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PHOTOELECTRONIC PROPERTIES OF ZINC PHOSPHIDE CRYSTALS, FILMS AND HETEROJUNCTIONS

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PURPOSE

The purpose of this research program is to investigate the photoelectronic properties of zinc phosphide (Zn_3P_2) in single crystal form, in thin-film form, and in heterojunctions in which Zn_3P_2 forms one of the elements. This research will be directed toward understanding the role of crystalline defects and impurities in Zn_3P_2, the nature of the electronic charge transport in single crystal and thin-film material, and the properties of photovoltaic heterojunctions involving Zn_3P_2. The scope of the program extends from basic investigations of materials properties on single crystals to the preparation and characterization of all-thin-film heterojunction devices.

One of the principal motivations behind this research program is the realization that Zn_3P_2 is a relatively uninvestigated yet ideal component for photovoltaic heterojunction use in solar energy conversion. The proposed program will concentrate on the bais materials problems involved with Zn_3P_2, providing the kind of information needed for other more developmental programs directed toward actual practical cells.

ABSTRACT

An increase in crystal growth rate for Zn_3P_2 was achieved by a vacuum baking step before crystal growth designed to reduce the pressure of excess gases in the ampoule. An analysis of the problem indicates that results are consistent with expectations. Samples have been submitted to SERI for mass spectroscopic evaluation and SIMS analysis.

Construction of suitable equilibrium defect distribution diagrams for Zn_3P_2 was initiated. Typical diagrams with their interpretation will be included in the next report.

Good rectifying diodes were prepared by vacuum evaporation of Mg onto etched surfaces of Zn_3P_2. A barrier height of 0.75 eV was measured from C-V data in good agreement with the published value of 0.80 eV. If the Zn_3P_2 surface was given a heat treatment in oxygen before Mg evaporation, the Mg made an ohmic contact indistinguishable from the normal ohmic Ag contact to Zn_3P_2. If the Zn_3P_2 surface was given a heat treatment in hydrogen before Mg evaporation, good diode characteristics were observed, with strong forward current saturation above 1 V.

The resistivity of Zn_3P_2 films deposited by CSVT in Ar is 1500 ohm-cm before laser annealing and 1200 ohm-cm after laser annealing. Laser annealing apparently produces a preferred orientation of these films.

Microprobe analyses of the films deposited by CSVT and vacuum evaporation indicate that these films are almost always Zn-rich with an average 69 atomic % Zn and 31 atomic % P. Films deposited by vacuum evaporation, on the other hand, are strongly P-rich. Variations in stoichiometry with position on a single film are also observed.

I. MATERIAL PREPARATION

The procedures described in PR #2 have now become routine for the preparation of Zn_3P_2, as well as for its purification. These processes are able to provide good quality materials for the purposes of this project.

II. CRYSTAL GROWTH

In PR #2 we mentioned that high initial nucleation rate and slow transport are problems for controlling good single crystal growth in the closed-tube horizontal vapor transport method. This method, however, was shown capable of providing low-resistivity as-grown material. In view of its advantages, we have investigated increasing the growth rate by eliminating residual gases inside the ampoule, and we have also looked at the thermodynamics involved in the residual gas problem.

Crystal growth procedures follow those described in Figure 3 of PR #2. In order to get rid of excess gases, an additional step was introduced. The growth ampoule was placed into a clean quartz tube and was vacuum baked at 1000°C for 4 hr after cleaning and coating. Immediately after cooling, the ampoule was loaded with Zn_3P_2 source material and was again vacuum baked at 500°C for 2 hr before sealing. All other parameters were kept the same as described in Figure 3 of PR #2. The purpose of the baking step is to stabilize the carbon coating and hopefully to reduce the background gases.

A growth run made with this additional baking step did show some interesting results. The general growth pattern was not changed: high initial nucleation, slowing of the growth rate with time, and requirement of a low source temperature for the first stage of the growth. The difference was that the source temperature had to be reduced to 790°C, rather than the value of 830°C previously used,

in order to keep the growth rate at an average value of 0.45 to 0.55 mm/hr. If a higher source temperature were used, the transport would have been too rapid to allow formation of a single nucleus. This run was also the first time that all the source material was transported to the crystal growth in a 1 week growth period. These results indicate some effect of the background gases on the crystal growth; this effect can be reduced by more careful preparation and loading.

Abernathey et al.[1] proposed a simple model in which the growth velocity is inversely proportional to the difference of the total pressure and the partial pressure of the growth species in the ampoule. Variations in this difference were found capable of changing the growth rate by up to an order of magnitude. This result seems consistent with our investigation of the residual gas problem. According to this model, even non-stoichiometry will tend to decrease the growth rate, because (unlike the effusion hole method, which fixes the ratio of the zinc partial pressure to the phosphorus partial pressure at a value of 4.36 kinetically[2]) the ratio of zinc to phosphorus partial pressure can increase (zinc rich) or decrease (phosphorus rich) continuously in the closed tube method in such a way as to slow down the growth rate with time.

Another phenomenon that has been noticed is that the distance between the source and the crystal (one important parameter affecting the transport) becomes larger with time, because the crystal is more compact than the source material. This probably also contributes to the reduction in growth rate with time.

To evaluate the problem of residual gases, consider the following reaction involved in the decomposition of SiO_2:

$$SiO_{2(s)} + 2\,CO_{(g)} \rightarrow Si_{(s)} + 2\,CO_{2(g)} \qquad (1)$$

The standard free energy of reaction at 900°C is $\Delta G^{o}(900^{o}C) = 76.9$ kcal/mole

with a ratio of CO partial pressure to CO_2 partial pressure of 1.46×10^7 at equilibrium. These data can be taken directly from the Ellingham diagram; other quantities such as the volume of the ampoule, the total oxygen pressure (about 1/5 of the total pressure sealed inside the ampoule), and the growth temperature are known. If these data are applied to the law of mass action from Eq. (1), the ideal gas law, the mass balance equation of oxygen and Dalton's law of partial pressures, one can calculate the amount of Si deposited in the system. Unfortunately, the results of the calculation depend upon the initial amount of CO and CO_2 present in the ampoule, which is not known because the amount of CO and CO_2 introduced by sealing is not known. In extreme cases, there can be about 20 torr of Si partial pressure for large initial amounts of CO, and there can be negligibly small Si partial pressure for small initial amounts of CO. If one expects that the vacuum baking step stabilizes the carbon coating and hence reduces the initial amount of CO or CO_2, one might expect less background gases with the vacuum baking step, and therefore a faster growth rate as observed.

Lorimor et al.[3] reported that unintentional doping of Si into GaP can be as large as 10^{18} cm^{-3} using an LPE method with a quartz tube, following this reaction:

$$H_{2(g)} + SiO_{2(\text{vitreous})} \rightarrow H_2O_{(g)} + SiO \qquad (2)$$

Vacuum baking, which is also expected to reduce the amount of water in the system, may eliminate also other possible sources for the background gases.

We have not yet evaluated the electrical conductivity of the crystal grown in this way. It will be of great interest to see whether possible reduction in Si-doping during growth has affected the electrical conductivity as well as the growth rate. We have submitted samples to SERI for mass

spectroscopic evaluation.

III. EQUILIBRIUM DEFECT DISTRIBUTION

Using the available data and the proposed interstitial phosphorus acceptor model,[4] it is possible to calculate the equilibrium defect distribution in Zn_3P_2 as a function of zinc or phosphorus pressure for various temperatures. Such a diagram can also be calculated to include doping effects by donors and acceptors. These diagrams are useful for practical considerations of modifying the electrical properties, and of determining the pressure range within which a stable phase is maintained. Since one piece of data is missing: the standard free energy of formation of the metal-rich defect species, the evaluation has to be careful and general. We expect to provide some typical diagrams with their interpretation in the next progress report.

IV. Mg/Zn_3P_2 JUNCTIONS

Mg/Zn_3P_2 junctions have been prepared by the vacuum evaporation of a thick layer of Mg onto Zn_3P_2 single crystals to evaluate the electrical properties of these junctions. A Ag layer was evaporated over the Mg to prevent oxidation, and ohmic contacts to the Zn_3P_2 were made with Ag.

Almost all as-prepared junctions show good rectification. C-V measurements indicate a hole density of 5×10^{16} cm^{-3}, a value that is consistent with our measurements of a resistivity of less than 50 ohm-cm, if we use the reported hole mobility of 20 to 40 $cm^2/V\text{-sec}$. The C-V measurements also indicate an insulating layer about 150A thick for some junctions; this is expected since the Mg was in contact with air during loading, and can presumably be eliminated by more careful procedures and our better vacuum station. A barrier height of about 0.75 eV measured with these junctions is consistent with the reported value of 0.8 eV.[5]

The effect of different surface treatments of the Zn_3P_2 before de-

positing the Mg was investigated. Three surface treatments were used: (1) as-etched, (2) etched plus 5 min hydrogen heat treatment at 420°C, and (3) etched plus 5 min oxygen heat treatment at 575°C. For the oxygen heat treated surface, the Mg becomes an ohmic contact and all diode properties are lost. For the hydrogen heat treated surface, good rectification properties are obtained, but the forward current undergoes radical saturation above about 1 V. The extrapolated diode behavior exhibits potentially very good J_{sc} and V_{oc} if retained under illumination in a suitable cell. Several samples with different heat treatment were sent to SERI for SIMS analysis.

V. CLOSE-SPACED VAPOR TRANSPORT FILMS OF Zn_3P_2

Films of Zn_3P_2 were deposited by CSVT on amorphous Si_3N_4 (1000A thick) coated on Si. The following results were obtained from a series of preparations and laser annealings:

(a) If the films are more than 100 μm thick, they peel off easily upon laser annealing.

(b) The resistivity of the films before and after laser annealing were approximately 1500 ohm-cm and 1200 ohm-cm respectively. Micrographs of the cross section of the films beofre and after laser annealing are shown in Figures 1 and 2.

(c) Spectral response of photoconductivity was measured for a CSVT film about 30 μm thick. The current was increased by about 50% maximum under monochromator illumination, showing a sharp maximum at 7000A. Taking the maximum photoconductivity to correspond to an absorption constant equal to the reciprocal of the film thickness, indicates an absorption constant of 333 cm^{-1} at 7000A; the absorption curve of Figure 10 in PR #2 on an evaporated Zn_3P_2 film would predict an absorption constant about two orders of magnitude larger for 7000A

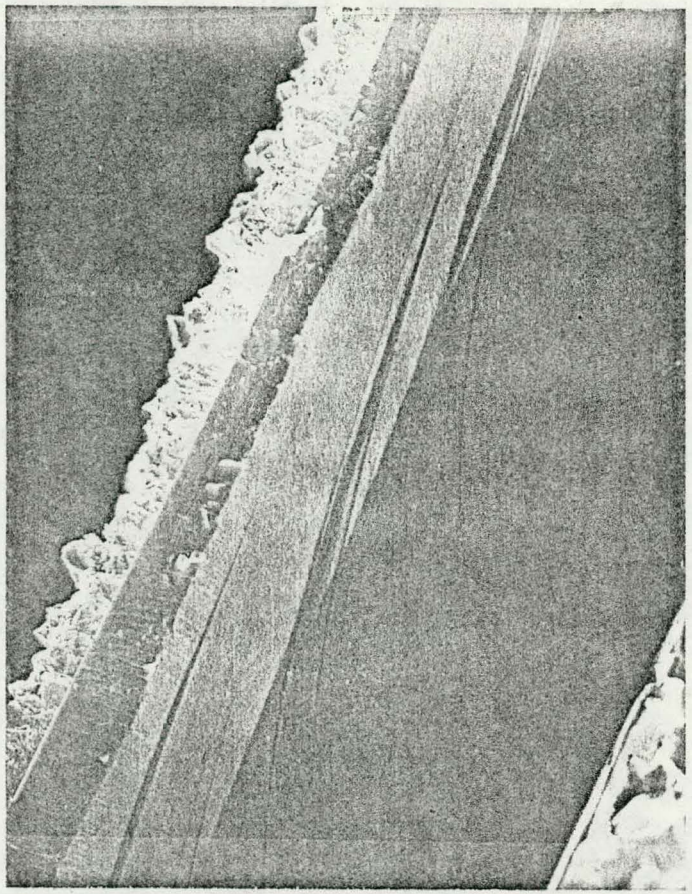

Figure 1a. Electron micrograph of the cross section of Zn_3P_2 film grown on Si_3N_4 on Si.

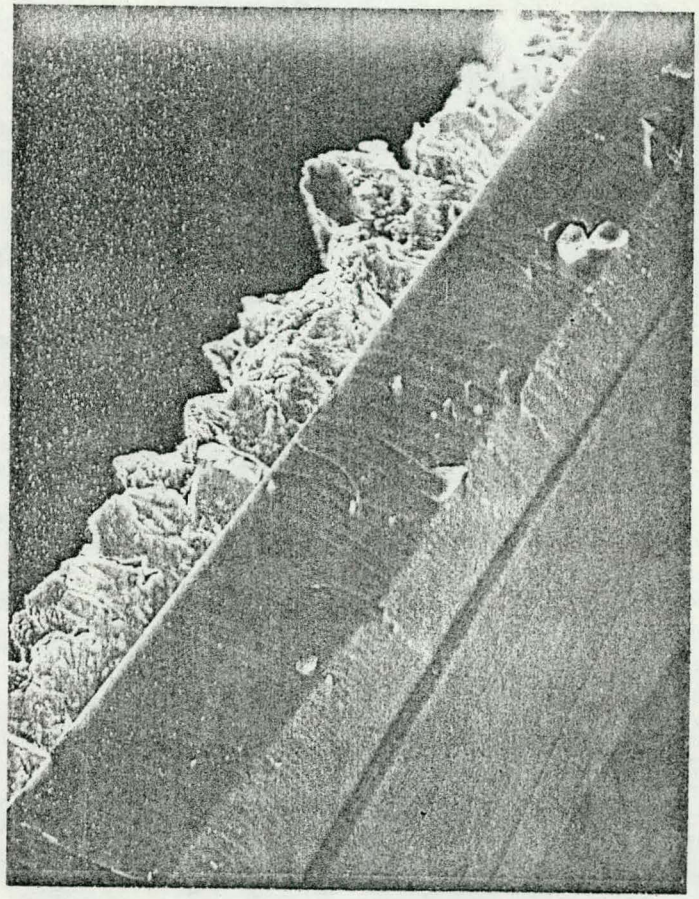

Figure 1b. Electron microgaph of the cross section of Zn_3P_2 film grown on Si_3N_4 on Si.

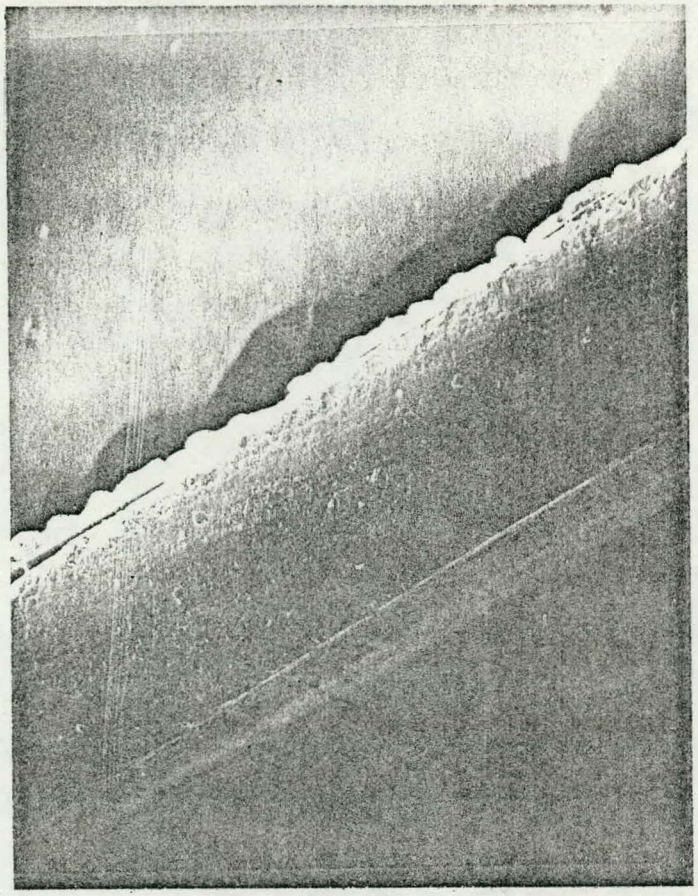

Figure 2a. Electron micrograph of the cross section of a Zn_3P_2 film grown on Si_3N_4 on Si, after laser annealing.

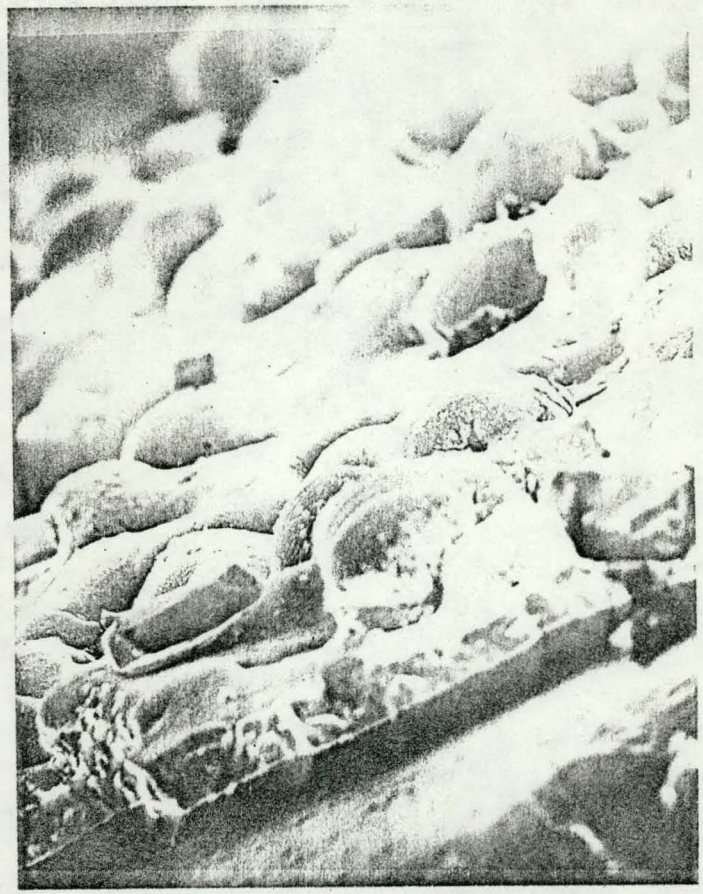

Figure 2b. Electron micrograph of the cross section of a Zn_3P_2 film grown on Si_3N_4 on Si, after laser annealing.

(however, the composition of the evaporated film is in serious question as indicated below, the composition of the CSVT film is closer but not exact, and the thickness of the CSVT film is not exact).

(d) X-ray diffraction was used to examine the films, both in powder form and on the substrate. The powder from the thin films before and after laser annealing show the same diffraction pattern. But X-ray diffraction on the films themselves shows differences before and after laser annealing; the as-grown films show diffraction peaks for all the planes, but the diffraction pattern of the film after laser annealing shows peaks that correspond to the following set of diffraction planes: (220,004), (224,400), and (008). Evidently, therefore, the Zn_3P_2 films show preferred orientation after laser annealing.

(e) Microprobe analyses were made on the crystal, films grown by CSVT from a crystal source, films grown by CSVT from a powder source, and films after laser annealing in air, argon and forming gas. The results are shown in Table I. They indicate serious questions as to the composition of the films deposited in this way. Only the films deposited from a single crystal source appear to have the proper composition. The relative proportions of Zn and P do not change appreciably upon laser annealing. A film of zinc phosphide deposited by vacuum evaporation previously was also microprobed; major deviations from Zn_3P_2 are indicated with stoichiometry varying across the surface.

Other microprobe analyses shown in Table I for CSVT-deposited films show that stoichiometry deviations across the film length are also a problem.

VI. REFERENCES

1. J.R.Abernathey, D.W.Greenwell, and F.Rosenberger, J.Cryst.Growth 47, 145 (1979)

2. A.Catalano et al., "Zn_3P_2 as an Improved Semiconductor for Photovoltaic Devices," Final Report, DOE, Appendix A. DOE-EX-76-C-05-2460.

3. O.G.Lorimor, S.E.Haszko and P.D.Dapkus, J.Electrochem.Soc. 122, 1230 (1975)

4. See Ref. 2, Appendix C.

5. See Ref. 2, Appendix E.

TABLE I

Microprobe Analyses on Zn_3P_2 Films

Sample	Description	Atomic % Zn	Atomic % P
A0	Single crystal	61	39
A1	Thin film grown by CSVT from powder	72	28
A2	Thin film grown by CSVT from crystal	61	39
A3	Thin film grown by CSVT from powder; laser annealed in Ar	76	24
A4	Thin film grown by CSVT from powder; laser annealed in forming gas	62	38
A5	Thin film grown by CSVT from powder; laser annealed in air	72	28
A6	Thin film grown by CSVT from powder.		
	Laser annealed in Ar.	74	26
	Laser annealed in forming gas.	68	32
	Laser annealed in air.	64	36
A7	Thin film grown by vacuum evaporation		
	Area (1)	54	46
	Area (2)	34	66
	Area (3)	23	77
	Area (4)	27	73
B0	Thin film grown by CSVT from crystal		
	Area (1)	76	24
	Area (2)	99	1
B1	Thin film grown by CSVT from powder.		
	Area (1) unannealed	68	32
	Area (2) unannealed	74	26
	Area (3) laser annealed in air	69	31
B2	Thin film grown by CSVT from powder.		
	Area (1) unannealed	71	29
	Area (2) unannealed	78	22
	Area (3) laser annealed in Ar	67	33

TABLE I - Continued

Sample	Description	Atomic % Zn	Atomic % P
B3	Thin film grown by CSVT from powder		
	Area (1) unannealed	69	31
	Area (2) laser annealed in forming gas	65	35
	Average of all CSVT Films	69 $\pm$ 4	31 $\pm$ 4

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