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**PHOTOELECTRONIC PROPERTIES OF ZINC PHOSPHIDE CRYSTALS,
FILMS AND HETEROJUNCTIONS**

Quarterly Progress Report No. 6, July 1–September 30, 1980

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Solar Energy

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QUARTERLY PROGRESS REPORT NO. 6

PHOTOELECTRONIC PROPERTIES OF ZINC PHOSPHIDE
CRYSTALS, FILMS AND HETEROJUNCTIONS

for the period

July 1 - September 30, 1980

Subcontract No. XJ-9-8031-1

Solar Energy Research Institute
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Golden, Colorado

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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 basic materials problems involved with Zn_3P_2 , providing the kind of information needed for other more developmental programs directed toward actual practical cells.

ABSTRACT

Growth of single crystal Zn_3P_2 using iodine transport shows enhanced growth rate for 5-10 mg/cm^3 of iodine.

The contact resistance of evaporated Au contacts on a sublimation-grown crystal was equal to 2.0 ohm-cm^2 and independent of temperature or bulk resistance over a factor of 30 increase in bulk resistance with decreasing temperature. Au or Ag contacts on iodine-transport grown crystals, however, showed significant increases in contact resistance as the bulk resistance was increased by a factor of 500 by cooling to 77°K .

The sublimation-grown crystals have two dominant acceptors. The deeper of these has an ionization energy of $0.14 \pm 0.02 \text{ eV}$, and the shallower $0.02 \pm 0.01 \text{ eV}$. Both levels are distributed monotonically along the length of a boule, the deeper level decreasing with length of growth time, and the shallower level increasing in density. These same activation energies appear to occur in the polycrystalline or iodine-transport grown crystals as well, but here phenomena are more complicated. Evidence for iodine compensation in iodine-transport grown crystals is observed.

A 40 sec, 300°K heat treatment in H_2 has dramatically different effects on a polycrystalline sublimation-grown crystal, for which it decreases the conductivity by a factor of about 30, and on an iodine-transport grown crystal for which it strongly increases low-temperature conductivity by many orders of magnitude.

The maximum mobility for all samples lies between 10 and $20 \text{ cm}^2/\text{V-sec}$. At high temperature all samples show a mobility varying as T^{-n} with $n \sim 1$. At low temperatures in some samples charged impurity scattering with $\mu \propto T^{3/2}$ is observed; exceptions are the polycrystalline sample for which the mobility is thermally activated with an energy of 0.07 eV , and the last-grown iodine

transport grown crystal which also has a much more rapid temperature dependence.

Initial results with a source temperature of 672°C indicates that a strong dependence of conductivity of Zn_3P_2 films deposited by close-spaced vapor transport on substrate temperature exists. Films with apparent conductivity as high as $2.5 \times 10^{-2} (\text{ohm-cm})^{-1}$ have been prepared. Thermoelectric power measurements will be made.

I. CRYSTAL GROWTH

Crystal growth by sublimation with iodine chemical transport has been investigated. Iodine, in proportions between 1 and 25 mg/cm³ was loaded with the Zn₃P₂. The distance between source and crystal was 6". The best temperature profiles were 790-800°C at the nucleation control stage and 830-860°C at the crystal growth stage for the hot zone, and 700-720°C for the cool zone. An enhanced growth rate of 0.65 mm/h was found for 5-10 mg/cm³ of iodine, whereas a reduction in growth rate was found for 25 mg/cm³ of iodine. Such a maximum growth rate at an intermediate iodine proportion is expected.¹

The chemical reaction involved in this case is

Although Zn₃P₂ melts congruently and crystal growth by chemical transport is not necessary, use of iodine chemical transport does provide an enhanced growth rate for appropriate iodine proportions. Since Zn is considered to be the slower transport species between Zn and P,² the formation of a higher partial pressure of ZnI₂ at the source region compared to that for Zn₃P₂ allows more Zn to transport to the crystal growth region. Iodine transports the Zn from the source to the crystal growth region, ZnI₂ decomposes there and the iodine returns to the source region for a repeat reaction. If more iodine is loaded, however, than is needed for this process, the excess iodine becomes a third vapor species in the growth ampoule, and, like P, prevents the transport of Zn to the growth interface. This effect is quite similar to the effect of excess gases that reduce the growth rate, as discussed in Progress Report No. 3.

II. CRYSTAL CHARACTERIZATION

The electrical properties of crystals grown by sublimation and by iodine chemical transport have been measured extensively as a function of temperature using the Hall effect. Samples were cut from different sections of the various boules grown.

Contacts using Ag, Au or Ag-Au alloy were evaporated on Zn_3P_2 . All contacts have a linear I-V curve over the temperature range of interest. The contact resistance, however, is often a function of temperature and/or the bulk resistance. Figure 1 shows a plot of the contact resistivity in ohm-cm^2 vs the product of the bulk resistance and its cross-section area (hence also in ohm-cm^2), as both vary with changes in temperature between 300° and 77°K . For a sublimed crystal, for which the bulk resistance did not increase above 30 ohm-cm^2 at 77°K , Au contacts showed a relatively constant value of 2 ohm-cm^2 for their contact resistivity independent of temperature or bulk resistance. For an iodine-transported crystal, on the other hand, for which the 77°K value of resistance was close to 500 ohm-cm^2 , both Ag and Au contacts showed appreciable increases in resistivity to values as high as 500 ohm-cm^2 for the Ag contact and 80 ohm-cm^2 for the Au contact at 77°K ; the Ag contact showed appreciably higher contact resistivity at all temperatures below room temperature than the Au contact. The general shape of the Au and Ag contact resistivity suggests a dependence on bulk resistance, rather than on temperature only.

Figure 2 shows typical temperature dependence of electrical conductivity for several typical sublimed crystal samples. Curves 1 through 3 are for samples cut from the early, intermediate and latter portion of the same crystal boule. Curve 4 is cut from a polycrystalline Zn_3P_2 boule grown by sublimation with grain size of the order of mm.

Figure 1. Contact resistivity vs bulk resistance (resistance times cross sectional area) for Ag and Au contacts on Zn_3P_2 . The upper two curves are for samples cut from the same iodine-transport grown boule, and the lower curve is for a sublimation-grown sample. Points on the curve are obtained by varying the temperature from 300° to 77°K .

Figure 2. Conductivity vs T for sublimation-grown crystal. Curves 1, 2, and 3 are for samples cut from the early, middle and later portion of the same boule. Curve 4 is for a polycrystalline boule. Curve 5 is effect of 40 sec, 300°C heat treatment in H_2 on sample 4.

Curve 5 shows the change in sample 4 caused by heat treatment in hydrogen for 40 sec at 300°C, multiplied by a factor of 10 so that it could be plotted on the same scale.

Figure 3 shows typical temperature dependence of electrical conductivity for several crystal samples grown by iodine chemical transport. Curves 6 through 8 are for samples cut from the early, intermediate and latter portion of the crystal boule.

Figure 4 collects that Hall mobility vs temperature data for samples 3, 4, 6, 7 and 8, and for sample 1 after heat treatment in Ar, labeled curve 1'. At low temperatures, samples 3, 6 and 7 show a variation of mobility with $T^{3/2}$, typical of scattering by charged impurities. All of the samples at high temperature show a variation of mobility with T^{-n} , representative of lattice scattering; for all samples except sample 1', n is of the order of 1. The maximum mobility for all of the samples lies between 10 and 20 $\text{cm}^2/\text{V-sec}$. The temperature variation of the mobility at low temperatures is much more rapid for the polycrystalline sample 4 and for the last-grown sample from the boule grown by iodine transport. If the data for sample 4 are plotted on a $\log \mu$ vs $1/T$ plot, an activation energy of 0.07 eV is obtained.

Figure 5 collects data on the temperature dependence and magnitude of the hole density in samples 1', 3, 6, 7 and 8. Hole densities are of the order of 10^{16} cm^{-3} and relatively independent of temperature for sample 3, typical of the sublimation-grown crystals in which only shallow acceptor levels dominate. Heat-treated sample 1' shows the highest hole densities measured, almost 10^{17} cm^{-3} at room temperature; sample 1 even before heat treatment (see Figure 2) had a high temperature region in which thermal activation from a deeper acceptor was evident. Somewhat surprisingly the hole density in sample 6, grown by iodine chemical transport, is about twice that for sample 3, grown by sublimation. The last-grown

Figure 3. Conductivity vs T for iodine-transport grown crystal. Curves 6, 7, and 8 are for samples cut from the early, middle, and later portion of the same boule.

Figure 4. Hall mobility vs T for samples 3, 4, 6, 7, 8 as on Figures 2 and 3. Curve 1' is for sample 1 from Figure 2 after heat treatment in Ar.

Figure 5. Hole density vs T for samples 1', 3, 6, 7 and 8, using the same sample designations as on Figure 2, 3 and 4.

iodine-transport sample 8 shows anomalous low-temperature hole density behavior as well as low-temperature hole mobility behavior (see Figure 4); the strong temperature dependence of conductivity shown for this sample in Figure 3 apparently has contributions from both a temperature variation of hole density and a temperature variation of hole mobility.

If all of the conductivity, Hall mobility and Hall carrier density data are analyzed with a little interpretation to fill in the gaps, it appears that the sublimation-grown crystals have two dominant acceptors. The deeper of these has an ionization energy of $0.14 \text{ eV} \pm 0.02 \text{ eV}$, and the shallower has an ionization energy of $0.02 \pm 0.01 \text{ eV}$. Both levels appear to be monotonically distributed in density along the length of a boule, with the 0.02-eV level dominating in the crystals grown last (sample 3) and the 0.14-eV level dominating in the crystals grown first (sample 1). These same activation energies appear to occur in the polycrystalline and iodine-transport grown crystals as well, but here phenomena are more complicated. The general decrease in conductivity with position in the boule from front to back found for the iodine-transport grown crystals (Figure 3) suggests that increasing compensation by iodine occurs along the boule.

Figure 6 shows changes after heat treatment of iodine-transport grown crystal 8. The heat treatment was 40 sec at 300°C in hydrogen, the same as that used to produce sample 5 from sample 4. Unlike the latter case, where for polycrystalline material grown by sublimation this heat treatment produces a marked increase in resistivity (by a factor of 10 to 100), the same heat treatment produces a complete conversion from the anomalous behavior in which both hole density and mobility are thermally activated before heat treatment to a situation in which the iodine-transport crystal behaves very similarly to a

Figure 6. Temperature dependence of hole mobility and density for sample 8 before and after heat treatment for 40 sec at 300°C in H_2 .

sublimation-grown crystal with only small temperature dependence of hole density and hole mobility, higher temperature values being retained at low temperatures. The reasons for these changes and the difference in behavior between polycrystalline and iodine-grown crystals is not presently known but provides a fascinating area for investigation.

Attempts were made to excite photoluminescence using an Ar ion laser, such as has been successfully used to excite luminescence in CdTe and InP crystals, in a variety of crystalline samples produced in this work. Unfortunately no detectable signal was found to date. Huldt³ suggests the existence of non-radiative recombination paths involving shallow levels with an activation energy of about 0.06 eV.

III. THIN FILM GROWTH

Apparently a small contamination of the H_2 , used for close-spaced vapor transport growth of Zn_3P_2 films, by O_2 still exists and results in the formation of ZnO on the source surface if the source temperature is low. This limits the lowest usable source temperature. We are overcoming this difficulty by installing a H_2 catalytic purifier.

A preliminary series of film growths were made with a source temperature of $672^\circ C$ and substrate temperatures between 300° and $500^\circ C$. Initial results indicate that the conductivity of the films increases exponentially with substrate temperature between values of $2.7 \times 10^{-7} \text{ (ohm-cm)}^{-1}$ at $387^\circ C$ to $2.5 \times 10^{-4} \text{ (ohm-cm)}^{-1}$ at $460^\circ C$. If these results can be reproduced, a clue to the preparation of high conductivity films by CSVT will have been achieved.

The thickness of deposited Zn_3P_2 films is being measured using an Alpha Step instrument. The best etch for the film to form a sharp step to determine film thickness appears to be a mixture of HNO_3 , HF and alcohol; HNO_3 forms a layer of oxide on the surface that is removed

by the HF. The alcohol helps to reduce the surface tension so that the etch can diffuse more rapidly.

The modified CSVT apparatus (not the newly designed apparatus) includes a quartz tube through which gas or liquid can be passed to cool the substrate. As expected, water is more effective in cooling than is N_2 , but there appears to be a gap between the lowest temperature attainable with N_2 and the highest temperature attainable with flowing water. Choice of another coolant should alleviate this problem.

IV. THIN FILM CHARACTERIZATION

The thermoelectric power apparatus has been repaired and suitably modified for operation. We expect to be able to analyze transport in the thin films via thermoelectric power measurements in the near future.

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