ELSEVIER

Nuclear Instruments and Methods in Physics Research B 146 (1998) 362–366

NIM B
Beam Interactions with Materials & Atoms

Excitonic model of track registration of energetic heavy ions in insulators

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Abstract

The consequence of generation of dense electronic excitation along the paths of energetic heavy ions is discussed, emphasizing the fates of electron–hole pairs. It is pointed out that a substantial part of the energy imparted to electron–hole pairs in the materials in which excitons are self-trapped is converted directly to defect formation energy but do not contribute to heating. However, the thermal spike model can be an appropriate macroscopic model of the track registration of the materials in which excitons are self-trapped, because energy deposited to the material remains along the ion paths. The energy imparted to electron–hole pairs is diffused away from the ion paths in the materials in which excitons are not self-trapped. This explains the reason why the critical stopping power for track registration is higher in these materials. The difficulty for application of the thermal spike model to these materials is pointed out and it is suggested that nominal defects in densely excited region nucleate fragmental tracks.

PACS: 61.80Az; 61.82Ms; 61.80Jh; 71.35Aa
Keywords: Swift heavy ion; Radiation effects; Electronic excitation; Heavy-ion track; Thermal spike; Exciton; Self-trapped exciton; Amorphisation; Defect cluster

1. Introduction

The registration in solids of the tracks of heavy ions of energies above 1 MeV per nucleon is one of the few phenomena which link geological time-scales to events occurring in femtoseconds. Track formation occurs for incident ions which have above a critical (threshold) stopping power. The track radius observed by transmission electron microscopes can be scaled by electronic stopping power of the materials [1]. Clearly, the process has its origin in the electronic excitation of material. The presence of the critical stopping power implies that the density of this electronic excitation must exceed a critical value for tracks being registered.

Table 1 lists the threshold stopping power for a number of inorganic materials. The tracks can be continuous or fragmented. Continuous tracks are registered by heavy ions of stopping power in the range of 1–5 keV/nm in some materials, including SiO_2 and $LiNbO_3$ [2,3]. Tracks are amorphous for

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0168-583X/98/$ – see front matter
PII: S0168-583X(98)00448-0

Table 1
The threshold stopping power for track registration and defect formation in materials

Material	Threshold stopping power (keV/nm)	Ref.
SiO_2	2	[2]
mica	5	[1]
$LiNbO_3$	7	[3]
$Y_3Fe_5O_{12}$	4	[1]
Al_2O_3	21	[6]
MgO	20	[7]
Bi	31	[8]
Si	–	[9]

these materials. For alkali halides, the threshold stopping power has not been obtained with the same accuracy as for the materials listed in Table 1. Heavy ions of stopping power of about 10 keV/nm creates tracks in LiF, detected by chemical etching and small angle X-ray scattering. Tracks are even larger than that for SiO_2 [4,5]. However, in some insulators, such as MgO and Al_2O_3, the threshold critical stopping power is much higher, in the range of 20 keV/nm, and the tracks formed by ions near the critical stopping power are fragmented [6,7]. Even higher critical stopping powers are needed for track registration of high-temperature oxide superconductors [1], metals [8] and semiconductors [9]. Track registration depends strongly on the properties of the materials.

The mechanism of track registration is still controversial. Fleischer et al. [10] first suggested that the cause of track registration is dielectric breakdown due to electric field induced between electrons ejected from an ion path and positive ions left after ionization. An alternative model, the thermal spike mechanism, assumes that the portion of solids that exceeds the melting point is amorphised or damaged. The thermal spike appears to be able to explain the dependence of track radius on stopping power for those insulators for which the critical stopping powers are in the range of 1–5 keV/nm [3], and also for metals [8]. In the thermal spike model, it is assumed that all energy imparted to electronic excitation is transferred to phonon energies within 0.1 ps.

Both these models are incomplete. It is not clear just what "breakdown" means in terms of basic atomic processes, and so the character of the damage cannot be predicted. Nor is it clear just how the electronic excitation energy is transformed into thermal energy for the thermal spike to be effective. The energy of the incident ions is first imparted to some class of electronic excitation and only subsequently becomes ionic motion. It is important to trace the conversion of energy from electronic to lattice. We believe that both processes should recognise the potential self-trapping of excitons [11] in the track-forming materials, whether as the energy localisation process causing damage (as in the breakdown model [12]) or as the route by which electronic energy is transformed into heat within 1 ps. Indeed, the process of exciton self-trapping gives a further possible description of track registration, and one which can be regarded as including the other two descriptions [13,14].

The purpose of the present paper is to examine the consequences of electronic excitation along the paths of energetic heavy ions in insulators. We emphasise that the consequences of the generation of excitons and electron–hole pairs at high densities must be taken into account. We believe that the differences in the critical stopping power in the insulators, described above, can be explained in terms of the strength of exciton–phonon coupling. Self-trapping of a dense cluster of excitons (with a local density close to the molecular density, i.e. one exciton for almost every molecular unit) induces either amorphisation or heavy damage. Although the thermal spike model appears to be an appropriate macroscopic description of the phenomena for insulators in which excitons are self-trapped as well, and although it appears to work for metals as well, the model appears to be oversimplified. Closer examination of the consequences of the formation of exciton clusters is needed.

2. Excitation along the ion path

The primary interaction of energetic heavy ions with non-metals excite electrons from the valence band and core bands, producing energetic electrons, called δ rays. The δ rays cause further excitations of the same nature, and also interact with phonons. Electronic excitation by δ rays

continued for a time of order 10 fs, so long as their energy is higher than the band-gap energy. Since the excitation cross section is inversely proportional to the excitation energy, the number of core holes will be less than the number of holes in the valence band. Furthermore, the core holes are filled with electrons from the valence bands, emitting Auger electrons, within about 10 fs. Therefore, in about 10 fs after the incidence of an energetic heavy ion, the energy is imparted to the creation of energetic holes in the valence bands and energetic electrons in the conduction band, and these have low energies, and are incapable of further ionisation. Since the ranges of δ rays are short, the energy deposition is confined within a short distance along an ion path. Thus, dense electron–hole pairs are generated along an ion path, accompanied by heating. Given the high density of electron–hole pairs, they should convert to excitons in a short time, forming an exciton cluster [15].

The number of electron–hole pairs created by ionising radiation at low excitation densities is estimated to be E/W, where W is a parameter 2–3 times the band-gap energy E_G [16]. Thus, from a half to 2/3 of the input energy is converted to phonons: it consists of the energy ($<E_G$) possessed by the electrons and holes decelerated to an energy below the band-gap energy after a series of ionising collisions, and the energy imparted to phonons directly from energetic δ rays. The extremely high density of excitation along ion paths may alter the cross section of δ rays, as described later, but the pictures described above will be maintained along the densely excited part of the ion path.

The range of δ rays can be evaluated using formulae developed by Katz et al. [17]. These formulae give the density of electron–hole pairs in ion tracks in SiO_2, for which track radii have been evaluated by transmission electron microscopes [3]. It is found that the average concentration of excitons in the track is approximately 0.8 of the molecular density of the material [14]. This relation holds over the range of stopping power from the critical stopping power 3 to 20 keV/nm. Since the range of δ rays does not depend strongly on material, we can presume that the density of excitation per molecule in solids become almost unity at a stopping power of ~5 keV/nm.

3. Relaxation of densely excited tracks

The fates of the excitons in the exciton cluster are threefold [18,19]: Auger recombination, diffusion from the ion path, and lattice deformation (damage or heating) due to the self-trapping process of the excitons. The first (Auger) process converts the energy possessed by electron–hole pairs to heat; the second (diffusion) process takes energy away from the path. The last process, which occurs only in material in which excitons can self-trap, converts the energy of electron–hole pairs to lattice deformation. The deformation can involve defect production; it may also involve large thermal vibrations.

In materials with weak exciton–phonon interaction, as is well documented in Si and Ge, the excitons at low temperatures form exciton molecules and exciton droplets, in which excitons are separated typically by the exciton Bohr orbital. At high temperatures, because of low binding energy between excitons, they undergo diffusion separately. In any case, in the weakly coupled materials for which excitons are not self-trapped, the excitons diffuse away from the ion paths, and either interact with defects or are annihilated by radiative recombination. Diffusion takes at least 1/3 of the electronic energy away from the ion paths.

In materials in which excitons are self-trapped, lattice relaxation competes with diffusion and with Auger transitions. According to the measurements of the lifetime of free electrons in SiO_2 [20], self-trapping of an isolated exciton takes place 160 fs after excitation. The self-trapping time may be shorter for dense excitons because of their interaction. The diffusivity of excitons has not been measured, but it is governed by diffusivity of holes, which is too small to be measured. Suppose that the diffusivity of excitons is of the order of 1 cm^2/s. The time constant for a jump over a molecular unit is then of the order of 10 fs, so that the motion of excitons before self-trapping is extremely limited.

Auger recombination of excitons in an exciton cluster can be regarded as a resonant energy transfer from recombination luminescence of an exciton to electron-excitation of a neighbouring exciton. Following Dexter [21], we estimate that

the resonance energy transfer from a molecule in solid to a neighbouring molecule of SiO_2 requires more than 100 fs. Thus, it appears that the cluster of excitons will relax before other two competing processes (Auger and diffusion) can be effective. A highly distorted region should form along the path. It is likely that almost all input energy to electronic excitation will be localised along the ion path, as either the defect formation energy or thermal energy, if excitons are self-trapped. Clearly, the self-trapping of excitons can influence the critical threshold.

Self-trapping of an isolated exciton involves local rearrangement of bonding and accompanied by a large lattice distortion [22]. The relaxation of a cluster of excitons is somewhat similar to a hot zone in collision cascades; every atom in the lattice is highly displaced, and there is an electronic excited state [23]. Electronic excitation will clearly affect the interatomic bonding, and amorphisation is an obvious possible consequence of the relaxation of such an exciton cluster. This is especially so in materials such as SiO_2, which are easily amorphised; in alkali halides, which are not easily amorphised, the formation of a defect cluster is expected. We note that excitons are self-trapped in all materials of which the critical stopping power is 1–5 keV/nm. Thus, our arguments seem to be valid for all materials in Table 1, of which the critical stopping power lies near 5 keV/nm. In view of a large volume change due to formation of self-trapping of excitons [24], our model explains also experimental observation of swelling accompanied with track formation [25].

The relaxation of a cluster of excitons, whether it leads to defect clusters or to amorphisation, is accompanied by heating. The thermal spike calculation indicates that the temperature reaches a maximum about 10 ps after the passage of ions and then starts to fall afterwards. Furthermore, the energy used for amorphisation or formation of defect clusters directly from exciton clusters does not contribute to temperature rise therefore, the thermal spike model appears to overestimate the temperature rise. A further problem for the thermal spike model is that the range of δ rays increases as the density of excitons approaches the molecular density, since the ionisation cross section is inversely proportional to the excitation energy. Thus, the local density of energy near the ion path cannot increase in proportion to the stopping power, even though a Gaussian form of energy deposition is assumed in the thermal spike model. However, these difficulties are avoided within an exciton self-trapping description. Qualitatively, the essential feature of the thermal spike model is energy input along ion path, and this feature can be retained. Apart from a certain unknown parameter, such a thermal model may be able to predict qualitatively some of the features of track registration, such as the track radii, even in the case where heating is not the direct cause of track registration. The same key qualitative features can be explained equally if we use a mechanism based on the relaxation of excitons.

In materials in which excitons are not self-trapped, the critical stopping power is higher by a factor of 4–8. Since there is no source of localisation of electron–hole pairs, at least 1/3 of the energy will diffuse away from the ion path. It may be argued that 2/3 of the input energy at the stopping power of 20 keV/nm is sufficient to cause melting. However, the density of excitation along the path is again almost equal to the molecular density for a stopping power of 5 keV/nm. It follows that, for 20 keV/nm, the range of δ rays is much longer. Again there is a problem of the overestimation of the energy input along the path of heavy ions. Alternatively, the localisation of electron–hole pairs can occur at defect sites, resulting in formation of local exciton clusters, which can be converted to a highly distorted region. Since the exciton density is of the order of molecular density, the formation of such local defect cluster in a cluster of excitons can be regarded as nucleating defect clusters or amorphisation. This model can explain why the tracks are fragmented in these materials.

4. Conclusion

The occurrence of the self-trapping of excitons influences the critical stopping power for track registration in insulators. Those materials in which excitons are self-trapped have critical stopping powers near 3–5 keV/nm, those in which excitons

are not self-trapped have values near 20 keV/nm. The difference can be ascribed to the localisation of electronic excitation energy along the ion path. The density of excitation along ion path at stopping powers of 3–5 keV/nm is approximately equal to the molecular density; it is likely that a cluster of excitons formed in the materials in which excitons are self-trapped collapses to an amorphous structure or a defect cluster. This damage process is probably similar to some of the atomic processes which occur during electrical breakdown. It is likely that the thermal spike model is adequate as a macroscopic model for cases in which all energy imparted to electronic excitation is localised along the track. On the other hand, when describing track registration for insulators in which excitons are not self-trapped, the thermal spike model may overestimate the energy deposition along ion paths. We suggest that defects in the densely excited region nucleate fragmental tracks.

Acknowledgements

The authors are grateful to M. Toulemonde for valuable discussions.

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