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Germanium phosphide coatings from the atmospheric pressure chemical vapour deposition of GeX_4 ($X = Cl$ or Br) and $PCyc^{hex}H_2$

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Abstract

Atmospheric pressure chemical vapour deposition of germanium phosphide thin films was achieved on glass substrates from the reaction of $GeCl_4$ or $GeBr_4$ with $PCyc^{hex}H_2$ at 600 °C. These coatings show good uniformity and surface coverage. They are reasonably adherent, passing the Scotch tape test. The films were translucent in appearance with regions of birefringence. The films were X-ray amorphous. Scanning electron microscopy showed surface morphologies consistent with an island growth mechanism. X-ray photoelectron spectroscopy binding energy shifts for $GeP_{1.00}$ were 1218.2 eV for Ge $2P_3$ and 131.5 eV for P $2p_{3/2}$. Energy dispersive X-ray analysis and electron probe studies gave elemental ratios that were in agreement indicating films which varied from being germanium rich (Ge_3P) to phosphorus rich (GeP_2), with negligible chlorine or bromine incorporation dependent on deposition conditions. No Raman scattering was observed. Sheet resistance measurements indicated the films were poor conductors. Optically the films showed poor reflectance (5–10%) and 60–80% total transmission from 400 to 1000 nm. UV–Vis spectroscopy indicated an indirect band gap of 1.1 eV. Contact angle measurements were in the range 60°–80° and showed no significant change after 60 min irradiation with 254 nm UV light.

Keywords: Germanium phosphide; Thin film; APCVD

1. Introduction

Metal phosphides are known for all transition elements [1] and a variety of structures and stoichiometries are known [2]. They have been used as rodentacides [3], investigated as catalysts [4], explored as diffusion barrier layers in microelectronic device production [5], and exploited as semiconductors [6]. Many transition metal phosphides are hard, refractory materials [7], and in some cases resistant to oxidation [8]. Whereas the corresponding metal nitrides have significant technological applications [9] only the main group phosphides, namely InP and GaP, have been extensively studied [10].

Bulk metal phosphides have been prepared by a variety of routes including: direct combination of the elements [11,2], reduction of metal oxides in the presence of phosphorus and iodine [12], reaction of a metal with Ca_3P_2 [13], and via solid state metathesis reactions [14].

Formation of metal phosphide films (other than gallium and indium) has received little attention, especially by the use of chemical vapour deposition (CVD), though single and dual source routes to titanium and tin phosphides have been studied [15]. To our knowledge no work has been published on the formation of thin films of germanium phosphides by any technique. Bulk germanium phosphide (GeP) has been prepared and known for some time [16]. The thermodynamic properties of the germanium phosphide system have also been investigated [17]. Crystal structures of the only known stoichiometric bulk materials GeP and GeP_3 have also been published [18].

Germanium phosphide (GeP) is a semiconductor with a band gap of 0.95 eV [19]. This band gap nestles between crystalline silicon (1.14 eV) and crystalline germanium (0.77 eV) [20]. For a thin film of material to find application as a photo-voltaic it must ideally have a band gap between 0.95 and 1.7 eV [20]. It is

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therefore surprising that thin-film germanium phosphide has been overlooked as a possible photovoltaic-thin film semiconducting material. Here we report the first instance of a germanium phosphide film prepared by dual source atmospheric pressure chemical vapour deposition (APCVD).

2. Experimental

Nitrogen (99.99%) was obtained by BOC and used as supplied. Coatings were obtained on SiO_2 coated float glass. APCVD experiments were conducted on 150 mm × 45 mm × 3 mm pieces of glass using a flat bed cold walled APCVD reactor. The glass was cleaned prior to use by washing with petroleum ether (60–80 °C) and isopropanol and then dried in air. A graphite block containing a Whatman cartridge heater was used to heat the glass substrate. The temperature of the substrate was monitored by a Pt–Rh thermocouple. Independent thermocouple measurements indicated that temperature gradients of up to 50 °C were observable at 600 °C across the surface of the glass. The rig was designed so that four independent gas lines could be used. All gas handling lines, regulators and flow valves were made of stainless steel and were 1/4″ internal diameter except for the inlet to the mixing chamber and the exhaust line from the apparatus that were 1/2″ in diameter. In these experiments three gas lines were used. Gases came directly from a cylinder and were preheated by passing along 2 m lengths of stainless steel tubing, which were curled and inserted inside a tube furnace. The temperatures of all the gas inlet lines were monitored by Pt–Rh thermocouples and Eurotherm heat controllers.

Germanium (IV) chloride (99.99%) was obtained from Strem Chemicals and used without further purification and was placed into a stainless steel bubbler. The bubbler was heated to 60 °C by a heating jacket and $GeCl_4$ introduced into the gas streams by passing hot nitrogen gas through the liquid. $PCyc^{hex}H_2$, was purchased from Strem Chemicals, handled in a glove box and used without further treatment. The two components of the system were mixed by the use of two concentric pipes of 1/4″ and 1/2″ diameter, respectively, the inner pipe being 3 cm shorter than the outer pipe. The concentric pipes were attached directly to the mixing chamber of the coater. Gas flows were adjusted using suitable regulators and flow controllers. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. All of the apparatus was baked out with nitrogen at 150 °C for 30 min before use. Deposition experiments were conducted by heating the horizontal bed reactor and the bubblers to the desired temperatures before diverting the nitrogen line through the bubbler and hence to the reactor. Deposition experiments were timed by use of a stopwatch and were conducted typically for 1 min. The maximum possible deposition temperature with this equipment was 600 °C. At the end of the deposition only nitrogen was allowed to flow over the glass substrate until the substrate was sufficiently cool to handle (~ 60 °C). Cool, coated samples were handled and stored in air. The large coated glass sample was cut into smaller samples (1×1 cm^2) for analysis by X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray analysis (EDXA), scanning electron microscopy (SEM), electron probe, transmission/reflectance and UV absorption studies. Larger pieces of glass (4 cm × 4 cm) were used for sheet resistance, X-ray powder diffraction, contact angle and Scotch tape tests.

X-ray powder diffraction patterns were measured on a Siemens D5000 diffractometer using filtered (Cu $K\alpha_1$, $\lambda = 0.15406$ nm) radiation in the reflection mode using glancing angle incidence (1.5°). SEM images were acquired on a Hitachi S570 instrument. EDXA was conducted using a JEOL 35-CF instrument. Electron microprobe analysis was obtained on a JEOL EMA and referenced against germanium and phosphorus standards. X-ray photoelectron spectra were recorded with a VG ESCALAB 220I XL instrument using a focused (300 μm spot) monochromatic Al $K\alpha$ radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging and the binding energies were referenced to an adventitious C 1s peak at 284.6 eV. Depth profiling measurements were obtained by using argon beam sputtering.

UV–Vis spectra were obtained using a Helios double beam instrument. Reflectance and transmission spectra were recorded between 300 and 1150 nm by a Zeiss miniature spectrometer. Measurements were standardised relative to a rhodium mirror (reflectance) and air (transmission). Raman spectra were acquired on a Renishaw Raman system 1000 using a helium–neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. Contact angle experiments were determined by measuring the spread of a 1 μl droplet of water on the film surface, and applying a simple trigonometric program. Electrical properties were determined by using a 4 probe device.

3. Results

APCVD of germanium phosphide films were achieved on glass substrates from the dual source CVD reaction of $GeCl_4$ or $GeBr_4$ and cyclohexylphosphine ($Pcyc^{hex}H_2$). The process was studied at different substrate temperatures and flow rates of precursor (Table 1).

No film could be grown at substrate temperatures below 550 °C, however, uniform films were obtained at 600 °C. The films grown from dual source CVD reactions of $GeCl_4$ or $GeBr_4$ and cyclohexylphosphine were

Table 1
Experimental conditions and microanalytical results for the APCVD reactions of GeX_4 (X = Cl or Br) and $PCyc^{hex}H_2$

Substrate temperature, °C	Nitrogen flow through GeX_4 bubbler, $l\,min^{-1}$ (GeX_4) [bubbler temperature, °C]	Nitrogen flow through R_xPH_{3-x} bubbler, $l\,min^{-1}$ (R_xPH_{3-x}) [Bubbler temperature, °C]	Nitrogen flow of make up gas, $l\,min^{-1}$	EDAX and electron probe analysis
600	0.3 ($GeBr_4$) [140]	0.3 ($CyhexPH_2$) [120]	1.0	Ge_2P
600	0.3 ($GeBr_4$) [140]	0.3 ($CyhexPH_2$) [120]	0.6	Ge_2P_3
600	0.3 ($GeBr_4$) [140]	0.3 ($CyhexPH_2$) [120]	0.3	$GeP_{1.00}$
500	0.3 ($GeBr_4$) [140]	0.3 ($CyhexPH_2$) [120]	0.6	No film
550	0.3 ($GeBr_4$) [140]	0.3 ($CyhexPH_2$) [120]	0.6	No film
600	0.3 ($GeBr_4$) [140]	0.5 ($CyhexPH_2$) [120]	0.6	$GeP_{1.20}$
600	0.3 ($GeBr_4$) [140]	0.7 ($CyhexPH_2$) [120]	0.6	$GeP_{1.20}$
600	0.5 ($GeBr_4$) [140]	0.3 ($CyhexPH_2$) [120]	0.6	$GeP_{1.10}$
600	0.7 ($GeBr_4$) [140]	0.3 ($CyhexPH_2$) [120]	0.6	$Ge_{1.10}P$
600	0.3 ($GeCl_4$) [55]	0.3 ($CyhexPH_2$) [120]	1.0	$GeP_{1.00}$
600	0.5 ($GeCl_4$) [55]	0.3 ($CyhexPH_2$) [120]	1.0	Ge_5P_3
600	0.7 ($GeCl_4$) [55]	0.3 ($CyhexPH_2$) [120]	1.0	Ge_3P
600	0.3 ($GeCl_4$) [55]	0.5 ($CyhexPH_2$) [120]	1.0	GeP_2

translucent, those grown at 600 °C exhibited birefringence due to thickness effects. The films were not reflective. All of the films passed the Scotch tape test. They could not be marked with a wet towel but could be marked with a brass stylus or steel scalpel. The films showed no optical change after storage in air for 3 months.

Compositional analysis of the films was determined by EDXA and electron probe measurements (summarised in Table 1). The results show that the films are free of chlorine (or bromine if $GeBr_4$ was used) and contain only germanium and phosphorus. In all cases some breakthrough to the underlying glass was observed with oxygen and silicon being observed. This was corrected for based on a sample of plain glass. These results show that it is possible to create films with a selection of stoichiometries, ranging from Ge_3P to GeP_2 (including non-stoichiometric phases such as $Ge_{1.1}P$) which were free from oxide or phosphate. The analysis showed that there was a slight variation in composition across the surface of the glass substrate of a single film, for example films with composition Ge_2P_3 had a composition of $GeP_{1.00}$ at the extreme edges. Backscattered electron images indicated a homogenous single phase film except at the extreme edges.

SEM analysis of the films showed that the deposition reaction proceeded via an island growth mechanism. A representative micrograph is shown in Fig. 1. SEM indicated a film thickness of 300–600 nm. This corresponds to a growth rate of 300–600 nm^{-1}.

The optical properties of the films were studied by reflectance/transmission measurements and UV absorption between 300 and 1100 nm. All samples showed a shift in the absorption edge relative to the plain glass substrate. The films showed poor reflectivity (10%), similar to the glass substrate. The transmission spectra indicated slight hazing; this is due to scattering of light by particles in the film of a similar dimension to the wavelength of the light.

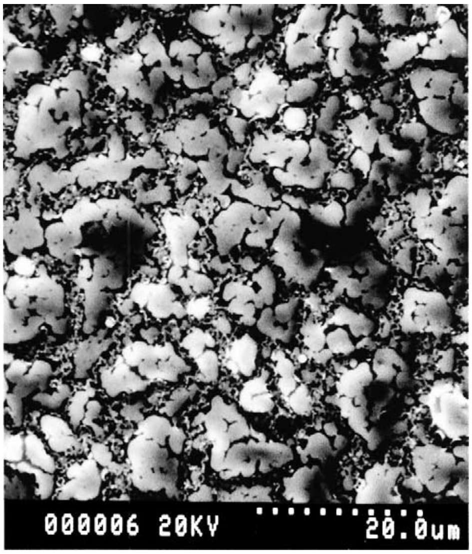

Fig. 1. Secondary electron SEM image of a germanium phosphide ($GeP_{1.00}$) film formed from the APCVD reaction of germanium tetrabromide and monocyclohexylphosphine at 600 °C.

The XPS peak profiles for the GeP films observed after sputtering (Fig. 2) are consistent with one environment for both germanium and phosphorus, although at the surface the shifts are slightly higher indicating perhaps, the presence of germanium phosphate. This is confirmed by observing a peak in the oxygen O_{2s} region which is not due to surface oxygen. After the first sputtering there is no evidence for the presence of germanium oxides or phosphate from the XPS profiles—the bulk of the film corresponds to GeP. XPS measurements on a sample of the film prepared by the dual source APCVD reaction of $GeCl_4$ and

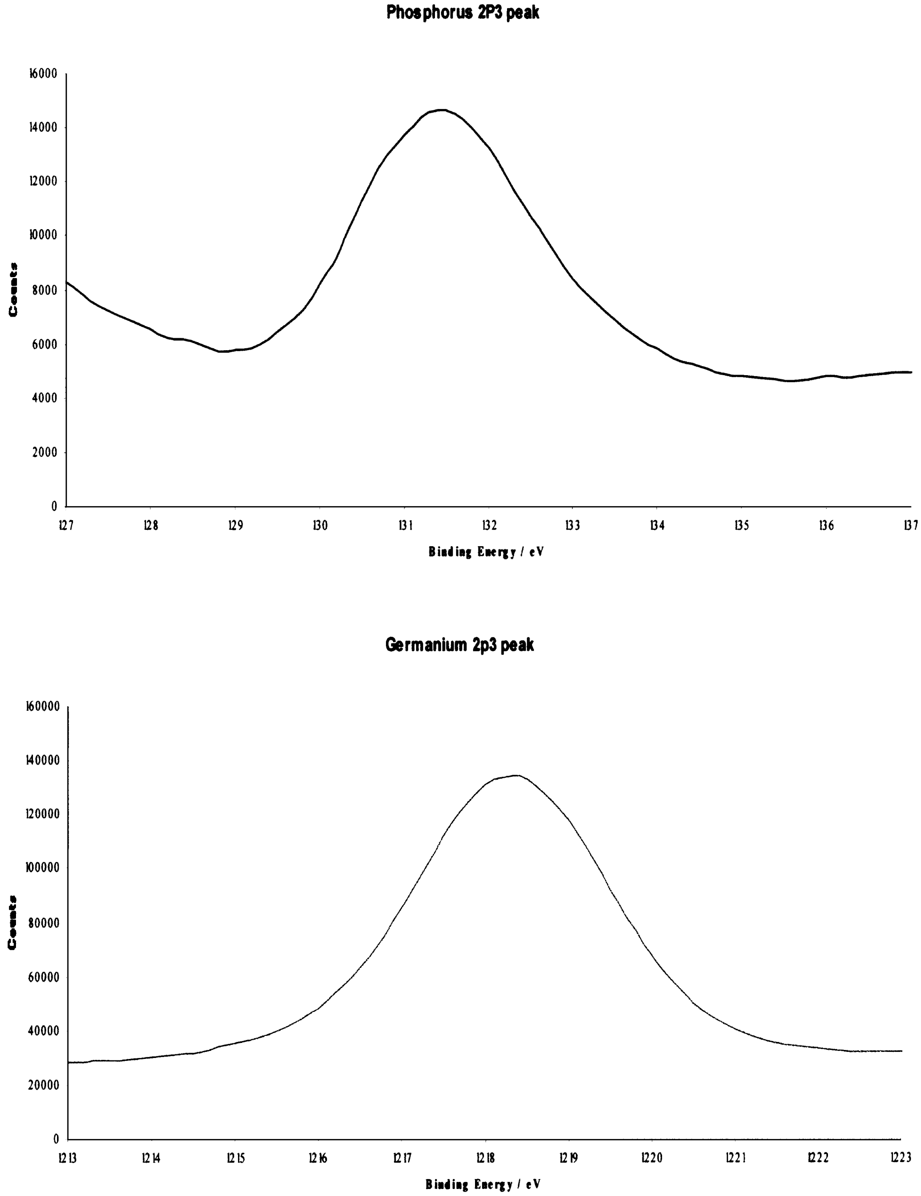

Fig. 2. The XPS peak profiles for a $GeP_{1.00}$ sample showing on the left of the phosphorus $2p_3$ region and on the right of the germanium $2p_3$ region.

$PCyc^{hex}H_2$ gave a composition of $GeP_{1.00}$. This film revealed binding energy shifts of 1218.2 and 131.5 eV for Ge $2p_{3/2}$ and P $2p_{3/2}$, respectively. To our knowledge the XPS spectra of GeP has not previously been reported. The Ge $2p_{3/2}$ binding energy is intermediate between 1217.0 eV in elemental Ge and 1219.5 eV in GeS_2. The P $2p_{3/2}$ binding energy in $GeP_{1.00}$ is similar to 133.5 eV for tin phosphide [21].

Raman microscopy was used to investigate all of the films. In all cases no Raman scattering was observed. This implies that germanium phosphides are poor Raman scatterers. No free carbon was detected by Raman microscopy. Previous work shows that free carbon as graphite is detectable by Raman a levels of approximately 1–2% [22].

The indirect band gap was calculated from the UV–Vis spectra using the Tauc method [23]. The sample of $GeP_{1.00}$ had a band gap of 1.1 eV similar to previous literature values for bulk material (0.95 eV) [20]. The germanium phosphide films were X-ray amorphous. Sheet resistance measurements indicated that the films were poor conductors, values were typically in the region of 600 Ω/□. The films were shown to have contact angles to water droplets of 60°–80°. The contact angle did not change significantly after irradiation with 254 nm UV light for 1 h. This contact angle is similar to that of plain glass 50°–75°. The films show no photocatalytic activity for the destruction of a stearic acid over layer using 254 nm light.

4. Discussion

Reaction of $GeCl_4$ or $GeBr_4$ and cyclohexylphosphine ($PCyc^{hex}H_2$) under APCVD affords translucent films of germanium phosphide on glass substrates. A range of germanium phosphide film stoichiometries ($Ge_3P \rightarrow GeP_2$) could be made depending on the deposition conditions. A number of non-stoichiometric films were also produced. It is unlikely that these films contain significant elemental germanium or phosphorus as these would be detected in the analysis. The precursor halides and $PCyc^{hex}H_2$ were chosen for this study as they are volatile and give sufficient carryover for APCVD. $PCyc^{hex}H_2$ is commercially available and does not have the toxicity and extreme pyrophoric characteristics of PH_3.

The mechanism of this reaction was not determined in this study. It is likely that HCl is produced in the reaction as well as $Cyc^{hex}Cl$ or HBr and $Cyc^{hex}Br$ if using $GeBr_4$ [24]. It is plausible that the reaction occurs via the formation of an adduct as some solid material was recovered from the exhaust which was not starting material. Previous work also suggests that similar deposition processes occur via adducts [25].

These films show no Raman spectra. The films shift the absorption edge, and undergo less transmission and reflection than SiO_2 coated glass due to scattering haze. EDAX and electron probe results suggest that the composition over the surface of the glass is similar. SEM shows that whilst various morphologies are possible, one predominates in samples of germanium phosphide films. Backscattered electron images indicated that films consist of a single homogenous phase.

Germanium content in the films increased with the flow rate of the germanium precursor, a similar trend was not observed with the variation of flow rate of the phosphorus precursor. It appears to be the case that the concentration of germanium precursor in the reactor is the limiting reagent. Where the flow of nitrogen gas is higher less phosphorus incorporation into the final film was observed.

A Tauc plot based on the UV–Vis spectra of a $GeP_{1.00}$ sample indicated an indirect band gap of 1.1 eV. This is similar to previously published values [19]. Our value is slightly higher than the previous value. We anticipate that this is the case because of confinement effects. As the films are at most 600 nm thick the particles are significantly smaller than in the bulk material and as such confinement effects cause the band gap to increase [26]. In any case we have demonstrated here that thin film GeP can be made by CVD and that in thin film GeP has a band gap of 1.1 eV. This band gap is in the required range for application as a photovoltaic material.

5. Conclusion

Reaction of $GeCl_4$ or $GeBr_4$ and cyclohexylphosphine under APCVD affords translucent films of germanium phosphide on glass substrates. The films show good surface coverage, adhesion and reasonable uniformity. Germanium phosphide films with a range of stoichiometries (Ge_3P–GeP_2) could be obtained. These were all translucent in appearance and poor electrical conductors. A Tauc plot indicated that germanium phosphide films are semiconducting with an indirect band gap of 1.1 eV.

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