TABLE I Comparison of calculated d-spacings [4] with those observed from electron diffraction

hkl	$d_{calc.}$ (nm)	$d_{obs.}$ (nm)
010	1.002	–*
100	9.932	–*
110	0.683	0.686 (8)
020	0.501	0.501 (7)
200	0.466	0.470 (7)
120	0.441	0.441 (7)
210	0.423	0.428 (6)
210	0.423	0.422† (6)
021	0.372	0.372† (5)
220	0.341	0.345 (4)
030	0.334	–*
130	0.315	0.319 (4)
300	0.311	–*
310	0.297	0.302 (4)
310	0.297	0.299† (3)
230	0.272	0.273 (3)
320	0.264	0.268 (3)
040	0.251	0.252 (2)
231	0.244	0.247† (2)
140	0.242	0.243 (2)
321	0.239	0.237† (2)
141	0.222	0.222† (2)
132	0.208	0.208† (2)
150	0.196	0.195 (1)
042	0.186	0.186† (1)
251, 520	0.175	0.175† (1)
242	0.173	0.173† (1)
033	0.162	0.162† (1)

*Unobserved.
†Observed in tilted diffractograms.
Numbers in parentheses are the estimated errors in the last decimal place.

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Electrical conductivity of zinc phosphide thin films

Optical and electrical properties of GaP and similar phosphides belonging to III–V compounds have been thoroughly investigated and some of these materials are already being used for commercial purposes in opto-electronic devices [1–3]. Similar studies on the phosphides of zinc and cadmium, of the $A^{II}B^{V}$ type, are limited. Recent investigations on the physical and chemical properties of these phosphides indicate that they may also be useful in semiconductor devices [4–6]. Very recently, the potential use of Zn_3P_2 in terrestrial solar cells has been stressed by Möller *et al.* [7]. Continuing efforts to find new materials are very important to the progress of the electronic industries. Some aspects of polycrystalline Zn_3P_2 have also been studied by us, for example, energy storage properties and electrical conductivity. The Zn_3P_2 was prepared in our laboratory using commercially available chemicals [8, 9]. Luminescence and conductivity have been attributed to the formation of complexes such as Zn–O and Zn–P. In this note the results of further investigations on electrical conductivity, measured in the temperature range 130 to 550 K, of thin films of Zn_3P_2 deposited on glass substrates under vacuum by an evaporation technique, are reported and discussed.

Zinc phosphide powders, used in the vacuum deposition of thin films, were essentially prepared by the two methods described in an earlier paper

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[8], namely, (i) by the chemical reaction of a stochiometric mixture of AR grade zinc dust, spectroscopically-pure carbon and pure orthophosphoric acid (S_1) and (ii) by the carbon reduction of pure zinc phosphate in vacuum at 600° C (S_2). Films were deposited on glass substrates at room temperature (30° C) under a vacuum of 10^{-6} torr using a Hind Hivac Beam Electron Evaporator. The thickness of the films, measured by a conventional weighting method was found to be 250 μm. Ohmic contacts were obtained by applying silver paint to both the ends of the films. The films were then transferred to the vacuum chamber where the conductivity cell was fixed; the experimental details are described in an earlier paper [9]. Using a 9 V battery, the current passing through the films was measured in the range 130 to 550 K using a Model EA–813 digital pico-ammeter; all the measurements were carried out under a vacuum of 10^{-3} torr. The temperature of the film was determined using a copper–constantan thermocouple fixed near the surface. A variac thermostat was used to vary the temperature. The film was allowed to equilibrate at each temperature and then the current was measured. The usual precautions were taken to avoid stray electrical pick-up. Several samples were studied in this way and the results were compared with those films prepared using commercially available zinc phosphide powders (S_3). Since all the samples in a particular batch exhibited similar trends, the following results are presented and discussed for Sample 1 in each case.

The conductivity of all samples, in general, is very low at room temperature and its variation with temperature (log σ against $1/T$) is shown in Fig. 1. The conductivity plot of Fig. 1 essentially indicates two linear regions, one from 130 to 450 K and the other from 450 to 550 K. The temperature variation was found to be similar in all cases. The activation energy calculated from the slopes are 0.08 and 1.54 eV for regions I and II, respectively. X-ray and scanning electron microscopy (SEM) studies of these films have revealed that the films are amorphous in nature. The same structural features were also reported by Catalano *et al.* [10].

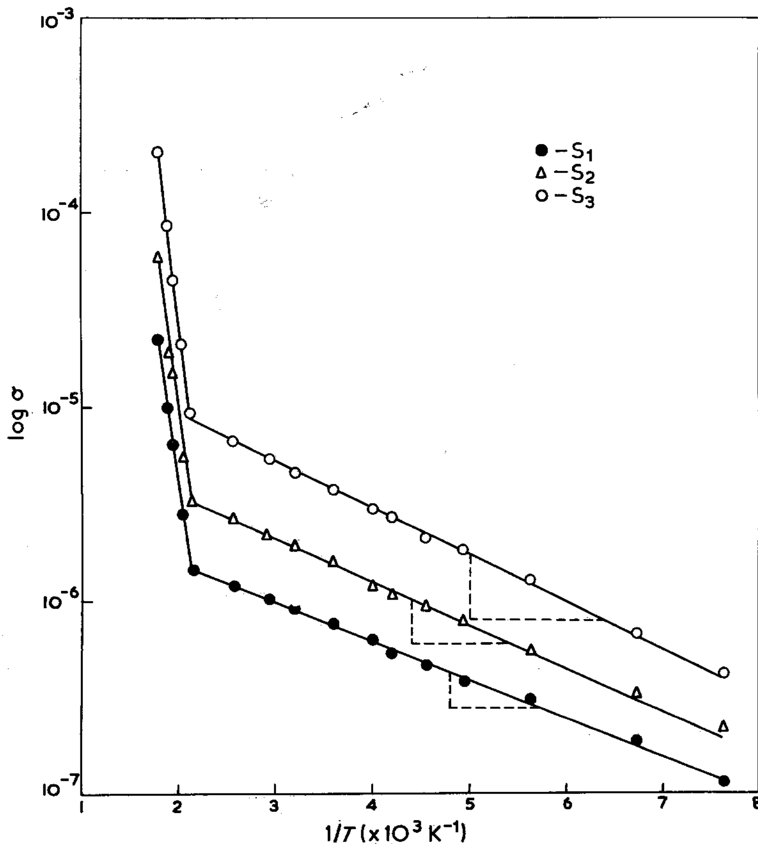

Figure 1 Variation of conductivity of zinc phosphide thin films with temperature. S_1 – Sample prepared by the chemical reaction between AR grade zinc dust, pure orthophosphoric acid and carbon. S_2 – Sample prepared by carbon reduction of zinc phosphate in vacuum. S_3 – Commercial zinc phosphide.

The optical and electrical properties exhibited by most of the amorphous semiconductors compared with their single-crystal forms were reviewed by Stuke [11]. In view of these properties the low value of conductivity and the low activation energy of region I, observed for Zn_3P_2 films in our investigation, may be attributed to the disorder in the material due to dangling bonds produced during evaporation. The other possibility of attributing them to the presence of impurities in the material is unlikely in view of the fact that the activation energy in this temperature range, for the impurity-doped samples, is always reported to be higher (0.4 to 0.8 eV) [7]. Thus, the thin films of zinc phosphide studied in this investigation have exhibited all the features that are normally observed in amorphous semiconductors, i.e. a higher value of activation energy in the intrinsic region (greater than the optical band-gap which is about 1.2 eV [5]) and a relatively small influence due to impurity atoms in the extrinsic region.

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Dependence of defect density and activation energy on deposition rates in copper films

Vacuum evaporated films posess a high value of resistivity compared with that of the bulk because of the incorporation of a large number of defects frozen into the film during atom condensation of the film. The resistivity of the film can be decreased substantially by removing these defects by annealing and ageing. Due to size effects, the resistivity of a very thin annealed film becomes comparable with that of the bulk. Many theories [1–3] have been proposed relating the electrical resistivity with the defects and with the kinetics of their removal during the ageing and annealing processes.

Several investigations [4–10] have been made on different metals and alloys studying the effect of annealing on the electrical properties of thin films and on the distribution of defect density on various deposition parameters such as residual gas pressure, film thickness, rate of deposition etc. Making use of Vand's theory [1], they studied the lattice vibration energy spectra of the as-grown films. In the present investigation the influence of deposition rate on the defect density $F_0(E)_{max}$, and activation energy E_{max} has been studied and discussed on the basis of the sheet resistance of the film before heat treatment.

Copper films of equal thickness (610 Å) were deposited onto well-cleaned glass substrates kept at room temperature. The pressure maintained during the evaporation was $\approx 10^{-5}$ torr. The deposition rate which was changed by altering the heating current through the filament, was estimated making use of a quartz crystal thickness monitor. The film thickness was measured by the

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