Chemical vapour deposition of crystalline thin films of tantalum phosphide

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Abstract

Tantalum phosphide coatings were prepared by chemical vapour deposition reaction of $TaCl_5$ and PH_2Cy at 350-500 °C. The films are hard, stable to corrosive environments and show reflection properties in the Infra-red.

Key words

Chemical vapour deposition

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1. Introduction

Transition metal phosphides form an interesting series of compounds with several potential applications. Titanium phosphide (TiP) is a hard-wearing metallic conductor that is extremely resistant to oxidation [1]. It has been suggested in a patent for use as a diffusion barrier for Al/W-metallization [2]. A number of transition metal phosphides, including tungsten (WP) and molybdenum (MoP), have been found to be active catalysts for hydrodesulfurisation and hydrodenitrogenation reactions [3]. Additionally, metal-rich molybdenum phosphides have been found to be super-conducting with Mo_3P having the highest T_c (7 K) among binary metal phosphides [4]. Whilst synthetic routes to many bulk transition metal phosphides are well known [5, 6] the production of thin films of these materials remains relatively unexplored. Films of titanium phosphide (TiP) [7] and niobium phosphide (NbP) [8] have been produced from single source precursors using low pressure CVD conditions; a thin layer of TiP has been produced by annealing titanium nitride in phosphine at 450 °C[2] and recently crystalline thin films of TiP have been grown from the reaction of $TiCl_4$ and tertiarybutylphosphine (^{t}BuPH$_2$) under Atmospheric Pressure (AP)CVD conditions [9]. Additionally, Watson et al have reported the synthesis of thin films of amorphous chromium phosphide via low pressure pyrolysis of the precursor $Cr(CO)_5(PH_3)$ [10]. Thin films of γ-Ta_2N have been produced from $TaCl_5$ in a hydrogen/nitrogen atmosphere at atmospheric pressure at temperatures between 850 °C and 1000 °C [11]. The use of sputtered tantalum phosphide (TaP) as a diffusion barrier layer in semiconductor devices has also been reported [12] but there are no reports of the production of TaP thin films using a CVD process. Stimulated by this lack of a low-cost route to a material with potentially important commercial applications an investigation into the production of a tantalum phosphide thin film using APCVD techniques was undertaken.

2. Experimental

Films were grown on silica-coated float glass (15 x 4 cm) using a purpose built cold-wall reactor [13]. The precursors were diverted into the gas stream by passing the nitrogen carrier gas through heated bubblers. Reactions of $TaCl_5$ and cyclohexylphosphine ($CyPH_2$) were studied under APCVD conditions at temperatures between 350 °C and 500 °C. Cyclohexylphosphine was chosen because it is easy to handle (a liquid) gives

good transport and does not have the problems associated with PH_3 (toxic, explosive in air). At temperatures of 350 °C and below no deposition was observed from the reaction of $TaCl_5$ and $PCyH_2$. At temperatures between 400 °C and 500 °C even deposition of the substrate was observed with increased thickness at the higher temperatures. At a substrate temperature of 500 °C with a run time of 3 minutes it was found that a silver mirror-like film was produced which completely covered the substrate. The low volatility of the solid $TaCl_5$ (Mp 216 – 200 °C) was overcome by using high N_2 carrier flows. However due to the propensity of the solid to re-condense at cold spots in the CVD apparatus it was found the best results were obtained with the bubbler temperature maintained below the melting point of the solid. Sufficient vapour pressure of the metal source was achieved under these conditions for relatively rapid deposition to take place. The lack of equilibrium conditions in the bubbler makes calculating the amount of $TaCl_5$ used during reaction difficult although it can be assumed that the phosphine component was in excess.

3. Results and Discussion

One of the films produced at 500 °C was analysed using EDAX, SEM, glancing angle XRD and XPS. EDAX analysis showed the film was homogenous over a number of points and was nearly stoichiometric TaP. After etching through the surface contamination layer XPS revealed a film with no detectable carbon or chlorine contamination and a stoichiometry of TaP. The P 2p ionisation was centred on a binding energy of 128.6 eV which is indicative of a transition metal phosphide [8, 9, 14]. A small P 2p peak at 133.4 eV was also visible in the first two etched layers, indicative of oxygen contamination in the form of phosphate [8]. An O 1s peak was visible in the first two atomic layers at 530.8 eV but was evidently formed from two separate peaks. The Ta 4f showed a set of major peaks with Ta $4f_{7/2}$ at 21.8 eV and Ta $4f_{5/2}$ 23.6 eV with minor peaks observed with Ta $4f_{7/2}$ at 26.2 eV and Ta $4f_{5/2}$ at 28.0 eV in the first two etched layers. In Ta_2O_5 the O 1s peak appears at 530.4 eV [15] and the Ta $4f_{7/2}$ peak at 26.8 eV [16]. This suggests the tantalum phosphide film formed during reaction is contaminated with a small amount of surface oxide and phosphate from post-reaction oxidation. Analysis of the film using glancing-angle XRD showed the film was crystalline with a tetragonal unit cell with dimensions *a* = 3.30 Å (0.01) and c = 11.57 Å (0.09) which matches the literature values for β-TaP [17]. An SEM image (figure 1) showed that the film was an agglomeration of approximately 250 nm sized spherical particles.

Films produced at lower temperatures were X-ray amorphous and the SEM of these films were relatively featureless. Conductivity measurement using a four-point probe gave a sheet resistance of 5 Ω/sq, a value similar to a thin metal film, hence TaP is a good electrical conductor. Film thickness was not directly determined but from the EDAX break through measurements was of the order of 0.5 - 1 micron.

All films produced were adherent to the substrate, passed the Scotch tape test and were not abraded by brass or steel. The films were resistant to common solvents and concentrated nitric acid but were removed by concentrated hydrochloric acid in approximately 1 week. These results indicate that films of tantalum phosphide are more chemically resistant than those of titanium phosphide films produced using a similar CVD method [9]. This result is in accordance with the findings of Ripley during the analysis of bulk materials [1].

Water droplet contact angle measurements of theTaP films showed that they were hydrophobic. The films were opaque to UV, visible and near infra-red radiation but showed good reflection across these regions with slightly greater reflection observed towards the red/near infra-red region. The films showed no photocatalytic activity towards the decomposition of stearic acid. Low temperature magnetism measurements performed on the films showed that they were paramagnets with no evidence for superconductivity down to 4 K.

4. Conclusion

The first low temperature route to thin films of high purity tantalum phosphide is presented. Both crystalline and amorphous forms could be grown dependant on the substrate temperature. The ease of film production, the low temperature of deposition combined with the inherent advantages of the CVD methodology suggest that the full properties of thin films of TaP may now be more easily investigated.

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