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Electrical and thermoelectrical properties of Zn$_3$P$_2$ films grown by the hot wall epitaxy technique

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Zinc phosphide thin films were prepared by the hot wall epitaxy technique. The transport properties of films grown at different substrate temperatures from 200 to 350 °C were studied from room temperature up to 600 °C. Films were also grown in pure oxygen and nitrogen atmospheres at a pressure of 10^{-6} Torr, and the conductivity of the films was measured *in situ*. Thermoelectric measurements on films grown on mica were also done at various temperatures ranging from 300 to 800 K. Arrhenius plots of electrical conductivity yielded an electronic band gap of 1.32 eV and acceptor levels of 0.21 and 0.49 eV corresponding to interstitial phosphorus and absorbed oxygen levels, respectively. Variation of growth temperature, pressure, and nature of the gas present inside the chamber during growth are shown to result in a range of electrical resistivities and to be responsible for changes in carrier concentration. The sign of Seebeck coefficient was found to change from positive to negative at a temperature of 240 °C for a film grown on mica at a substrate temperature of 350 °C.

INTRODUCTION

Zinc phosphide has gained importance as a promising, low cost semiconductor for large-scale terrestrial photovoltaic applications,[1,2] owing to its chemical and thermal stability, large optical absorption coefficient at a band edge of 1.42 eV, a minority-carrier diffusion length of 8–10 μm, and the easy availability of constituent elements.

An extensive literature is available on band structures,[3,4] optical properties,[5,6] photoconductive properties,[7] and transport properties[8,9] of Zn$_3$P$_2$ single crystals. However, relatively little work has been done on the thin films of Zn$_3$P$_2$.[1,8,10] To the best of our knowledge, there is no reported literature available on the thermoelectrical properties of thin films.

Using the hot wall epitaxy (HWE) technique we have grown polycrystalline Zn$_3$P$_2$ films on mica and glass substrates. In this paper the electrical properties of Zn$_3$P$_2$ films grown at different substrate temperatures, for various ambient atmospheres, and the thermoelectric behavior of the polycrystalline films are reported. A typical optical absorption spectrum and x-ray diffractograms are also included.

EXPERIMENTAL TECHNIQUES

The source material Zn$_3$P$_2$ was synthesized by direct combination of stoichiometric proportions of high-purity zinc and red phosphorus.[1] The powder obtained was confirmed as Zn$_3$P$_2$ by x-ray analysis. An x-ray diffractogram of the powder indicated the presence of single-phase Zn$_3$P$_2$. The hot wall epitaxy system used in this work was based on a computer-aided design of Ramachandran and Vaya,[11] and the dimensions are optimized experimentally for large-grain polycrystalline film growth for a wide range of source and substrate temperatures. The experimental details of the film growth are published elsewhere.[12] Freshly cleaved mica and chemically cleaned glass plates were used as the substrate material. The films were grown at substrate temperatures ranging from 200 to 350 °C, keeping the source and wall temperatures at 630 and 650 °C, respectively.

Since Zn$_3$P$_2$ vaporizes congruently, it is assumed that the stoichiometry of the vapor is maintained during growth by keeping the vapor leak rate sufficiently low. The leak rate was kept low by minimizing the gap between the substrate and quartz wall of the hot wall epitaxy system.

The *in situ* conductivity measurements on films grown in pure nitrogen, oxygen, and air ambients were carried out using a measurement setup as follows. The films were coated on glass plates, the two ends of which are precoated with silver paint for contact purposes. Pressure contacts were made on these silver paint coatings and the connecting leads were taken out of the chamber using vacuum feedthroughs. The whole setup is fixed on a substrate manipulator with the substrate heater and placed on the quartz wall of the hot wall epitaxy system. A mask with a rectangular hole (0.5 × 1.5 cm^2) was placed in between the opening of the quartz wall and the substrate, in order to obtain a regular film shape. The film was detached from the mask and quartz tube using the substrate manipulator for measurement, thereby avoiding the passage of current through wall coating or through coatings on the mask. The film was allowed to cool. Then conductivity measurements on this film was carried out at temperatures from 300 to 400 K, during both heating and cooling cycles, inside the evacuated chamber, without ex-

TABLE I. Electronic parameters of Zn_3P_2 HWE films compared with the available data on bulk Zn_3P_2.

Quantity	Method of measurement	Parameters obtained from present study	Reported values of bulk Zn_3P_2	References
Energy gap				
(a) Optical	Optical absorption spectrum	1.42 eV	1.32 eV 1.49 eV	5 13
(b) Electrical	Arrhenius plot	1.32 eV	...	...
Carrier concentration at 300 K	Hall effect	$10^{13}/cm^3$	10^{14}–$10^{20}/cm^3$	8,13
Hall mobility	Hall coefficient and electrical conductivity	28 cm^2/V s	10–50 cm^2/V s	8
Acceptor levels	Arrhenius plot	0.21 eV 0.49 eV	0.14 eV 0.23 eV 0.25 eV 0.47 eV	 8,9 13
Thermoelectric power at 300 K	Seebeck coefficient measurement	1.8 mV/K	...	...

posing the freshly grown films to atmosphere. After admitting appropriate gases inside the chamber, the transport properties of these films were carried out by the two-probe method under a dynamic vacuum of 10^{-3} Torr.

Hall measurements were done at room temperature on a relatively thick film ($\sim 10 \mu m$) on a mica substrate especially grown at 330 °C for this purpose by putting a mask of area 2×0.5 cm^2 below the substrate. Silver paint contacts were made. The Hall coefficient R_H, carrier concentration p, and Hall mobility μ_H were calculated by the usual formulas, and the values are listed in Table I.

Thin films of 1.0×0.5 cm^2 size on mica substrates were used for thermoelectric measurements. The experimental setup for varying, controlling, and measuring the temperature, temperature gradient, and thermoelectric voltage are described below. The specimen selected for measurements was attached to a relatively thick mica sheet of 8×1 cm^2. Two nearly identical flat heaters were provided on either end of this mica sheet. This assembly had two thermocouples and connecting leads which were inserted inside a small quartz tube furnace (2 cm diam) which served as the ambient heater. The whole setup was placed in the evacuation system and a dynamic vacuum of 10^{-3} Torr was maintained during measurement. While maintaining the average temperature T, a desired temperature gradient ΔT in either direction could be set up across the active portion of the sample by using the small heaters. The Seebeck coefficient was obtained using data taken over a ΔT range of ± 10 K. No correction was applied for thermoelectric power due to the contact material. The thickness of the films was measured using an optical microscope with 10^3 magnification to an accuracy of ± 0.5 μm.

RESULTS AND DISCUSSION

In the x-ray diffractograms a number of peaks corresponding to (220), (004), (224), (400), (212), etc., are present. The films appear to be oriented at higher substrate temperatures and the orientation becomes preferential as (220). Typical x-ray diffractograms for Zn_3P_2 films grown on glass at substrate temperatures of 300 and 350 °C are shown in Fig. 1. The optical absorption spectra of the films grown on mica and glass are shown in Fig. 2. The parameters derived from the figure are listed in Table I.

The thin films grown on mica substrate at lower substrate temperatures are found to be relatively less resistive, but have a very poor adhesion to the substrate. Hence the
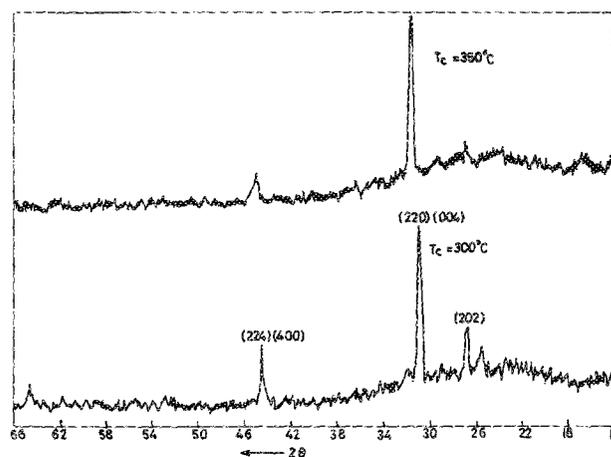

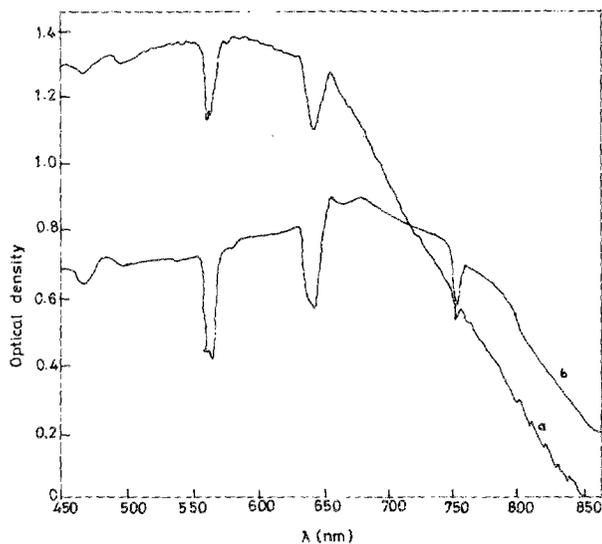FIG. 1. X-ray diffractograms of Zn_3P_2 films grown on glass at a substrate temperature of 300 and 350 °C.

FIG. 2. Optical absorption spectra of Zn_3P_2 films coated on (a) mica, (b) glass.

transport measurements were not possible on these films at high measurement temperature. Good sticking was obtained for films grown at 330 °C and above on mica. The dark resistivity of these films were estimated as 10^6 Ω cm at room temperature. Figure 3 shows the variation of conductivity with temperature at different growth temperatures. The curves do not coincide at the conductivity region corresponding to the intrinsic conductivity of the semiconductor
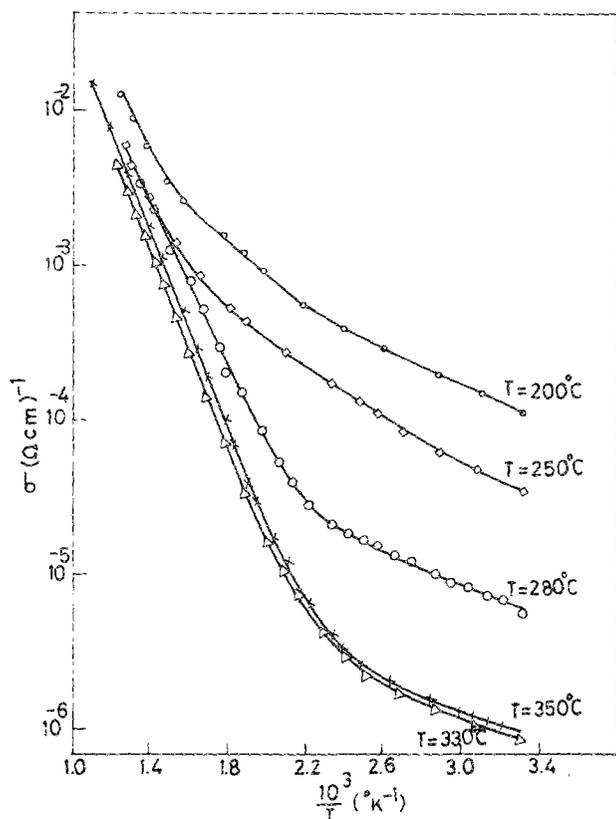

FIG. 3. Arrhenius plots of Zn_3P_2 films grown on glass at various substrate temperatures coated on mica, at a pressure of 10^{-6} Torr in air.

probably because of error in the thickness measurement. The conductivity of the films decreases as the crystallinity improves with increasing substrate temperature. Grain boundaries were shown to be inactive with respect to the electronic properties of Schottky barrier solar cells on polycrystal Zn_3P_2 by Bhushan.[14] The electrical conductivity of the films is controlled mainly by the excess phosphorus present in the material, which is a function of growth temperature. The conditions for more phosphorus atoms to be buried in the grown films are highly favorable at lower growth temperatures. At high temperatures more and more excess phosphorus atoms will be expelled from the material and hence conductivity falls even though there is an enhancement in mobility due to better crystallinity. The higher intrinsic temperature (corresponding to the transition from extrinsic conductivity to intrinsic conductivity) of the films grown at lower growth temperature also shows the higher carrier concentration in these films. The majority-carrier mobility seems to play only a minor role in controlling the conductivity. A more thorough investigation is necessary to determine the exact reasons for this behavior. The activation energy of the acceptor level, which is believed to be due to phosphorus intestitials, is found to be 0.21 eV in well-oriented films varying slightly with crystallinity of the sample. The electrical band gap is calculated from the intrinsic region of the plot to be 1.32 eV.

Figure 4 shows the variation of *in situ* conductivity with temperature for films grown in oxygen, air, and nitrogen environments. A rapid increase in conductivity was observed immediately after exposing the films to oxygen or air. The initial resistivity was never regained by reevacuation to the same pressure in which the films were grown. This implies that oxygen atoms were either adsorbed or that the material was doped by the oxygen. An additional impurity level is present in the films grown in oxygen (unlike the other
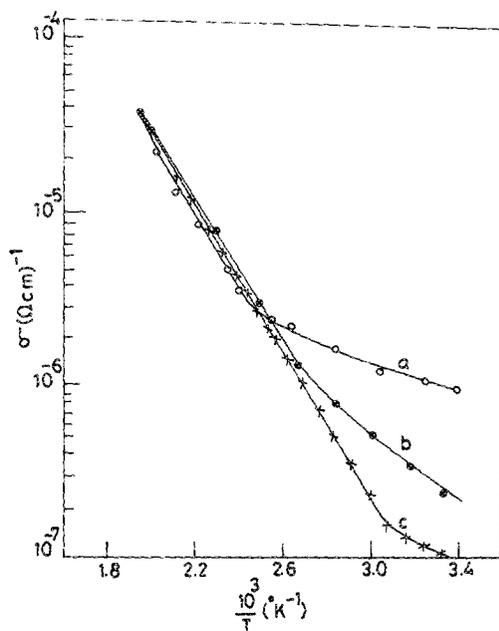

FIG. 4. *In situ* conductivity of Zn_3P_2 films grown on glass in (a) air, (b) oxygen, and (c) nitrogen environments.

curves) with an activation energy 0.49 eV. A deep impurity level (hole trap) has been detected by Suda and Bube at 0.48 ± 0.02 eV for sublimation-grown Zn_3P_2 polycrystal, using deep level transient spectroscopy (DLTS) with Mg Schottky contacts.[15] This hole trap can be attributed to oxygen atoms incorporated into the crystals during growth. The variation of conductivity with temperature for these films after exposing them to air is presented in Fig. 5. The films grown in nitrogen atmosphere appear to be relatively pure, because throughout the temperature region of measurement the conductivity remains in the intrinsic region. In a recent publication, Casey, Fahrenbruch, and Bube[16] have reported the behavior of Schottky barriers using Mg formed on polished and etched Zn_3P_2 samples heated in various gases: air, hydrogen, nitrogen, and argon. Though heat treatment in any of these gases could change the reverse saturation current of the diode by three to four orders of magnitude, the diodes formed on the samples heated in reactive gases such as air and hydrogen were the most affected. This shows that the surface of Zn_3P_2 is vulnerable to heat treatment in the presence of gases. Our results indicate that (Fig. 4) the bulk electronic properties are affected only by oxygen and air (the effect of hydrogen has not been tested). The typical range of thickness of the films used in these measurements was 6–7 μm for which bulk electronic properties are expected to be dominant. The drastic change in conductivity during exposure can only result from surface effects. The surface charge concentration becomes so high that it is capable of changing the conductivity of the whole sample (7 μm thick), considering the fact that the measurement contacts are on the back surface of the films in contact with the substrate or effective-

ly from the bulk. Annealing in vacuum was found ineffective in significantly altering the resistance on films grown at high substrate temperatures.

The variation of thermoelectric power of a Zn_3P_2 film coated on mica at a substrate temperature of 350 °C in air ambient with temperature is shown in Fig. 6. At lower temperatures the sign of Seebeck coefficient (α) indicates that the material is p type. The sign of α is reversed at temperatures above 240 °C. In the intrinsic region the contribution of the electrons to the thermoelectric power exceeds that of the hole contribution, due to high mobility of electrons and hence the reversal of sign occurs.

The value of α at 370 K was calculated from the measured value (Hall measurement) of carrier concentration ($5 \times 10^{13}/cm^3$) and by assuming the value of effective mass as 0.3 m. The usual formula for the calculation of Seebeck coefficient for an extrinsic nondegenerate semiconductor was used and the scattering parameter γ was assumed to have a value of $-\frac{1}{2}$, corresponding to acoustic deformation scattering. It was in perfect agreement with the measured value. But at temperature between 300 and 370 K, there was a discrepancy of up to 0.3 mV/K between the calculated and measured values. This may be attributed to phonon drag effect, which can be prominent at this temperature due to low mobility of the carriers. The Seebeck coefficient α could not be calculated in the bipolar conduction region of the semiconductor, where α turns from positive to negative, because the parameters such as the effective masses and mobilities are unknown.

The carrier concentration and Hall mobility were calculated from Hall coefficient and electrical conductivity data.
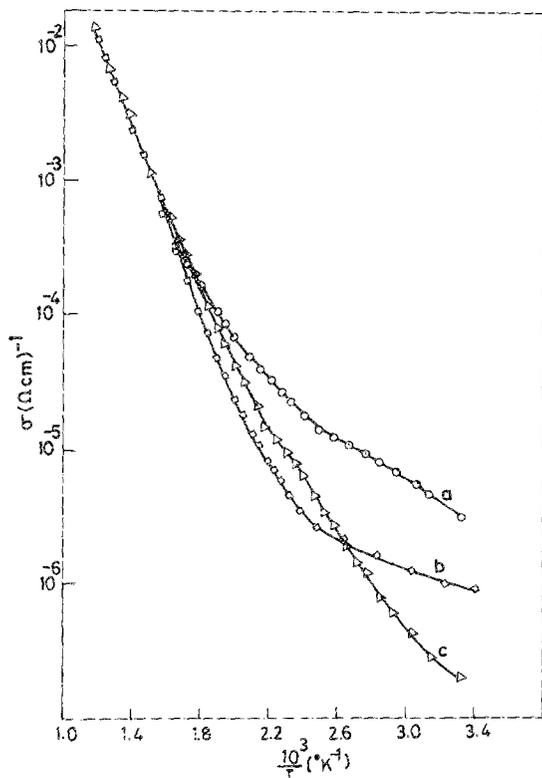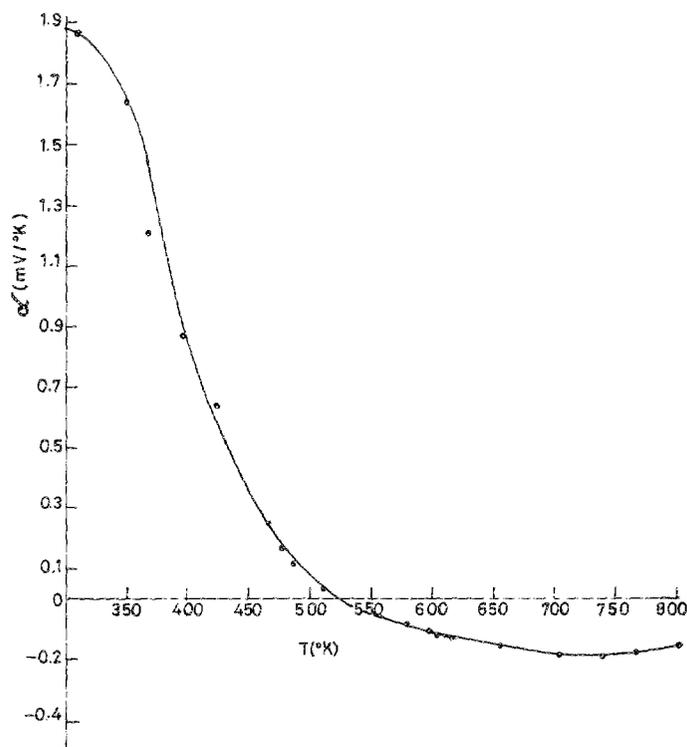

FIG. 5. Conductivity of the Zn_3P_2 films grown under different ambient atmospheres: (a) oxygen, (b) air, and (c) nitrogen after exposure to air.

FIG. 6. Thermoelectric power vs temperature for Zn_3P_2 film on mica at a pressure of 10^{-6} Torr in air.

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The Hall mobility was 28 cm^2/V s, which agrees reasonably with the reported values.[8] The carrier concentration in the unintentionally doped Zn$_3$P$_2$ films were found to be 10^{13}/cm^3 for a film grown at a substrate temperature of 350 °C on a mica substrate. The carrier concentration was found to change with the preparation conditions. A strong dependence of the optical absorption coefficient on substrate temperature for thin films of isostructural materials like Cd$_3$P$_2$ and Cd$_3$As$_2$ is reported in the literature.[1]

CONCLUSIONS

The conductivity of the Zn$_3$P$_2$ films is shown to depend on the growth temperature, background pressure, and the nature of the ambient atmosphere. However, the nature of the substrate and the crystallinity of the sample do not appear to be influential to control the resistivity of the films. Unintentionally doped Zn$_3$P$_2$ films have a very high dark resistivity and the majority carriers are holes at room temperature. Exposure to oxygen or air resulted in a drastic change in conductivity. Oxygen appeared to create a deep acceptor level in the Zn$_3$P$_2$ bands at 0.49 eV. The decrease in conductivity with the improvement of crystallinity added evidence for defect dominated conductivity as reported by Catalano and Hall.[8] The reversal of Seebeck coefficient sign near the intrinsic region implies a large difference in the mo-

bilities of electrons and holes. The electrical properties suggest that well-oriented Zn$_3$P$_2$ films can be successfully used for device applications if prepared under optimized conditions.

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