Materials Characterization 58 (2007) 730 – 734

MATERIALS CHARACTERIZATION

Electrical conduction in zinc phosphide thin films

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Received 30 June 2006; received in revised form 5 October 2006; accepted 16 November 2006

Abstract

Zinc Phosphide (Zn_3P_2) films were deposited by vacuum evaporation under a pressure of 1.3×10^{-5} m bar onto well-cleaned glass substrates. *I–V* measurements show Ohmic and non-ohmic behavior for lower and higher fields, respectively. The field-lowering coefficient was calculated theoretically and experimentally and it was found that the possible conduction mechanism in these films is Richardson–Schottky type. The activation energy decreases as the voltage increases. The zero-field activation energy was found to be 0.97 eV and this zero field activation energy decreases with an increase in film thickness. The capacitance measurements were made at room temperature. The flat band potential was found to be ~1.5 V. The ionized charge density and the total number of interface states were calculated and the values were found to be $5.30\times10^{16}/cm^3$ and 4.18×10^{17} cm^{-2} eV^{-1} respectively.

Keywords: Zn_3P_2 thin films; Vacuum evaporation; Electrical conduction; Richardson Schottky mechanism; *C–V* characteristics

1. Introduction

Zinc Phosphide (Zn_3P_2) is a II-V compound with a direct band gap of about 1.5 eV [1,2], which matches with the solar spectrum in the visible region [3]. Since both Zinc and Phosphide are extremely abundant and cheap, Zn_3P_2 has recently been considered as one of the most promising materials for the production of solar cells [4 5] and also Zn_3P_2 films find their application in infrared (IR) and ultraviolet (UV) sensors [6]. In addition zinc phosphide films have a long minority carrier diffusion length (13 m) and large optical absorption coefficient [6–8]. Recently thin films of both polycrystalline and amorphous Zn_3P_2 have been prepared by different techniques [9,10] such as CVD [11,12], vacuum evaporation [13], hot wall epitaxy [14] and RF sputtering [15]. So far the problem faced with Zn_3P_2 films is the occurrence of micro-cracks and differences in sticking coefficients. However not much work has been carried out on electrical conduction studies of thermally-evaporated Zn_3P_2 thin films; and as a potential candidate for solar cell application it still requires detailed investigations on electrical conduction. Hence this paper reports the *I–V* and *C–V* characteristics of thermally-evaporated Zn_3P_2 thin films.

2. Experimental details

Zinc Phosphide (99.999%, Sigma Aldrich Chemicals Ltd.) films were prepared by vacuum evaporation using a “Hind Hivac” coating unit (12A4D) onto well-cleaned

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1044-5803/$ - see front matter
doi:10.1016/j.matchar.2006.11.014

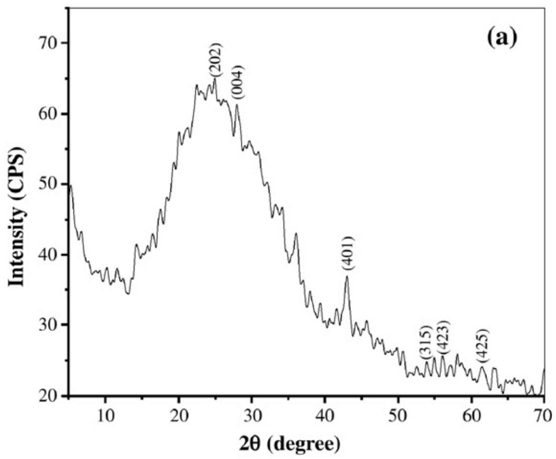

Fig. 1. XRD pattern of a Zn_3P_2 film of thickness 3000 Å.

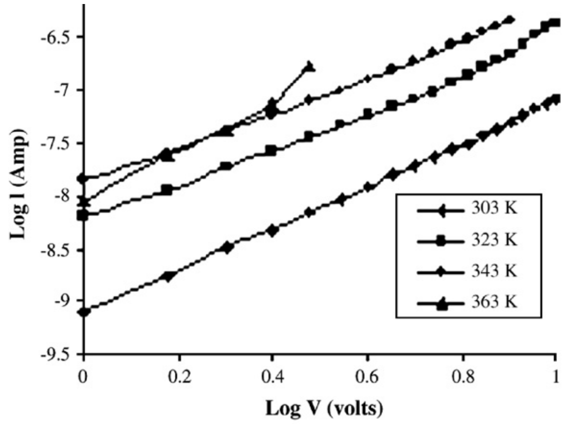

Fig. 2. Log I vs. Log V curve for a Zn_3P_2 thin film of thickness 3000 Å.

glass substrates. A rotary drive was employed to obtain uniform thickness. The thickness of the films was measured by a quartz crystal monitor. Aluminium (Al) is first evaporated on glass substrate through a suitable mask to form a base electrode. A Zn_3P_2 layer is then formed by a thermal evaporation technique under a pressure of $\sim 1.3 \times 10^{-5}$ m bar over the base aluminium electrode. Finally a metallic electrode (Al) is evaporated as the top electrode, so as to form a Al–Zn_3P_2–Al (MSM) sandwich structure. The current–voltage characteristics were studied employing a Digital Pico Ammeter (DPM3, Scientific Equipment, Roorkee) in series with a capacitance and voltage source and all the studies were performed under a vacuum (rotary pump). The capacitance measurements were made at room temperature using a digital LCR meter (LCR-819, GW instek, Good Will instrument company Ltd., Taiwan). The bias-dependent capacitance of the MSM structure was studied by applying forward bias voltages (0–2 V) at various frequencies.

3. Results and discussion

An X-ray Diffraction (XRD) pattern of a Zn_3P_2 film of thickness 3000 Å is shown in Fig. 1. The structure of the film is found to be mixed (amorphous/microcrystalline) in nature. The structure of a film is found to be polycrystalline at higher thicknesses. The variation of current as a function of voltage at different temperatures in a Zn_3P_2 film of thickness 3000 Å is shown in Fig. 2. It is observed that the current exhibits a voltage dependence of the form $I \propto V^n$, where n depends on the field and temperature. From the figure it is observed that the current (I) exhibits a linear dependence with applied voltage (Ohmic behavior).

The field dependence of current for the film of thickness 3000 Å at different temperatures is shown in Fig. 3. It is seen that the plots became linear, which indicates that the conduction mechanism may be of either Richardson–Schottky (RS) or of the Poole–Frenkel (PF) type [16]. Both the mechanisms involve a relation of the type:

$$I \alpha \exp\left(\frac{e\beta F^{1/2}}{k_B T}\right) \quad (1)$$

where I is the applied current, F the applied field, β the field lowering coefficient and k_B the Boltzmann constant. The possibility of an Space charge limited current (SCLC) conduction behavior is ruled out, because the slope in the I–V characteristic curve is less than two for all the voltage range studied [17].

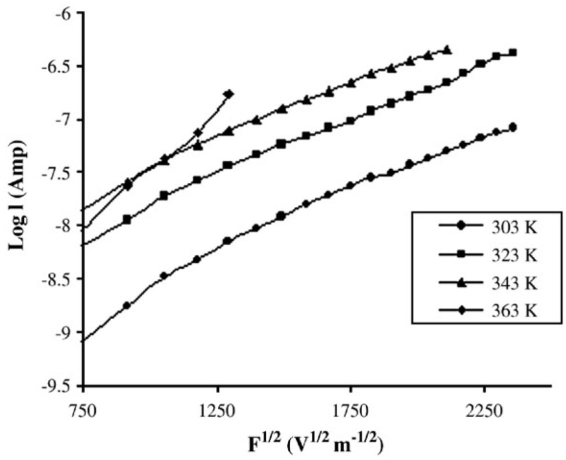

Fig. 3. Variation of current vs. square root of field for Zn_3P_2 film.

Table 1
Theoretical and experimental values of β for Zn_3P_2 film

Temperature (K)	β ($\times 10^{-5}$ eVV$^{-1/2}$cm$^{1/2}$)		
	Experimental	Theory	
		β_{SC}	β_{PF}
323	5.984	5.625	0.113
363	6.379		
403	8.130		

To determine the conduction mechanism we calculated the theoretical field lowering coefficient (β_{Theory}), which is then compared with that of the experimentally-determined (β_{exp}) given by:

$$\beta_{Theory} = \left[\frac{e}{a\pi\varepsilon_o\varepsilon_r}\right]^{1/2} \tag{2}$$

where $a=1$ for PF emission and $a=4$ for RS emission, e is the electronic charge, ε_o the permittivity of free space and ε_r the high frequency dielectric constant of the material. Theoretical values obtained using Eq. (2) for Schottky (β_{SC}) and Poole–Frenkel (β_{PF}) are 5.625×10^{-5} eV V$^{-1/2}$cm$^{1/2}$ and 0.113×10^{-5} eV V$^{-1/2}$ cm$^{1/2}$, respectively. The experimental β values were determined from the plot log J vs. $F^{1/2}$ and the values are given in Table 1. From Table 1 it is clear that the experimental value is closer to the calculated β_{SC} than β_{PF}. Hence it is proposed that the dominating conduction mechanism for thermally-evaporated Zn_3P_2 thin films is of the Schottky type. The small discrepancy observed between the theoretical and experimental values of β_{SC} can be attributed to the accumulation of electronic charge close to the injected electrode, which reduces the effective field [18]. Therefore, a mere coincidence of the experimental β_{SC} with the theoretical value cannot be taken as a deciding factor for the conduction mechanism responsible [19].

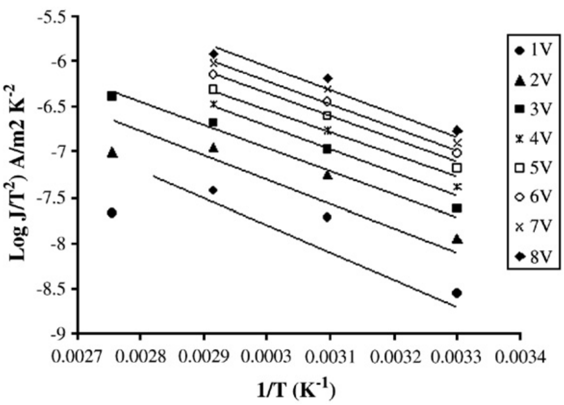

Fig. 4. Plot of log (J/T^2) versus $1/T$.

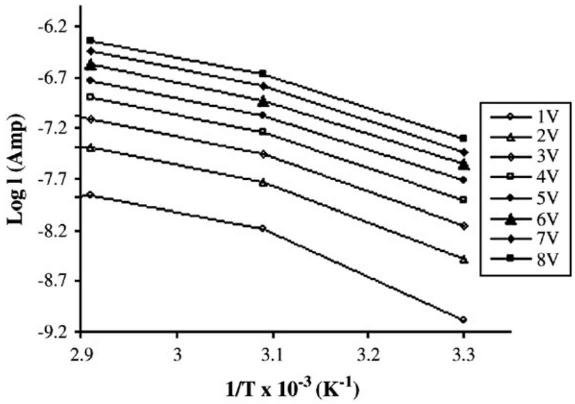

Fig. 5. Logarithmic current versus inverse absolute temperature.

Moreover, Schottky emission depends on the barrier height, which again depends on the electrode work function. In contrast, PF conduction depends on internal emission in the dielectric value and is independent of the electrode work function. Therefore, in order to confirm the observed β_{SC} dependence with theoretical values of β, a Schottky plot between log (J/T^2) and $1/T$ was drawn for different voltages (Fig. 4). The resulting straight line observed in the figure confirms the Schottky type of conduction mechanism in Al/Zn_3P_2/Al devices [20].

Further, to confirm the Schottky mechanism, a graph is presented in Fig. 5 to show the relation between log I and $1/T$ for different applied voltages. The resulting straight line confirms the Schottky type conduction mechanism in these films. The activation energy has been determined at different applied voltages using the relation:

$$I\alpha\exp\left(\frac{-\Delta E}{KT}\right) \tag{3}$$

Estimated values of the activation energies are given in Table 2. It is seen that the activation energy decreases

Table 2
Field-dependent activation energies for Zn_3P_2 film

Voltage (V)	Activation energy (ΔE) in eV
1	0.88
2	0.79
3	0.65
4	0.63
5	0.53
6	0.47
7	0.59
8	0.39
ΔE_o	0.97

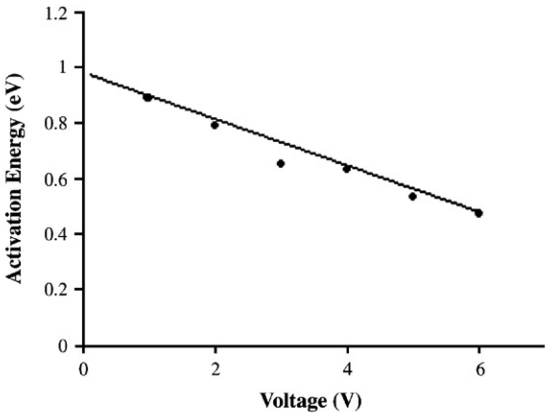

Fig. 6. Variation of activation energy with applied voltage for film.

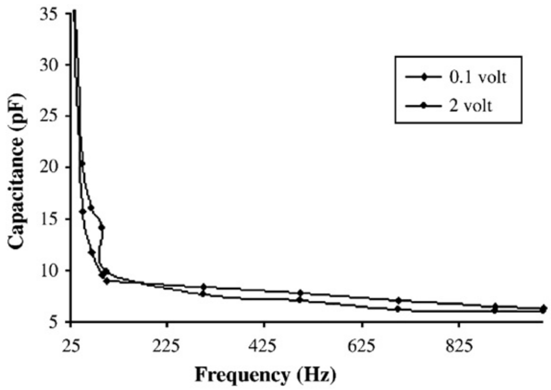

Fig. 8. Frequency dispersion of capacitance for Zn_3P_2 film.

with an increase of applied voltage, indicating that the potential barrier has been lowered in the presence of an external electric field. Fig. 6 depicts the activation energy versus applied voltage. The zero field activation energy is calculated from the graph and found to be $\Phi_0=0.97$ eV.

4. *C–V* characteristics

Capacitance was measured in the dark as a function of reverse applied bias .The variation of capacitance with voltage is given in Fig. 7 for Zn_3P_2 film of thickness 3000 Å. By extrapolating the graph in the reverse bias region the flat band potential was estimated and the value was found to be 1.5 V [13]. Fig. 8 depicts the frequency dispersion of capacitance at 300 K for a 0.1 V bias. From the plot it is observed that at low frequency the capacitance shows a larger value. Such a high value of capacitance at low frequency is due to the ac signal response for deep levels [14,15]. The decreasing behavior of the capacitance with increasing frequency suggests that there is a slow deep level state at or near the interface.

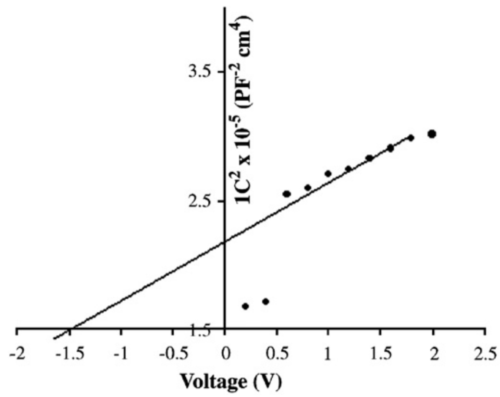

Fig. 7. Mott–Schottky plot for Zn_3P_2 film.

The ionized charge density (N) was calculated by taking the slope close to zero from the $1/C^2–V$ plot and the ionized charged density was calculated as $N=5.30\times10^{16}/\mathrm{cm}^3$ [13]. The total number of interfacial states due to the depletion layer and interface can be measured from the capacitance at lower frequency whereas the capacitance at higher frequency is associated with depletion layer only [6]. The number of states can be calculated from the measured capacitance at low frequencies using the relation [7]:

$$N_{\mathrm{IS}}=\left(\frac{C_{\mathrm{LF}}-C_{\mathrm{HF}}}{q}\right) \tag{4}$$

where N_{IS} is the total number of interfacial states, C_{LF} and C_{HF} are the capacitance at lower and higher frequencies respectively, q is the electronic charge and the value of N_{IS} was found to be $4.18\times10^{17}\ \mathrm{cm}^{-2}\ \mathrm{eV}^{-1}$.

5. Conclusions

The DC electrical parameters and conduction processes in thermally-evaporated Zn_3P_2 films were investigated by studying the current–voltage characteristics. The conduction mechanism in Zn_3P_2 films was found to be Schottky type. The estimated activation energy is found to decrease with an increase in the applied field. *C–V* measurements reveal that there is a slow deep level near the interface.

Acknowledgements

The authors wish to acknowledge the Secretary and the Management of Kongunadu Arts and Science College, Coimbatore for their encouragement and support to carry out this work. One of the authors (RS) wishes to acknowledge University Grants Commission, New Delhi for a UGC Research Award to carry out this work.

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