occurring in the plume, in practical deposition terms the exact theoretical value for n is relatively unimportant as it will be masked by a number of factors. For example, pitting of the target and movement of the substrate during scanning both complicate or randomise the variation in film thickness as a function of  $\theta$ . The value of **n** is not strongly dependant on the laser fluence or repetition rate but decreases gradually with increasing background gas pressure (Ohkoshi - 1994, Kools - 1993),.

The forward directed nature of the plume does however limit the substrate area that can be covered by PLD and various solutions to this problem are mentioned in section **1.2.2.2**.

### **1.2.1.4 Film Growth of Films at High Background Gas Pressures.**

The synergy of reactive gases and high energy ions is a very powerful combination that sets PLD and sputtering apart from nearly all other deposition regimes. The reason for this is that the ions present in PLD are produced as part of the ablation process whereas other techniques such as IVD rely on the post ionisation by electron bombardment. Generally such methods involve components such as hot filaments which are sensitive to aggressive gases such as oxygen commonly used in PLD and more particularly O<sup>+</sup> ions that result from the ionisation process. In contrast the high energy ionised material present during PLD are well contained within the ablation plume.

The use of oxygen is vital in the deposition of many of the materials that have fuelled recent development of the PLD process; particularly the complex metallic oxides that constitute the superconducting ceramics and perovskite ferroelectrics.

Other background gases such as nitrogen are occasionally used in the growth of nitrides such as TiN, (for example Craciun and Craciun - 1992) and water vapour in the growth of hydroxylapatite, (Cotell - 1993). N<sub>2</sub>O and NO<sub>2</sub> can also be used as an alternative oxidising environment in, (Morimoto *et al* - 1990), and are found to have a higher reactivity than O<sub>2</sub> in producing CuO<sub>2</sub> in the ablation plume from an YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> target, (Otis *et al* - 1992).

### 1.2.1.5 High Deposition and Instantaneous Deposition Rates

The mixture of high available laser energy coupled to the target and the directional nature of the resultant plume leads to a fast average, and an extremely high instantaneous, film growth rate. The magnitude of the instantaneous growth rates are unique to PLD and result in part from the short duration of the plume, (roughly ~10-100 $\mu$ s, Geohegan - 1992). If the growth rate is 0.1nm per pulse, which is typical of my own observations, at 10Hz. this corresponds to an average growth rate of 1nm per sec. and an instantaneous growth rate of at least 10 $\mu$ m per sec.

Figure **1.3** gives a comparison of time averaged deposition rates in competing technologies; note that for all the methods apart from PLD the instantaneous deposition rate is equal to the averaged deposition rate.

A high deposition rate can be advantageous in that the surface of the film is exposed to possible contaminants arising from a poor vacuum for a shorter period, an effect which is exaggerated by the instantaneous growth rate.



*Figure 1.3 - Comparison of time averaged deposition rates in competing thin film deposition techniques* 

## 1.2.1.6 Congruent Evaporation of Multicomponent Materials

One of the major advantages of PLD, which sets this technique apart from the great majority of deposition methods, is the ability to co-evaporate a number of separate elements in a multicomponent target in the same ratios as the original material. As mentioned earlier the temperatures that can be reached during the few nanoseconds of the laser pulse are sufficient to vaporise all components of a multicomponent target irrespective of their melting points and the plume is generally stoichiometrically representative of the target. Nevertheless, the laser fluence may need to be adjusted to assure stoichiometric transfer particularly when one of the components is particularly volatile. An example is in the lead zirconate titanate system where PLD at low

fluences can lead to a lead excess (Saenger *et al* - 1990) and a fluence of  $8J/cm^2$  is necessary (see chapter 7 particularly figure 7.3).

In the majority of competing deposition methods congruent evaporation entails careful calibration for each compound. For example, in any technique based on thermal evaporation ( electron beam evaporation, MBE, IVD ), the rate of evaporation and rate of transfer of each individual film component must be carefully controlled. Thus the complication and cost of the process increases with the number of elements present in a complex compound. Chemically based processes such as sol gel and MOCVD can give excellent stoichiometric control provided that suitable chemical precursors can be found.

Table **1.2** summarises some of the comparisons between competing deposition processes particularly with a view to complex electronic ceramic thin film deposition. Some categories need explanation:

"simple stoichiometric transfer" indicates those techniques which require no particular adjustments to maintain stoichiometry.

"Naturally oriented films" indicates orientation without post deposition processing.

"Control", PLD has low thermal inertia allowing rapid modulation of the growth profile.

chapter one - Introduction

The sources for this table are mainly J.L.Vossen and W.Kern -1991, D.B.Chrisey and G.K.Hubler-1994, Roy and Etzold 1990 and L Sheppard-1992.

#### 1.2.2 Special Adaptations to the PLD System

The box in table 1.2 entitled "possible problems" for PLD has two entries: surface debris and uniformity, this section will deal some of the adaptations that have been made to the simple apparatus described in section **1.1** to overcome these problems.

	PLD	SPUTTERING	MBE	IVD	TE	MOCVD	Sol gel
reactive gas during depo	Y	Y	N	N	N	Y	N
simple 1. stoichiometric transfer	Y	Y/N	N	N	N	N	¥
naturally 2. oriented films	Y	Y	Y	Y	N	N	N
dry process	Y	Y	Y	Y	Y	Y	N
large area	Y/N	Y	Y	Ν	Y	Y	Y
energetic ions	Y	Y	N	Y	Ν	N	N
high cost	Y	Y	Y	Y	Y	Y	N
possible problems	debris, uniformity		limited range of materi als				multiple coating, cracks
special advantages	control 3.						
commercially established	N	Y	Y	N	Y	Y	Y

#### Table 1.2 - comparison of thin film deposition techniques

Table **1.2** indicates that for complex materials PLD is often the ideal deposition technique provided that the difficulties of surface debris and uniformity of film thickness can be minimised.

## 1.2.2.1 Measures for Decreasing Surface Debris.

Surface debris occurs on thin films grown by PLD for two main reasons.

1. "Large" lumps of material, (e.g.  $\sim 1\mu m$  diameter), are ejected directly from the target and arrive intact on the substrate.

2. Material condenses from the plume to form agglomerations of particles which are deposited as features on the surface of the substrate which are generally smaller than those derived directly from the target.

The fact that large particles are present in the plume and not solely created on the substrate can be seen from the mass distributions of particles ejected from an YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> target during ablation with a Nd:YAG laser (Becker and Pallix 1988).The use of a reflecting TOF spectrometer with photo ionisation reveals the presence of particles up to 18,000 amu.

In ablation of mixed alkali halide targets Yang and Xia *et al* - 1991 found that the clusters emitted from a target consisting of pure CsI and pure CsCI powders showed no sign of alloying. This evidence is consistent with cluster formation only by direct ejection from the target under the conditions described in the paper.

The number of droplets is generally observed to increase with laser fluence, but this effect is dependant on the target material and some authors (van de Riet *et al* - 1993) note the opposite effect with certain metal, silicon and FeSiGaRu targets.

These authors also note that rough target surfaces lead to more droplets and in a more recent paper, (van de Riet *et al* - 1994), relate a method of varying the azimuthal angle of the laser during ablation to minimise the formation of target roughness. A corresponding decrease in droplet formation is observed with this method with FeSiGaRu targets and Riet and Nillesen find a decrease in droplet formation in metals at very high fluences in contrast to the behaviour with oxide targets.

In certain materials droplet emission can be eliminated by the use of a molten target (Cheung - 1992) which maintains a smooth target surface during ablation. The only drawback with this method is that it limits the chose of

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material to one which has an acceptably low vapour pressure at its melting point which is the case among commonly used materials only for germanium. The most common method to decrease the number of type 1 particulates is by changing the laser wavelength to one which is more strongly absorbed, this generally dictates the use of ultra-violet wavelengths with oxide targets. (Koren *et al* - 1989, J.Perriere - 1992) and can lead to a dramatic reduction in particulates.

Work based on the scattering of a second laser by particles emitted from the target, (Murakami - 1992), corroborates for the existence of at least two components in the plume using time and space resolved measurements.

By using four Nd:YAG wavelengths, ( $\lambda$ ,  $\lambda/2$ ,  $\lambda/3$ ,  $\lambda/4$ ), Murakami observed that the number of particulates in the plume decreases with wavelength.

Several other methods of particulate suppression exist including the use of a second laser pulse, similar to that which causes the target ablation but aimed at the plume, (Becker and Pallix - 1988 and Murakami -1992). The second laser is triggered with a time delay relative to the first, timed to coincide with the passage of the micron sized particles in the plume; a representative delay would be 275ns. This results in a decrease in number of particles arriving at the substrate and an improvement in the temperature-resistivity relationship of  $YBa_2Cu_3O_{7-\delta}$  thin films deposited with the use of this two laser pulse technique.

A similar technique using a pulse of gas timed to catch the large particles and a also a mechanical shutter were employed with some success, (Murakami -1991).

By using a rotating disc which was later analysed by SEM Dupendant *et al* - 1989 were able to show that the micron sized particles lag behind the atomic particles by a sufficient degree to be separated on a rotating disc, (Figure 1.4).



Figure 1.4 - Rotating substrate for velocity discrimination

This source of information has been used to build a velocity filter similar in principle to figure **1.5** with which some authors report films grown with greatly reduced surface debris, (Venkatesan *et al* – 1992).

Surface debris formed by plume condensation can normally be controlled by appropriate choice of laser fluence and spot size such that the plume above the target is not fully saturated.



## 1.2.2.2 Measures for Helping Deposition Uniformity

As a direct result of the plume's narrow angular distribution discussed in section **1.2.1.3**, thin films are normally deposited by PLD on small substrates in contrast to the other techniques of table 1.2. This is not necessarily a disadvantage in research when complex epitaxial films are grown on expensive single crystal substrates which are themselves small. However, if PLD is to become economic in a manufacturing environment, a method must be developed to coat large areas uniformly, i.e. >50mm diameter. The distance between target and substrate can be increased for monocomponent films in high vacuum, but in general, ideal growth conditions dictate the target substrate geometry. The most common methods rely on four methods either alone or in combination.

1. Rastering the laser spot on a, (large), target, (Greer 1992 and 1993).

2. Translating the substrate, (Foltyn *et al* - 1991).

3. Arranging the target with the ablated surface displaced at a small angle to its the plane of rotation or using targets with curved surfaces.

4. Using multiple targets and more than one laser beam.

Method 1. may also carry the additional advantage of minimising the formation of surface structures on the target which would otherwise lead to increased particulate emission. (van de Riet *et al* - 1993)

## 1.2.2.3 Special Advantages of PLD

The box in table 1.2 entitled "special advantages" for PLD has "control" as an the entry.

This refers to the fact that the thermal inertia in the PLD system is very low i.e. the plume is created within nanoseconds of the laser pulse and dies microseconds after the laser pulse ends. This allows very tight control over the deposition and, with the use of a number of targets contemporarily or an evaporation source (Cheung and Sankur - 1992), the rapid control of the composition of the growth in layers within the thin film.

#### 1.3 The Development of the Plume

It is beyond the scope of this thesis to give a detailed description of the often mathematically complex models that have been used to account for the formation and expansion of the ablation plume. However, much of the experimental work presented here is on the analysis of the plume. Therefore a general description of the theoretical concepts, underlying assumptions and predictions is given to shed light on the energy and mass spectra presented later in the thesis.

#### 1.3.1 Power density Effects

The nature of the laser-target interaction clearly depends on a number of factors, particularly:

- 1. the peak laser power density at the target surface
- 2. the absorption coefficient of the target material
- 3. the laser wavelength.

If the power density or fluence of the laser radiation coupled to the target is low the heating effect will approximate a simple thermal source. The energy and angular distribution of the ejecta will be the same as that from thermal evaporation, peaking at below 1eV with temperatures below the critical temperature of the evaporant and a  $\cos\theta$  angular distribution (where  $\theta$  is measured relative to the target normal). The conditions for this behaviour are low laser energy, long pulse length or large absorption depth. Below the threshold for laser ablation, particles will be desorbed but no visible crater is observed where the laser strikes the target and the constituents of the vapour will not necessarily reflect the proportions in the target.

Above a threshold fluence the rate of evaporation increase markedly and the laser leaves a visible mark on the target surface, a visible plume appears above the target and the angular distribution of the ejecta changes from a

cosθ to a cos<sup>n</sup>θ (see section **1.2.1.3**). The value is clearly dependant on the target material, laser pulse length and wavelength but as an example, a typical figure for threshold fluence, would be 250-300mJ /cm<sup>2</sup>, (O'Brien *et al* - 1992) for an YB<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> target and a KrF excimer laser ( $\lambda$ =248nm and fwhm of 23ns ). For comparison the ablation threshold for MgO is 3 J/cm<sup>2</sup>, (Dirnberger *et al* - 1993) at 248nm and 10J/cm<sup>2</sup> for refractory metals such as Tungsten, 1064nm, 10ns, (Kools - 1994).

# **1.3.2 An Overview of the Interaction between the Laser with the Target and Plume.**

As the laser beam strikes the target during PLD, a proportion of its energy, (which will be a function of temperature and state), is reflected and/or scattered while the rest is absorbed and transmitted into the volume of the target by conduction. This creates a molten layer which, rapidly vaporises. If the laser pulse is in the nanosecond range, the thermal diffusion time constant will be long compared to the pulse length leading to the vaporisation of the target surface over a period similar to the pulse width.

The nature of the interaction between the laser and target clearly changes as the target is transformed from solid to liquid to vapour and then at high laser fluences to plasma. As light is an electromagnetic radiation it can only effect or be effected by the particles that have a net charge. The strength of the laser- target coupling depends on the density of charged particles, principally electrons, and on how strongly they are bound.

Initially as laser radiation strikes the target surface, the interaction will be dominated by volume absorption by electrons and phonon interactions in the lattice. However, at very high fluences, the electric fields within the target due to the extreme laser power levels are so high that dielectric breakdown occurs in all materials. Under these conditions the general electronic structure of the target material may not be the critical factor determining ablation (Cheung and Horwitz -1992). As an example of this effect, the absorption coefficient of MgO found from the ablation rate at 248nm has been reported as  $4 \times 10^4$  cm<sup>-1</sup>,

much higher than that from transmission measurements at normal light levels, i.e. those well below threshold ablation levels, (Dirnberger *et al* - 1993).



(adapted from Cheung and Horwitz - MRS Bulletin Feb92)

*Figure 1.6 -* The interaction between a high power laser pulse and a target at fluences well above the ablation threshold, ( adapted from Cheung and Horwitz-1992 ).

As the target temperature rises, the mechanism changes to surface absorption by free carriers in the molten layer. Finally, if the fluence is high enough and the plasma sufficiently dense, plasma absorption of the laser light will occur just above the surface of the target.

The attenuation may be strong enough to reduce the energy reaching the target surface to below the threshold for plasma emission, so the plume dies and the full laser fluence can again reach the surface. This is a self limiting effect and can dictate the rate of ablation at high fluences.

### 1.3.3 Mechanisms Initiating the Onset of Ablation

From a theoretical standpoint the mechanism which initiates ablation in high band gap oxides may be very different to that in metals and semiconductors due to the absence of unbound electrons at room temperature.

Traditionally it has been believed that pulsed laser ablation of a material follows from the rapid thermal heating of the surface since thermalisation times even in insulators are much shorter than the pulse duration. However some authors (Haglund and Itoh - 1994) believe that electronic effects may be dominant in non-metallic materials. The role of electronic effects will be particularly apparent at lower fluences and in strongly insulating materials.

There are two distinct regimes for laser ablation depending on the ablated material and the wavelength of the laser used. In materials where free electrons are present or where the photon energy, hv, is higher than the band gap, the absorption coefficient will be high. The interaction of laser radiation with electrons promoted to, or naturally present in, the conduction band raises the surface temperature and can cause thermal evaporation above a threshold fluence. The rate of conversion of laser energy into heat depends on electron lattice interactions such as the scattering of electrons by phonons and phonon emission.

By contrast in metallic materials, light is almost completey reflected from the surface for laser frequencies below the plasmon frequency in the metal and absorption rises steeply at higher laser frequencies (Kools - 1994). The absorption coefficient is high for wavelengths commonly used in PLD giving a typical absorption depth of below 50nm due to absorption by the conduction electrons. In a metal the absorbed energy is coupled to the lattice by the

electron- phonon interactions on a time scale of the order of 1-4 picoseconds (Elsayid-Ali *et al* - 1987) causing heating and eventual evaporation.

For 12ns u.v laser pulses near the ablation threshold the heating efficiency in metals is proportional to, (Kelly and Rothenberg - 1985).

## (1-R )(M/KpC)<sup>1/2</sup>

where **R** is the reflectivity, **M** the molecular weight ,**K** the thermal conductivity,  $\rho$  the density and **C** is the heat capacity.

In materials with a wide band gap relative to the laser photon energy, (such as the perovskite ferroelectrics but not high temperature superconductors), the absorption coefficient may be extremely small and the ablation mechanism may be far more complicated including absorption at point defects and electronic laser sputtering, (Helvajian and Welle - 1989).

Possible sources of absorption of sub band-gap energy photons are multiphoton bulk absorption, single photon absorption by surface states and defects in the bulk and on the surface. Photons absorbed by surface states and defects may cause heating below the surface by the transfer of thermal energy generated by non radiative processes. Energy absorption from bulk defects is unlikely to cause desorption since typical laser photon energies are of the order of a few eV which is insufficient to cause ejection (Nakai *et al* - 1991).

A mechanism suggested by Haglund and Itoh takes into account the role of excitons which constitute energy levels within the band gap which act as sites for subsequent photo ablation. The pathway for laser induced particle emission depends on the degree to which excitons and holes become self trapped in the material. In semiconductors, MgO and CaO excitons and holes will not become self-trapped whereas in alkali halides and SiO<sub>2</sub> for example they will. Ferroelectric materials are expected to lie between the two extremes represented by the two classes of material mentioned above. The sequence of events which leads to ablation is as follows.Photons interact with the surface producing either excitons or electron-hole pairs or both depending on the photon energy. Self trapping and electron -hole capture leads to a relaxed excited state which then decays to a metastable state through a non radiative defect reaction. Subsequent photo excitation of this state will lead to a

vacancy and an emitted atom and further photo excitation still will lead to vacancy clusters and emitted atoms. The interaction between the solid surface and laser photons produces defects by altering the electronic and physical structure of the surface and bulk by laser induced particle emission.

The combination of altered optical absorption and the evolution of defect clusters which grow in number with subsequent laser pulses produces large numbers of weakly bonded atoms which can be dislodged at relatively low fluence creating conditions for massive ejection of surface material.

The electronic processes described above will also be present in materials with band gaps below the photon energy but are unlikely to be dominant at high fluences since total dielectric breakdown is likely to occur irrespective of the initial electronic structure of the material.

A characteristic of electronic processes is the super linear increase in particle emission with increased laser fluence in contrast to a purely thermal processes in which the particle emission would be linear until plasma shielding becomes important.

The threshold for laser ablation in ceramic oxides is, nevertheless, normally lower than for the refractory metals whilst amongst metals the threshold varies from 0.1 J/cm<sup>2</sup> for lead and cadmium to  $\sim$ 2J/cm<sup>2</sup> for transition metals to  $\sim$ 10J/cm<sup>2</sup> for refractory metals such as Tungsten, 1064nm, 10ns, (Kools - 1994).

The high temperature superconductors YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and BiSrCaCuO are unusual among ceramic oxides in that as well as being superconductors at liquid nitrogen temperatures they are ohmic conductors at room temperature and the presence of conduction electrons indicates that these materials will exhibit some similarities with the metals in terms of absorption of high intensity laser radiation.

## **1.3.4 Plasma Absorption**

Although materials related effects are important at relatively low fluences, at higher fluences plasma effects may come to dominate the ablation process so completely that the original chemistry of the pre-irradiated solid target becomes almost irrelevant.

The plasma absorption coefficient a is given by (Singh and Narayan - 1990):

 $\alpha_{ib} = 3.69 \times 10^8 \ (\textbf{Z}^3 \ \textbf{n_i}^2 \ / \ \textbf{T}^{\ 0.5} \ \nu^{\ 3}) \{1 - \exp(-\textbf{h}\nu \ / \ \textbf{k}\textbf{T})\} \qquad \text{ in cm}^{-1}$  where...

Z is the average charge,  $n_i$ , the plasma ion density, (cm<sup>-3</sup>), T the plasma temperature, v the laser frequency, h Planck's constant, k Boltzmann's constant. The plume of vapour can be heated by this process (which is called inverse-bremsstrahlung) to temperatures which may be well above the critical temperature of the target material, (where the solid and vapour densities are equal), by absorption of the laser light in free-free transition of electron-ion pairs.

The dependence on  $n_i^2$  indicates why the laser pulse will only be absorbed very near to the target surface where the ion density is high, whereas the v<sup>3</sup> factor dictates that photon absorption coefficients are generally lower for ultra violet wavelengths in plasmas. This is in contrast to solids where ultra violet absorption coefficients are generally far higher than for visible or infra-red radiation.

Consequently the absorption of energy and the transfer of that energy to the surface will be mediated by the free electron plasma  $10^{-2}$  cm above the surface (Dreyfus - 1992). In this region the electron density may reach the so-called "critical density", (Phipps and Dreyfus - 1993) where laser absorption rises rapidly at first and where, at even higher densities, incident radiation is totally reflected. The critical density has a very high value of  $10^{21}$  to  $10^{23}$  /cm<sup>3</sup> (compare this to  $10^{22}$  to  $10^{23}$  /cm<sup>3</sup> for the atomic density of a solid) for visible laser wavelengths. There is consequently an extremely high pressure created near the surface on the order of 100kbar (Phipps and Dreyfus - 1993) and the absorption zone may be as short as the laser wavelength such that the region of interaction between the laser and the plume will be essentially two dimensional even for very small laser spot sizes.

The Saha equation predicts the ratio of singly charged ions to neutrals in a gas in local thermodynamic equilibrium to be...

$$n_i/n_n = 2.4 \times 10^{15}$$
. (T<sup>3/2</sup>/ $n_i$ ). exp(- $u_i/kT$ )

where ..

 $n_i$  is the ion density in cm<sup>-3</sup>,  $n_n$  the neutral density in cm<sup>-3</sup> and  $u_i$  the first ionisation potential in eV.

For T=3000K and  $U_i$  =7eV this gives the percentage of ions in the plume as only 0.01%.. However this percentage rises rapidly to 80% at 10000K.

Relating this to laser parameters is of course dependant on the factors mentioned earlier but Phipps and Dreyfus for LIMA quotes a figure of 5GW/cm<sup>2</sup> as the approximate power density at which the ionisation fraction approaches unity (Phipps and Dreyfus - 1993). The ionisation fraction will fall rapidly at lower irradiance.

Figure 1.7 is an illustration of three regions of the plume; but should not be seen as a snapshot since these regions will not necessarily exist contemporarily. The figure shows three regions with rapidly decreasing particle densities and the velocities increasing and becoming more forward directed with increasing distance from the target.



**Figure 1.7 -** Schematic of three distinct physical regions present at various times in the high fluence ablation plume (adapted from Phipps and Dreyfus - 1993), not drawn to scale.

#### 1.3.5 The Role of the Knudsen Layer

In the region close to the surface of the target the velocity and the angular distribution of the particles leaving the target may differ markedly from those at greater distances and the extent of this effect will depend on the laser fluence. At low fluences the particles will escape the solid surface without mutual interaction and go into free flight, their velocity spectra being described by a Maxwellian distribution.

When the rate of particle emission approaches something of the order of 0.5 monolayers in nanoseconds the particles collide sufficiently to come into equilibrium (NoorBatcha *et al* -. 1987 and 1988, Kelly and Dreyfus - 1988 a and b) and they will acquire a flow or centre of mass velocity and an angular distribution of the form  $cos^4\theta$ . The velocity distribution will evolve from a half range Maxwellian to a shifted Maxwellian with v replaced by v-v<sub>cm</sub>, where v<sub>cm</sub> is the centre of mass or flow velocity, (see Appendix ).

The use of a Maxwellian, shifted or not should nor be taken to imply a thermal primary mechanism since the distribution is simply the result of collisional processes immediately above the target, independently of the primary mechanism.

In this regime the high temperature plasma immediately above the target is dense enough to form a thin layer in which a sufficient number of collisions occur to form a partially thermalised region this region is called the "Knudsen layer". The number of collisions needed to form this layer may be as low as 3 to 4, and is thought that the kinetics of this region are responsible for the forward directed nature of the plume.

A further consequence of the Knudsen layer is that certain energetic particles from the plume will strike the target surface causing re-condensation and either further target heating or cooling.

Beyond the Knudsen layer plume expansion eventually makes the transition to multidimensional flow, particle interactions become less common and the plasma density is too low to effect the passage of the laser.

## 1.3.6 Expansion of the plume on leaving the Knudsen layer

A detailed discussion of the mathematics of various attempts to model the behaviour of particles in the ablation plume is beyond the scope of this thesis. However an understanding of the physics of the key ablation mechanisms is outlined in order to complement the kinetic energy data presented later in this thesis.
# 1.3.6.1 Singh, Holland and Narayan 1990 (adiabatic expansion model).

The model of Singh *et al* also assumes that the rapid expansion of the plasma arises from the density gradients in the plasma. The plasma represents a heated high pressure gas kept in a small volume and then suddenly allowed to expand in a vacuum. The particle density in the plume during the initial stages of expansion is very high ( $10^{19}$  to  $10^{20}$  cm<sup>-3</sup>) and collisions are consequently numerous so the plasma behaves as a compressible fluid. Expansion is divided into two regimes, firstly an isothermal expansion phase during the laser pulse followed by an adiabatic expansion after the laser pulse.

The model assumes a linear decrease in the number of particles in the plasma from a maximum number where the laser strikes the target to zero at the expanding edge of the plume during particle emission. The particle velocities show an opposite trend increasing linearly from zero at the target surface to a maximum at the plume's leading edge.

The expansion velocity and initial acceleration are found to be determined by the dimensions of the plasma being greatest where the dimensions are smallest. Clearly the region above the target where the laser interacts with the plume is very small (typically 1  $\mu$ m.), compared to the lateral dimensions of the spot and for this reason the density gradients are greatest along the target surface normal. This leads to a far greater plume velocity in the outward direction from the target than parallel to the surface and in consequence the plume is highly forward directed for macroscopic spot sizes.

After the laser pulse has ended the plume is assumed to expand adiabatically into free space since there is no further energy input into the system. The rate of expansion in a particular direction is, again, inversely proportional to the dimensions of the plume in that direction and hence the plume remains highly forward directed.

The model makes predictions on the spatial thickness variations of deposited films which follow directly from the predicted three dimensional form of the plume. It also predicts a (Fluence)<sup>0.2-0.75</sup> dependency of ion velocities which will attain values well above thermal energies. In addition the predicted velocities of particles of different mass will vary with (Mass)<sup>-1/2</sup>.



Figure 1.8- The density, pressure and velocity profiles according to the Singh and Narayan model (from Singh et al - 1990)

The expansion of the laser plume is not isotropic, expanding most rapidly where the initial dimensions were smallest, as discussed in section **1.3.6.2**.

# 1.3.6.2 Kools ( elliptical temperatures)

Kools *et al* have suggested that the angular distributions derived from laser etching copper in a chlorine environment at  $5 \times 10^{-5}$  mbar can only be fitted with a form of Maxwell-Boltzmann distribution with a stream velocity and "elliptical temperatures".

The particle velocities are expressed as three independent velocities in the x, y and z directions and a stream velocity i.e. the centre of mass, (c.o.m), velocity of the plume :

dx dy dt ~ exp{-m/2kT<sub>xy</sub> {  $(x/t)^2+(x/t)^2$  } - m/2kT<sub>z</sub> {(z/t)-u}<sup>2</sup>} dx dy dz

$$n(x_{i},t)dxdydt \propto t^{-3}exp\left[-\frac{m}{2kT_{xy}}\left(\left(\frac{x}{t}\right)^{2}+\left(\frac{y}{t}\right)^{2}\right)-\frac{m}{2kT_{z}}\left(\left(\frac{z}{t}\right)-u\right)^{2}\right]dxdydz$$

where:  $T_{xy}$  and  $T_z$  are called transversal temperatures and longitudinal (elliptical temperatures)

k is Boltzmann constant,

u is the stream velocity,

and m is the particle mass .

Kools also employs a Monte Carlo simulation to model the effect of background gases on the development of the plume.

In his model, Kools, assumes that the plume process can be divided into two separate expansion processes, (Kools - 1993) in a similar way to Singh and Narayan. The pressure of the gas cloud on the surface dictates that the initial expansion is dominated by a one-dimensional element along the target normal. This is followed by a three-dimensional expansion at distances further from the target driven solely by density gradients, and at increasing distances the plume densities are so low that the expansion approaches free flight. Specifically, Kools calculates that the deviation from free flight is less than 10% within a microsecond, corresponding to an expansion of approximately half a millimetre under what he describes as typical ablation conditions. The assumption that the initial expansion is equivalent to expansion into a vacuum can be justified provided that the mean free path for the background gas is greater the 0.5mm of the initial, (one-dimensional ), expansion region, which limits the application of the model to background pressures of 760mTorr.

#### **1.3.7** Ion Acceleration Mechanisms

Other authors have introduced specific adaptations to the basic model to explain the high particle energies recorded in time of flight mass spectrometry and optical spectroscopy (see table **3.1**). The relative increase in velocities relative to the predicted value is a factor of  $\sqrt{10}$  according to Phipps, (Phipps and Dreyfus - 1993). They also note that suprathermal ion energies had been

noted as long ago as 1966, (Langer et al -1966; their reference) with up to 1keV for Cu<sup>2+</sup> ions from targets irradiated at 10GW/cm<sup>2</sup>. Gurevich et al -(1973) have proposed a model in which electrons being lighter than ions expand rapidly causing a self consistent field to be generated which accelerates the slower ions to much higher energies than would be expected from inverse bremsstrahlung alone.

## 1.4 Conclusions

Pulsed laser deposition in essence is a very simple technique with many similarities to other physical deposition processes. There are many advantages with PLD apart from its simplicity. Perhaps the two most important ones being the energetic nature of the plume which can aid the formation of specific crystalline thin film states and the ease with which correct stoichiometric transfer can be obtained.

The situations in which PLD can become more complicated are when large uniform areas are required which are totally free from surface debris. The measures that can be taken to overcome these problems have been discussed.

Unfortunately the underlying physics of the creation and development of the ablation plume is complicated. This partially ionised plasma is formed in a time scale of nanoseconds and never reaches equilibrium, further complications arise from the laser-plasma interaction which may lead to the extinction and re growth of the plume in rapid succession. Theory does not predict the energies of ions ejected from the target for high fluences as noted in section 1.3.7. The only way to ascertain the actual energy of particles in the plume is by direct measurement of the plume under conditions similar to those used for deposition.

chapter one - Introduction

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# 2.0 PEROVSKITE FERROELECTRIC MATERIALS

In this chapter we will discuss the basic crystallographic and electronic properties of perovskite ferroelectrics and briefly review some of the devices that can be made from ferroelectric thin films.

Ferroelectric materials are a subset of the class of dielectrics known as piezoelectrics. They are distinguishable from other piezoelectrics in possessing a remnant polarisation whose direction may be reversed by the application of an electric field.

The term ferroelectric is somewhat misleading and derives from the analogy between ferroelectric and ferromagnetic behaviour. Both ferroelectrics and ferromagnets obey the Curie-Weiss law and their anomalous behaviour will disappear above a certain, material specific, temperature. In addition, the polarisation of ferroelectric materials is organised in domain structures analogous to ferromagnetic domains. However, there is no suggestion of a common mechanism governing the two effects and iron has no special relevance to ferroelectricity.

## 2.1 The Crystal Structure of Ferroelectric Compounds

From a crystal symmetry point of view piezoelectricity occurs only in structures that lack a centre of inversion; this applies to twenty one of the thirty two point groups. For a material to be ferroelectric, in addition to the above stipulations it must also have a non equivalent direction. This leaves 10 point groups with ferroelectric crystal structures within the twenty one piezoelectric types.

## 2.1.1 Perovskites

This is probably the most commercially important group of ferroelectrics.

The general formula for a perovskite is  $ABO_3$ , where A and B are cations and A has a larger radius than B, their valences may take almost any value such that A+B = 6.

Not all perovskites are ferroelectric and in fact no ferroelectrics are known where **A** and **B** both have valences of 3. Knowledge of the radii of the cations is useful in predicting how closely a perovskite type will approach the ideal cubic perovskite structure. The packing can be characterised by a tolerance factor, **t** where...

$$\mathbf{t} = (\mathbf{R}_{A} + \mathbf{R}_{O}) / (2)^{1/2} (\mathbf{R}_{B} + \mathbf{R}_{O})$$

R being the ionic radius of the ion referred to by the subscript, as in the formula  $ABO_{3}$ .

When t = 1 the packing is ideal; when t > 1 the B ion is "loose" in its octahedra of six nearest oxygen ions and can move around. For a stable perovskite, generally: 0.9 < t < 1.

Barium titanate is a classical example of a perovskite ferroelectric and its ferroelectric nature was discovered towards the end of the second world war making it the first of its class to be discovered. Above  $120^{\circ}$ C barium titanate is an ideal cubic perovskite and paraelectric, ( point I in figure. 2.1 ) whilst below this temperature the titanium and oxygen ions shift to form a tetragonal ferroelectric phase, ( II in figure. 2.1 ). Below  $0^{\circ}$ C an orthorhombic, ferroelectric phase forms, (III in figure. 2.1) which becomes rhombohedral and still ferroelectric below -90°C, (IV in figure. 2.1).

**N.B.** in figure  $\check{2.1}$ ,  $P_s$  denotes the direction of spontaneous polarisation relative to the original cubic cell

to the original cubic cell.

Barium titanate has an extremely high dielectric constant which

led to early interest in its use in capacitors, however the value is extremely temperature dependant.

Figure **2.3** shows how the perovskites of the general type,  $A^{2+}B^{4+}(O^{2-})_{3}$  can be classified according to the ionic radii of the constituents.

The figure illustrates how the structural modifications from the ideal cubic result from the substitution of various ions. The thick dotted line in figure **2.3** indicates the points joining  $PbTiO_3$  and  $PbZrO_3$ , the small black square is  $BaTiO_3$ .



**Figure 2.1 -** Pseudo-cubic cell of the different phases of BaTiO $_{3}$ 



**Figure 2.2.** The perovskite structure, (a) the unit cell, (b) the unit cell seen as a network of  $BO_{6}$  oxygen octohedra, (from Xu - 1991).



**Figure 2.3 -**  $A^{2+}B^{4+}(O^{2-})_{3}$  perovskites plotted against ionic radii ( from Xu - 1991).

## 2.1.1.1 Lead Zirconate Titanate (PZT)

PZT is probably the most important material in this class of perovskite. It is formed from a solid solution of lead zirconate and lead titanate and has a general structure similar to that of barium titanate with  $Ti^{4+}$  and  $Zr^{4+}$  ions occupying the **B** sites at random and Pb<sup>2+</sup> occupying the **A** sites. The general formula is  $Pb(Zr_{x} Ti_{(1-x)})O_{3}$  for the whole spectrum of compounds with properties ranging from lead zirconate to lead titanate and allowing for a degree of tuning for a specific application.

In general ferroelectric behaviour is most marked in a material when it is near to a phase boundary where the crystal structure is changing, for example due to temperature variation (see figure. 2.1). This leads to ferroelectric materials which undergo a phase change near room temperature having very elevated piezoelectric and ferroelectric properties and some of the highest dielectric constants known. Unfortunately, these materials can be difficult to exploit practically with properties changing wildly with small variations in temperature.

An alternative approach to the maximisation of ferroelectric properties is to find materials which are close to a phase boundary by virtue of the balance of components.

The PZT family of ferroelectrics would occupy the thick dotted line on the diagram of figure **2.3** between  $PbTiO_3$  and  $PbZrO_3$  passing through two phase boundaries and this is one of the reasons for its commercial importance as a piezoelectric and ferroelectric material. The lattice parameters and properties of PZT can be varied by simply altering the composition, leading to a more stable PZT device.

PZT exhibits anomalous behaviour in terms of dielectric constant, piezoelectric coupling factor and some physical properties as the lattice parameters change abruptly near the morphotropic phase boundary i.e. at points close to structural reorganisation Zr/Ti = 53/47 and the majority of formulations of the PZT family of ceramics are close to this ratio.

Figure **2.4** shows the phase diagram of different PZT compositions illustrating the position of the morphotropic phase boundary.

The morphotropic phase boundary is the ratio of lead to zirconium for which the most interesting properties occur in PZT, for example the dielectric constant and the electromechanical coupling factor change rapidly near to the boundary.



**Figure 2.4** PbZrO<sub>3</sub>-PbTiO<sub>3</sub> subsolidus phase diagram, (from Jaffe, Cook and Jaffe 1971)

# 2.2 The Behaviour of Ferroelectric Elements in a Circuit

The nature of the ferroelectric effect can be illustrated from an electric circuit point of view by the behaviour of the most simple ferroelectric element, the ferroelectric capacitor in a Sawyer-Tower circuit (Sawyer and Tower - 1930), figure 2.5. The X plates of the oscilloscope are connected to the alternating voltage driving the normal dielectric capacitor, C, and the ferroelectric capacitor  $C_x$  in series, and the Y plates to the voltage on a floating node between the two capacitors.



Figure. 2.5 - The Sawyer-Tower Circuit

The hysteresis loop of polarisation, **P**, versus electric field, **E**, across a ferroelectric capacitor generated on the oscilloscope and has several important features as shown in figure **2.6**.



Figure 2.6 - A P-E hysteresis loop for a ferroelectric capacitor,

A small electric field will not be sufficient to reverse the polarisation of the test material and it will behave like a normal (paraelectric) dielectric exhibiting a linear relationship between **P** and **E**; **O** to **A** in figure **2.6**.

When the field strength is increased a number of domains in the ferroelectric sample that are polarised in the opposite direction to the field will switch over, i.e. reverse direction, and the polarisation increases rapidly (AB on graph). Eventually all the domains are aligned with the field (BC on graph) and the crystal is saturated and becomes a single domain, the polarisation at this point is called the saturation polarisation,  $P_s$ .

As the field is decreased some of the domains remain aligned even at zero field,  $P_r$  is defined at this point and called the remnant polarisation. The field required to reduce the polarisation to zero is called the coercive field strength,  $E_c$ , and is an important factor in determining the working voltages of a ferroelectric device. An ideal ferroelectric would have an almost square hysteresis loop and bulk crystalline materials tend to approach this ideal

more closely than existing thin films.

## 2.3 Ferroelectric devices

Many of the ferroelectric devices which have only recently become practicable due to recent advances in thin film processing over the last ten years were first investigated in the 1950s. This is true particularly of non volatile memory applications where single crystal or thick ceramic form dictated too high operating voltages see figure **2.6**, (Paz de Araujo *et al* -1990)

There is now considerable research and development interest in the use of ferroelectric materials (Ishibashi *et al* - 1993), particularly for non-volatile, high speed ferroelectric random access memories (Ramesh *et al* - 1994, Scott *et al* 1991, Dey and Zuleeg - 1990, Scott - 1988).

Other components which can be made using ferroelectric thin films include i.c. neural network components (Clark *et al* -1991), optical switches, (Masuda - 1990), pyroelectric detectors, (Dijkamp *et al* - 1987) and SAW devices, (Sreenivas and Sayer - 1988, Shimizu- 1988).

chapter two - Ferroelectric Materials

The leading candidates from a materials standpoint for many of these devices continue to be the lead zirconium titanate family of ferroelectric perovskites. However many other important ferroelectric materials continue to be studied including LiNbO<sub>3</sub> and LiTaO<sub>3</sub> which are important in many electro-optical devices, (Alfonso *et al* - 1992), (Agostinelli *et al* - 1993), and  $(Ba_{1-x},Sr_x)TiO_3$  which has many similar properties to PZT in terms of piezoelectric, dielectric and electro-optical properties.

Although a detailed description of these components is out of the scope of this discussion, a general overview of a few devices is appropriate.

Figure **2.7** shows the simplest form of memory architecture; composed of an array of ferroelectric capacitors. However, this design has proved unsuccessful due to the lack of a well defined and stable ferroelectric switching threshold (coercive voltage, figure **2.6**), which leads to memory loss due to the half select pulses applied to unselected cells (Bondurant - 1990).



*Figure 2.7 - Ferroelectric memory made from cross point matrix of ferroelectric capacitors* 

There are several ways to improve on this design; one is to build each memory element with a field effect transistor whose gate insulator has been replaced by a ferroelectric layer. This design gives two distinct values for the threshold voltage depending on whether the dipoles of the ferroelectric are oriented up or down.. The advantages are: a degree of amplification, unlimited read cycles (fatigue is only caused by information being written to it) and high packing density as only one device per cell is necessary. Unfortunately such devices are difficult to build reliably partly because of the need for low resistance electrodes for low switching voltages. This is problematic particularly for the bottom electrode which is a ferroelectric-silicon interface without prejudicing the characteristics of the transistor. In addition movement of charge through the ferroelectric can lead to the two threshold voltages becoming indistinguishable over a time period which may be as low as a few seconds.



Figure 2.8 - (FRAM) cell

Figure 2.8 shows a ferroelectric random access memory (FRAM) cell.

Another memory element configuration is that of a ferroelectric capacitor with metal electrodes which is written to by a voltage greater than the coercive voltage causing alignment of the dipoles in the material. Reading is achieved by applying another voltage across the capacitor causing a current to flow. The nature of this current will depend on whether the dipoles are oriented in the direction of the read voltage field. If they are, the current is simply the charging current of the capacitor, if they are not a greater current flows which is the some of the charging current and of the capacitor plus the switching current of the ferroelectric dipoles. This system is not sensitive to charge movement and information is preserved even when the voltage across the device is zero.

Alternatively ferroelectric materials can be used in dynamic random access memory devices simply as charge storage memory cells by virtue of their high dielectric constants (Chikarmane *et al* -1991).



Figure 2.9 -SAW device

Surface acoustic wave (SAW) devices are used in filters, resonators and oscillators and rely on the piezoelectric properties of a ferroelectric to send a transverse wave across the surface of a substrate. The waves emanate from an inter digital electrode are then picked up by another similar electrode, provided that the properties of the electrodes, piezoelectric and substrate allow for the specific frequency of the surface waves involved.

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# 3.0 ENERGY AND MASS SPECTRA OF ELECTROCERAMICS

This chapter comprises a review of the major plume analysis methods and discusses the experimental results from previous work and the conclusions that can be drawn about the internal dynamics of the plume. The main methods discussed are optical imaging, optical emission spectroscopy, optical absorption spectroscopy and mass spectroscopy.

## 3.1 Practical Considerations for Depositing Oxides

The PLD of oxides varies from that of, for example, metals and polymers in several important respects.

Although the transfer of material from target to substrate may be stoichiometrically representative of the target material, the film may be deficient in a volatile constituent which does not recombine quickly to form a non volatile material on the film surface. In practice this leads to oxygen loss in the deposition of oxide materials and the oxygen level must be controlled by the presence of an oxidising gas, (nitrous oxide, ozone or more commonly oxygen itself) in the ablation chamber, (Otis *et al* - 1992, Morimoto *et al* - 1990). This frequently necessitates the use of substrate heaters which can maintain temperatures of up to 900°C without being degraded by the aggressive environment in the chamber (see figure 7.1).

In the absence of an oxygen environment, low melting point metals with a higher melting point oxide will form films which are deficient in the metal when grown in high vacuum. The addition of oxygen oxidises the metal in transit and more particularly on the substrate, thus ensuring its availability in the film more details of this effect in PZT will be given in chapters **5** and **7** on PZT deposition.

A typical example of the complexities introduced by depositing metal oxides is that of the high temperature superconductor  $Y_1Ba_2Cu_3O_{7-x}$ . In order to produce single phase material with desirable superconducting properties three factors must be taken into account.

- 1. incongruent melting at high temperatures,
- 2. decomposition at low oxygen partial pressures,
- 3. low cation mobility at low temperatures.

 $Y_1Ba_2Cu_3O_{7-x}$  is generally deposited at substrate temperatures between 650°C and 800°C and oxygen pressures of 0.1 to 2mbar. However  $Y_1Ba_2Cu_3O_{7-x}$  crystallises into the non superconducting, tetragonal phase  $Y_1Ba_2Cu_3O_6$  above 600°C and must be converted to the superconducting orthorhombic phase,  $Y_1Ba_2Cu_3O_{7-x}$  by oxygenation.

 $Bi_2Sr_2CaCu_2O_8$  also can present problems in oxygenation which necessitate the use of a nitrous oxide, (N<sub>2</sub>O) environment. (Kanai - 1989).

Ferroelectric perovskites present different problems in terms of the loss of volatile components and in having several crystal structures which are stable at different temperatures, more details of the specific case of PZT will be discussed in detail in chapter 7. However the general conclusion that can be drawn is that although film growth conditions need to be carefully controlled to ensure high quality film growth, the intrinsic simplicity of the PLD apparatus can accommodate this.

## 3.2 Energy and Mass Analyses of the Ablation Plume

Information must be pieced together from a number of independent sources in order to fully understand the particle types and their energies in the ablation plume. The main methods of analysing the ablation plume are simple optical absorption, high speed photography, optical spectrometry, mass spectrometry, and ion probes. Each separate technique sheds light either on a particular region of the mass /energy spectrum or particle type or allows the validity of a theory of the PLD process to be evaluated.

## **3.2.1 Light Absorption Techniques**

A broad indication of the range of particles travelling in the plume can be gained by the simple technique of directing a low power laser through the plume and onto a fast photo diode whilst observing the change in signal as the plume develops. The strength of this method is that it allows a very broad range, perhaps unparalleled by other techniques, of particle types and energies to be detected; however the information that can be gathered is quite limited.

As shown in figure **3.1**, the variation in signal from a second laser, (HeNe), passing through the plume during ablation, can be used to study the temporal behaviour of the plume, (K. Murakami - 1992). Data obtained with laser ablation at 1064nm, 532nm, 355nm and 266nm radiation using an YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-8</sub> target indicates that up to three velocity components are present. The values quoted in the reference are  $1 \times 10^4$  m/s,  $2 \times 10^3$  m/s and  $2 \times 10^2$  m/s for the three components. Comparative light emission experiments indicate that the two slower components above are associated with non luminous particles and are much more pronounced at 1064nm and 532nm ablation. In addition the first dip in transmission is associated with the second of the peaks in fluorescence experiments indicating that in total may be up to four different components in the plume, two luminous and two associated with large slow moving non luminous particles. The latter components are difficult to identify in the majority of experiments and constitute the material which may cause surface imperfections in the eventual thin film.



Figure 3.1 -Timing measurements of plume particle velocity using HeNe laser deflection from Murakami - 1992.(1)

## 3.2.2 Imaging Techniques

More detailed qualitative spatial and temporal information and some quantitative information of the development of the plume is can be obtained from high speed photography. This technique is particularly useful for understanding the development of the plume and nature of the interaction between the plume and the atmosphere in the ablation chamber. Additional generalised information on the velocity of the plume as a whole can also be gathered. However this method on its own cannot furnish a great deal of knowledge about the chemistry and energies of the individual particles in the ejecta.

A gate intensified ccd array (Geohegan - 1992) can be used to record the plume giving up to 3.8ns resolution and with sufficient sensitivity at 20ns exposure times to image the plume up to nearly 5cm from the target, streak cameras have also been used (Dyer and Sidhu - 1988) although with a lower sensitivity.

Photography of the plume relies either on the presence of excited states or collisional excitation kinetics in high density regions of the plume and is particularly useful for showing the region where the shock front interacts with the background gases.

It should be noted that much of the plume is invisible since only the more energetic particles will be self luminous whilst the slower neutral states and massive agglomerations require an additional light source to be detectable.

The recorded images of the plume from ablating an  $YBa_2Cu_3O_7$  target at  $10^{-6}$  mbar with a KrF laser at  $1J/cm^2$  (Geohegan - 1992) show the plasma initiating on the target surface and then separating into two components. One is essentially stationary and extending out to 1mm from the target and visible for up to 2µs. The other component expands rapidly away from the target normal for 0.5µs. and detaches itself from the target surface whilst expanding freely in a highly forward directed manner. The leading edge velocity of the forward expanding part of the plume is constant at  $10^4$ m/s.

The stationary region is associated with collisions between particles in the plume in a high pressure region near the target surface where particles move in all directions and is thought to be associated with the Knudsen layer.

When images are recorded for similar ablation parameters with an oxygen pressure of 0.133mbar the result is almost indistinguishable during the first microsecond (1cm) of the plume, but then a luminous crescent shaped front appears at the forward outer edge of the plume which expands outwards and slows to 600m/sec. after 8 $\mu$ s. The almost stationary component is also observed within 1mm of the target emitting light for up to 2 $\mu$ s.

A similar effect is observed by streak camera in the ablation of the polymers PET and Kapton (Dyer and Sidhu -1988) although the time scale is somewhat compressed. A small spot expands to a spherical region at 100ns. which then detaches from the target until two components are visible at 300ns with a luminous region almost stationary close to the target.

Similar experiments carried out with an ArF excimer (Palau -*et al*) result in vacuum velocities of  $2 \times 10^4$  m/s. and indicate that the appearance of a luminous front and a slowing of the plume by the ambient gas at  $5 \times 10^{-2}$  mbar.

High speed photography of ablated magnesium with a KrF excimer (Dirnberger 1994) indicates that the plume expansion velocities are a function of laser fluence varying from  $10^4$  m/s at 3.5J/cm<sup>2</sup> to  $2.5 \times 10^4$  m/s at 11.7J/cm<sup>2</sup> at  $2 \times 10^{-5}$  mbar. Although the photographic techniques mentioned

show a remarkable consistency in terms of particle velocity, values as high as  $10^5$  m/sec. have been reported, (Anan'in - 1991), for extreme fluences  $9000J/cm^2$  ablating carbon and aluminium with a Nd:YAG laser This corresponds to an energy of up to 600eV for carbon and 1400eV for aluminium ions.

Photographic techniques in laser ablation are useful for understanding the nature of the interaction between the plume and the background gas, and the detail of the temporal change in the expansion velocity can be used to distinguish between different theoretical models of the gas plume interaction. The two models commonly referred to in the literature are known as the "drag" model and the "shock" model (Marine *et al* -1990 and 1991).

The shock model was developed to describe the propagation of a shock wave through a background gas where the mass of the material setting up the shock wave is small compared to the mass of the background gas set in motion. This last assumption may not be valid for the laser ablation plume. The equation of motion for an explosion in a gas described by this model for a spherical shock wave radius R is ..

$$R = \xi_0 (E/p_0)^{1/5} t^{2/5}$$

where,  $\xi_0$  is a constant, E is the energy of the ablated material,  $p_0$  is the density of the background gas and t is time.

Attempts at curve fitting the available R - t data for ablation plumes with this equation are generally unsuccessful, predicting greater propagation distances than those observed.

A closer fit is provided by generalising the equation to...

where n is nearer 3/5 than 2/5 and where a is a constant.

An alternative approach assumes that the plume behaves as if it were experiencing a viscous drag i.e one where the decelerating force is proportional to the velocity, this is called the drag model (Geohegan -1992).

At low pressures the drag model provides better agreement with experimental data (Palau J., Geohegan 1992, Ohkoshi 1994) but at higher pressures, high atomic mass gases (e.g. Xenon) and longer time scales the shock model is applicable. The reason that the data approaches a shock model curve over longer time scales is that the plume will compress a mass of gas a head of it and, as the mass of this compressed gas increases, the initial assumptions of the relative masses of ejecta and background gas in the shock model become more relevant.

## 3.2.3 Spectrographic techniques

Further information on the development of the ablation plume comes from analysing the emission and absorption spectra. The information available from this technique compliments the imaging techniques described earlier in that the spectra may be resolved both temporally and spatially. More importantly, however, the addition of the facility to analyse the spectrum of light emitted or absorbed by the plume allows the identification of many of the particles in the plume. The strengths of this method are:

- 1. a wide range of individual particles; ions, neutrals molecules, can be detected;
- 2. the analysis is compatible with almost all gases and geometries used in PLD and the plume spectra can be sampled at discrete locations;
- 3. spectrographic data can be collected during deposition allowing direct comparison between the condition of the plume and the resultant thin film made at a later date.

The weaknesses are:

- 1. Higher mass clusters and lumps cannot not be seen
- 2. There is a degree of ambiguity in the interpretation of the data as the spectra must be compared with standard tables which will have been compiled in under dissimilar conditions..
- 3. Although information is gathered in real time detailed interpretation of the data has to be carried out at a later date making this technique imperfect as an *in situ* diagnostic technique.



Figure 3.2 -Typical arrangements for spectroscopic studies of the ablation plume

Figure **3.2** is a composite diagram showing some of the general arrangements needed for spectroscopic analysis of the ablation plume by three different methods: emission, absorption and laser induced fluorescence.

For simple emission spectroscopy, the plume, or a small part of the plume, is imaged onto the slit of a spectrometer. The spectrum which is analysed for discrete emission or absorption bands originates from electrons, ions, excited neutrals and molecules undergoing conversion to lower energy states spontaneously within the plume.

The spatial development of the plume species can be monitored by imaging discrete areas at different points at the same time and the temporal development is monitored by triggering the output from the spectrometer after a controlled delay time from the laser pulse. By these two procedures

the velocities of different species can be calculated throughout much of the plume and the position of peak fluorescence measured in a variety of different conditions.

The number of species that can be monitored by spectroscopy may be augmented by the addition of a dye laser to stimulate specific absorption bands, (this is sometimes called LIF, laser induced fluorescence), or a by the use of a broad band illuminator such as a xenon flash lamp to allow the analysis of the absorption spectrum. Both these methods allow the observation of non excited neutrals much in the way that fluorescent spectroscopy allows the observation of naturally excited species.

In this way, spectroscopy allows a picture of the plume to be drawn by piecing together evidence of different particle types, target materials and deposition conditions.

## 3.2.3.1 Picosecond Laser Ablation

Although uncommon in PLD, the use of picosecond pulses for ablation has several advantages for studies of the plume by spectroscopy. The chief of these is that heat flow calculations indicate that practically no evaporation occurs during the first picoseconds of ablation pulse and the effects of laser-plume interaction are greatly reduced. This is corroborated by photo acoustic studies (Dyer *et al* - 1991). The velocity distribution is therefore that of the particles leaving the Knudsen layer without the interaction between the vapour and laser taking place.

For picosecond ablation of silicon, ( 35psec., 1064nm and 2.5J/cm<sup>2</sup> ), two velocity components can be seen, (W.Marine *et al* - 1992). The faster component has a velocity of the order  $10^5$ m/sec., (=1.5keV for atomic Si ), and appears immediately after the laser pulse and the slower component, ( $10^3$  m/sec. = 0.15eV), is delayed 10-50 ns. from the laser pulse and is present for a period some 10 times greater than that of the faster component. The particle velocities are proportional to their charge and the ionic particles show an inverse square root dependence on the mass. The dependence of velocity; this clearly leads to a charge separation in the plume appearing to

corroborate the Coulomb expansion model. Similarly, high plume velocities are found for  $YBa_2Cu_3 O_{7-\delta}$  ablation which translated into particle energies are 8.3eV - 1.4 keV for O+ ions and 71eV - 12keV for Ba+ ions.

Near the target surface the spectrum will typically consist of a broad featureless continuum representative of free-free or free-bound electronic recombination. There is a high concentration of particles in this region (typically  $10^{20}$  /cm<sup>3</sup>) and the frequent collisions lead to an averaged velocity.

At greater distances, (2-3mm, 50-90ns), time integrated spectra are dominated by more clearly defined emission peaks and particle velocities are determined from those with peak intensities at a certain distance from the target. These spectra are characteristic of the interaction between the plume and the background gas. Marine and Scotto d'Aniello, (W.Marine, *et al* -1992), suggest that the fact that the relationship between velocity and mass varies with distance from the target is due to space charge formation.

## 3.2.3.2 Nanosecond Ablation

Spectrographic studies of  $YBa_2Cu_3O_7$  ablation with an ArF laser at low fluences, (  $0.168J/cm^2$  ), show the presence of Y, Y<sup>+</sup>, YO, Ba, Ba<sup>+</sup>, and Cu in the plume but no Cu<sup>+</sup> (W.A.Weimer -1988 ). This is attributed to the relation between the ionisation potential of copper, (7.726eV), relative to other the species in the plume, (i.e. 6.378 eV for yttrium and 5.211eV for barium ) and the photon energy of the ArF laser radiation (6.42 eV). However other authors do find emission lines of Cu<sup>+</sup>, (Marine *et al* - 1992), (Girault *et al* - 1990) at higher fluences.

Emission spectroscopic studies of BiSrCaCuO under ablation with ArF radiation from 0.2 to 4 J/cm<sup>2</sup> (Gonzalo, *et al* - 1994), show the presence of Bi, Sr, Ca, Cu, Ca<sup>+</sup>, and Sr<sup>+</sup>, but no Bi<sup>+</sup>, Cu<sup>+</sup>, or diatomic oxide molecules were found. The maximum oxygen pressures used for these studies was  $7 \times 10^{-1}$  mbar.

Very highly ionised species have been found at high laser fluences. On ablating a silicon target at  $14J/cm^2$  with 532nm radiation, Si<sup>4+</sup> can be detected in the plume by X-ray absorption (K.Murakami - 1992), however

they are not present at 3.5 J/cm<sup>2</sup>. More recently (Sakeek *et al.* - 1994), report the formation of oxides at the contact front of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> plume in an oxygen environment.

There is some variability among spectroscopic studies concerning the velocities of the luminous components for different materials. For  $YBa_2Cu_3O_7$  typical quoted values vary between 1 - 1.3 × 10<sup>4</sup> m/s, (corresponding 45ev for Y<sup>+</sup> ions), (Girault *et al* - 1990, Fried *et al* - 1994), to up to  $13 \times 10^4$  m/s (corresponding to nearly 8keV for Y<sup>+</sup> ions), (W.Marine *et al* - 1992), with the velocity of individual ions found to be proportional to their charge and proportional to the inverse of the square root of the mass.

Similar velocities are found for Silicon targets i.e.  $1.3 \times 10^4$  m/s, (= 24eV ),

for Si<sup>+</sup> with ArF ablation 1-4 J/cm<sup>2</sup>, (15ns.FWHM), (W.Marine *et al* - 1994) also with a double peaked velocity distribution with the slower peak having half the velocity of the faster peak in broad agreement with picosecond ablation (W.Marine *et al* - 1992). Laser induced fluorescence, (LIF), studies of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> plumes, (K.Wanniarachchi *et al* -1993) show that the velocity of yttrium atoms and yttrium oxide molecules is consistent with a shifted Maxwell distribution and that the transition from drag to shock model takes place at a background pressure of 133mbar. Other authors, Otis and Goodwin (1993), report YO molecules from an YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> target follow a shifted Boltzmann distribution but that atomic species do not, they also find bimodal distributions in neutral atomic species and energies up to 200eV for Ba<sup>+</sup> ions.

Spectrographic monitoring during laser ablation is useful for determining the chemical as well as physical interaction between plume and background gases. In comparing suitable oxidising environments, the ablation products of an YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> target, LIF spectroscopy indicates that oxidisation does occur within the plume , (T. Okada *et al* - 1992 )and the majority of yttrium atoms are oxidised in the plume at oxygen pressures as low as 80mbar, (K.Wanniarachchi *et al* - 1993 ).

In addition it is possible to differentiate among oxidising gases. As mentioned earlier, Cu atoms need a greater energy input to oxidise in the plume than either barium or yttrium however LIF spectroscopy indicates that more CuO is present in an N<sub>2</sub>O environment than O<sub>2</sub> and more still in NO<sub>2</sub> by a factor of approximately two, (N<sub>2</sub>O), and four, (NO<sub>2</sub>), (Otis *et al* - 1993). In

addition, the optimum pressure for production of CuO can be gauged and is found to be a function of fluence, wavelength and gas type, (e.g. optimum at 193nm  $1.9J/cm^2$ , 266mbar (NO<sub>2</sub>), 330mbar (O<sub>2</sub>)).

In summary, spectroscopy is a useful technique particularly for monitoring of the material present in the plume in conditions identical to those employed for PLD.

The technique can be used in various guises to detect a wide range of monoatomic and diatomic ions and neutrals and to see them in different areas of the plume, up to within  $100\mu$ m of the target. In this context the technique has been invaluable in giving insight into reactions between the plume and the background gas and for giving insight into the existence and nature of the Knudsen layer.

In addition some information is available on the position of the shock wave of the plume within the ambient gas and this can be used to establish an optimum target substrate distance for deposition, (K.Wanniarachchi *et al* - 1993).

The disadvantages of optical spectrometry are that, although velocity information is available for specific particle types, it is generalised at best and is inferred from a set of experiments and, therefore cannot be used to for *in situ* monitoring or detailed energy analysis.

Other disadvantages of ablation plume spectrometry are:

a. the limited mass range of detectable particles which means that the clusters cannot be detected and

b. the need to have a complex array of separate pieces of equipment to detect both excited and non excited particles and their velocities.

## 3.2.4 Mass Spectrometric Techniques

Mass spectrometry can show an enormous range of breakdown products from the ablated target from single atoms and ions to relatively large agglomerations of particles almost up to the dimensions of the particles which constitute surface debris on the growing film. However, in the case of electronic ceramics, by far the most common components observed in the spectra produced by this method are the single atomic species and simple oxides. The energies of the particles in the ablation plume can often be measured more directly by their behaviour in an electric field, and by either measuring the time of arrival onto a suitable detector or by the use of an electrostatic analyser such as a cylindrical mirror analyser. The most common method used in this area is Time Of Flight Mass Spectrometry, (TOF mass spectrometry).

The advantages inherent in this technique are

- 1 It is very sensitive to ions ejected from the laser irradiated surface.
- 2. It can be extended to the study of neutrals by a system of preionisation such as electron impact ionisation, (EI), or by the use of a second laser, normally one with a high photon energy to ionise some of the neutral particles in the plume. In this way the data gathered with the ionising, laser on can be compared with data gathered with the ionising laser off.
- 3. A full spectrum of masses and energies can be obtained with far greater definition than the methods discussed so far allowing detailed comparison between separate ablation conditions.
- 4. Whereas, for example, spectrometric measurements of the plume are at best ambiguous for particles consisting of more than a few atoms mass spectrometry commonly allows atomic mass units of up to 600amu to be seen and in some cases (Becker and Pallix -1988) up to 400000amu.

The disadvantages of the mass spectrometric techniques are

 The most sensitive detectors need to be maintained in high vacuum (typically 10<sup>-6</sup> mbar) to function and hence are rarely used over the range of pressures employed for oxide deposition.

(The use of differential pumping does allow the deposition chamber to be maintained at a higher pressure than the analysis chamber but the skimmer needed for this is generally so small that the throughput of the system is severely limited when accompanied by a long drift region).

2. Time-of-flight systems either require large detector distances, (e.g. 201.5cm, Chrisey *et al* - 1991), or retarding voltages to ensure sufficient

velocity resolution at high particle velocities: these are not typical of deposition conditions.

 One possible disadvantage of any pre-ionisation system is that clusters may be broken up and hence some of the observed particles may be creations of the measuring system. Electron energies in impact ionisation systems must be limited to minimise this effect (Chrisey *et al* - 1991). This problem is not confined to mass spectrometry.



*Figure 3.3 - Typical time of flight mass spectrometer attached to a laser ablation chamber , (adapted from Chrisey et al - 1991).* 

Figure 3.3 shows a typical system for measuring particle energies and masses by time of flight. The differentially pumped region between the ablation chamber and ioniser can be designed in a number of ways to enable accurate timing of particle arrival and collision free transit. The simplest system is that shown in the diagram: particles leaving the ablation chamber enter a field free, differentially pumped drift region before entering the mass spectrometer.

The ions are separated from neutrals by electrostatic deflection plates and the signal coming out of the mass spectrometer is timed using the laser pulse as the zero point.

One common variation is to accelerated or decelerate ions passing down the drift tube either by a constant voltage or a pulsed voltage, (Murray and Peeler -1992), and is designed to sample ions within a discrete region and time interval. A disadvantage of this technique is the need to use a model to calculate kinetic energies from arrival times to allow for the convolution of the initial particle velocities by the external fields in the drift tube, (Wiedeman *et al* - 1991).



**Figure 3.4** - Velocity measurement by selective ionisation. Particles are ionised by a femtosecond laser pulse with a time delay, τ, after the laser pulse at distance d from the target. Ionised particles are passed to a mass spectrometer. (Späth and Stuke -1992)

One further approach to timing neutrals in the plume is to selectively ionise them with another pulsed laser. If this is done after a measured delay in a region of the drift tube from which ions have been excluded, (Späth and Stuke -1992), only neutrals within a certain velocity range will be present in the ionisation region. The velocity is calculated from the ionising laser pulse delay and mass can be calculated after passing the newly created ions through a mass spectrometer.

## 3.2.4.1 Mass spectrometry of electronic oxides

Mass spectrometry of the ablation plume with  $YBa_2Cu_3 O_{7-\delta}$  targets frequently indicates the presence of metal ions and metal monoxides and many authors observe more complex materials in the plume such as ions of BaCuO,  $Ba_2O_2$ ,  $YBa_2O_3$ ,  $YBa_2O_6H_2$ ,  $YBa_2O_6$ , (Venkatesan *et al* - 1988). Particles of mass 80 - 100 amu have been seen in the plume from an  $YBa_2Cu_3 O_{7-\delta}$  target (Izumi *et al* - 1991). In addition some very massive particles have been observed including regularly spaced peaks of mass up to 7300amu with an interval of 226amu between the peaks corresponding to the mass of  $Y_2O_3$  or YBa, (Becker and Pallix -1988). However this work was carried out with an unusual mix of wavelengths having both the fundamental and the second harmonic of the Nd:YAG laser, (i.e. 1064nm and 532nm), together and the mass spectrometer has an unusually high mass range so it is difficult to equate these findings with other mass spectrometer work.

In common with the spectrometric methods mentioned above CuO is sometimes absent or depleted in the plume relative other metal oxides, (Späth and Stuke -1992, Wiedeman *et al* - 1991, Alimpiev *et al* -1994; Izumi *et al* - 1991).

Above threshold fluences some authors, (Wiedeman *et al* - 1991) find that the ratio of YO<sup>+</sup> to Y<sup>+</sup> is increased with fluence.

In the case of LiNbO<sub>3</sub> ablation (Haglund *et al* - 1991), both dimers and trimers are found, Li<sup>+</sup>, Li<sub>2</sub>O<sup>+</sup>, NbO<sup>+</sup> and (Nb<sub>x</sub>O<sub>y</sub>)<sup>+</sup> indicating that in this case, as in that of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> particles of unit cell type dimensions can exist in the plume alongside the atoms and micron-sized particles.
### 3.2.4.2 Mass spectrometry of other materials

Another commonly analysed material studied by this technique is carbon, (generally in the form of pyrolytic graphite) which provides an interesting contrast to the behaviour of metals and ceramic oxides in its tendency to form stable groups as high as  $C_{60}$  known as buckminster fullerenes which can be synthesised by PLD, (Curl and Smalley, 1991).

Mass spectra show that many multi-atomic ionised species can also occur in the plume i.e.  $C_2^+, C_3^+, C_4^+$  with an increased proportion of  $C_4^+$  at 45° to the target normal (Murray *et al* - 1992; ).

Curiously, no C<sup>+</sup> is observed normal to the target in the above study. This is also the case with a study SiC, (Tench *et al* - 1990), although Si<sup>+</sup> is observed.

Although most research effort has been focussed on neutrals and positively charged ions, negative ions also exist in the plume. O<sup>-</sup> and LiNbO<sub>3</sub><sup>-</sup> ions have been observed by mass spectrometry in the plume from a LiNbO3 target, (Haglund *et al* - 1991) and Cu<sup>-</sup>, Y<sup>-</sup>, Ba<sup>-</sup> in the YBa<sub>2</sub>Cu<sub>3</sub> O<sub>7-δ</sub> plume with energies up to 350 eV, which are similar to the energies reported for positively charged ions (Alimpiev *et al* -1994).

#### 3.2.4.3 Energy Dispersive Mass Spectrometric Techniques

There is a great deal of variation in the details of the published energy spectra obtained by mass spectrometric methods. In part this may be due to the large number of possible arrangements of laser, fluence, spot size, target material, (both chemical and physical condition), and particle flight times which mean that no two experiments are identical.

Different measurement schemes inevitably will be more sensitive to particular parts of the energy spectrum than others. For example, electron bombardment ionisation is more efficient in ionising lower velocity neutrals, (Chrisey *et al* - 1991) although laser ionisation, (Späth and Stuke -1992), is very nearly velocity insensitive. However, in the latter case the ionisation

efficiency depends on the ionisation potential of the different atoms relative to the laser wavelength.

TOF measurements often require extended particle flight times and may reflect a lower proportion of ions in the plume than would be found at particle flight times typical in ablation conditions.

Nevertheless some general patterns do emerge.

Mass spectrometric investigations of ions naturally present in the ablation plume show higher energies than those of neutrals, (e.g. Wiedeman *et al* - 1991, Schenck *et al* - 1989) and where energy spectra of neutrals do show high energy components, particularly at higher laser fluences, they appear to be associated with ions that have undergone recombination in the plume, (Bykovskii *et al* -1987).

Much of the energy analysis in this area has taken  $YBa_2Cu_3O_{7-\delta}as a$ material to study due to its potential economic importance as well as the fact that the majority of PLD research is still on this material. Fukushima et al (1993) finding energies of up to 425eV for Y+ ions. Generally however, a representative range of kinetic energies found by TOF mass spectrometric techniques broadly reflects those found by TOF optical techniques (see table 3.1). A low energy thermal component is frequently observed together with high energy, (normally ionised), components which are not predicted by simple models of adiabatic expansion, or inverse bremsstrahlung effects, (e.g. Izumi et al - 1991). The explanation for this may well lie in the discussion of section 1.3.7. For an YBa<sub>2</sub>Cu<sub>3</sub> O<sub>7-δ</sub> target, energies of up to 300eV with no peak below 1eV have been reported for Ba+ ions ablated with an XeCl laser (308nm) at 0.78J/cm<sup>2</sup>, (Alimpiev et al -1994). These results were taken using an electrostatic filter: more commonly however, time based spectrometers report peak energies below 10eV and tails up to 50eV, (Venkatesan et al - 1988, Chrisey et al - 1991) with lower energies reported near the ablation threshold, (Späth and Stuke -1992, Wiedeman et al -1991).

It should be noted that extremely high kinetic energies have been reported using TOF techniques with Faraday cups as collectors, for example up to 2.4 keV in graphite ablation (Diaz *et al* -1992), and 1.7 keV for Zr<sup>+</sup> ions in ZrO<sub>2</sub> ablation (Sankur *et al* - 1987). However despite the fact that these energies

seem very high they are well within the range of picosecond spectroscopic analysis discussed in section **3.2.3.1**.

At low laser fluences, kinetic energy distributions generally approximate a Maxwellian distribution with temperatures < 10,000K and many authors find an improved fit with the addition of a drift or centre-of-mass velocity factor, (Nishikawa *et al* - 1994, Venkatesan *et al* - 1988, Späth and Stuke -1992).

At higher fluences the energy distributions of many materials no longer exhibit a simple Maxwellian distribution but may have much higher energies and multiple peaks, (Chrisey *et al* - 1991; Alimpiev *et al* -1994; Bykovskii *et al* - 1987; Murray and Peeler -1992, Venkatesan and Wu - 1988).

One possible explanation for multiple peaks in the energy spectra is that the more highly charged ions have separate, higher kinetic energy distributions, and that recombination effects in the plume cause a lowering in the ionisation number whilst retaining the kinetic energy, (Bykovskii *et al* -1987), (Alimpiev *et al* -1994).

However not all authors report higher energy peaks appearing even at high fluences for example, even at 80 J/cm<sup>2</sup>, (Schenck *et al* - 1989), do find multiple energy peaks, but they use a Maxwell Boltzmann curve fit of 8000K for the highest energy component which would indicate peak energies of only a few eV even for 'very hot' Cu<sup>+</sup>.

Higher energies are thought to occur, (Kools and Dieleman - 1993), in the ablation plume at the point at which gas phase heating becomes important, at higher fluences at a given wavelength and at lower fluences at longer wavelengths due to the increase in the absorption coefficient of the plasma. It should be noted that this is at variance the picosecond spectroscopic analysis discussed in section **3.2.3.1**.

Double peaks have also been observed by mass spectrometric techniques in the particle energy spectra during PZT ablation, (Leuchtner *et al* -1993) but at lower energies. They report double peaked distribution in the TOF spectra of neutral species, the lower velocity part of which can be fitted by a Maxwell Boltzmann distribution with temperatures of a few thousand Kelvin implying a thermal origin. The higher energy peaks are attributed to ionised

species which have been neutralised by free electrons in the plasma or perhaps arise from electronic ablation processes.

### 3.3 Patterns Emerging From Measured Kinetic Energy

The quantitative nature of data obtained by mass spectrometry allows detailed analysis of the photo ejected ions from an ablated target at different fluences.

Below the ablation threshold, increasing fluences lead to a linear increase in ion signal. When the threshold is reached the signal increases with fluence raised to a power (n) whose value is representative of the laser wavelength, (Wiedeman *et al* - 1991, Nishikawa *et al* - 1994, Haglund *et al* - 1991, Strupp *et al* -1991), the straight line of log. signal versus log. fluence implying a multiphoton absorption process as in figure **5.3**. The slope decreases with increasing wavelength and the slope, if constant, indicates the number of photons involved in the ablation process.

Well above the threshold for ablation, two interesting features are often observed in kinetic energy spectra. Beyond a certain point, increased fluence does not lead to an increase in either the position of the energy peak or the count rate.

Firstly the plateau in the signal is thought to be caused by plasma shielding, (Alimpiev *et al* -1994). Secondly the energy at which signal peaks occur generally follow a similar trend.

At lower fluences, (e.g <1J/cm<sup>2</sup> at excimer wavelengths), the kinetic energies are normally relatively low, i.e.<1eV (this is below the point at which space charge and plasma acceleration would be expected to take place), and the energy peak then moves to higher energies with increasing fluence, but only up to a point, (Wiedeman *et al* - 1991, Nishikawa *et al* - 1994).

However, at higher fluences, (e.g.  $2-8 \text{ J/cm}^2$ ), there is some evidence that a plateau appears in ion energy peak position versus fluence, (Nishikawa *et al* - 1992) and the position of the peak itself will be high (e.g. 60eV in the above reference). This is consistent with plasma shielding as with the plateau in signal intensity. However it should be noted that the maximum detectable energy in the above reference is close to the measured energy peak. Kools

and Dieleman find a plateau in the evaporation temperature of copper at lower fluences (starting at 1.35 J/cm<sup>2</sup>) which they ascribe to a catastrophic decrease in laser/target coupling at the critical temperature, (Kools and Dieleman - 1993).

For very high fluences, ( $15 - 200 \text{J/cm}^2$ ), in  $\text{ZrO}_2$  ablation giving the very high energies mentioned earlier Sankur finds the plume velocities to be proportional to the cube root of fluence, (Sankur H., J. DeNatale - 1987).

However, high kinetic energies are not found exclusively at high laser fluences, and their are situations in which kinetic energies of several hundreds electron volts are measured under very ordinary conditions, , (0.1- $1.5 \text{ J/cm}^2$ , 308nm, 15ns, YBa<sub>2</sub>Cu<sub>3</sub> O<sub>7- $\delta$ </sub> target ), (Alimpiev *et al* -1994). In this case increased fluences do lead to higher kinetic energies even though the maximum fluences are 0.78 J/cm<sup>2</sup>. The only unusual feature in this study apart from the high energies quoted is the electrostatic energy filter used.

### 3.3.1 Variation of Ejecta Velocity with Particle Mass

The velocities of the different mass components of complex target have been extensively studied, and under most conditions, the spread and peak velocities of plume ejecta decrease with increasing mass. In the higher laser fluence regime, a relationship sometimes appears of the form:

 $v = K(1/m^{1/2})$ , with v the particle velocity, m the mass and K a constant.

Chrisey and Horwitz find that this relationship holds true for oxide neutrals but not atomic species and clearly implies a constancy of kinetic energy over different masses, (Chrisey *et al* - 1991). This is consistent with some of the observations from optical TOF spectrometry, (Marine *et al* -1992).

However, for negative ions a constant average velocity among the monoatomic metals in the  $YBa_2Cu_3 O_{7-\delta}$  plume has been reported (Alimpiev *et al* -1994).

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### 3.3.2 Ageing Effects In The Target

The change in the physical nature of the target as the ablation progresses effects both the physical and under, non-ideal conditions, the chemical nature of the target. The most obvious effect is that of pitting in the target, which is particularly noticeable when the laser follows a repeated path across the target under such conditions a visible trough is quickly formed. In some circumstances a complicated structure of microscopic cones angled toward the laser is formed on the target surface, (Thomas et al - 1992). Clearly, under these conditions, cone shaped structures may cause the segregation of material. Hence the energy and mass spectra obtained from an ageing target can be expected to contain a proportion of particles emanating form oblique surfaces. The effect of this is not straightforward but it can leave to the suppression of certain energy peaks in complex neutral energy distributions. More specifically, the neutral copper component of an YBa<sub>2</sub>Cu<sub>3</sub> O<sub>7- $\delta$ </sub> ablation plume looses a higher energy peak but not the other metals, (Chrisey et al - 1991). Becker and Pallix observe a marked change in the mass spectrum in an eroded target with the regularly spaced high mass peaks are more clearly defined but with a lower signal relative to the background level (Becker and Pallix -1988).

### 3.3.3 Plume modelling from energy spectra.

What insights can be gained from mass spectrometry into the physics of the ablation plume and the consequences for thin film formation ?

Kinetic energy / velocity spectra with lower energies can normally be modelled by a classical Maxwell Boltzmann distribution sometimes with the addition of a centre of mass velocity ( see appendix). If the velocity measurements give angular dependant information the concept of elliptical temperatures can be tested as discussed in section **1.3.6.2** (Kools and Dieleman - 1993 ). The temperatures which fit the observed energy distributions often remain high compared to the critical temperatures of the target material even for distributions in the lower range of those reported. Kools and Dieleman point out that particles moving backwards in the Knudsen layer will recondense on the target surface and will be removed from the distribution. This will have the effect of increasing the effective, calculated temperature above the expected limitation of the critical temperature.

One of the main problems arising from the plume kinetic energies found both by TOF optical and mass spectroscopy is that the energy values are often far higher than would be predicted by thermal desorption processes even taking into account the proviso mentioned above. The strength of mass spectrometric techniques are that they may be more conducive to putting detailed numbers on the data which allow comparison with theory.

Work on the ablation of  $Bi_2Sr_2CaCu_2O_8$  and  $YBa_2Cu_3O_{7-\delta}$  at low laser fluences, (Wiedeman *et al* -1991), and of LiNbO<sub>3</sub>, (Haglund *et al* -1991), illuminates the role of electronic ablation mechanisms in the formation of the ablation plume that were discussed in section **1.3**.

The slope of a straight line in a Log (fluence) versus Log (signal) graphs gives the number of photons involved in a possible multiphoton process and the product of the photon energy and the slope should correspond to the excitation energy of ion ejection. If this value is constant for different laser wavelengths, added credibility can be given to the existence of multiphoton processes.



The relationship between ablation laser photon energies and the energy bands can be related to the onset of ablation, (Haglund *et al* -1991).

VALENCE BAND

**Figure 3.5** - Energy level diagram of LiNbO<sub>3</sub> in relation to Nd:YAG wavelengths with arrow lengths representing the photon energies.

Figure 3.5 shows how a Nd:YAG laser can be used to probe the energy levels in  $LiNbO_3$  and explains the difference in the onset of ablation with fluence for different laser wavelengths, (Haglund *et al* -1991).

The maximum kinetic energies of Cu<sup>+</sup>, Sr<sup>+</sup> and Bi<sup>+</sup> ions measured by Wiedeman and Kim in the  $Bi_2Sr_2CaCu_2O_8$  plume show broad correspondence with the energy that is predicted by Knotek-Feibelman theory, (Knotek and Feibelman - 1978). In this theory a subshell excitation will undergo Auger decay and may create a localised two hole pair. The resultant Coulombic force can eject one of the ions with a maximum kinetic energy which can be calculated from

K.E.<sub>max</sub> =  $e^2 / R_0$  where  $R_0$  is the bond length.

Wiedeman and Kim show broad agreement between the maximum recorded kinetic energies and those predicted from the bond lengths, (the kinetic energy values in question are low being 7.0 eV for the Cu-O bond, 6.3 eV for Bi-O, 5.5 eV for Si-O but are a great deal higher than would be predicted by thermal processes ). The conclusion of this work is that the kinetic energy of emitted ion cannot be explained by a thermal desorption model but are consistent with a Knotek-Feibelman excitation coulombic explosion process. Higher fluence and high kinetic energy data can be more difficult to interpret. Many authors report that the energy spectra of the plume ejecta are very complex and to not lend themselves to simple analysis. The work of Chrisey and Horwitz with YBa<sub>2</sub>Cu<sub>3</sub>  $O_{7-\delta}$  energy spectra, finds a high quantity of neutral particles above 10eV and multiple irregular peaks; it is difficult to model the data with existing mechanisms and they remark that there is even some variation between targets. They ascribe this complexity to the target itself and point out phase, local stoichiometry and density changes which take place in a complex multi component target such as YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> during ablation. However the  $1/M^{1/2}$  (where M is mass) relationship for oxides does appear to corroborate the adiabatic expansion model of Singh, (Singh and Holland - 1990)

Kinetic ion energies as high as 200eV in the YBa<sub>2</sub>Cu<sub>3</sub> O<sub>7- $\delta$ </sub> plume, (Izumi *et al* - 1991), are even more difficult to explain by laser solid interactions or subsequent laser absorption in the plasma. The authors suggest acceleration of ions by self consistent electric fields during ablation following the model proposed by Gurevich *et al* - 1973. In this model the lighter electrons expand more rapidly than the ions, setting up a self consistent electric field in the plume which accelerates the ions to the high energies observed, (hundreds of eV).

#### 3.4 Other Plume Analysis Methods

The interaction between the laser beam and the plume has been investigated by measuring the reflectivity of the ablation plume for a silicon target under 193nm radiation well above the ablation threshold, (Tokarev *et al* -1994). The results indicate that three photon absorption is the dominant mechanism under these conditions and that inverse bremsstrahlung absorption has a negligible influence. Figure **3.6** below shows how these measurements are obtained.



*Figure 3.6 -* Arrangement for measuring the reflection from the plume (Tokarev et al -1994).

Light directly from the laser is used to trigger the oscilloscope and the light reflected in the opposite direction is filtered to eliminate the emissions from the plume and taken as the measure of plume reflectivity.

A novel approach that has been used to monitor the temporal development of the plume during ablation utilises the transient pressure produced on the target by the ejected material, (Dyer *et al* - 1991). The method uses a piezoelectric transducer attached to the rear of the target. Results from KrF ablation of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> indicate that ablation begins during the 10ns laser pulse and indicate that species of high average mass are ejected in the initial ablation step.

### 3.5 Conclusions

The evidence furnished by mass spectrometric methods is particularly useful in illuminating the detailed processes happening within the plume at low pressures where the interaction between plume and gas is limited, (below  $5 \times 10^{-2}$  mbar judging from optical measurements ). This allows plume modelling in detailed way and there is a good agreement between theory and experiment in the low energy regime. Unfortunately, when high kinetic energies occur, there is much contradictory evidence about the actual kinetic energies found within the plume. Although it is often stated that high plume energies are found at high laser fluences and long wavelengths due to the effects of inverse bremsstrahlung this is not always the case (Alimpiev *et al* -1994). The disparity in energy spectra among published data is illustrated by table **3.1** which looks at some of the energy spectra for some metal oxides ceramics both of optical and electrostatic measurement methods.

Table 3.1 shows some of the published data on the energy spectra of metal oxides showing the range in energy spectra that have been gathered. There appears to be no consensus or clear trend. Whereas some authors find high energies at u.v. wavelengths and low fluences, (Izumi and Alimpiev) and low energies at longer wavelengths despite high fluences (Shenk), the highest reported energies are for low fluence, (Alimpiev, Marine) and very high fluence, (Sankur). This indicates the difficulties involved in finding a consensus of opinion in this area, implying that instrumental and material

factors may be important. However this table does bring into question the simple assertion that high plume energies result from laser/plume interactions which are strongest for high fluences, long wavelengths and long pulse durations. Bimodal distributions are reported frequently (e.g Chrisey *et al* -1991, Schenck *et al* - 1989, Alimpiev *et al* - 1994, Bykovskii *et al* - 1987, Murray -1992) generally being ascribes to recombination effects however for low energies peaks (well below 1eV) a possible source may be from neutral materials in the liquid phase (Wakata *et al* - 1994).

FIRST AUTHOR	LASER (nm)	FLUENCE (J/sq.cm)	max ENERGY (eV)	ENERGY peak (eV)	TARGET	IONS/ NEUTRALS
IZUMI	193	1.0	200	20	YBCO	
CHRISEY	248	2.9	50	0.5	YBCO	N
VENKATESAN	266	60	40	7.0	YBCO	N
ALEMPIEV	308	1.5	300		YBCO	(+,-)
SHENCK	532	80	6	1.0	YBCO	N+I
STUKE	248	0.2	1.3	0.3	BISCC O	N
NISHIKAWA 1992	248	7.5		60+	SrTiO3	1
SANKUR	10500	200	1700		ZrO2	1
GIRAULT *	248	4	78	46	YBCO	1
MARINE 1*	1064	2.5	8000	46	YBCO	1
MARINE 2*	193	1.4	25	25	Si	1

**Table 3.1** - Comparative table of the energy ranges of particles found in<br/>ablation plumes by TOF mass spectrometry and (\*) time resolved<br/>spectroscopy. Energies that have been calculated from velocities are taken<br/>for the mass of yttrium in the case of YBCuO and for an average mass of the<br/>compound for other materials.

FIRST AUTHORS	LASER (nm)	FLUENCE (J/sq.cm)	max ENERGY (eV)	ENERGY peak (eV)	TARGET	IONS/ NEUTS
Tyrrell & York 1994	532	4 - 13	400	100	Fe	1
Tyrrell & York 1994	532	0.43	50	5-30	YBCO	1
Tyrrell & York 1995	532	0.9	30	15	BSCCO	I
Tyrrell & York 1995	532	4	250	150	BSCCO	I
Tyrrell & York 1996	248	7	160	20 & 120	PZT	1
Tyrrell & Coccia 1996	248	5	60	10 &30	Cu	I

Table	3.2 - Com	oarative t	able of	the e	nergy	ranges	of particles	found	in
	ablation	plumes b	y techr	niques	descri	ibed in	chapter 4.		

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## 4.0 ANALYSIS OF THE ABLATION PLUME

Much of the work presented in this chapter and subsequent chapters on the analysis of the ablation plume and deposition of lead zirconate titanate has been published in a series of four papers.

1. Kinetic Energy and Mass Distribution of Ablated Species formed during Pulsed Laser Deposition - G.C.Tyrrell, T.H.York, N.Cherief. D.Givord, J.Lawler, M.Buckley and I.W.Boyd., *Microelectronic Engineering*, Volume **25** (1994) pages 247 to 252.

2. Characterisation of Ionic Species Generated During Ablation of  $Bi_2Sr_2Ca_2Cu_3O_{10}$  by Frequency Doubled Nd:YAG Laser Irradiation.-G.C.Tyrrell, T.H.York and I.W.Boyd., *Applied Surface Science*, Volume **86** (1995) pages 50 - 58.

3. Kinetic Energy Distributions of Ions Ejected During Laser Ablation of Lead Zirconate Titanate and their Correlation to Deposition of Ferroelectric Thin Films - G.C.Tyrrell, T.H.York, L.G.Coccia and I.W.Boyd. (1996) *Applied Surface Science*, in press.

4. Energy Distribution and Mass Spectrometry of High Energy Ions Generated During KrF Excimer and Frequency Doubled Nd:YAG Laser Ablation of Metals. - G.C.Tyrrell, , L.G. Coccia T.H.York and I.W.Boyd. (1996) *Applied Surface Science*, in press.

In order to understand the nature of ablation plume, a series of experiments were carried out designed to analyse both the energy and mass of ionised species within the plume, simultaneously. In contrast to some of the earlier work discussed in this area, the aim of these experiments is primarily to gain insight into the actual conditions in the plume during PLD. Consequently the targets are not generally single crystal or highly polished and are allowed to age over a similar period to those involved in deposition.

The second aim of these experiments is to evaluate the possibility of developing an *in situ* analysis tool for PLD to optimise the deposition

에는 것 같은 것은 것을 가지. 같은 것 같은 것은 것 같은 것을 가지? conditions in real time. Detailed knowledge of the ablation plume is particularly useful in that it allows the researcher to separate plume and substrate effects in film deposition. Substrate effects (i.e. the deposition rate, the substrate temperature, the substrate material and the reaction between the growing film and the ambient gases) can also be measured *in situ* but detailed analysis of the thin film is more commonly measured *ex situ* ( see appendix).

An energy dispersive mass spectrometer manufactured by VG quadrupoles and based on concepts developed by Ron A. A. Hack, Ivo J. M. M. Raaijmakers and Jan Visser at Philips Research, Eindhoven, (J. Krumme *et al* - 1991) was used for this study. The equipment was originally developed to analyse plasmas in magnetron sputtering and a similar one was used by Shi *et al* - (1989 and 1990), to obtain real time mass and energy spectra of ions in the laser ablation plume.

Figure 4.0 shows the arrangement employed for this analysis.

In essence the system is identical to that used for pulsed laser deposition except that the position of the substrate holder is taken by a cylindrical mirror analyser, (CMA), which leads into a quadrupole mass spectrometer, (QMS). The distance between the entrance to CMA and the target was 65mm for all experiments unless otherwise stated.

A Q-switched Nd:YAG laser, (maximum output - 0.5J/ pulse, repetition rate - 10Hz. and pulse width - 4ns), was used as the ablation source operating at 532nm.

The analysis section of the apparatus, beyond the CMA entrance aperture, (**fig 4.1**), is differentially pumped by a 200l/sec. turbomolecular pump allowing a pressure of up to  $10^{-1}$  mbar to be maintained in the ablation chamber whilst allowing the CMA/QMS to remain at a working pressure of below  $10^{-6}$  mbar.



Figure 4.0 - Overview of plume analysis experiment

In contrast to some of the time of flight arrangements discussed in section **4.2.4.4** this does not severely limit the transmission of the system as the CMA is placed relatively close to the substrate.

The combination of QMS and CMA allows spectra of the ions in the plasma to be obtained in two ways

In 'energy mode' the ion energies are scanned for a set value of mass per unit charge. In this mode the energy pass window of the CMA is scanned continually, allowing all particles of a given energy, specified by the point of the CMA in its scan, to pass through the QMS. The QMS then allows only those ions with a specific mass to charge ratio to pass to the channeltron detector. In 'mass mode' the mass per unit charge is scanned at a fixed energy. This mode is the complement of the energy mode, in that the CMA is set to pass a fixed energy and the QMS pass mass window is scanned. Figure **4.1** shows the analysis section in more detail.



Figure 4.1 - Passage of ions through CMA/QMS

Particles enter from the ablation chamber by first passing through an entrance orifice (aperture), lens 1 in figure 4.1, which forms the boundary between the two chambers, they then pass the ion transfer optics, (einzel lens) with an acceptance angle of ~1degree and pass the repeller.

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Figure **4.2** is a detail of the cylindrical mirror analyser used for this experiment. This design differs from the conventional one in that it accepts particles from a parallel source rather than the a point source.



Figure 4.2 - Detail of cylindrical mirror analyser and voltages

Within the CMA, ions can pass only with a certain energy, (Epass), typically between 10 and 25V, determined by the electrode geometry's and voltages  $V_T$  and  $V_B$ , . To enable the CMA to analyse a spectrum of ion energies, the incoming ion energy is scanned by ramping  $V_{cma}$  such that ...

original ion energy =  $E_{pass}$ +  $eV_{cma}$ 

Thus  $V_{cma}$  will act as a retarding potential when passing ions with energies higher than  $V_{cma}$  and an accelerating potential for ions with an energy less than  $V_{cma}$ . As  $V_{cma}$  is ramped, ions passing the CMA at energy  $E_{pass}$  actually represent incoming ions within a narrow energy window determined by the formula above.

The CMA creates a diverging beam at an optimum angle of 42.3 degrees from the broadly parallel beam entering the system and, in conjunction with an Einzel lens, injects a re-collimated beam into mass spectrometer at an energy of typically 3eV which maximises the QMS throughput. This is achieved through the pole bias facility which floats the quadrupole rods relative to earth potential.

i.e., original ion energy = pole bias + 3ev

The energy and mass ranges are 0-500eV with ~0.7 eV resolution and 0 - 600amu with ~1amu resolution, respectively.

lons exiting the QMS are detected by a channel electron multiplier operating in pulse counting mode sending signals to a rate meter.

The repetition rate of the laser used for these experiments was 10Hz. unless otherwise stated and the rate meter was set to a gate time of 0.1 sec. and a slew delay of 1ms. This enables efficient sampling of the plume without triggering the laser.

Since the gate time is very much larger than the plume duration, each reading will correspond to one laser pulse and one individual plume.

The choice of entrance aperture is a trade off between ion throughput and differential pumping efficiency. Above  $10^{-6}$  mbar the channeltron detector, (channel electron multiplier), becomes noisy and an aperture below about 0.1mm gives an impractically small signal for practical target-substrate geometries and laser spot sizes. In practice an aperture (orifice or lens 1 in figure **4.1**) of 0.45mm was used for the majority of the spectra obtained and this limits the pressure in the ablation chamber to a maximum of  $10^{-1}$  mbar, a more detailed discussion of the effect of aperture size on energy spectra will be given later.

There are a number of advantages to maximising the intervals between opening the system to atmosphere.

Even with a small laser spot size and low laser power the target suffers from rapid ageing. This is particularly problematic when a series of experiments are being undertaken comparing energy spectra at range of fluences or masses, which might entail 10 minutes of continual ablation. In addition the channeltron can suffer from degassing which affects its response immediately after evacuation, (Kurz, 1979). It takes at least an hour to evacuate the system to 10<sup>-6</sup> mbar and therefore a multiple target holder was designed with a novel

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mechanism that allows four targets to be selected and rotated using a single vacuum feedthrough, (fig 4.3).



FRONT VIEW

SIDE VEW

*Figure 4.3 -* The multiple target holder used for plume analysis experiments.

The device is made of stainless steel and PTFE with no metal-to-metal bearing surfaces. Four 13mm pressed ceramic targets can be held at one time.

The central shaft passes through a rotary feedthrough and is made to rotate by a stepper motor. When the shaft is made to rotate in one direction it causes the targets to turn by virtue of the central steel cog which turns the PTFE cogs behind each separate target holder. The body of the mechanism prevented from turning by the spring steel ratchet system. However, turning the shaft in the opposite direction causes the body of the holder to rotate as well as the targets. The targets have a higher rotational friction relative to the rotation of the main body and therefore the whole body of the holder rotates bringing a different targets in line with the laser.

The multiple target holder is protected by a steel mask, (not shown), with an orifice the size of the target in it, preventing the targets from being contaminated by back sputtering when not in use. An incidental advantage of

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this target holder is that the slight wobble of the main drive shaft during rotation allows the laser spot to ablate a new region of the target for over ten rotations.

The first set of experiments used iron as a target.

Iron is a simple monocomponent material which was found to give a stable plume, with energy spectra that vary little over extended scan times. In this context iron provides an ideal material to characterise the system and establish ideal operating conditions to use as a springboard for the analysis of complex multicomponent metallic oxides.

# 4.1 The Importance of Correct Plasma Sampling.

A large number of obstacles have to be overcome before this equipment can be used to manipulate the partially ionised, rarefied gas which is the ablation plume. As mentioned earlier the system was originally designed to work with conventional plasmas and the difficulties encountered when adapting it to work with the laser plume illustrate some of the differences between the plume and a stable plasma.

The importance of differential pumping was illustrated by initial experiments performed before the differential pumping arrangement was employed, under these conditions no energy spectra are obtained, instead simply a series of regularly spaced lines across the entire energy range were visible.

After the system had been adapted, a 3mm aperture, (orifice or lens 1 in figure **4.1**), was fitted in the entrance to the CMA forming the beginning of the differentially pumped region, with the result that many of the energy spectra had the general form shown in figure **4.4**.

The energy spectrum in the figure 4.4 is part of a range of data collected with the QMS passing 56amu and optical filters placed in front of the focusing lens to vary the fluence, with a spot size of  $3.55 \times 10^{-2}$  cm<sup>2</sup>, (the other readings are not shown). At lower fluences a full spectrum of energies up to 200eV was observed but as the fluence was increased parts of the spectrum began to disappear normally the high energy part. The other conditions were those used for the majority of the experiments described i.e. laser-532nm, 10Hz..

repetition rate, 4ns. pulse duration and the CMA adjusted to detect externally generated ions with a pass energy of 25eV.



**Figure 4.4 -** A typical Fe<sup>+</sup> ion spectrum with a laser fluence of 1.33J/cm<sup>2</sup> at 532nm. and with a large (3mm) orifice at the entrance of the CMA and spot size  $3.55 \times 10^{-2}$  cm<sup>2</sup>.

Two counter intuitive features stand out immediately from this series of experiments :

1. The total, integrated count rate is lower for higher fluence ablation conditions above a certain point, ( $7.4J/cm^2 - 10191counts$ ,  $1.33 J/cm^2 - 11479counts$ ,  $0.75J/cm^2 - 60429$  counts). This is not in itself impossible but the energy cut-off is very sharp and occurs at a laser fluence of less than  $2J/cm^2$  and remains for all fluences above that value.

2. In the case of all the ablations from 7.4 J/cm<sup>2</sup> to 1.33 J/cm<sup>2</sup> there are no counts above 50 eV; and the 0.74 J/cm<sup>2</sup> ablation spectrum is very jagged with the counts varying wildly from point to point.

These results are typical of a number of experiments with different materials and a 3mm orifice and are difficult to explain in terms of a real physical effect.. Above 0.75J/cm<sup>2</sup> all spectra obtained under these conditions show the features visible in the spectrum above. Other, smaller orifices were tried with the result that the fluence at which spectra typical of figure **4.4** were obtained increased with decreasing orifice size.

A working assumption was made that high particle fluxes may prejudice the passage of ions in the CMA leading to unreliable readings particularly at higher laser fluences.

Re configuring the system with a smaller orifice, (.45mm), and a smaller spot size gave the spectra reproduced in figure **4.5**.



**Figure 4.5-** A typical Fe<sup>+</sup> ion spectrum with a laser fluence well above the ablation threshold at 532nm and with a small (.45mm) orifice at the entrance of the CMA and spot size  $3.55 \times 10^{-2}$  cm<sup>2</sup>.

The spectrum of fig **4.5** is characteristic of medium to high fluence spectra obtained with iron targets once the 0.45mm orifice had been installed. This particular example was obtained at a fluence as high as 13 J/cm<sup>2</sup> and a spot size of  $2 \times 10^{-3}$  cm<sup>2</sup> and illustrates the importance of using a small orifice and small spot sizes to limit the number of ions in the CMA.

Two main features are clearly visible

1. an initial steep rise in count rate from very low values at thermal energies rising to a maximum at between 20eV and 35eV.

2. a general flatter distribution of energies between 50eVand 250eV and then a gradual fall off to300eV.

Above 300eV there are very few counts with iron targets at these laser fluences.



4.2 Objective Criteria for Appraising Energy Spectra.

**Figure 4.6** - Oscilloscope trace of the voltage drop in V<sub>cma</sub> superimposed on an energy spectrum of Fe<sup>+</sup> collected with a 3mm orifice.

Although the behaviour of the spectrum appeared more predictable with the smaller orifice it was realised that a more objective test was needed before any confidence could be placed in the energy spectra obtained with the CMA. Running a series of CMA scans at different fluences and spot sizes indicated that the onset of unreliable readings began with certain parts of the spectra disappearing under conditions of large spot size and high fluence.

The CMA was therefore partially dismantled and all the voltages on the different electrodes measured during operation, to see whether they were being controlled correctly.

Figure **4.6** shows the result of an experiment to gauge the voltage drop in the central element of the CMA during deposition under conditions, (laser fluence spot size) chosen to maximise the quantity of ablated material. The energy curve data has been smoothed to aid presentation and allow the two curves to be superimposed since the raw data curve varies widely. The oscilloscope data was obtained with the system set in mass mode at 56amu and the set energies indicated in the graph. Figure **4.6** shows that high fluences can have a pronounced effect on the voltage  $V_{cma}$ , with this voltage differing by up to 6V from the set voltage, furthermore at the points of greatest voltage drop the energy spectrum disappears completely. Therefore by recording this voltage it is possible to monitor the reliability of the collected data; the condition for reliability being that for which  $V_{cma}$  is within one volt of its correct value throughout the entire range.



**Figure 4.7** - Oscilloscope trace of the voltage drop in  $V_{cma}$  superimposed on an energy spectrum of Fe<sup>+</sup> collected with a 0.45mm orifice.

By contrast with figure **4.6**, figure **4.7** shows a similar graph under more typical ablation conditions. There is still a very slight drop in  $V_{cma}$  at the point of greatest signal indicating that the peak energy may be somewhat

underrepresented at that point only but their is no deviation in  $V_{cma}$  at all over the rest of the spectrum .

The above information provides a basis for further work with the CMA/QMS. The oscilloscope data can be used to check that the CMA voltages are not being distorted when an energy or mass spectrum is being gathered and particular care is taken when high particle fluence is expected or unforeseen gaps in the spectra occur.

## 4.3 Curve Fitting for Simple Energy Distributions in Iron Ions.

Working under the conditions described above in which the number of ions passing through the CMA is limited by the use of a small, (0.45mm), aperture, and spot size ( $2 \times 10^{-3} \text{cm}^2$ ) whilst monitoring the  $V_{cma}$ , the energy spectra obtained can be analysed with confidence that they represent a genuine reflection of the conditions within the plume.

At first sight data such as that shown in figure **4.5**, which is a typical high fluence energy spectrum, does not fit a simple Maxwell-Boltzmann distribution. However, superposition of Fe<sup>+</sup>, (singly charged iron ions) and  $Fe^{2+}$ , (doubly charged iron ions) energy distributions suggests that the distribution of figure **4.5** may composed of two parts, (see fig **4.8**).

The higher energy part of the Fe<sup>+</sup> spectrum appears to follow the distribution of the  $Fe^{2+}$  ions, suggesting either that there may be a physical association between the two spectra or that there are two separate mechanisms dictating the shape of the ion spectrum.

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*Figure 4.8 -* Energy spectra of iron ions with standard target-orifice distance (65mm)

The former possibility would imply that some of the Fe<sup>+</sup> ions are remnants of former  $Fe^{2+}$  ions that have gained an electron in transit between the target and the CMA entrance aperture.

Further evidence for this hypothesis comes from comparing spectra taken under similar conditions with different target orifice distances ensured by replacing the 10cm spacer in front of the CMA with a 26cm spacer

In figure **4.9** the lower energy part of the Fe<sup>+</sup> spectrum has almost disappeared whereas the higher energy portion remains; implying that the majority of the remaining Fe<sup>+</sup> ions originated from Fe<sup>2+</sup> ions.

A similar effect is seen with other metals and with carbon see section **4.4**. With iron targets the singly charged distribution splits into two components with increasing CMA-target distance, and there is a slight increase in maximum energy.



**Figure 4.9** - Energy spectra of Fe<sup>+</sup> and Fe<sup>2+</sup> ions with the target-CMA distance increased to 225 mm relative to conditions of figure 4.13.



*Figure 4.10 -Simple Maxwell Boltzmann curve fits for the energy distribution of iron ions.* 

If the spectra for Fe<sup>+</sup> is taken as a composite of two simple curves then Maxwell-Boltzmann distributions with different temperatures can be used as an approximate fit. An example of this is shown in figure 4.10.

The formula for Maxwell Boltzmann, (M-B), curve fits used for the plot of figure 4.10 is .

 $f(E) = A_1.(E^{3/2}).exp(-E/kT_1) + A_2.(E^{3/2}).exp(-E/kT_2)$ 

Where E is the ion energy, T the plasma temperature,  $A_1$  and  $A_2$  are scaling constants to allow for the arbitrary count rate and k is Boltzmann's constant i.e. 8.6×10<sup>-5</sup> eV/K

The two specific curve fits whose sum forms the thicker line in figure 4.17 are for  $T_1 = 130000$ K and  $A_1 = 10$  for the lower energy part of the spectrum and  $T_2 = 1200000K$  and  $A_2 = 0.1$  for the higher energy component.

Although the general trend of the composite curves follow the Fe<sup>+</sup> spectrum the higher energies are clearly badly represented. This is due to the fact that the plasma temperature for the high energy curve fit  $(T_2)$  is too high leading to a long high energy tail despite the fact that the peak energy is more or less correctly positioned.

A better fit can be found by modifying the standard Maxwell-Boltzmann (M-B) through the introduction of the concept of a stream velocity, (NoorBatcha et al, 1987 and 1988, Kelly and Dreyfus 1988 a and b) which alters the distribution, (in terms of velocity distributions), to...

 $f(v)=A.v^3.exp[-m(v-v_{cm})^2/2kT_{eff}]$ 

Where  $V_{cm}$  is the centre of mass, (or stream velocity), of the particles in the plume, T<sub>eff</sub> is the effective plasma temperature and A is a scaling constant. Replotting the data from figure 4.10 as velocity, rather than energy, versus count-rate and using the sum of two stream velocity M-B distributions, gives the result shown.

The curve fit of figure 4.11 is clearly an improvement on distributions based on a Maxwell-Boltzmann distribution without taking the centre of mass velocity of the plume into account. The disparity between the real data and the curve fit is still greatest at higher velocities, ( $>3 \times 10^4$  m/sec.), although not to the same extent as the curve fit of figure **4.10**. Further disparities are noticeable at intermediate velocities, ( $1.75 \times 10^4$  m/sec.), however this is an area that can show greater variation as the target ages.



Figure 4.11 - Velocity distribution of Fe ions with M-B curve fits with allowance for stream velocity adaptation.

### 4.4 Energy spectra of Iron lons at different pressures.

Figure **4.12** shows the change in high fluence,  $(13J/cm^2)$ , energy spectra from an iron target as argon is introduced into the chamber. Between  $10^{-7}$  and  $10^{-5}$  mbar little change is observed in the overall energy distribution but at  $10^{-3}$  mbar a clear decrease in the quantity of ions detected between 100 and 200eV is observed and more particles appear between 0 and 20eV.

At 10<sup>-2</sup> mbar argon pressure the energy distribution changes fundamentally with the energy range of 100 to 200eV being subject to a particularly decrease in Fe<sup>+</sup> population. However despite the clear distortion in energy distribution brought about by the presence of argon gas it is interesting to note

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that the broad range of ion energies detected is similar throughout the entire pressure range with particle energies reaching over 200eV even at 10<sup>-2</sup> mbar.



**Figure 4.12** - Energy spectra in the range 0 to 500eV of Fe<sup>+</sup> ions from an iron target at different argon pressures, (10exp(-n) mbar signifies 10<sup>-n</sup> mbar).

The loss of lower energy ions with increasing gas pressure implies that the most frequent background gas/plume interactions take place with the lower velocity ions and the higher energy ions appear to pass through the background gas relatively unaffected. The consequences for thin film formation would be that the high energy ions that may cause resputtering of the growing film may be present even at quite high gas pressures. It should also be noted that interactions between particles in the plume are strongest

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when the masses of the gas and particle are close, in this case the atomic mass of iron is 56amu and argon is 40amu.

The lower energy part of the Fe<sup>+</sup> spectrum is particularly interesting as can be seen in figure **4.13**.



**Figure 4.13** - Energy scans under the same conditions as those of figure 4.12 scanned in the range 0-20eV

Scanning ion energies in this range underlines the low frequency of ions detected at energies in the range between 0 and 8eV despite a small energy peak around 3eV. As with the higher energy range the spectra change little between  $10^{-7}$  and  $10^{-5}$  mbar but at  $10^{-3}$  mbar the 3eV peak increase considerably until at  $10^{-2}$  mbar the peak grows to 200counts. This peak is most probably associated with collisions between iron neutrals or ions and argon atoms.

### 4.4 Carbon energy spectra

As a contrast with the iron, carbon is an interesting target to study to illuminate the relationship between material related and plume related energy effects.



**Figure 4.14 -** Energy spectra of Carbon ions at 1.3J/cm<sup>2</sup> (this is the lowest fluence for which ions are detected) N.B. no C<sup>2+</sup>ions are detected at this fluence.



**Figure 4.15 -** Energy spectra of Carbon ions at 13J/cm<sup>2</sup> the energy spectra at higher fluences are similar

The behaviour of Carbon is very interesting, at the lowest fluence for which ions can be detected (1.3J/cm<sup>2</sup>, for 532nm radiation) the initial scan shows no ions at all but if the target (pyrolytic graphite) is allowed to rotate a few times so that the laser strikes areas for the second time an energy spectrum will suddenly appear and remain constant for successive scans. As with iron targets the doubly charged ions only appear at higher fluences and appear with the energy range which corresponds to the additional energies that appear in the singly charged spectrum at higher fluences.

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**Figure 4.16-** Energy spectra of (a)  $C^+$  and (b)  $C^{2+}$  ions from a pyrolytic graphite target and standard target -CMA distance (65mm).



**Figure 4.17-** Energy spectra of (a)  $C^+$  and (b)  $C^{2+}$  ions under the same conditions as figure 4.16 with target -CMA distance increased to 225mm.

Figures 4.16 and 4.17 are a set of energy spectra for ablated carbon showing the increase in ion energies at increasing distance from the target reflecting the behaviour of Fe<sup>+</sup> Fe<sup>2+</sup> ions reproduced in figure 4.9. The energy increase is particularly noticeable for  $C^{2+}$  ions with the peak energy rising from about 120eV to approximately 220eV.

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# 4.5 CONCLUSIONS

The conclusions that can be drawn from these spectra are the following :

1. Mass and energy distributions of ablated ions can be obtained in real time provided that suitable precautions are taken to limit the flux of incoming particles.

2. The energies of ions within the plume appear to increase with increasing charge since the higher energy peaks in Fe<sup>+</sup> can be identified as originating in Fe<sup>2+</sup> ions that have gained an electron after having attained high kinetic energy.

3. The energy distributions of Fe<sup>+</sup> ions show a similar form to that obtained from two Maxwellian distributions with centre of mass velocities added together. This is strong evidence in favour of the Knudsen layer model of ablation. However the 'temperatures' needed to give the high energies observed are well above the critical temperature of iron and clearly cannot be directly associated with any real physical temperature on the surface of the target. This problem is discussed in the reference Kelly and Dreyfus 1988, the temperature used for a Maxwell Boltzmann distribution is a kinetic temperature. Therefore, if the similarity in form between the observed energy distributions and the Maxwellian distributions is more than mere coincidence then the high energies observed may result from an acceleration process in the plume which is proportional to charge as discussed in section **1.3.7**. The Maxwellian form of the energy spectrum would then be seen as a remnant of the pre-acceleration distribution.

4.The effect of ambient gas pressure on the energy distribution of Fe<sup>+</sup> ions from an iron target indicate that interactions between the plume and ambient only become noticeable at  $10^{-3}$  mbar and that high energy particles (i.e. above 100eV) are still detected at  $10^{-2}$  mbar argon pressures. This would imply that it is not possible to cut out high energy ions from reaching the substrate by simply increasing the gas pressure even if the total concentration of high energy ions is decreased.

5. The low fluence carbon energy spectrum only appears when the laser strikes an area that has already been irradiated before. This would imply that either

a. a surface protective layer is removed by the first laser pulse or

**b**. surface damage by the first laser pulse causes a physical change in the graphite structure which exposes areas with facets facing the laser directly and thus increasing the effective local laser fluence or

**c**. an electronic damage process is occurring which allows ablation by subsequent pulses through electronic defects within the graphite. This would increase the number of absorption sights and lower the ablation threshold.

With a material such as pyrolytic graphite which is not a single crystal it is difficult to envisage electronic damage having any noticeable effects over and above the naturally occurring defects. This argument favours the second explanation.

In terms of broad energy range, the energies encountered in the iron spectra are similar to those found in the chemically dissimilar carbon targets. This tends to indicate that the energy of particles in the plume is dominated by acceleration effects within the plume itself rather than by light/solid interactions.

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# 5.0 ENERGY AND MASS SPECTRA OF PLUMES FROM ABLATED PZT TARGETS

This chapter continues from chapter 4 in the analysis of the energy and mass spectra of the ablation plume of a more complex material, lead zirconate titanate (PZT). All the spectra were obtained with a frequency doubled Nd:YAG laser emitting at 532 nm, 4ns pulse width and 10Hz. repetition rate. Some of the work presented in this chapter has been published as, 'Kinetic Energy Distributions of lons Ejected During Laser Ablation of Lead Zirconate Titanate and their Correlation to Deposition of Ferroelectric Thin Films' - G.C.Tyrrell, T.H.York, L.G. Coccia and I.W.Boyd. (1996) *Applied Surface Science*, in press.

Firstly the mass spectra are analysed and then the energy spectra of the PZT plume with the separate elements and oxides being studied individually. Possibilities are discussed for equating the data with current theories of the ablation plume including electronic ablation mechanisms and the Knudsen layer. Finally the change in the energy and mass spectra of PZT is discussed in the presence of oxygen at similar pressures to those used in PLD of PZT.

Lead zirconate titanate is a buff coloured ceramic with a number interesting electrical properties, such as ferroelectricity, piezoelectricity and an extremely high dielectric constant and was discussed in detail in chapter 2. The structural diversity, (this material can grow as either a perovskite or pyrochlore structured material), creates difficulties in the growing of thin films by more conventional techniques and it is therefore an ideal candidate for pulsed laser deposition. However, little is known about the nature of the plume during PLD and the effect that the ion energies have on the crystal structure of the growing film.

The target used for these experiments was supplied by GEC-Alsthom and is a hot pressed high density ceramic with a composition  $Pb(Ti_{.45}Zr_{.54}) O_3 + Nb(1\%)+Sr(0.6\%) +AI$  (trace), (see chapter 7). The apparatus used for the study of PZT energy spectra is essentially identical to that described in the previous section on iron ion energy distributions.

#### 5.1 Mass Spectra of Ablation Plumes from a PZT Target.

The mass spectrum of figure **5.0** is a composite of 25 scans at a range of particle energies from 0 to 150eV with a laser fluence of 1.4 J/cm<sup>2</sup> at 532 nm, 4ns pulse length and shows the naturally occurring positively ionised species present in the plume without the addition of an external ionisation source.



*Figure 5.0 -* Mass spectrum of ablated PZT target : composite of 25 scans with energies from 0-200 eV showing the major peaks only.

The major peaks can be identified as those of the singly ionised atomic species from the constituent elements of the commercial hot pressed PZT used as the target; since the background pressure was below 10<sup>-6</sup> mbar we can assign the oxygen ion peaks directly with the PZT ablation. Clearly then,

at least for the ionic content of the ablation plume below 600amu, most of the material transferred during PLD is carried in monoatomic form.

Their are a number of smaller peaks which are not visible on the scale shown in figure **5.0**. The most prominent of these is ZrO<sup>+</sup> followed by those of Nb<sup>+</sup>, Sr<sup>+</sup> and Al<sup>+</sup> we consider the last three as irrelevant to the principle properties of the material. A mass spectrum showing the smaller mass peaks is shown in figure **5.1**.



*Figure 5.1 -* As figure 5.0 but showing details of mass peaks appearing at lower count rates and not visible in fig 5.0.

Two anomalies stand out: one is that the quantities of the oxides of titanium detected in the plume are negligible compared to the zirconium oxides, as shown by table **5.0**, despite the fact that in the bulk material titanium and zirconium take up the same positions in the unit cell (figure **2.2**) and in similar quantities ( the ratio Zr/Ti in the target is 1.2). This is difficult to explain in terms of, for example, the bond strength of zirconium to oxygen which is only slightly greater than that of titanium to oxygen (see table **5.0**) and less than the lead to

oxygen bond strength. This anomaly has also been noted by other authors (Leuchtner and Chrisey - 1993) and later work (Tyrrell and York - 1996) with KrF ( $\lambda$  =248nm, hv = 5eV), irradiation indicates that TiO+ is present in the plume below 1J/cm<sup>2</sup> but disappears rapidly at higher fluences.

Metal ion,	Ratio MO+/M+	Bond Strength of	Bond Strength of
(M+)	as %	M-O, (eV).	M-O, (KJ/mole).*
Pb+	0.5%	3.96	382
Zr+	6%	8.04	776
Ti+	0.2%	6.96	672

**Table 5.0** - Comparison of the ratio of metal oxides ions to metal ions in the PZT ablation plume and their bond strengths; \* source: CRC Handbook of Chemistry and Physics - CRC Press Inc. - Florida 1988.

One explanation may be that, at the wavelength used (532nm, 2.33eV), the TiO bond can be broken by 3 photons whereas the ZrO bond requires 4 photons. However both these events would have a very low probability and do not explain the relative abundance of PbO<sup>+</sup> to TiO<sup>+</sup>.

The other anomaly is the disproportionate peak height of  $Ti^{2+}$  compared to  $Zr^{2+}$ , a factor of over ten to one when the graph is analysed at high resolution to separate the peaks. It is possible that the relative abundance of  $Ti^{2+}$  relative to  $Zr^{2+}$  and the lack of TiO+ relative to ZrO+ are related in the way that specific ablation processes split up the PZT matrix. Alternatively it may point to an instability in the TiO+ ion.

Some of the peaks in the mass spectrum correspond to very highly ionised states, for example there is a peak for  $O^{3+}$  with 11 counts on the scale of figure **5.0**. This indicates that very energetic processes are occurring in the plume (the ionisation potential of  $O^{3+}$  is 54eV, over twenty times the photon energy of the (532nm) laser radiation which rules out multiphoton ionisation in this particular case).

The height or area of the peaks from figures **5.0** and **5.1** should not be used to compare the abundance of materials with widely differing masses in the ablation plume due to the mass dependence of the transmission of ions through the system which decreases at high masses and the ionisability of the separate components.

#### 5.1.1 Behaviour of PZT ions at Lower Laser Fluence.

Under the conditions described for this analysis the visible plume appears at between approximately 0.09J/cm<sup>2</sup> and 0.175J/cm<sup>2</sup> and this point coincides with onset of a detectable signal in the system. The absolute values for laser fluence are presented only as a guide but the use of carefully calibrated neutral density filters allows the relative values within a set of data to be well within 10% of the stated value.

The behaviour of the plume of PZT near the ablation threshold is quite different from that observed at higher fluences and nature of PZT energy spectra at different fluences is divided into two parts.



Figure 5.2 - Graph of the variation in total ion emission with laser fluence from a PZT target. 532nm , 10Hz., 4ns.

At low laser fluences (.09J/cm<sup>2</sup> to 0.7J/cm<sup>2</sup>) the number of ions emitted varies greatly with fluence. Figure **5.2** is a composite graph showing the total number of counts from different energy spectra at different scanned masses. Figure **5.2** shows the output of the ions from PZT plume and the ratio lead to titanium plus zirconium, the data is a composite of the integrated counts from a

number of different energy scans, with 532nm laser fluences just above the limit of detectability for the CMA / mass spectrometer.

The graph shows that the lead output is particularly sensitive to fluence and the increase in ratio of Pb<sup>+</sup> to Ti<sup>+</sup> and Zr<sup>+</sup> ions (an important parameter for perovskite film deposition, see chapter 7) is driven mainly by the increase in the number of Pb<sup>+</sup> ions with fluence. No very clear ablation threshold is visible, as has been noted before (Lichtenwalner *et al* -1993,) with PZT.



*Figure 5.3* - Log - Log graph of the variation in ion outputs with laser fluence from a PZT target.

Figure **5.3** is a log-log curve from figure **5.2** and indicates the variation in the total number of ions emitted from a PZT target with fluence on a log.- log. scale. The slope of this graph as discussed in section **3.3.3** can be used to indicate the nature of the ablation process following, Wiedeman, Kim *et al* -1991. If a straight line can be drawn through the points on a Log Fluence v. Log Signal graph the value of the slope is equal to the number of photons in a multiphoton ionisation process section **3.3.3**.) In the case of figure **5.3** the variation in individual ion outputs generally do not appear to follow a straight line except for the case of ZrO<sup>+</sup> ion for which such a line exists within the error

bars. The error bars in this case were calculated by taking the variation in total ion output from scan to scan with constant laser fluence for a similar set of experiments over the same time period since it was felt that the manufacturers quoted figures are not applicable to this application of the CMA.

The slope for the ZrO<sup>+</sup> trace is 1.3 which would, if taken as an indication of an electronic desorption process as explained in section **3.3.3**, would indicate that the excitation energy of that process were  $1.3 \times hv = 3eV$ .

An attempt to put a straight line through the data of the Zr<sup>+</sup> points which does not fit within the error bars but would indicate a slightly greater slope of 1.54 indicating an excitation energy of 3.54eV.



*Figure 5.4 -* Log - Log graph of the variation in ion outputs with laser fluence from a PZT target at high laser fluences.

At higher fluences of 1.3 to  $50J/cm^2$ , (figure **5.4**) the ion output appears to reach a plateau implying the onset of plume shielding, (Wiedeman, Kim *et al* -1991; Alimpiev, Belov *et al* -1994) and, in the case of lead particularly, the integrated ion emission appears to decrease slightly at very high fluences.

Once again the anomaly in this general trend is ZrO<sup>+</sup> whose output appears to rise throughout the entire range of fluences but with a greatly reduced slope, (0.43 compared to 1.3 at lower fluences).

## 5.2 Energy Distributions of Low Energy lons in the PZT plume

More a detailed insight into the nature of the plume at different laser fluences can be gained from the energy distributions.

Figure 5.5 shows the energy spectrum of Pb<sup>+</sup> ions at a range of lower fluence levels starting from the lower limit of detectability with the equipment.,  $0.09J/cm^2$  up to  $0.7J/cm^2$ . There are four points to note.

1. There is no signal below 5eV.

2. As the fluence increases a second distribution appears at higher energies which comes to dominate the spectrum leading to a bimodal distribution with a range of 100eV compared to a range of 40eV at lower fluences.

3. The threshold for detectability is between 0.09 and  $0.175 \text{J/cm}^2$  fluence. 4.The increase in Pb<sup>+</sup> ion output at  $0.7 \text{J/cm}^2$  is much more pronounced for Pb<sup>+</sup> than for the other metal ions shown in subsequent graphs (note the scale of the .0.7 J/cm<sup>2</sup> spectrum).

It should be noted that the "bimodal distribution" has previously been reported by a number of separate authors and materials, including  $YBa_2Cu_3 O_{7-\delta}$ , (Chrisey *et al* -1991), (Alimpiev, *et al* -1994), various metals (Bykovskii, *et al* - 1987) and in Carbon, (Schenck *et al* -1989), (Murray *et al* -1992).

The energy distribution of Zr<sup>+</sup> ions, figure **5.6**, is more complicated. At lower fluences the recorded spectra show a broad irregular peak between 5 and 40eV but at 0.7J/cm<sup>2</sup> another peak appears at higher energies showing a clear bimodal distribution with a complicated peak rising sharply from 32eV peaking at 35eV and falling gently to 83eV.

The behaviour of Ti<sup>+</sup> ions (not shown) is very similar to that of Zr<sup>+</sup> ions, a broad peak centred at just below 20eV can be seen at all fluences and a bimodal distribution appears at 0.7J/cm<sup>2</sup> with the second peak centred on around 40eV.



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**Figure 5.5 -** Energy distributions of Pb<sup>+</sup> ions, 0.09 to 0.7 J/cm<sup>2</sup> showing a rapid increase in both ion energy and quantity at 0.7 J/cm<sup>2</sup> , note that the graph for 0.7J/cm<sup>2</sup> has a scale of 0 to 200.



**Figure 5.6** - Energy distributions of Zr+ ions, 0.09 to 0.7 J/cm2 showing a similar progression of energies to the Pb+ data but with a more gradual change in ion output with laser fluence .



**Figure 5.7** - Energy distributions of ZrO+ ions, 0.09 to 0.7 J/cm<sup>2</sup> note the scale of the 0.7J/cm spectrum.

Figure 5.7 shows the energy distribution of ZrO<sup>+</sup> ions and, although the development of the spectra is similar to that of the metal ions shown previously, the general energies are significantly lower than any of the metal ion distributions and although the 0.7 J/cm<sup>2</sup> fluence energy peak is bimodal the lower energy peak remains dominant throughout.

Figure 5.8 shows the energy distribution of O<sup>+</sup> ions in the fluence range 0.09 to 0.7 J/cm2. Once again the energy range is from approximately 5eV to 80eV as with the metal ions. The main difference is the fact that the total ion output at  $0.7 \text{J/cm}^2$  does not increase to the same extent as the metal ions. The distributions are bimodal and the threshold of ion detectability (and visible luminescence in the plume), is 0.09eV. As with the other ions shown there are no ions detected below 5eV once again showing that the ions do not have a thermal origin.



Figure 5.8- Energy distributions of O<sup>+</sup> ions, 0.09 to 0.7 J/cm<sup>2</sup>

# 5.2.1 Mass Distributions of Multiply Charged lons

Figure 5.9 shows the spectra of  $Zr^{2+}$  and  $Ti^{2+}$  ions at  $0.7J/cm^2$  which is the lowest fluence for which they are detected. The distribution is quite different to that of the singly charged species presented earlier, there are no doubly charged particles detected below 10eV and the distribution is centred around the higher energy limit in the low fluence spectra of singly charged species.



Figure 5.9- Energy Distributions of Multiply Charged Ions (Log counts).

# 5.2.2 Dependence of Particle Velocities in the Plume on their Mass.

The adiabatic expansion model, (Singh and Narayan, 1990) predicts a  $1 / \sqrt{(Mass)}$  velocity dependence for dissimilar particles in the ablation plume. The components of PZT which are well spaced in mass from 16 to 207amu provide an ideal opportunity to test the validity of this assertion. In figures **5.10** to **5.13** the energy spectra of a typical low fluence (0.35 J/cm<sup>2</sup>), ablation spectra are plotted as velocity spectra and the lower energy part of the curves are fitted with a centre of mass Maxwell Boltzmann distribution so that the peak velocities as defined by the peak of the curve fit can be plotted against mass. The conditions for the curve fits are purely subjective i.e the constants are chosen to give the Maxwellian which most closely mirrors the values plotted.

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*Figure 5.10 -* Velocity spectra of O<sup>+</sup> ions ablated at 0.35J/cm<sup>2</sup> with a Maxwell Boltzmann fit for the first peak



*Figure 5.11-* Velocity spectra of Ti<sup>+</sup> ions ablated at 0.35J/cm<sup>2</sup> with a Maxwell Boltzmann fit for the first peak



Figure 5.12 Velocity spectra of Zr+ ions with a Maxwell Boltzmann fit .



*Figure 5.13 - Velocity spectra of Pb+ ions ablated at 0.35J/cm<sup>2</sup> with a Maxwell Boltzmann fit .* 



**Figure 5.14-** Centre of mass velocities of the first peaks from Figures 5.10 to 5.13 plotted against masses on a Log -Log scale with the slope being -0.48. Also shown is the log velocity of each curve plotted against log atomic weight and the slope is shown for the metal ions alone -0.39.

Figure **5.14** shows the results of plotting positions of the first peak centre of mass velocities against mass for Pb<sup>+</sup>,  $Zr^{+}$ , Ti<sup>+</sup> and O<sup>+</sup> : the points fall in a straight line with a slope of -0.48. If O<sub>+</sub> is omitted the straight line fit is excellent, this time with a slope of -0.39. Where peak velocities are plotted (Pk.Vel on graph) the straight line is less convincing but has a similar slope as the centre of mass velocities. This is a very slightly weaker dependence of velocity on mass (which according to Narayan and Singh would be -0.5), in accordance with the discussion of Narayan and Singh in the same paper which they ascribe to the problem of 'mixing in a multicomponent target'. Once again ZrO<sup>+</sup> behaves differently from the other materials lying well below the line of the metal ions.

### 5.3 Higher Fluence Energy Distributions

The behaviour of the plume at higher fluences is quite different from that at the near threshold fluences described previously. The particle energies of the singly charged metal ions rapidly reach a value many times that found at lower fluences, with a maximum of nearly 250 eV. However, as in the case of the total ion flux, the maximum energies of the ions in the plume also reach a plateau with increasing fluence so that above 1.3 J/cm<sup>2</sup> the maximum energy varies very little. This is illustrated by figures **5.15** and **5.16**. All the distributions shown are broadly similar in having an initial peak between 0 and 30eV followed by a dip and then an extended flat plateau reaching up to around 200eV.



**Figure 5.15-** Energy distributions of Pb<sup>+</sup> ions at fluences from 1.3 to 36.5  $J/cm^2$ .

Figure **5.15** shows the energy distributions of Pb<sup>+</sup> at fluences from 1.3 to 36.5J/cm<sup>2</sup>. The spectra change little with increasing fluence and show no simple distribution which would lend itself to modelling by a Maxwell Boltzmann distribution. However in general terms the graph is reminiscent of high fluence the Fe<sup>+</sup> graphs discussed in chapter **4** with a high proportion of the ions contained within a region below 50eV followed by a long flat curve extending up to 200eV. One interesting feature is the flux at low energies; at 1.3J/cm<sup>2</sup> there are very few counts below 25eV whereas at 36.5J/cm<sup>2</sup> the gap has filled almost completely.



Figure 5.16- High fluence energy spectra of Zr<sup>+</sup> ions from 1.3 to 36.5J/cm<sup>2</sup>

Although the Zr<sup>+</sup> distribution of figure **5.16** seems almost random at first there are interesting trends discernible in the lower energy part of the spectrum. Between about 10 to 30 eV there is a sharp peak in the Zr<sup>+</sup> energy spectrum which corresponds in position to the ZrO<sup>+</sup> spectrum peak, fig **5.17**. This peak is visible throughout the range of fluences from 1.3 to 36.5 J/cm<sup>2</sup> in the Zr<sup>+</sup> curves and completely dominates the entire spectrum of ZrO<sup>+</sup>. Other peaks are

also visible in this region, Pb<sup>+</sup> ions in particular peak around 25 to 30eV and the peak shifts position with fluence in a regular and predictable manner. The position of these peaks as a function of fluence is shown in figure **5.18**. The ZrO<sup>+</sup> spectra of figure **5.17** is somewhat different from the metal ions in having just a single peak reminiscent of the lower energy portion of the Zr<sup>+</sup> spectrum.



Figure 5.17- High fluence energy spectra of ZrO+ ions.



*Figure 5.18* Peak position of dominant low energy peaks in Pb+ , Zr+ and ZrO+ as a function of fluence

The titanium ion energy spectra in this fluence range (not shown) are similar to the zirconium ions but completely lack the sharp high energy peak below 25 eV.

#### 5.3.1 Multiply Charged lons

The energy distribution of multiply charge ions at high laser fluences has no low energy component much below 50eV, in marked contrast to the distribution of singly charged ions but consistent with the low fluence graphs of figure **5.9**. However at higher fluences the centre of the distribution moves to much higher energies (150ev in the case of figure **5.19**). Clearly any attempt to fit a Maxwell Boltzmann curve to these distributions would require an enormous centre of mass velocity to shift the peak to such high energies.



**Figure 5.19 -** Zr<sup>2+</sup> and Ti<sup>2+</sup> ions at a laser fluence of 12J/cm<sup>2</sup> (the data has been fitted by a cubic spline to allow superposition).

#### 5.4 Measurements of the Plume under Typical PLD Conditions

PZT is typically deposited under conditions of high laser fluence and high oxygen background pressures, i.e.  $3-12 \text{ J/cm}^2$  and  $1-3 \times 10^{-1}$ mbar of oxygen. The effect of high background gas pressures can be seen directly by analysis of the energy distributions in the ablation plume. The most dramatic effect is on the distribution of Zr<sup>+</sup> ions as shown in figure **5.20** with a dramatic decrease in the total ion count and a distortion of the entire distribution with the ions with energies between 90 and 140eV and below 25eV decreasing most markedly. In contrast the Pb<sup>+</sup> ions appear to be far less effected by the presence of oxygen in the chamber, figure **5.21**. This is partly understandable in terms of the momentum of the Pb<sup>+</sup> ions relative to Zr<sup>+</sup> which would be higher by a factor of 1.5 for the same energy and therefore would be less effected by the collisional process taking place in the presence of a background gas. The effect of oxygen pressures on the oxide ions in the plume is noticeable but not

dramatic. Normally there are practically no detectable PbO<sup>+</sup> ions visible in the plume as can be seen from the mass spectrum of figure **5.1** but with the introduction of oxygen into the chamber a certain number of PbO<sup>+</sup> ions do appear, figure **5.22**. The relatively small increase in oxides detected at high oxygen pressures is puzzling especially as some estimates (Elastal *et al* - 1995) of the gas phase chemical combinations in YBa<sub>2</sub>Cu<sub>3</sub> O<sub>7- $\delta$ </sub> targets made by spectroscopic absorption and emission spectra indicate that more than 95% of ablated yttrium and barium combine with oxygen in transit.



**Figure 5.20** - The effect of  $10^{-1}$  mbar of oxygen on the distribution of Zr<sup>+</sup> ions in the energy spectrum of the PZT ablation plume at a fluence of  $12J/cm^2$ .



**Figure 5.21** - The effect of oxygen pressure on the energy distribution of  $Pb^+$  ions in the energy spectrum of the PZT ablation plume at a fluence of  $12J/cm^2$ .



**Figure 5.22 -** The increase in the population of PbO<sup>+</sup> ions in the energy spectrum of the PZT ablation plume at a fluence of 12J/cm<sup>2</sup>.



**Figure 5.23 -** The decrease in the population of ZrO<sup>+</sup> ions in the energy spectrum of the PZT ablation plume at a fluence of 12J/cm<sup>2</sup>.

Strangest of all is the effect of oxygen pressure on the ZrO<sup>+</sup> (figure **5.23**) population which appears to cause a severe decrease in population and a slight shift to higher energies.

#### 5.5 Discussion

This section has dealt with the energy and mass spectra of ionised particles ejected from a PZT target under ablation. The conclusions that can be drawn fall into two categories.

1. The insight which can be gained into the nature of the ablation process.

2. Information with implications for film growth with a view to using the technique of energy and mass analysis as an *in situ* tool to assist the fine tuning of the process.

For insight into the ablation process the data is interesting and suggestive, if not ideal. The spectra were taken from standard targets, identical to those used for deposition, and are therefore smooth rather than polished and polycrystalline rather than single crystal. In addition although every attempt was made in the alignment of the laser to prevent 'hot spots' forming in the beam profile, the profile was not ideal. Nevertheless certain points stand out clearly once more. The ions are clearly not of thermal origin the kinetic temperatures are far too high and there is a complete lack of low energy ions in the majority of the energy spectra. The spectra indicate agreement with the predictions of Knudsen layer theory in having a full range shifted Maxwellian distribution with a centre of mass or flow velocity.

It has been shown from log-log curves that the total ion content does not for the most part appear to increase with fluence in a way that would imply that electronic processes were solely responsible for ablation. However, as discussed in section **1.3.3**, ferroelectrics represent a class of materials which might be expected to show some electronic effects in terms of the ablation. Evidence in support of this case comes from the spectra of ZrO<sup>+</sup> ions which do not follow the general trends of the metal ions and is anomalous in nearly all respects. The energy distributions are highly peaked and have practically no contribution above 20eV. This fact is illustrated by figure **5.24**, the Maxwell Boltzmann curve fit indicates a kinetic temperature of only 1200K despite the high fluence of 23 J/cm<sup>2</sup>.



**Figure 5.24 -** The energy distribution of ZrO+ ions and shifted Maxwellian curve fit in the energy spectrum of the PZT ablation plume at a fluence of 23J/cm<sup>2</sup>.

This temperature is a little lower than that for the other curves presented and would seem to imply a thermal origin were it not for the fact that there are no low energy ions.

The evidence for an electronic process in  $ZrO^+$  formation is further enhanced by figure **5.3** and the ablation process for  $ZrO^+$  appears to be connected with the low energy peak of the  $Zr^+$  energy spectra of figure **5.16**. Further evidence comes from the fact that the peaks in the  $ZrO^+$  spectra are centred between 7.5 and 8.5 eV for fluences of 23J/cm<sup>2</sup> and above, (figures **5.17** and **5.18**) which is very close to the bond strength of zirconium to oxygen, (8.04 eV, table **5.0**).

The Maxwell Boltzmann curve fits were of the general form

 $f(v) = \mathbf{A}v^{3} \exp[-m(v - v_{CM})^{2}/2kT).]$  (see appendix)

The particular constants used for the plots shown at .35J/cm<sup>2</sup> are: For Pb<sup>+</sup>

A=9×10<sup>-11</sup>; m=208amu; Vcm=3800m/sec.; T=8000K

For Zr+

A=1×10<sup>-9</sup>; m=91amu; Vcm=5250m/sec.; T=3000K

For Ti+

A=5×10<sup>-10</sup>; m=48amu; Vcm=6900m/sec.; T=1400K

For O+

A=7.0×10<sup>-11</sup>; m=16amu; Vcm=13700m/sec.; T=9000K

However these particular curve fits appear very poor and should only be taken as a measure of centre of mass velocities for which there is less ambiguity than there is for the effective temperatures.

For comparison Leuchtner *et al* report values of Vcm=240m/sec. and T=2000K for Pb atoms in the ablation of a PZT target at 1.3 J/cm<sup>2</sup>, (Leuchtner *et al* - 1993). Plasma temperatures of 20300K in vacuum falling to 8000K for oxygen pressures of 0.1 mbar have also been reported for Maxwell Boltzmann curve fitting of optical emission spectroscopy data (Cheng - 1995) for PLZT (PZT with 5%.lanthanum substitution of the lead).

The high ion energies observed at greater fluences, (above 1J/cm<sup>2</sup>) are indicative of the ion - ion repulsion mechanisms mentioned in section **1.3.7**.

The implications for deposition are also interesting :

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Firstly, both the total ion output and the maximum energy changes little between 1 and 36.5 J/cm<sup>2</sup> indicating that this area would be fluence for deposition where tight control of thickness is important. Unfortunately the maximum energies in this regime are high with possible implications for ion damage of the growing film as mentioned in the introduction in section **1.2.1.2**. The ionic lead content in the plume is particularly sensitive to fluence at low fluences (figure **5.2**), illustrating that higher fluences will be beneficial.

Although ion energies are reduced by the addition of relatively high pressures of oxygen the effect is only partial particularly for Pb<sup>+</sup> ions meaning that high velocity ions are still striking the substrate surface.

Secondly, there is some evidence of oxidisation of in the plume in the case of lead but the in the case of zirconium oxide the ions appear to be dissociated by collisions with the ambient oxygen. This fact is contrary to certain reports such as that from the laser induced fluorescence spectroscopy, (LIF), of (Wanniarachchi K.*et al* -1993) of YBa<sub>2</sub>Cu<sub>3</sub> O<sub>7- $\delta$ </sub> .which find the producton of YO in the ablation plume.

This implies that if the growing thin film is to be entirely oxidised it must rely on reactions between the background oxygen and the growing film itself. Assuming that at  $10^{-1}$  mbar a monolayer of oxygen will form in  $4 \times 10^{-5}$ seconds for a unit sticking coefficient and approximately one monolayer of PZT is deposited every pulse i.e. in 0.1 seconds for a 10Hz. repetition rate this gives sufficient time for reactions to take place on the surface of the film. The perhaps surprising conclusion that little oxidation occurs within the plume even at guite high pressures is consistent with the results of emission spectroscopy of germanium in an oxygen environment, (Vega et al -1993) BiSrCaCuO (Gonzalo, et al -1994) and strontium titanate (Hiratani et al -1995), but not with fluorescence measurements of PZT, (lembo et al -1993) and Elastal et al -1995). This disparity may be partly explained by the observation that the quantity of oxides observed in the ablation plume in an oxygen environment increases with distance from the target, (Amoruso et al -1995, Morrow et al - 1994) and also that the gas phase ionisation occurs outside the area in which high energy ionising electrons are present. Furthermore the greatest effects on the energy spectra of adding oxygen appears at lower energies and since neutrals species in the plume are

generally thought to have lower energies it is likely that the reactions that are observed between oxygen and the background gases are between neutral species.

It is also interesting to note that Geohegan (Geohegan - 1992) used the results of his gate intensified high speed ccd array photographs to conclude that the fast ions were remove from the plume by the background gas pressures often used in PLD ( a few hundred mbar ) which would be in contrast to the results suggested by the work presented here ( see figure **5.20** to **5.22**). However more recently (Geohegan - 1995) it has been suggested that this is not the case and that a relatively high proportion of the high energy ions do react on the substrate even at high gas pressures.

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chapter six - energy /mass spectra of other electroceramics

# 6.0 ENERGY AND MASS DISTRIBUTIONS OF OTHER ELECTROCERAMICS

This chapter discusses the analysis of the ablation plume from a target of the high temperature superconductor BiSrCaCuO ablated with a frequency doubled Nd:YAG under the same conditions described in chapters 4 and 5. The majority of the work in this chapter has been published as 'Characterisation of Ionic Species Generated During Ablation of Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> by Frequency Doubled Nd:YAG Laser Irradiation.'-G.C.Tyrrell, T.H.York and I.W.Boyd., *Applied Surface Science*, Volume **86** (1995) pages 50 - 58.

The 2223 phase of the system,  $Bi_2Sr_2Ca_2Cu_3O_{10}$ , has a T<sub>c</sub> of 110K and has been extensively studied world-wide (Sajjadi and Boyd - 1993, Kanai *et al* -1989, Tabata *et al* - 1990). The tailoring of the superconducting BiSrCaCuO system to develop accurately controlled layer structures has led to an interest in those growth parameters which may influence the quality of the interface, (Kanai *et al* - 1989, Tabata *et al* - 1990). For example, the presence of ions in the laser ablation plasma may be detrimental to thin film growth if their energies are above the sputtering threshold of the growing thin film. However, as mentioned before, kinetic energies in the range 10-100eV may be beneficial to the growth process.

Using a novel multi-layering technique (Sajjadi and Boyd - 1993), frequency doubled Nd:YAG (532nm) laser radiation has produced BiSrCaCuO thin films of comparable quality to those of the best achieved with u.v lasers. The constituents of the plume, however, and the kinetic energy associated with them has not previously been studied at this wavelength. The photophysical processes occurring upon u.v irradiation of the BiSrCaCuO system have already been studied for near threshold fluences (Wiedeman L., H.S.Kim and H. Helvajian, 1991-1and 2) as discussed in section **3.3.3** where electronic multiphoton photoejection processes were studied. Saenger has studied the time-resolved optical emission of the Bi $_{1.7}$ Sr $_{1.3}$ Ca $_2$ Cu $_3$ O<sub>x</sub> plume generated by 193nm laser radiation (at 2.5-3.5 J cm<sup>-2</sup>) and found a two component velocity distribution for Sr<sup>o</sup> neutrals (3eV, 20eV) and a narrow non-Maxwellian distribution at 50eV for Sr<sup>+</sup> ions (Saenger K.L., 1989).

## 6.1 Measurement of ions from $Bi_2Sr_2Ca_2Cu_3O_{10}$ in vacuum:

Figure **6.0**, shows a low fluence spectrum obtained for ablated Sr<sup>+</sup> ions at  $0.9J/cm^2$ . The ion signal initially increases with laser fluence and the position of the maximum intensity of ejected ions is always centred around 14 eV. Some studies (Wiedeman *et al* - 1991-1) have reported a major Sr<sup>+</sup> peak at 5eV when ablating BiSrCaCuO with 351 nm excimer radiation while Saenger detected both a 3eV and a 20eV peak for Sr<sup>0</sup> neutrals for 193nm ablation using optical emission spectroscopy (OES)(K.L. Saenger, 1989). The FWHM for the major peak in Sr<sup>+</sup> KE distribution in these studies is approximately 10-20eV which is much greater than the 2eV FWHM observed by Wiedeman. We have no explanation for these differences and further investigation is necessary to isolate whether they are due to the effect of wavelength, or different ion ejection mechanisms in action.



Figure 6.0 - The kinetic energy distribution of Sr<sup>+</sup> ions ejected from a BiSrCaCuO target at 0.9 J/cm<sup>2</sup> (532nm)

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Figure 6.1 shows a Log-Log plot of the integrated ion signal for individual ions as a function of laser fluence. No Bi<sup>+</sup> ions were detected at these low fluences. This plot shows a linear power law dependence in similar way to the PZT plots of chapter 5. However the slopes once again are lower than those reported for u.v laser irradiation of 2212 BiSrCaCuO (Tabata *et al* - 1990). The excitation energy for ion emission is obtained by multiplying the slope by the photon energy for 532nm radiation, (2.33 eV). Thus the excitation energies for O<sup>+</sup>, Ca<sup>+</sup>, Cu<sup>+</sup> and Sr<sup>+</sup> ions are calculated to be 4.56, 2.65, 5.30 and 4.26 eV respectively. These values do not compare well with the observed emission lines associated with those singly charged ions. Lines for Cu<sup>+</sup>, Ca<sup>+</sup> and Sr<sup>+</sup> have been observed at 8.9, 3.15 and 3.04eV respectively. So, a multiphoton ion desorption process does not seem likely. Alternatively, these ions could derive from charge exchange processes from fast neutrals. Fast Sr<sup>o</sup> neutrals with velocities up to 7.5 x 10<sup>5</sup> cm/s (20eV) have been observed (Saenger - 1989).



Figure 6.1 - log-log plot of the total ion output of an ablated BiSrCaCuO target against laser fluence for 532nm radiation.
At higher fluences more complex energy distributions are observed which cover a greater energy range and also represent different energising processes within the plasma as was the case for PZT. For Bi, for ablation at higher fluence (4 J cm<sup>-2</sup>), ion energies of up to 250eV are observed.

# 6.2 Measurement of ions from Bi2Sr2Ca2Cu3O10 in a nonreactive ambient gas (Ar).

Figure 6.2 shows the effect of the pressure of argon on the ion energy distribution of Ca<sup>+</sup> ions ejected at a laser fluence of 4 J cm<sup>-2</sup>. Figure 6.2 a. shows this energy spectrum at high vacuum ( $10^{-7}$  mbar), revealing a bimodal distribution. An increase in argon pressure results in little change to the observed energy spectrum until the argon pressure reaches  $10^{-2}$  mbar when the collisional influences of the ambient gas are evident. Figure 6.2 b shows a pronounced change in the energy spectrum where the low energy component is attenuated and exhibits a reduced FWHM. No high energy species are observed at energies greater than 170eV.



**Figure 6.2 -** two graphs showing the dependence of the energy distribution of Ca<sup>+</sup> ions from a BiSrCaCuO target on ambient argon pressure, a is ablated at a chamber pressure of 10<sup>-7</sup> mbar of argon and b at 10<sup>-2</sup> mbar.

Further investigation of the low energy component was performed to isolate the character of the narrow FWHM value. Figure **6.3a** shows the high

resolution energy spectrum of the Ca<sup>+</sup> ions at high vacuum. This spectrum shows a fairly uniform distribution of ion population over the energy range 0-20eV with a barely discernible increase in intensity between 4-8eV. A remarkable contrast with this can be seen for the high resolution spectra at 10<sup>2</sup> mbar argon pressure, shown in Figure **6.3b**. The spectra exhibit two distinctly defined peaks between 2 and 5eV. The first is a narrow high-count distribution centred at 2.6eV with a FWHM of 0.5eV. The second appears at 4.5eV and possesses a broader near-Maxwellian peak shape with a FWHM of 3eV. Low energy spectra for other ions from the BiSrCaCuO material show slightly different peak shapes and positions. This is clearly at variance from the peak types reported by Wiedeman et al for low fluence ablation in vacuum. In the case of the Cu<sup>+</sup> products shown in figures 6c and 6d a broad highly resolved peak occurs at 5eV for argon pressures of 10<sup>-2</sup>mbar, while only a very small peak is observed at 7eV in the high vacuum example. Figures 6.3e and 6.3f show the energy spectrum for Sr<sup>+</sup> ions in the range 0-20eV in vacuum and at 10<sup>-2</sup> mbar. The broad high vacuum distribution extending between 7 and 20eV and peaking just above 8eV is seen to narrow significantly to between 3 an 10eV, peaking at 4eV. There is also weak evidence for a second peak around 12eV which is reduced to around 6eV. All these species have clearly lost energy or are produced via collisions with the ambient Ar atoms.

Interestingly, optical emission spectroscopy studies, (Saenger, 1989) extracted mean velocities of  $2.5-3 \times 10^5$  cm/s for the Sr<sup>o</sup> species, which is similar to the 4.5eV ( $3.12 \times 10^5$  cm/s) and 6.5 eV ( $3.75 \times 10^5$  cm/s) Sr<sup>+</sup> peaks observed in this study. This strongly indicates that the majority of the ablated species possess these energies, and that in rarefied gas environment collisional charge exchange processes appear. The ion KE distributions at high argon pressures are intriguing and difficult to explain using conventional collisional gas kinetic arguments.



**Figure 6.3 -** Energy spectra of Ca<sup>+</sup>, Cu<sup>+</sup> and Sr<sup>+</sup> ions at 10<sup>-2</sup> and 10<sup>-7</sup> mbar from a BiSrCaCuO target ablated at 532nm showing the low energy distributions.

These ion signals may be due either to ions derived from neutrals via a charge exchange process or some electron-induced fragmentation process of clusters ablated from the surface. The energy loss upon collision will be primarily dependent on the relative masses of the two species. In this case the

order of energy loss would be  $Ca^+-Ar$ , >  $Cu^+-Ar$  >  $Sr^+-Ar$ . Except for the low FWHM distributions, which remain to be further studied.

### 6.3 Mass Spectra of YBaCuO and CeO<sub>2</sub>

This very brief section is intended as a discussion on where molecular ions are present and why, with reference to two ceramics, YBaCuO and CeO<sub>2</sub>, to test the assertion that molecular ions are present in proportion to their bond strength.

The mass spectra of the plume from an YBCuO target at 10<sup>-3</sup> mbar of oxygen pressure (figure **6.4**), indicates that very few metal oxides are present in the plume at this pressure. The ablation of an YBCuO at 532nm leads to ions which are almost entirely monatomic and there is no evidence of oxidation in the plume during transit, at least at this pressure.

This is not the case with all materials however, in the case of the electronic buffer layer material cerium oxide(Amirhaghi *et al* - 1992) much of the material retains its diatomic form even at high fluences and a pressure of  $10^{-7}$  mbar. The proportion of CeO+ ions to Ce+ ions in figure **6.5** is about 42%, much higher than the metal to metal oxide ratio found in the other oxides studied.. The explanation for this effect, which is noticeable at all fluences, may be related to the high bond strengths of Ce-O relative to Y-O, Ba-O, of table **6.1** and Ti-O, Zr-O, table **5.0**. It has been reported, (Gibson -1995), that the quantity of CeO+ to Ce+ from the trivalent cerium tungsten oxide target is greater than that from the tetravalent CeO<sub>2</sub> target.

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**Figure 6.4 -** Mass distributions of ions in the YBCuO plume at 10<sup>-3</sup> mbar of O<sub>2</sub>, (532nm radiation, 10Hz.). TOP- 1500 counts full scale, BOTTOM - 16 counts full scale.



*Figure 6.5 -* mass scan composite of CeO<sub>2</sub> target ablation plume with a fluence of 6J/cm<sup>2</sup> and 10<sup>-7</sup>mbar pressure (532nm, 10Hz.)

Metal Ion (M+)	Bond Strengths M-O, (eV)	Bond Strengths M-O, (KJ/mole)	
Ce+	8.35	805.8	
Y+	7.45	719.7	
Ba+	5.82	561.9	

 Table 6.1 - comparison of bond strengths of certain metals discussed in this section with oxygen - source \* CRC Handbook of Chemistry and Physics - CRC Press Inc. - Florida 1988

#### 6.4 CONCLUSIONS

The energy distribution of various species ejected from BiSrCaCuO have been characterised and are shown to depend upon gas pressure and laser fluence. The majority of the ions in energy distributions for low laser fluences  $(1J \text{ cm}^{-2})$  are measured to be between 0 and 20eV. At high fluences (4 J cm<sup>-2</sup>), ion energies of up to 300eV have been shown. The introduction of argon at pressures of  $10^{-2}$  mbar causes energy loss from the high energy ions while a discrete and previously unobserved low energy distribution is discussed. This has tentatively been attributed to momentum and charge transfer processes between ions and neutrals in the plume.

Such a combined energy and mass spectrometric study can assist in providing significant information to aid in the optimised deposition of the BiSrCaCuO systems and other multicomponent oxide. The use of high gas pressures during the ablation process is clearly important in acting as a buffer from possible damage inflicted by high energy ablated ion species although this buffer is not completely successful in eliminating all high energy ions.

The presence of molecular ions can be very important in the growth of thin film it has been shown that molecular ions are present in the ablation plumes of ceramics where the metal atom to oxygen bond strength is sufficiently high. This assertion is supported by the evidence of the mass spectra from the cerium oxide and  $YBa_2Cu_3O_{7-\delta}$  ablation plume where the proportion of oxides present is in reasonable accord with their bond strengths.

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### 7.0 DEPOSITION OF THIN FILMS OF PZT.

This section gives some details of the process of optimisation involved in depositing thin films of lead zirconate titanate by pulsed laser deposition. It is not intended as an exhaustive treatment but as a practical description of the technique of PLD to contrast with the analysis of the ablation plume presented in chapter **5**. The final intention is that the technique of plume analysis can be married with practical knowledge of deposition so that the sxp/cma system can be used as an *in situ* analysis technique to aid in the optimisation of pulsed laser deposition of complex materials and multilayers.



#### Pulsed Laser Deposition System

Figure 7.0 - ablation system used for the deposition of PZT

The deposition of PZT thin films described here was carried out within the vacuum chamber, laser and accompanying optics shown in figure **7.0**. The vacuum chamber was made of stainless steel and employed a 200 l/sec. turbomolecular pump and a rotary backing pump, allowing a minimum pressure of  $10^{-6}$  to  $10^{-8}$  mbar to be reached within an few hours. The ablation source was a Nd:YAG laser focused to a spot with an area typically of 2.8mm<sup>2</sup>, the output energy was 0.5 J at 532nm and 0.07J at 266nm with a Q-switched pulse width of approximately 4ns FWHM in both cases.

The choice of substrate material is dictated by its lattice parameters, resistance to high temperatures in oxygen, coefficient of expansion, availability and price and for the experiments described here MgO was the substrate chosen.

A single crystal MgO substrate was heated either by a platinum resistance heater or a quartz lamp, (see figure 7.1), and held 4cm from a circular rotating target of PZT 13mm in diameter. The beam strikes the target at an angle of 45° after having passed through a number of neutral density Pyrex optical filters, a converging lens, three mirrors and the quartz window to the chamber. The targets used for these experiments were 13mm diameter pellets cut from a large piece of hot pressed PZT supplied by GEC Alsthom in Stafford with a composition Pb(Ti\_{45}Zr\_{54}) O\_3 +Nb(1%)+Sr(0.6%) +AI (trace). This is essentially Pb(Ti\_{45}Zr\_{54}) O\_3 with small quantities of niobium, strontium and aluminium added to stabilise the grain boundaries and to increase the permittivity, piezoelectric properties and the mechanical and dielectric losses in the bulk material. The density of the targets calculated by Archimedes principle was 7.7 grams/cm<sup>3</sup>, some 96% of the theoretical maximum target density.

PLATINUM RESISTANCE HEATER



**Figure 7.1 -** Two heater designs, the top heater (1. and 2.) is made of a platinum thick film deposited on an alumina base placed in a cut down stainless steel tube which was used for the earlier experiments. The lower diagram (3.) is a much higher power design using a quartz lamp to heat a stainless steel plate with a spot welded integral thermocouple. The quartz lamp design allows substrates to be heated up to 800°C at oxygen pressures up to 1 atmosphere.

The difficulties of maintaining the composition of the PZT film at high temperatures for different deposition techniques are well established, (Castellano and Feinstein 1979; Roy *et al* - 1990, Krishnakamur *et al* - 1990, Horwitz *et al* -1991).

There are two particular difficulties encountered when depositing PZT at high temperatures in partial vacuum.

**a.** The lead content : lead is a volatile material in elemental form and binds weakly to other elements, even oxygen and whilst it may be present in the plume it rapidly evaporates from the substrate at high temperatures unless combined.

**b.** The substrate temperature : There are two possible crystal structures for PZT, the perovskite structure of figure **2.2** and a pyrochlore structure which has very inferior properties. The structure of the PZT thin film depends on its thermal history and the lead content. A slight depression of the lead content or deposition at too low a temperature leads to a thin film with high pyrochlore content. There is only a narrow temperature window between the minimum crystallisation temperature for perovskite PZT and the maximum temperature that a thin film can sustain during ablation without severe lead loss, (Cotell and Grabowski - 1992).

One solution to this problem is to deposit the film at relatively low temperatures and oxygen pressures followed by a post deposition anneal in an oxygen environment. A potentially more useful solution is to deposit films which have the required crystalline characteristics *in situ* by careful control of the temperature and pressure.

## 7.1 Variation of Stoichiometry with Substrate Temperature

Early experiments were carried out to determine the optimum deposition temperature to ensure the stoichiometric growth of thin film PZT. The results of these experiments are shown in figure **7.2** 



**Figure 7.2** - Pb, Zr and Ti proportions in PZT; substrate temperatures 450°C -800°C, 0.25 mbar O<sub>2</sub>, 532nm, MgO substrates. EPMA data (error bars are the standard deviation of the set of readings at each point).

The lead loss shown in figure **7.2** is exaggerated by the cooling cycle and oxygen pressures employed for the depositions which took over 30mins to decrease by 200°C at an oxygen pressure of 50mbar.

The relative lead loss above 500°C presents a difficulty. The crystallisation temperature for the perovskite phase of PZT is between 550°C and 600°C, (Adachi and Wasa - 1990). To compensate for this a rapid cooling cycle was used in later depositions and the oxygen pressure increased rapidly to 1atmosphere after deposition, ( high oxygen pressures aid the oxidisation of elemental lead in the growing film and decrease its volatility).



7.2 Variation of Stoichiometry with Fluence

**Figure 7.3 -** Variation of lead ratio with fluence, silicon substrates deposited at 20° C, 532nm., 6× 10<sup>-3</sup> mbar, EDAX data.

The effect of laser fluence on lead content is shown in figure 7.3 from EDAX data. This type of data is not as reliable as EPMA data as reflected in the 10% error bars and the absolute values of lead content are not entirely in agreement with those obtained by EPMA, this may in part be due to the different sticking coefficient of the silicon substrate. However the trend of increased lead content with fluence is consistent and is in general accordance with that reported in the literature (e.g. Morimoto *et al* - 1990, Saenger *et al* - 1990).

Further support comes from the work summarised in figures **5.5** and **5.15**, where high fluences increase the quantity of ionic lead in the plume leading to a more chemically active lead content which can be expected to bind to the matrix of the growing film.

It is thought that the ablation process contains a thermally evaporated constituent together with the high energy, forward directed element of the plume, (Venkatesan *et al* - 1988), as mentioned in section **1.2.1.3**,. Since the

thermal component has a greater divergence, it will lead to a relative depression in the centre of the plume which for any constituent that is thermally evaporated and consequently a decrease in the content of that element on a small substrate placed in the centre of the plume. Lead has a very high vapour pressure even at low temperatures and it is expected to be the major constituent in the thermal component of the plume. Another factor which may also be important in growing PZT is illustrated by the effect of fluence in the PLD of YBa<sub>2</sub>Cu<sub>3</sub> O<sub>7- $\delta$ </sub> (O'Brien *et al* -1992) in which the authors link the effect of surface modifications to variations in stoichiometry in the film. They argue that at, medium fluences, pitting and cone formation act to decrease the effective fluence to below the ablation threshold at certain points leading to problems in the stoichiometric transfer. At high fluences ablation is so violent that this cannot happen, but they note that high fluences can lead to the increased instance of particulate deposition.

Clearly high fluences are advantageous in respect of maintaining the lead content and the ideal fluence was later confirmed by X-ray diffraction.

## 7.3 Variation of Stoichiometry with Oxygen Pressure

The third important factor is the oxygen partial pressure during deposition. High partial pressures are desirable to maintain the stoichiometry of the thin film (bulk material would normally be sintered in air or pure oxygen to maintain full oxidisation of the components) but too high pressures during deposition leads to poor, powdery film growth and reduction in plume size by collision between plume particles and the ambient gases. A compromise pressure appears to be between 0.2 to 0.3 mbar (Horwitz *et al* - 1991). The target substrate distance was maintained so that the substrate remained within the visible plume where the highest concentrations of fast ions is found leading to high reactivity and surface mobility.

Figure **7.5** shows the variation of lead ratio across the substrate for a deposition at 10<sup>-6</sup>mbar and 6.5J/cm<sup>2</sup> and it can be seen that at this high fluence at least the stoichiometry is consistent along the length to within at least 10% over 35mm. The dotted line in figure **7.5** is the silicon signal (from the glass substrate used for the deposition) multiplied by minus one and is

included as an indication of the film thickness. A low silicon signal is derived from the increased absorption of the EDAX electron beam by the thicker areas of PZT film and a subsequent absorption of the resultant X-rays (see the appendix for a description of EDAX and EPMA).

The detailed information of stoichiometric transfer thus obtained by EDAX and EPMA can be used to standardise a set of parameters for the deposition process which is described below. Subsequent data was obtained after the apparatus had been upgraded by installing a quartz lamp substrate heater with a thermocouple attached directly to the stainless steel base (figure 7.1).



Figure 7.4 -The variation in lead content of PZT thin films with oxygen partial pressure, (532 nm., 10Hz.).



**Figure 7.5** - Variation of lead content along a large glass substrate, 20°C, 10<sup>-6</sup>mbar, 6.5 J/cm<sup>2</sup>, 532nm, 10 Hz.

The thermocouple was calibrated by the use of a second thermocouple placed on the surface of the substrate, and subsequent quoted temperatures are derived from the calibration factor arrived which compensates for the displaced position of the thermocouple relative to the substrate. By using the information presented a standard set of conditions was arrived at.

Standard conditions for deposition:

- Single crystal MgO substrates were carefully cleaned with acetone, dried with a lens tissue and placed in the vacuum chamber which was closed and pumped down to below 10<sup>-6</sup> mbar.
- 2. The substrates were then heated to 750°C *in vacuo* and the pressure was allowed to stabilise in order to limit the effects of to degassing in the system during the deposition heating cycle. Oxygen was then let into system further oxidising any organic material left on the substrate surface and then the temperature was brought down to 560°C and the oxygen pressure stabilised at 0.25 mbar.

- Depositions were normally 2mins long with a target rotation speed of 5min<sup>-1</sup> and a substrate temperature of 560°C.
- 4. Immediately after deposition, oxygen was allowed to enter the system with the heater maintaining the substrate temperature. The effect of this process is to bring the oxygen pressure to 1 bar within a minute. When the pressure had reached 1 bar the heater was turned off and the system allowed to cool.

Further information on the deposition of PZT requires knowledge of the crystal structure of the film which can only be gained from X-ray diffraction data.

The figures below show the progression in the X-ray diffraction spectra with variation in, temperature, oxygen pressure and fluence using 532 nm laser radiation; the deposition conditions unless otherwise stated are as follows:

laser parameters	substrate.	Oxygen pressure:
12 J/cm <sup>2</sup> 532nm, 10Hz.	MgO, 560° C .	0.25 mbar.

The variation in the intensity of the of the 001 perovskite phase is shown in figure **7.6** as the deposition temperature is varied between 500°C and 600°C. At 500°C and 530°C there is a strong peak due to the 222 reflection from the pyrochlore phase at  $2\theta = 29^{\circ}$ . This peak disappears at 560°C and peaks due to the perovskite phase appear, both from 001 and 101 planes. At 600°C the perovskite phase is less evident , this is noticeable particularly by comparing the 002 reflection at 560°C and 600°C.

Figure **7.8** shows the effect of varying the oxygen pressure used during ablation. All these films are pure perovskite phase and highly oriented as evidenced by the small number of peaks. In particular there is a total absence of reflections from the 111 plane, and only a very small reflection from the 101 plane of the perovskite phase at the two higher pressures. The strongest reflection from 001 oriented perovskite PZT appears at an oxygen pressure of 0.25 mbar. The effect of laser fluence (figure **7.7**) is most dramatic. All the XRD spectra are of highly oriented, perovskite phase PZT but the intensity of the 001 peaks increases greatly at  $12J/cm^2$ , deposition times were varied to maintain a film thickness of approximately  $0.8 + \text{ or } - 0.2 \ \mu\text{m}$ . Above  $12J/cm^2$  the plume damages the film growing on the substrate by secondary sputtering for this target substrate distance.



XRD Pattern of PZT on MgO for 532nm Ablation at Various Temperatures









**Figure 7.8** - X-ray diffraction 20 plots of PZT thin films grown on MgO substrates with a laser fluence of 12 J/cm<sup>2</sup> ( $\lambda$  =532nm, 10Hz.) substrate temperatures of 560° C ,. and oxygen pressures of 0.1, 0.25, 0.5, and 0.76 mbar.

The conclusion that can be drawn from EPMA, EDAX and XRD data is that for the substrate to target distance of 4cm the optimised fluence is  $12J/cm^2$  at 532nm and an oxygen pressure of 0.25mbar with a substrate temperature of 560°C. Under these conditions, highly oriented single phase perovskite thin films can be grown without the need for post deposition annealing or the addition of more strongly oxidising gases such as N<sub>2</sub>O, NO<sub>2</sub> or O<sub>3</sub>.

Having seen that single phase perovskite films can be produced by the method described above, the next step was to a ascertain the physical quality of the films by the use of a scanning electron microscope (SEM).

The surface quality of films produced as described above was investigated with the use of a scanning electron microscope and here the limitations in the method became clear. The films are dominated by large blobs of material averaging approximately one micron in diameter and totally covering the substrate, (figure **7.9**). The influence of longer laser wavelengths and high fluences has been reported before, (Kate *et al* - 1990), suggesting that in order to achieve films with surfaces as free as possible from micron sized particulates the use of ultra-violet wavelengths is advisable. Unfortunately the ablation conditions which are optimal for stoichiometric transfer and perovskite film growth at 532nm appear to be those which are most conducive to particulate formation on the film surface. The nature of the particulates varies over the surface of the substrate, figure **7.10** is an SEM photograph taken towards the edge; but the quality is very poor over the entire surface.



**Figure7.9** - SEM photographs of PZT film deposited at 532nm on an MgO substrate with a laser fluence of 12J/cm<sup>2</sup>, and 0.25 mbar pressure of oxygen and 560° C , taken at a point 3mm from the point where the plume strikes the substrate



**Figure7.10** - SEM photographs of a PZT film deposited at 532nm, on an MgO substrate with a laser fluence of 12J/cm<sup>2</sup>, 0.25 mbar pressure of oxygen and 560° C , taken at a point a few mm. from the edge of the substrate

#### 7.4 PZT Deposition at 266nm.

There are a number of solutions to the problems of substrate particulates as discussed in the introduction, (section **1.2.2.1**). It was decided to choose the simplest development of the system which would allow the minimum change in the apparatus and consequently the maximum continuity of the experience gained in the optimisation of the deposition process Thus a shorter wavelength was chosen for the ablation laser. There are many similar photographs published in the literature contrasting the growth of films at different wavelengths (e.g. Koren *et al* - 1989, Kautek *et al* - 1990).

The Nd:YAG laser has the capacity for output at least four wavelengths, (see table 1.1), the fundamental, (1064nm), the second harmonic, (532nm), the third harmonic, (351 nm), and the fourth harmonic, (266nm). The advantages of shorter wavelengths stem from the fact such radiation generally interacts more strongly with matter and consequently is absorbed in a smaller volume on the target surface. In part this is due to the fact that short wavelengths, have higher photon energies and are able to promote valence electrons into the conduction bands of many insulators thereby initiating dielectric breakdown (see section 1.3.3)

In consequence, the laser was adapted to take a frequency quadrupler in line with the frequency doubler used to obtain 532nm output in previous depositions. The result is a 266nm output in parallel to 532nm, the two wavelengths being separated out by an harmonic beamsplitter. The maximum output at 266nm is greatly reduced compared to 532nm, in addition since 266nm is more strongly absorbed, losses are greater in the optics and in consequence a relatively small spot size is needed.

For subsequent PLDs the spot size was reduced so that the fluence on the target surface reached 3.8J/cm<sup>2</sup> and the deposition time was increased to 3min from 2minutes. The particular value for the spot size was chosen so that the visible plume reached the substrate as it had done with the longer wavelength. The reason for this choice is that it gives an indication of the proportion of ions in the plume since the visible plume is caused by the ion recombinations and is strongly effected by ambient gas interactions with the plume. Choosing a visually similar plume in this way can be a used as a short cut for some aspects of system optimisation when changing a specific

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parameter. In all other respects the deposition conditions were identical to those before the frequency quadrupler was installed. The results of X-ray diffraction data for these films is shown in figure **7.11**. The diffraction lines and full width half maxima are detailed in the table below.

(hkl)	2θ <sup>0</sup> (copper K α1)	FWHM °	Relative Intensity
MgO (200)	42.91	0.054	100
PZT(001)	21.69	0.19	5
PZT(002)	44.15	0.38	2.7
PZT(003)	68.57	0.69	0.04
Pyrochlore	29.48		0.04

Table 7.0 main lines in spectrum of PZT thin film deposited at 266nm

The conclusions to be drawn from the data from the table above is that a very highly oriented thin films of almost single, (perovskite) phase can be grown on MgO using the technique described with the 266nm as with 532nm line from the Nd:YAG laser. From the point of view of XRD the use of 532nm or 266nm makes very little difference apart from the fact that lower fluences can effectively be employed with the shorter wavelength. Rocking curves performed on the above results are....

PZT(001): 20 fixed fixed at 21.69°, top of curve at 10.91°, FWHM =  $1.66^{\circ}$  MgO(200): 20 fixed fixed at 42.91°, top of curve at 21.52°, FWHM =  $0.16^{\circ}$ 

The major difference is to be seen in the SEM pictures of the 266nm deposition shown in figure **7.12**.

There is very little evidence of the surface particulates visible in the 532nm deposition of figure **7.10** and the photograph of figure **7.12** is typical of the entire area of the substrate with occasional particulates and pinholes. Calculations indicate that the average number of particulates in the region of  $1\mu m$  diameter is  $1000-6000/mm^2$  and pinholes  $500-2000/mm^2$ . This compares with  $330000-750000/mm^2$  particulates above  $1\mu m$  diameter for typical 532nm PLD.









Figure 7.12-SEM of PZT film deposited at 266nm, 3.8 J/cm<sup>2</sup>, 0.25mbar  $O_{2.}$  and 560° C.

## 7.5 CONCLUSIONS

This chapter has described the deposition of lead zirconate titanate using a Q switched Nd:YAG laser both in frequency doubled mode, 532nm, and frequency quadrupled mode,266nm. The method by which the deposition parameters were optimised has been described and it has been shown that highly C axis oriented, single phase (perovskite) thin films can be grown with both frequencies. The FWHM of the films grown at 266nm are particularly encouraging and demonstrate that PLD of PZT at 266nm can compete favourably with any other competing thin film technique.

However it has also been shown that the surface quality of PZT thin films grown at 532nm is very poor with a high proportion of micron sized particulates on the films which perhaps indicates why so little is published on PLD of PZT at 532nm. With 266nm ablation the surface quality is improved enormously with the number of particulates decreasing by a factor of 330.

It could also be said that a Q-switched frequency quadrupled Nd:YAG laser is perhaps the ideal tool for PLD. The shorter pulse width compared to the more commonly used excimer lasers, the reliability and simplicity of the design which does not need regular, expensive and dangerous gas refills indicate that this source deserves more attention for PLD.

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### **8.0 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK**

In the introduction the technique of pulsed laser was described and discussed within the context of other thin film deposition processes and brief mention was made of the historical development of the process. Several important features of PLD were discussed and compared to other deposition processes and a few difficulties encountered with PLD were mentioned with steps that could be taken to overcome them.

A brief review of the theory of PLD was then discussed with the interaction of the laser radiation with the solid surface of the target and the ablation plume.

In the second chapter perovskite ferroelectric materials were discussed mainly referring to lead zirconate titanate as an example, and the importance for future and present device applications of this class of materials was mentioned.

In chapter three a review of previous work on the mass and energy distribution of particles in the plume of laser ablated materials was presented.

In chapter four a novel method of analysing the mass and energy spectra of ions in the ablation plume in real time was introduced and described using a cylindrical mirror analyser in tandem with guadrupole mass spectrometer. It was shown how this method can be used to determine both the mass distribution of ablated species in the plume at a given energy and the energy distribution for a given mass. It was seen that this technique can give unrivalled, detailed and accurate information during ablation. However it was demonstrated that the technique will give misleading and inaccurate information unless the quantity of ions entering the system and the voltages on the various electrodes of the cylindrical mirror analyser are carefully monitored. Energy and mass spectra were then presented particularly for iron targets, as this material was found to give reliable and easily repeatable results which could be used to test the system. It was discovered that the energy spectra were often highly complicated and did not lend themselves to modelling by a simple Maxwellian. However it was later shown that by employing two full range shifted Maxwellian distributions that a reasonable

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representation of the data could be obtained. This is in accord with the theory of Knudsen layer formation.

In chapter five the technique of energy and mass analysis was extended to a more complex multicomponent ceramic, lead zirconate titanate or PZT. The energy and mass spectra from the PZT plume were examined at various laser fluences and it was found that, whilst the singly ionised metal ions behaved in a similar manner, that the ZrO+ ion behaved anomalously in many respects. The variation in emitted ZrO+ flux with laser fluence point to a possible electronic ablation origin for this material. The PZT plume was then studied under similar conditions to those employed in PLD and it was shown that only a very small percentage of the ions combine with an oxygen ambient in transit and in fact a large number of ZrO+ ions are broken up by gas phase collisions. In chapter six other electronic ceramics were studied by the same technique and the behaviour of the high temperature superconductor BiSrCaCuO was analysed both in vacuum and in the presence of an inert gas.

Finally in chapter seven PZT was deposited on substrates of single crystal MgO and analysed by EDAX, EPMA and X-ray diffraction. It was shown that highly oriented single phase films could be deposited with a Q-switched Nd:YAG laser using a frequency doubler but that this resulted in films with a very poor surface quality but that by using a frequency quadrupling crystal that the quality could be greatly improved and that this is potentially an extremely useful way of depositing these films.

## Suggestions for Further Work.

There are two areas in which the analysis of mass and energy spectra could be extended, one would be to gain a greater understanding of the ablation plume and the other would be to further develop the technique as a practical tool for use in fine tuning the PLD process.

In the both areas the facility of post ionisation to allow the detection of neutrals would be extremely useful, this could either be performed by electron bombardment or by the use of a second, ultra violet laser.

If plume analysis is to be used for theoretical work then highly polished substrates and an extremely homogenous laser beam profile must be used Ideally the spectra should be obtained from surfaces that have not been previously ablated and further work should be carried out on the effect of increased target-analyser distances and target analyser angles. Angularly resolve data are particularly useful for insight into the behaviour of the ablation plume. The materials studied should also be extended to include ionic and semiconductor materials at extremely low fluences to further gauge the role of electronic ablation effects.

Perhaps a more useful application of the technique would be to study novel techniques used in PLD. For example the effect of different oxidising gases and gas mixtures could fruitfully be studied. Further, the efficiency of gas ionisation methods could studied with great simplicity to aid the rate of oxidisation of the film at the substrate.

One intriguing if perhaps distant possibility would be to extend the function of the CMA/QMS from simply a passive analysis tool to an active part of the deposition process. In this scenario a system similar to the one described in chapter four might be adapted for a very highly efficient throughput in order to extract material from the ablation plume and only allow a predetermined range of energies and particle types to strike the substrate which in this experiment would be in the place of the channeltron. The possibilities for tuning the particle energies to favour particular phases in film growth and for rapidly switching between particle types to allow the growth of highly complex multilayers would be perhaps unparalleled.

In terms of ferroelectric film growth there is an enormous amount of work to be done particularly in the areas of boundary layer and electrode growth. The use of conducting oxides is interesting here however I feel that PZT growth has got to a stage where the main interest lies in device applications. In this context in addition to the applications mentioned in chapter two the recent interest in microscopic mechanical devices will have important implications for PZT for its piezoelectric properties alone.

APPENDIX

#### APPENDIX

# A1. The Maxwell Boltzmann Distribution and Shifted Maxwell Boltzmann Distribution



**Figure A1 -** Maxwell Boltzmann distributions of the general form  $f(v) = A.v^3.exp \{-m (v-v_{cm})^2 / 2kT\}$  for m = 56amu showing the effect of a centre of mass velocities ( $v_{cm}$ ) and effective temperatures (T) on the distribution.

Figure A1 is a plot of the Maxwell-Boltzmann distribution of the form  $f(v) = A.v^3.exp(-m (v-v_{cm})^2 / 2kT_k)$  for several values of  $T_k$  and  $v_{cm}$ . Where  $T_k$  is the kinetic temperature or effective temperature of the plume, v is the particle velocity,  $v_{cm}$  is the centre of mass velocity of the plume itself, m the particle mass k is Boltzmann's constant, A, is an essentially arbitrary factor in terms of modelling a measured distribution since the actual count rate depends simply on the sensitivity of the measuring apparatus. The solid lined curves are all for  $v_{cm} = 0$ 

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with  $T_k = 170000$ , 500000 and 1000000 K and two curves are shown for  $T_k =$ 170000K the thicker line is normalised by a different constant (A) to have the same peak intensity as the  $T_k = 1000000$  K line. The dotted line represents the distribution of a "shifted" Maxwellian with a centre of mass velocity (vcm) of 20000m/sec. All lines are plotted for a mass of 56amu. The general contributions of the elements of the formula  $f(v) = A \cdot v^3 \cdot exp(-m (v \cdot v_{cm})^2 / kT_k)$  are made clear by the different examples plotted. For the same peak count rate a high temperature plume will have a broader distribution i.e. a larger full width half maximum (FWHM) and the peak count value will occur at a higher velocity. The effect of introducing a centre of mass velocity is mainly to move the peak to higher velocities whilst maintaining a similar FWHM. The effect of increased mass is less marked and is not shown. Higher masses lead to a smaller FWHM and a slight shift of the peak to lower velocities. The actual formula used for curve fitting in the text is  $f(v) = A.v^3.exp(-m (v-v_{cm})^2 / 16629 T_k)$  with v in m/sec. and mass measured in atomic mass units. The ragged nature of the data as gathered by the cylindrical mirror analyser makes exact curve fitting difficult and the curves presented are fitted by eye to give a best approximate fit.

# A2. Characterisation Techniques

This section deals with the characterisation techniques used to analyse the composition, crystal structure and surface morphology of the thin films discussed in chapter 7.

## A 2.1 X-ray Diffraction, (XRD)

The most widely used technique to determine the inter atomic distances of ordered and partially ordered solids is that of X-ray diffraction.

This technique relies on the diffraction of electromagnetic radiation by regularly spaced planes of atoms within the matrix of the solid under investigation. In order to achieve this, radiation has to be generated which has a wavelength which is similar to the spacing of the crystal planes within the solid. This is normally achieved by bombarding a metallic target with a stream of electrons which will ionise electrons within the K shells of the target atoms so that recombination from the higher energy L and M shells will lead to the emission of X-rays. In order to form vacancies in these inner electron shells, thermally generated electrons must be accelerated to extremely high energies in the electric fields of an electron gun. The spectrum of electromagnetic radiation emanating from a target bombarded in this manner is characterised by a number of sharply defined high energy peaks within the hump of a broad continuum of energies continuing down at decreasing intensity to lower energies. The broad continuum is either called white radiation or bremmstrahlung from the German for breaking radiation which refers to the origin of the radiation in the rapid deceleration of the electrons by interaction with the target atoms.

The X-ray wavelengths of the sharp peaks which are used as the source for XRD are the K $\alpha$  and K $\beta$  lines and are generally derived from targets of the metals copper, molybdenum and cobalt. The wavelength of X-rays emitted from a target


by electron bombardment decreases with the atomic number of the target material.



Figure A2 - Bragg reflection from crystal planes with spacing d<sub>hkl</sub>

In figure A2 a parallel beam of X-rays of wavelength  $\lambda$  is depicted as reflecting from a crystal plane with a spacing of d<sub>hkl</sub>. The condition for constructive interference of X-rays reflected at an angle  $\theta$  is ,

## $n\lambda = 2d_{hkl} \sin\theta$

where n is an integer called the scattering order, for the respective plane and h,k and I are the are integers defining the many possible planes within a crystal and are called the Millar indices. Analysis of the spacing between the many possible crystal planes allows the structure to be established and the intrinsic properties of the material can be inferred.

From a physical standpoint, the sample under analysis is fixed on a rotating platen which is placed in a diffractometer normally with the geometry shown in figure **A3**. The 20 scans presented in chapter **7** are obtained by scanning the detector and sample over the focusing circle as indicated in figure **A3** and the intensity of the signal in the detector is recorded for each value of 20. This arrangement is extremely sensitive to the spacing of the crystal planes to within

tiny fractions of an Angstrom due to the highly monochromatic nature of the X-ray source and the diffractometer geometry.

If the material under investigation is in the form of small randomly oriented crystals, (or a 'powder') then all the possible crystal planes will be presented to the X-ray source at all possible angles leading to a  $2\theta$  spectrum with a peak corresponding to each crystal plane. On the other hand a highly oriented crystalline material will only have a  $2\theta$  spectrum with peaks corresponding to the crystal planes which lie in the plane of the substrate holder.

This is useful from the point of view of gauging the degree of alignment of a material for which the material properties are sensitive to crystal orientation such as the ferroelectric materials discussed in chapter **2**. The disadvantage of course is that limited information can be gained about the crystal structure without the complete diffraction fingerprint.



Figure A3 - The parafocussing geometry of an X-ray diffractometer

## A 2.2 EDX (energy dispersive X-ray analysis)

The technique of EDX is used to gain information on the stoichiometric composition of a material. A beam of electrons, with energies of tens of keV, is

focused on sample so that X-rays are emitted in much the same way as the X-ray generation in the XRD source. As with the XRD source, the X-rays have clearly defined output peaks with wavelengths which are characteristic of the target and with an intensity proportional to the concentration of the particular element concerned. In EDX, the energies of the X -rays and their intensities are measured simultaneously in a solid state detector so that an X-ray spectrum is obtained for the target material with energy peaks for K,L and M transitions in the targets electron shells. For a quantitative measure the measured intensities are modified by a factor called the ZAF correction factor. This factor allows for,

a) the absorption of X-rays from within the bulk of the sample by other elements in the sample of lower atomic number (proportional to the atomic number, Z, of elements in the sample),

a) the absorption volume of the of the electrons in the sample, (inversely proportional to the atomic weight, A), and

c) X-rays emitted by fluorescence, (F), as a result of the absorption of X-rays of a shorter wavelength.

The advantage of this method is that the composition of a sample can quickly be obtained with the equipment which is normally used in conjunction with a scanning electron microscope, so features visible on the SEM can be quickly analysed for elemental composition.

The disadvantages are that the energy sensitive detector is limited in its ability to distinguish between closely spaced wavelengths and the accuracy of elemental compositional readings is only to within 10%.

## A 2.3 Electron probe microanalysis EPMA

This technique is essentially the same as EDX except that X-rays are distinguished by their peak positions after diffraction in perfect crystals as in a diffractometer in reverse. This method of analysing X-ray spectra is known as wavelength dispersive to distinguish it from the energy dispersive method of EDX. The advantage of EPMA is that the geometry of the system allows greatly increased resolution and very much greater accuracy in compositional analysis; up to 2% in an ideal system.

The disadvantages are the sensitivity of the system which is much lower than for EDX, dictating long measurement times and individual analysis of each element. The simplest way to increase the sensitivity of the system would be to increase the current of the electron probe, but the maximum current is limited by the heating effect on the sample and the fact that the probe must be focused to small spot to maintain wavelength resolution.

In addition ZAF corrections are not exact for complicated compositions and accurate measurements require calibration of the system with a standard sample of similar composition to the sample. In addition the geometry requires that the sample have a flat surface, ideally a polished one.

APPENDIX

## A.3 INDEX OF ACRONYMS

AMU	Atomic Mass Units
BISCCO	BiSrCaCuO
СМА	Cylindrical Mirror Analyser
EDX	Energy Dispersive X-Ray Analysis
EPMA	Electron Probe Microanalysis
FWHM	Full Width Half Maximum
IVD	Ionised Vapour Deposition
K.E.	Kinetic Energy
LIMA	Laser Ionisation Mass Analysis
LIF	Laser Induced Fluorescence Spectroscopy
MBE	Molecular Beam Epitaxy
MOCVD	Metal-Organic Chemical Vapour Deposition
Nd:YAG	Neodymium YAG, (Yttrium Aluminium Garnet)
PLD	Pulsed Laser Deposition
PZT	PbZr <sub>x</sub> Ti <sub>(1-x)</sub> O <sub>3</sub> (Lead Zirconate Titanate)
QMS	Quadrupole Mass Spectrometer
S	Sputtering
SEM	Scanning Electron Microscope
TE	Thermal Evaporation
TOF	Time Of Flight
XRD	X-ray Diffraction
CCD	Charge coupled device

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