Preparation and characterisation of Cd_3P_2 , a II–V group compound semiconductor

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MS received 27 February 1984; revised 18 January 1985

Abstract. Cadmium phosphide ($\alpha\text{-Cd}_3\text{P}_2$) a $\text{II}_3\text{-V}_2$ compound semiconductor has been prepared by C/H_2 reduction of cadmium phosphate. The reduction process is conducted at 550°C allowing the reaction to continue for 4 to 5 hr. The material always gets deposited on the walls of the quartz tube at different zones, which after analysis is found to contain, depending upon the location of the zone, Cd_3P_2 , CdP_2 and other cadmium rich phosphides. The resistivity of the pressed samples are of the order of $3 \times 10^{-4} \Omega\text{-cm}$. Optical absorption spectra of thin films, obtained by thermal evaporation on glass substrates, have exhibited broad bands around 620 nm.

Keywords. Cadmium phosphate; cadmium phosphide; reduction process; resistivity; optical absorption.

1. Introduction

Photovoltaic properties of phosphides belonging to $\text{II}_3\text{-V}_2$ group of compound semiconductors have been actively studied recently owing to their promising applications in solar energy devices (Catalano 1977; Zdanowicz and Zdanowicz 1975; Yashevchenko 1980). Cadmium phosphide the material of the present study, has also been used in IR detectors as well as in laser sources (Zdanowicz and Zdanowicz 1975). Amongst this $\text{II}_3\text{-V}_2$ group, Zn/Cd phosphides have been prepared by earlier workers by the direct reaction of their constituent elements Zn/Cd and P . In our laboratory attempts are being made to synthesize these compound semiconductors by C/H_2 reduction of Zn/Cd phosphates (Murali 1980). Some results on electrical and optical properties of Zn_3P_2 prepared by this method were already reported (Murali and Rao 1981, 1982).

Both the phosphides (Zn_3P_2 and Cd_3P_2) are direct band gap semiconductors having bandgap values around 1.5 and 0.5 eV respectively. Zn_3P_2 is reported always to exhibit p -type conductivity while for Cd_3P_2 n -type conductivity has been observed. Till date conventional doping procedures with suitable impurities to make Zn_3P_2 n -type and Cd_3P_2 p -type have not been completely successful. In view of this making p - n junction devices with either Zn_3P_2 or Cd_3P_2 still remains a challenging problem in the research area dealing with the synthesis of these materials. The present paper reports some results on the electrical and optical properties of cadmium phosphide prepared by C/H_2 reduction of cadmium phosphate.

2. Material preparation

The starting chemical cadmium phosphate was prepared by two different methods, (i) by using cadmium sulphate and (ii) by using cadmium acetate. These materials were initially characterised by x-ray diffraction technique and the background impurities estimated by using TSL and TSC techniques (Bagulasankrithyan and Rao 1984). The material prepared using cadmium acetate yields better quality Cd_3P_2 by the reduction process.

Cadmium phosphate prepared using Cd acetate was dried initially at 200°C and then used in the preparation of Cd_3P_2 . In the case of carbon reduction process the mixture containing stoichiometric quantities of cadmium phosphate and specpure carbon were kept in a tubular furnace at 550°C and the reaction was allowed to continue for 4 to 5 hr either in N_2 atmosphere or in vacuum (10^{-2} torr). In the case of H_2 reduction process the cadmium phosphate packed in a porcelain boat is placed at the central zone of the furnace, whose temperature is raised at the rate of $4.5^\circ\text{C}/\text{min}$ in a continuous flow of H_2 . The reduction by H_2 is conducted in this way finally at 550°C for 5 to 6 hr. By both the methods of reduction Cd_3P_2 has only been formed on the walls of the quartz tube; the schematic of the furnace used in the material preparation is shown in figure 1. The x-ray diffractograms of Cd_3P_2 , obtained by both these methods, have indicated apart from $\alpha\text{-Cd}_3\text{P}_2$ lines, presence of Cd rich cadmium phosphide (figure 2); the values of 2θ are indicated in table 1.

Figure 1. A. Schematic diagram of the tubular furnace. B. Coating on the walls of the tube.

(a)

(b)

Figure 2. X-ray diffractograms of $\alpha\text{-Cd}_3\text{P}_2$ prepared by **a.** Carbon reduction and **b.** H_2 reduction of $\text{Cd}_3(\text{PO}_4)_2$.

Table 1. X-ray diffraction data of bulk Cd_3P_2 .

Value of 2θ (in degrees)	
ASTM	Experiment
*14.5	14.7
*15.8	15.9
*17.3	17.3
19.0	19.6
*21.5	21.6
27.0	27.2
*27.5	27.7
30.4	29.5
33.3	33.0
35.5	35.4
38.8	39.2
40.8	40.8
43.9	43.6
46.0	45.6

* correspond to Cd.

3. Results and discussion

The electrical conductivity of the pressed samples (pellets of 10 mm dia were made by applying 5 ton pressure) was measured using the four probe method. All the samples in general indicated very low values of resistivity of the order of $3 \times 10^{-4} \Omega\text{-cm}$. The ρ values reported by other workers (Zdanowicz and Wojokowski 1965) are in the range of 9 to 25 m $\Omega\text{-cm}$. The low values of resistivity observed for Cd_3P_2 in this study has been attributed to the large fraction of Cd content present in the Cd_3P_2 obtained by the C/ H_2 reduction process.

Optical absorption of the thin films prepared by thermal evaporation on glass substrates at room temperature has been measured in the spectral range from 0.4 to 3 μ using an UV-visible-NIR recording spectrophotometer (Beckman model 5270). Very thin films (thickness < 1 μ) could only be obtained by the method of evaporation. They have all exhibited a broad absorption band around 600 nm; some typical results of the optical absorption spectra are shown in figure 3.

Comparing these results with those reported by Zdanowicz and Zdanowicz (1975), the broad absorption band around 2.06 eV (~ 600 nm) which is nearly equal to the band gap of $\alpha\text{-CdP}_2$, may be attributed to the presence of $\alpha\text{-CdP}_2$ in the material (thin films) obtained on glass substrates. No such clear absorption bands related to $\alpha\text{-Cd}_3\text{P}_2$ were obtained for these thin films beyond 1.4 and up to 2.5 μm (this wavelength region has thus not been depicted in figure 3). X-ray diffraction data of thin films did not also, however, indicate any of the prominent lines of either $\alpha\text{-Cd}_3\text{P}_2$ or $\alpha\text{-CdP}_2$. Because of the very low value of the thickness these lines could not be detected in the presence of the background lines of the glass plate itself.

Figure 3. Optical absorption of thin films (of thickness ●-0.95 μm and ○-0.86 μm) of cadmium phosphide.

4. Conclusions

Cadmium phosphide, synthesized by C/H_2 reduction of $\text{Cd}_3(\text{PO}_4)_2$, when prepared in the form of thin films on glass substrates by thermal evaporation, has been found to contain $\alpha\text{-CdP}_2$ phase. The composition of the bulk material, however, is Cd rich $\alpha\text{-Cd}_3\text{P}_2$ which indicated resistivity values of the order of mohm-cm.

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