CHEMICAL VAPOUR DEPOSITION OF THIN FILMS IN THE SYSTEM B-P

E.M. KELDER, A. GOOSSENS, P.J. VAN DER PUT and J. SCHOONMAN

*Delft University of Technology, Laboratory for Inorganic Chemistry,
Julianalaan 136, NL-2628 BL Delft, The Netherlands*

Résumé - L'effet de la composition initiale des gaz et de la température par CVD classique sous pression atmosphérique à partir de $\text{BBr}_3\text{-PBr}_3\text{-H}_2$ a été principalement étudié. La rugosité du substrat de silice fondue a été modifiée. Avec une augmentation de température et une décroissance du rapport $\text{BBr}_3/\text{PBr}_3$ on observe un changement de mécanisme de dépôt du monophosphure cubique (on passe d'un contrôle cinétique au contrôle diffusionnel).

Dans le régime limité par la diffusion, on n'observe pas le dépôt de BP cubique si le substrat n'a pas de sites de nucléation. Dans ce cas, un film amorphe de B_xP ($x > 1$) est obtenu; sa teneur en phosphore dépend du rapport $\text{BBr}_3/\text{PBr}_3$.

Abstract - The effect of the growth parameters on the deposition of boron phosphides B_xP by thermally activated atmospheric pressure CVD was studied for the boron tribromide - phosphorus-tribromide - hydrogen system, with main emphasis on the reactant molar ratio and the temperature. The surface roughness of the fused silica substrates was varied. With increasing temperature and with decreasing $\text{BBr}_3/\text{PBr}_3$ molar ratio a transition in the growth mechanism for cubic boron monophosphide BP from kinetically controlled to diffusion controlled is observed.

No deposition of cubic BP is observed in the diffusion controlled regime if the substrate exhibits a lack of nucleation sites. In this case a dense film of boron rich amorphous boron phosphide B_xP ($x > 1$) is observed with a phosphorus content depending on the $\text{BBr}_3/\text{PBr}_3$ molar ratio during deposition.

1 - INTRODUCTION

Chemical Vapour Deposition (CVD) is used for the fabrication of thin film semiconductor solar cells. With semiconductor electrodes immersed in an aqueous electrolyte direct conversion of solar energy to fuel or electricity is feasible. In such photoelectrochemical (PEC) cells, most semiconductor electrode materials, having a suitable bandgap, are subject to severe photocorrosion under irradiation. Several methods have been developed to prevent photocorrosion, i.e. adding stabilizing redox couples in the electrolyte /1,2/ or coating the electrodes with stable conductors /3-5/. Protection of an instable electrode surface by cubic boron phosphide (BP), a stable window material, has previously been shown to be feasible /6,7/. The synthesis and characterization of two crystalline boron phosphides have been reported, i.e. cubic boron monophosphide, BP /8-11/, and a rhombohedral boron subphosphide, B_{13}P_2 , having a structure derived from α -rhombohedral boron /12-14/. Amorphous boron phosphides have been described as boron rich boron phosphides /15/.

Cubic boron monophosphide (BP) is a semiconductor, having an indirect bandgap of 2 eV /16,17/. Cubic BP is quite hard /18,19/, and resistant to chemical corrosion /20/. It dissolves under hydrothermal conditions in concentrated nitric acid and alkali hydroxide solutions.

These properties match well with the required properties of a stable window material for semiconductors in aqueous electrolytes under irradiation.

The most common method to synthesize boron phosphides is by CVD using the hydrides /21-23/ or halides /21-24/, though chemical transport- /25/ and metal flux methods /26,27/ are also known. Here we report on the CVD of boron phosphides by bromide reactants in a hydrogen atmosphere.

In order to develop thin boron phosphide films for use as PEC electrodes a study is made of the CVD deposition conditions and kinetics of reaction to control the product properties.

2 - EXPERIMENTAL METHODS

Conventional, thermally activated CVD was used to synthesize the boron phosphide (B₂P₃) thin layers by adjusting boron tribromide and phosphorus tribromide partial pressures over a heated substrate under atmospheric hydrogen pressure. BBr₃ and PBr₃ were used because of the manipulative convenience of these reactants.

To obtain the reaction products as a function of temperature and reactant concentrations, a horizontal atmospheric pressure CVD (APCVD) quartz tube reactor (ID 4 cm) (Fig. 1a) is used. A flat quartz boat is used as sample holder on which tilted substrates are mounted. For the polycrystalline cubic boron monophosphide deposits the kinetics of the reaction were studied. A thermobalance CVD set-up equipped with a vertical quartz tube reactor (ID 2 cm) (Fig. 1b) is used to obtain growth rates of polycrystalline cubic BP as a function of temperature and reactant concentrations. A fused silica fiber is used to suspend the substrates in the hot temperature zone.

Fig. 1 - CVD reactor set-up.

- 1a - Horizontal reactor for studying formation of the boron phosphide compounds.
- 1b - Vertical reactor for monitoring the rate of growth of BP.

Hydrogen, purified with a palladium catalyst and dried by 4A Zeolyte was saturated with BBr₃ and PBr₃ by bubbling it through the liquids which were kept at the temperature corresponding to the required vapour pressure.

Depositions were carried out at different ratios of reactant partial pressures by adjusting the hydrogen flow rates through both liquids.

Substrates were optical quality fused silica and sintered alumina chips cleaned by the usual organic detergents, and preheated in air at 1000°C for several hours.

The samples were brought to the deposition temperature in a hydrogen flow. After about half an hour, the PBr₃-H₂ gas mixture was introduced, in order to avoid initial deposits of B₂P₃. The average of the total gas flux during the reaction was about 400 ml/min/cm². During cooling of the system till 700°C an excess phosphorus pressure was maintained.

The solid reaction products were characterized by means of Debye-Scherrer diffraction patterns. XPS spectra were recorded with a Physical Electronics spectrometer, equipped with a double pass cylindrical mirror analyser, and a 10 kV, 30 mA Argon ion gun which was defocussed for sputtering. The samples were sputtered during 10 minutes in order to clean the surface. No signs of preferential sputtering were detected. Element concentration were calculated by standard procedures from published ionization cross sections /28/. Electron micrographs were made with a JEOL scanning electron microscope (JSM 35).

3 - RESULTS AND DISCUSSION

Polycrystalline cubic BP and B₂P were identified by their XRD patterns. In Figures 2a and 2b a summary is given of the deposition results on alumina and fused silica. It is obvious from these Figures that the deposition regime is narrow for crystalline boron monophosphide and that the positions of this regime vary somewhat for the different substrates.

Fig. 2 - Process conditions for deposition of amorphous boron phosphide (B₂P) (A), and polycrystalline cubic boron monophosphide (BP) (X), on alumina (2a), and on fused silica (2b) at different temperatures, and BBr₃/PBr₃ molar ratios.

The B/P atomic ratios for depositions at 1213 K were determined by XPS analysis (Fig. 3). From this Figure a distinction is made between polycrystalline cubic BP and amorphous B₂P. The amorphous B₂P compounds change with the BBr₃/PBr₃ molar ratio where x varies from 4 to ^x6 (Fig. 3). The amorphous B₂P films are transparent red brown dense layers. Occasionally cracking occurs due to thermal stresses if the layer exceeds a thickness of 1 μm (Fig. 4). For the polycrystalline cubic BP films a B/P atomic ratio of about 1 is found by XPS in agreement with crystalline cubic boron monophosphide as determined by the XRD patterns. A plausible explanation for the deviation from stoichiometry of the amorphous layers is an excess of boron reactant in the reaction boundary layer. XRD along with optical microscopy (Fig. 5) of roughened fused silica reveal an amorphous B₂P layer, and near the scratch edges a clustering of grains in a regime where polycrystalline cubic BP is formed on alumina and amorphous B₂P on fused silica. These grains are probably polycrystalline cubic BP. The morphology suggests a diffusion controlled reaction mechanism under these deposition conditions.

Fig. 3 - Boron atom fraction in boron phosphide compounds at different BBr_3 - PBr_3 mole fractions at 1222 K determined from XPS spectra for amorphous boron phosphide (B_xP) (A), and polycrystalline cubic boron monophosphide (BP) (X).

2 μm

Fig. 4 - SEM micrograph of a cracked amorphous boron phosphide (B_xP) layer on fused silica.

100 μm

Fig. 5 - Optical micrograph of roughened fused silica with an amorphous boron phosphide (B_xP) layer and polycrystalline cubic boron monophosphide (BP) grains near the scratches.

On sintered alumina substrates, polycrystalline layers are found under the same deposition conditions (Fig. 6a). This Figure reveals a layer of grains, with a grain size of $5\text{ }\mu\text{m}$. This is probably due to the roughness of sintered alumina itself which contains many nucleation sites (Fig. 6b). We are inclined to believe that the grains on fused silica may also represent polycrystalline cubic BP.

At higher temperatures and PBr_3 vapour pressures few grains grow having different sizes due to a diffusion limiting growth mechanism (Fig. 6c).

The SEM micrographs of the low temperature (1174 K) deposits reveal a rather different pattern. On fused silica a dense layer is found (Fig. 6d) which is broken and peeled off, due to bad adhesion and thermal stresses. The alumina substrates were covered with a closed dense film following the substrate surface roughness (Fig. 6e).

These results could indicate a surface reaction controlled mechanism.

Fig. 6 - SEM micrographs of polycrystalline cubic boron monophosphide (BP) on alumina, and fused silica with $[\text{BBr}_3]/([\text{BBr}_3]+[\text{PBr}_3])$ mole fraction of 0.10.

- 6a - BP on alumina ; deposition temperature 1275 K.
- 6b - uncoated alumina substrate.
- 6c - BP on fused silica ; deposition temperature 1275 K.
- 6d - BP on fused silica ; deposition temperature 1174 K.
- 6e - BP on alumina ; deposition temperature 1174 K.

To identify the controlling parameters, a plot of the growth rate versus temperature is presented in Figure 7. An increase in the rate of growth with temperature is found, but beyond 1190 K the growth rate decreases. For three different temperatures (1094, 1161, 1222 K) the pressure profiles of BBr_3 and PBr_3 are presented in Figures 8a and 8b in order to obtain the reaction order in these reactants. We find a linear increase of BP growth rate with BBr_3 vapour pressure, followed by a vapour pressure independent regime for higher BBr_3 vapour pressures. The order in the BBr_3 reactant does not depend on temperature, whereas at higher temperatures a decrease of the maximum growth rate is found.

For PBr_3 we find initially a strong increase in the growth rate. The rate goes through a maximum and falls off exponentially. The maxima of the curves depend on the temperature but the order of reaction in the PBr_3 reactant does not depend on the temperature for both sides of its maximum.

Fig. 7 - Logarithmic plot of the growth rate for polycrystalline cubic boron monophosphide (BP) on alumina substrates versus the reciprocal absolute temperature. +($\beta=0.10$), 0($\beta=0.20$), *($\beta=0.35$); results of the reactor of Figure 1a, $X(\beta=0.10)$; results of the reactor of Figure 1b, where β is the mole fraction: $[BBr_3]/([BBr_3]+[PBr_3])$.

Fig. 8 - Growth rate plotted as function of the reactant pressures at 1093 K (+), 1161 K (*), and 1222 K (0).
 8a - Growth rate vs BBr_3 pressure. The PBr_3 pressure is kept constant at 280 Pascal.
 8b - Growth rate vs PBr_3 pressure. The BBr_3 pressure is kept constant at 35 Pascal.

A simple explanation is the rate limiting behaviour by the well-known Langmuir and Langmuir-Hinshelwood isotherms /29/.

$$S = \frac{k * K_a * K_b * [A] * [B]}{(1 + K_a * [A] + K_b * [B])^2} \quad (1)$$

$$k = k' * \exp[-\Delta H/RT] \quad (2)$$

$$K_a, K_b = k_a, k_b * \exp[\lambda_a, \lambda_b / RT] \quad (3)$$

where

S	growth rate
K_a	Langmuir adsorption coefficient for BBr_3
K_b	Langmuir adsorption coefficient for PBr_3
k	reaction rate constant
[A]	partial pressure of BBr_3
[B]	partial pressure of PBr_3
k'	pre-exponential factor in the Arrhenius equation
ΔH	activation energy in the Arrhenius equation
R	gas constant
T	absolute temperature
k_a	pre-exponential factor in the equilibrium equation for BBr_3
k_b	pre-exponential factor in the equilibrium equation for PBr_3
λ_b	heat of adsorption for BBr_3
λ_a	heat of adsorption for PBr_3

With equation (2) and the equilibrium equation (3) it is possible to fit the results of Figure 7 for certain values of constants.

This implies a reaction mechanism that does not change with temperature, but we noticed earlier that at 1190 K a change of reaction mechanism takes place from surface reaction controlled to diffusion controlled. It seems very likely that the maximum in Figure 7 is due to the same transition in mechanism.

4 - CONCLUSIONS

For CVD of crystalline cubic boron monophosphide from BBr_3 and PBr_3 in a hydrogen atmosphere a narrow regime of temperature and molar ratios of reactants is available. At relatively low deposition temperatures and high PBr_3 pressures, a surface reaction controlled mechanism is found. Under these conditions it is possible to synthesize homogeneous dense thin films of BP as a protective coating. At relatively high temperatures and low PBr_3 partial pressure, a diffusion controlled mechanism is found where grains of BP cover the substrate. Under these conditions it is difficult to synthesize a homogeneous layer. Amorphous boron subphosphide can be synthesized in the regime where a diffusion controlled mechanism takes place for cubic BP. The amorphous layers are homogeneous dense layers and may also be utilized as protective coatings.

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