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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 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

The closed tube horizontal growth method has been pursued for the growth of single crystals of Zn_3P_2. The rate of material transport was increased by increasing the temperature difference between source and growth regions and by decreasing the distance involved. A boule with only 2 grains in a 12 mm diameter has been obtained.

The as-grown resistivity of this single crystal Zn_3P_2 was 50 ohm-cm, which was reduced to 10 ohm-cm by subsequent annealing in hydrogen at $410^{\circ}C$.

Initial ZnO/Zn_3P_2 (CVD deposition of ZnO) and CdS/Zn_3P_2 (CdS by vacuum evaporation) heterostructures were fabricated using small samples of single crystal Zn_3P_2 sent from Tony Catalano at Delaware. Not surprisingly, only small photoresponse was obtained with these totally experimental cells.

Zn_3P_2 films deposited on glass by CSVT were shown to be amorphous whereas those deposited on single crystal CdS were polycrystalline. Indeed several samples showed appreciable large-grain columnar growth at an angle to the substrate plane. Laser annealing was shown to have dramatic effects in crystallizing Zn_3P_2 films deposited on Si_3N_4 film substrates on single crystal Si.

Thin films of Zn_3P_2 were deposited on glass substrates by vacuum evaporation. As-deposited film resistivities fell in the range of 10^6 - 10^8 ohm-cm; an apparently temporary decrease in resistivity by factors up to 50 could be obtained by annealing in hydrogen. Optical transmission and reflection spectra, as well as photoconductivity spectral response spectra were measured on a number of these films.

1. MATERIAL PREPARATION

The materials synthesis procedure outlined in Progress Report No. 1 has become routine with a slightly modified temperature profile. The temperature of the Zn end of the tube is still 850°C, but the temperature of the P end has been increased to about 325°C for more complete reaction. The process is illustrated in Figure 1.

The temperature profile for the purification process has also been slightly modified by raising the source temperature to 900°C to increase the rate. The purified material condenses below 750°C at about 3½" away from the source. This process is illustrated in Figure 2.

2. CRYSTAL GROWTH

In Progress Report No. 1 we described difficulties in crystal growth associated with slow transport and too high initial nucleation. We have concentrated on these problems during the present quarter. The closed tube horizontal growth method is still the primary method under investigation in spite of the fact that slow transport and rapid nucleation seem intrinsic to this method, because of other advantages that will be discussed.

The growth apparatus is pictured in Figure 3. The source temperature is chosen to be 830°C to reduce the driving force for easy nucleation, after many observations using our transparent furnace. A limited number of nuclei form, but the one at the ampoule tip is always the largest because the driving force is largest at the tip. A single clean-up step in which the temperature is increased briefly can easily remove the undesired nuclei, leaving only the large one at the tip to serve as the seed for later growth. Using a seed from the

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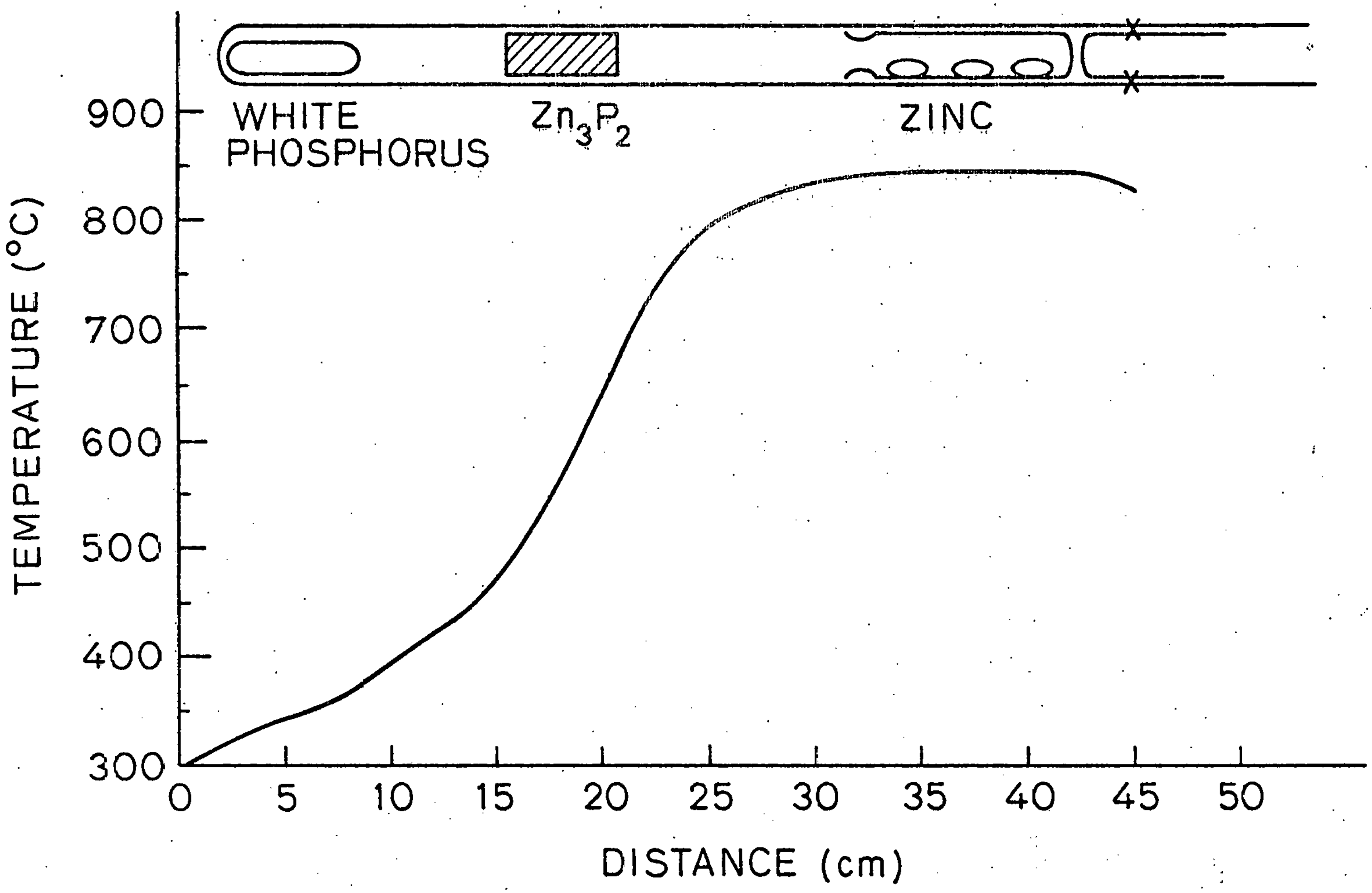

Figure 1. Conditions for the Zn_3P_2 material synthesis. The phosphorus has already undergone a special treatment to convert it to the white form.

PURIFICATION

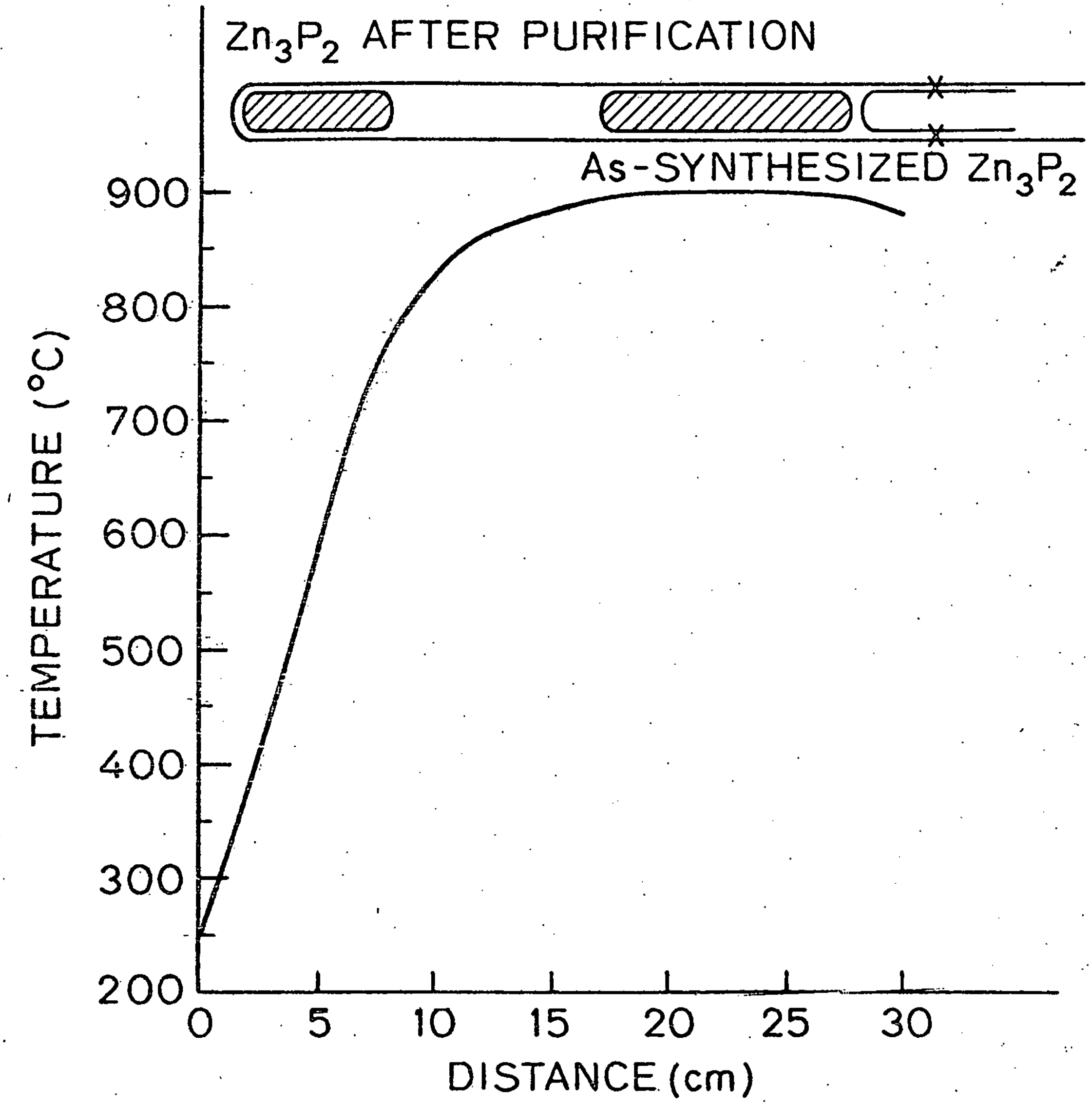

Figure 2. Conditions for the purification of Zn_3P_2. Specific temperatures and tube dimensions were selected to provide data on growth conditions.

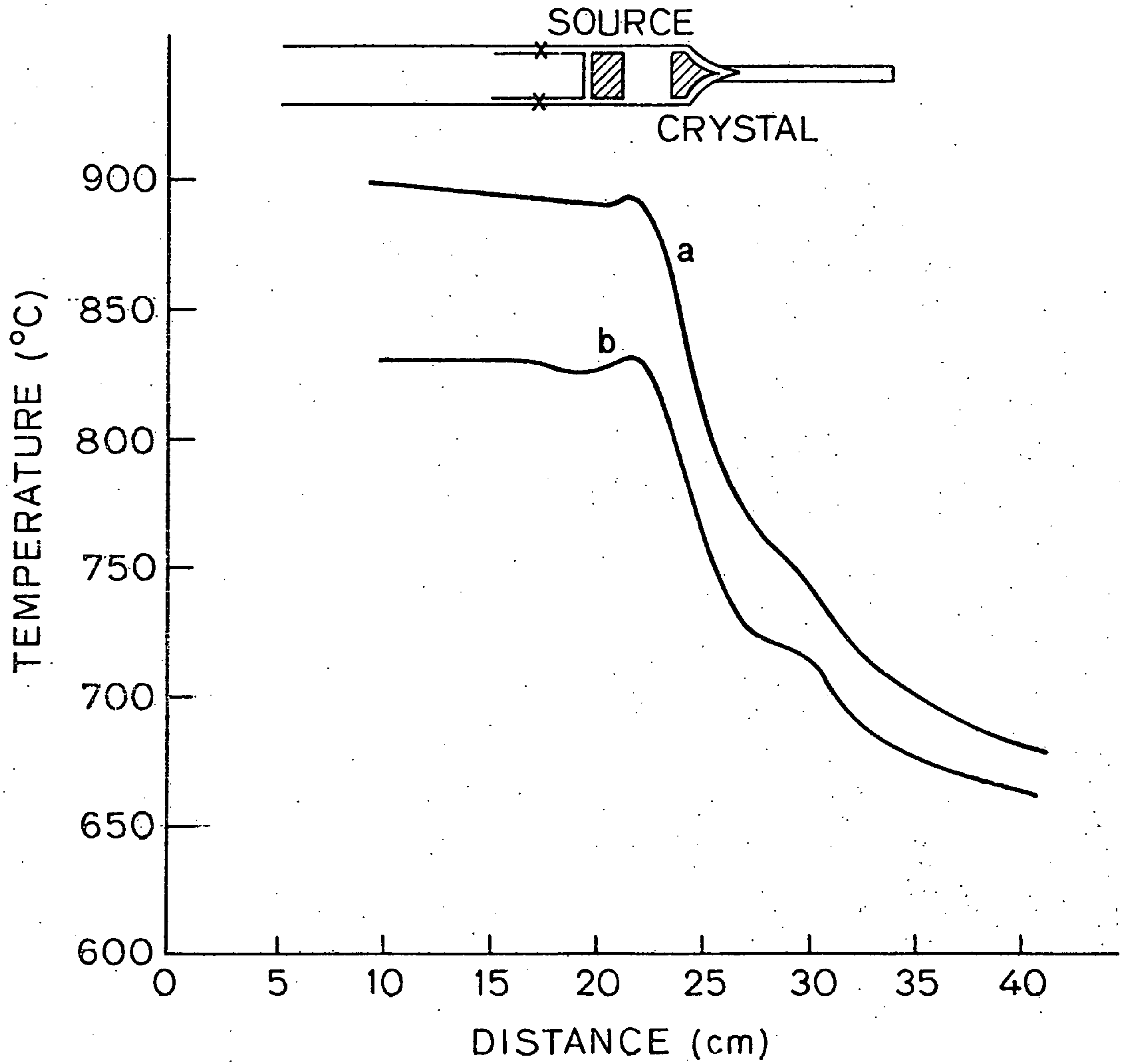
CRYSTAL GROWTH

Figure 3. Conditions for closed-tube horizontal growth of Zn_3P_2 single crystals. Curve b is the temperature profile used for initial nucleation control. Curve a is the temperature profile used for material transport.

beginning is another alternative that we may utilize in the future in alternative growth systems.

Two major modifications have been made to increase the rate of material transport. The temperature difference between the source region and the crystal region has been increased to 150°C, and the length of the ampoule has been decreased to 4", while keeping the pulling velocity a growth variable. Several processes for purification were investigated, not only for the purpose of purification, but also to serve to provide data that would enable us to select the appropriate temperature profile for crystal growth. Using the temperature profile of Figure 2, about 15 g of Zn_3P_2 could be purified in less than one day. Based on these results, we decided to use 900°C for the higher temperature zone, and 750°C for the lower temperature zone. The use of such a large temperature gradient has not been appreciably investigated in previous reports about this material.

Another way to increase the transport rate is to increase the concentration gradient of the vapor species for diffusion by decreasing the distance involved. The combined effect of these two modifications does show a faster transport rate, and the general pattern is consistent with that reported by the Delaware group.[1] The growth schedule starts with a faster growth rate of about 1 mm/h, and then gradually slows down to about 0.3 mm/h after several days. The pulling velocity can be varied as guided by observation of the interface shape.

A two-step process is therefore involved in the crystal growth. The first step is the initial nucleation control (curve b in Figure 3), and the second step is the material transport (curve a in Figure 3). The time needed for one growth run is about 5 days to a week, depending on the amount of material as well as other conditions. A typical result is shown in Figure 4. Only 2 grains in the 12 mm diameter of the boule

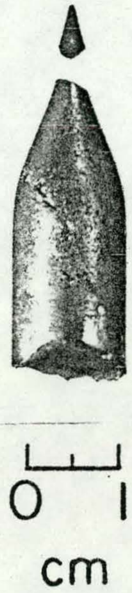

Figure 4. Typical Zn_3P_2 crystal grown by the closed-tube horizontal method shown in Figure 3.

were detectable, and the material was therefore quite suitable for device investigations.

As mentioned above, our data show that 15 g of material can be easily transported within one day using the temperature profile of Figure 2 in the purification process. The question then arises as to why the observed growth is so slow. Two possibilities may be suggested:
(1) kink site poisoning that limits the interface attachment kinetics, and (2) the occurrence of more than one reaction, so that different reactions are favored at different temperatures and pressures.
A detailed thermodynamical calculation and a correct estimate of the possible reactions are required to make a meaningful theoretical prediction. Since these questions are somewhat outside the main thrust of our program, we will not pursue them appreciably further.

Harman and McVittie[2] have reported that quartz ampoules decompose at high temperature. Residual gases of CO and CO_2 have been detected after the reaction in a closed tube. In some cases the vapor pressure of these residual gases can be as high as 70 torr, which is comparable to the partial pressure of the species driving the transport, e.g., the vapor pressure above the solid Zn_3P_2 is about 145 torr at 900°C according to Greenberg et al.[3] On the other hand, the residual gases were reduced appreciably after more careful treatment of the ampoule. In our case we have also observed these residual gases remaining in the tube after growth, but do not know how they may affect the crystal growth. More careful preparation steps including vacuum baking of the ampoule at high temperature, and selected loading sequence are currently under investigation.

If there is decomposition of the quartz and the residual gases CO and CO_2 are forming, an excess of Si should be expected in the ampoule which might be unintentionally doping the Zn_3P_2. A detailed impurity analysis will give more insight into whether this is occurring.

Although the effusion-hole crystal growth method has already been proven successful for Zn_3P_2,[1] the as-grown resistivity of crystals grown by this method are relatively high. In the event that the closed tube method should turn out to be intractable, we do have plans for an effusion-hole approach.

The source temperature of 900°C may prove troublesome in view of the phase transformation reported[4] at 880°C, which may affect the crystal growth through strain considerations or through the enthalpy of transformation. Not enough information about this transformation is available to permit a meaningful evaluation at this time.

3. RESISTIVITY

The as-grown resistivity of boule WZPB01 was found to be about 50 ohm-cm, and 5 min annealing at 410°C in a hydrogen atmosphere decreased the resistivity to 10 ohm-cm, which is in the acceptable range for device fabrication. These values are much lower than those reported for as-grown Zn_3P_2 of 10^6 ohm-cm, and 10^2 ohm-cm after phosphorus annealing.[1] The differences must be attributed to the method of crystal growth. Crystals prepared by the effusion hole method should be more stoichiometric and have a lower impurity content. The low resistivities obtained are one reason why the closed tube growth method is still of considerable interest.
Hall measurements and C-V measurements will be made in the future to more completely characterize the electrical transport properties of these crystals.

Evaporated Ag forms a good ohmic contact to Zn_3P_2 without annealing, which is improved still further by annealing. Evaporated

In contacts do not appear to be promising.

Hall measurements were attempted on one of the samples sent to us by the University of Delaware. The Hall voltage developed across the sample appeared to be very small, and was not measurable immediately because it could not be distinguished against the background of the misalignment voltage between Hall probes. A Van der Pauw method was attempted on another apparatus, but the same problem arose. We will increase the capabilities of our Hall apparatus by inserting a bucking voltage to eliminate the misalignment voltage.

4. HETEROJUNCTION DEVICES

Several samples of Zn_3P_2 kindly supplied by the Delaware group were used for experimental heterojunction devices. A ZnO film was deposited using our new CVD apparatus, and a CdS film was deposited by vacuum evaporation. The ZnO on the ZnO/Zn_3P_2 did not show acceptably low resistivity; the temperature required to have an as-deposited low resistivity for the ZnO film is high[5] and damage to the junction due to the large thermal expansion of Zn_3P_2 is expected. The CdS/Zn_3P_2 junction exhibited only a small photoresponse.

These early negative results are not surprising and we expect better performance and quantitative junction evaluation in the future.

5. Zn_3P_2 FILM DEPOSITION BY CLOSE-SPACED VAPOR TRANSPORT

Thin films of Zn_3P_2 were deposited on different substrates (glass, CdS single crystal, Si_3N_4) by the method of close-spaced vapor transport in an atmosphere of Ar. The steady-state temperatures of the source and substrate were 750°C and 460°C respectively. SEM studies showed that the films grown on glass were amorphous, while the films grown on CdS were polycrystalline.

Thin films were deposited on CdS single crystal substrates using the different types of source temperature/substrate temperature vs time profiles used in earlier investigations of CSVT deposition of CdTe on CdS.[6] Figure 5 shows electron micrographs of Zn_3P_2 deposited by CSVT on glass, and three different depositions on CdS single crystal substrates, all of which show fairly large columnar crystal growth at an angle to the substrate plane.

Zn_3P_2 was also deposited by CSVT on amorphous Si_3N_4 substrates (1000 A thick) coated on single crystal Si. An electron micrograph of the result is shown in Figure 6. A preliminary investigation was made of the effect of laser annealing[7] on grain size on these Zn_3P_2 films deposited on Si_3N_4, with the results shown in Figure 7. The relatively amorphous Zn_3P_2 as deposited on Si_3N_4 is apparently crystallized by the laser annealing. Effects of laser annealing on the electrical properties of these films will be investigated.

6. Zn_3P_2 FILM DEPOSITION BY VACUUM EVAPORATION[8]

Thin films of Zn_3P_2 have been deposited by vacuum evaporation in a system with base pressure lower than 5×10^{-7} torr. The starting bulk material Zn_3P_2 was placed in a molybdenum boat with a diaphragm containing a hole. The substrates were 1" x 1" Corning 7059 glass, located 8 cm from the boat, and capable of being heated to 400°C. For substrates at room temperature, the standard growth rate was 100A/s, whereas for substrates at 300°C, the growth rate was 55A/s. The dependence of film properties on film thickness was investigated.

Resistivity measurements were made using silver paint electrodes in the dark and under photoexcitation. Table I summarizes dark resistivity and film parameters for four typical films. The initial trends suggest that thinner films may have lower resistivity, and that there is no major difference in properties with substrate temperature between 30°C and 255°C.

Figure 5a. 300X electron micrograph of Zn_3P_2 deposited on single crystal CdS by close-spaced vapor transport using the temperature-time profile (1) of Ref. 6: substrate heated to final temperature before source.

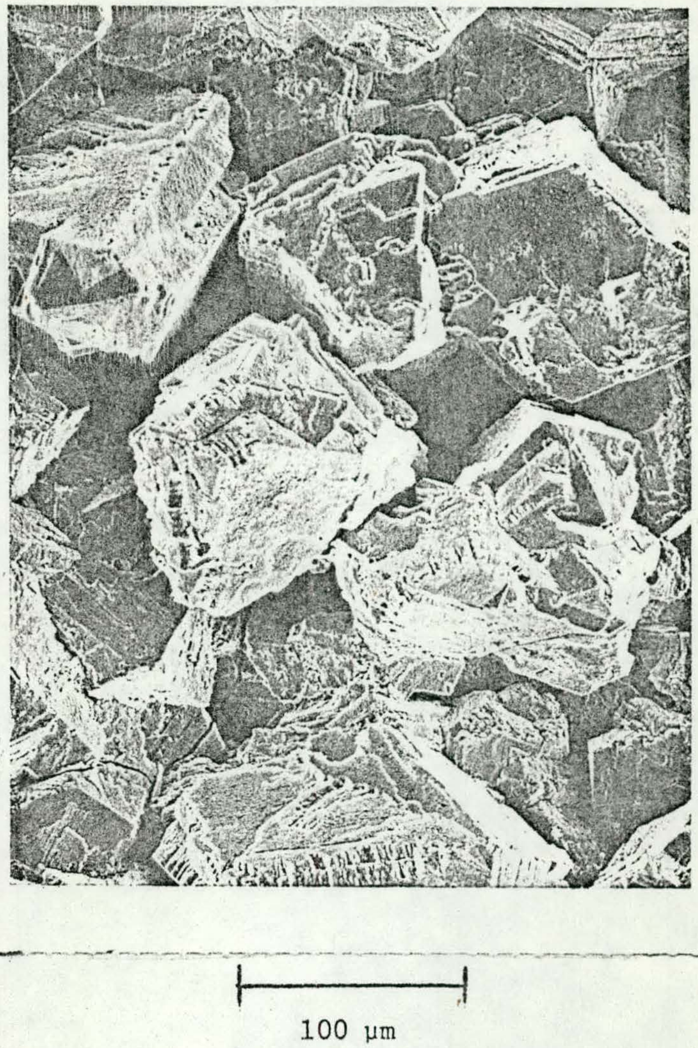

Figure 5b. 300X electron micrograph of Zn_3P_2 deposited on single crystal CdS by close-spaced vapor transport using the temperature-time profile (2) of Ref. 6: substrate thermally etched and then lowered to final temperature before raising source temperature.

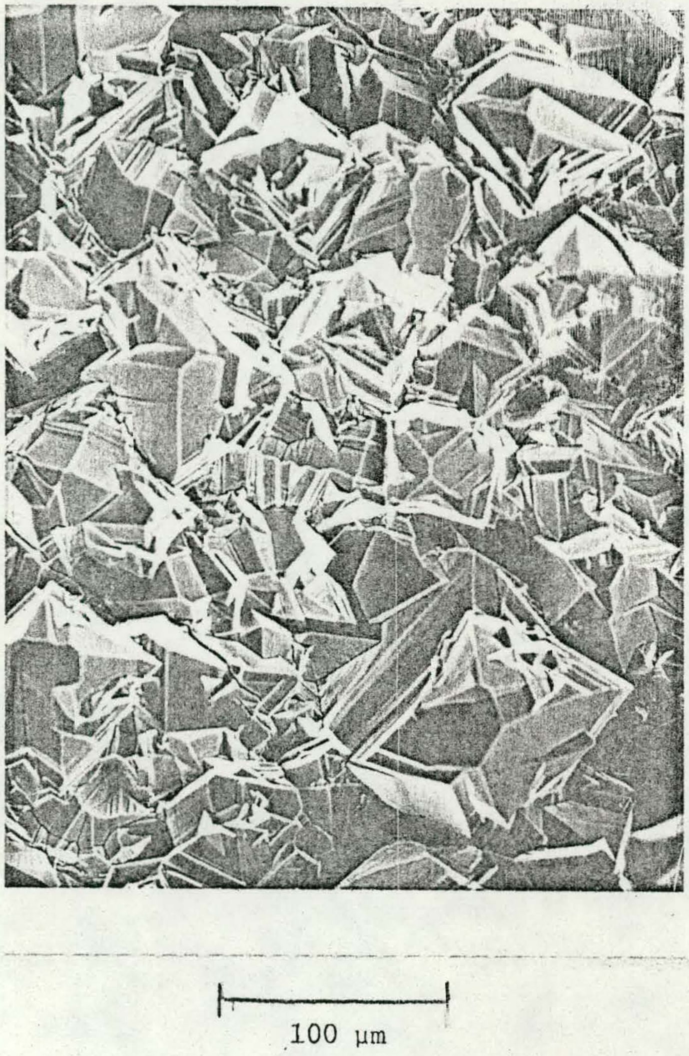

Figure 5c. 300X electron micrograph of Zn_3P_2 deposited on CdS by close-spaced vapor transport using temperature-time profile (3) from Ref. 6: substrate thermally etched and source raised to final temperature while substrate being lowered to final temperature.

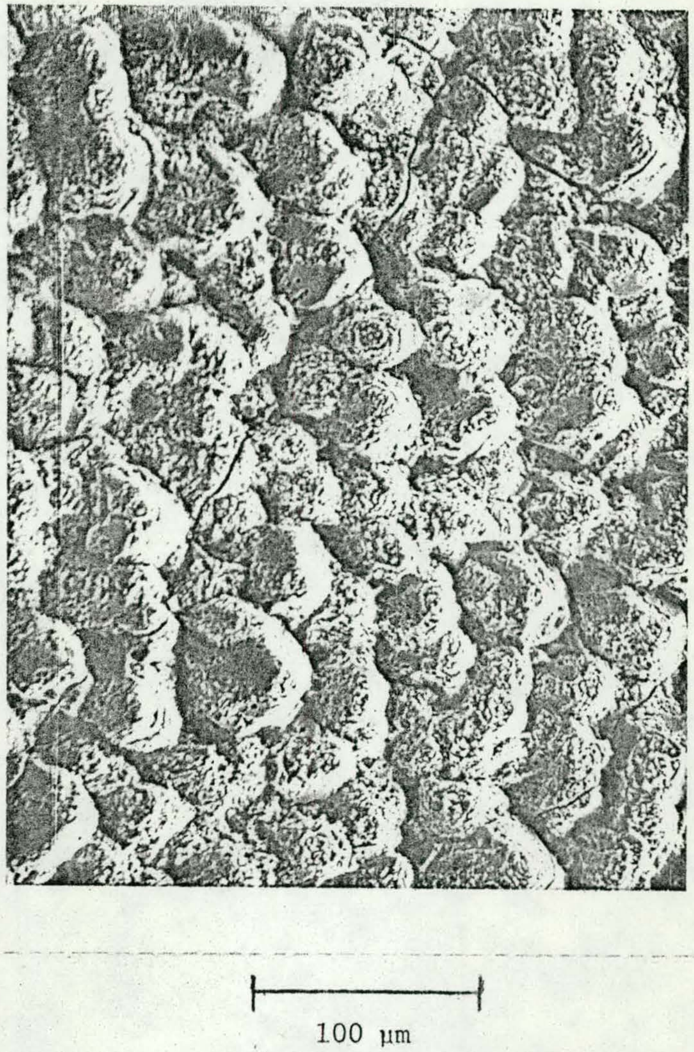

Figure 5d. 300X electron micrograph of Zn_3P_2 deposited by close-spaced vapor transport on glass.

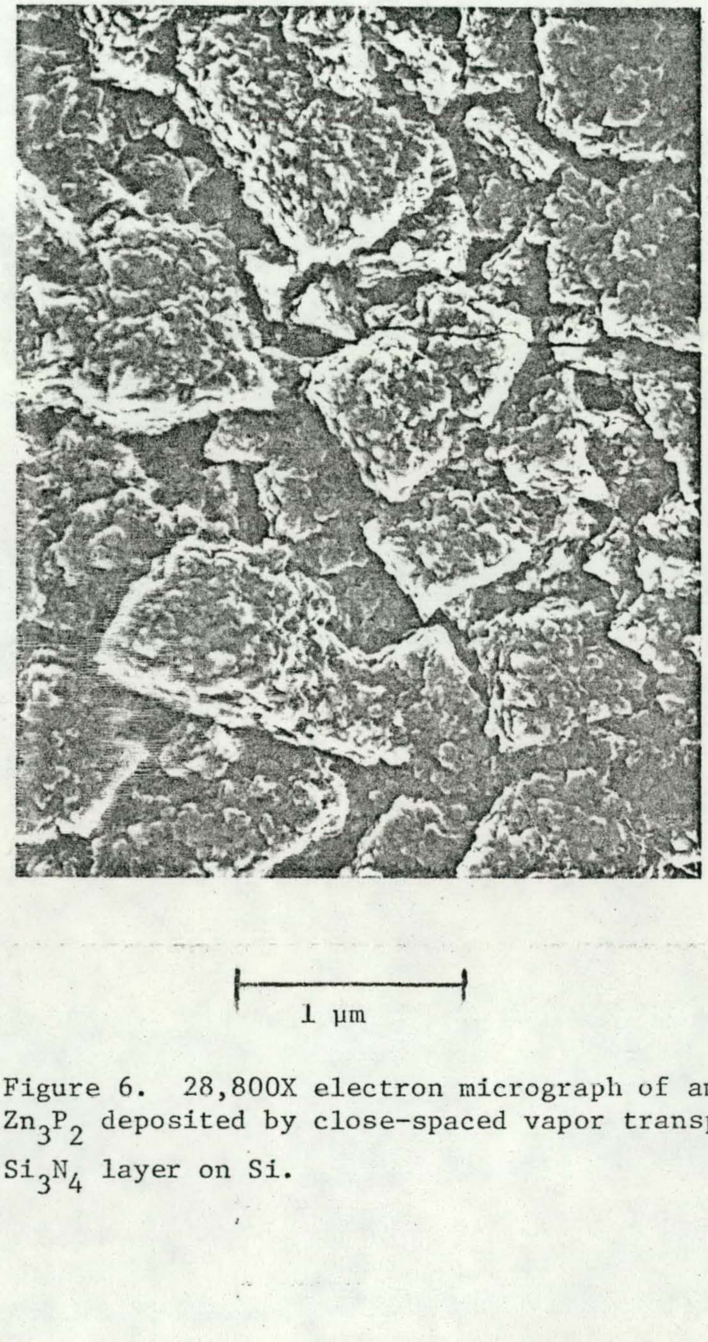

Figure 6. 28,800X electron micrograph of amorphous Zn_3P_2 deposited by close-spaced vapor transport on Si_3N_4 layer on Si.

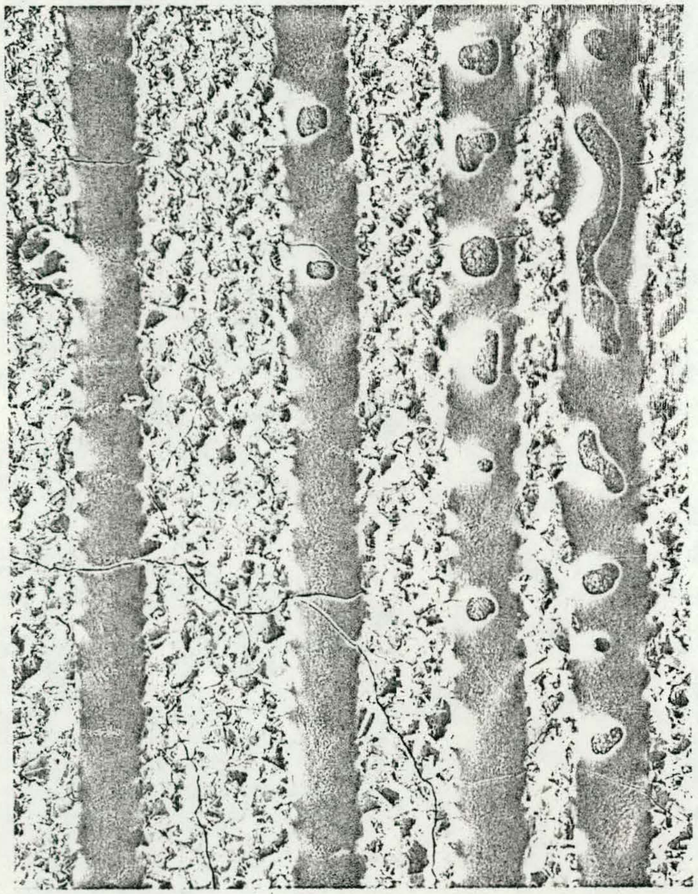

Figure 7a. 170X electron micrograph of Zn_3P_2 deposited on Si_3N_4 with laser annealing stripes corresponding to laser beam energies of (from left to right) 1.5W, 2.0W, 2.5W and 3.0W.

Figure 7b. 1000X electron micrograph of Zn_3P_2 deposited on Si_3N_4 after laser annealing with energy of 1.5W.

TABLE I

Resistivity of Evaporated Zn_3P_2 Films at 300°C

Sample #	Substrate T, °C	Dark Resistivity, ohm-cm	Thickness, μm	ρ_{dark}/ρ_{light}
2	220	2×10^7	1.87	70
3	220	6×10^6	0.2	-
5	255	3.8×10^7	2.84	-
10	30	7.2×10^7	4.95	10

Illumination by a tungsten microscope lamp reduces the resistivity by factors up to 100. As was found for single crystal Zn_3P_2, heat treatment in hydrogen between 400° and 500°C decreases the resistivity of some of our samples by a factor between 10 and 50. Aging subsequently at room temperature shows a tendency for the resistivity to be restored to its initial value; after one month the annealed samples have a resistivity only 5 to 20 times less than the initial values.

Transmission and reflectivity measurements between 0.2 μm and 2.5 μm have been made on these films using a Beckman 5270 Spectrophotometer and also a Cary 14 with an integrating sphere attachment. Figure 8 shows typical transmission curves for a thin sample (0.2 μm) and a thicker one (2.84 μm) deposited with substrate temperatures of 220° and 255°C respectively. When Zn_3P_2 is evaporated on a non-heated substrate, we always obtain a shift in the transmission edge to longer wavelengths, as illustrated in Figure 9. A shift in the reverse direction for Zn_3P_2 films deposited on non-heated substrates as compared to heated substrates has been reported by Zdanowicz and Pawlikowski[9], who proposed that films evaporated on non-heated substrates were amorphous whereas films evaporated on heated substrates (200°C) were polycrystalline. The cause of the shift that we observe is under investigation.

Figure 9 also shows the reflectivity coefficient for these two types of layers in the visible and near infrared. These results are in good agreement with those reported by Catalano[10] in the visible range, but they obtain a higher reflectivity coefficient (60%) than we obtain by averaging the interference oscillations for our layer (38%).

From transmission and reflection data near the absorption edge, the variation of the absorption coefficient for a sample deposited on a 250°C substrate has been determined, and is shown in Figure 10. This result is in complete agreement with published data.[10] Assuming a

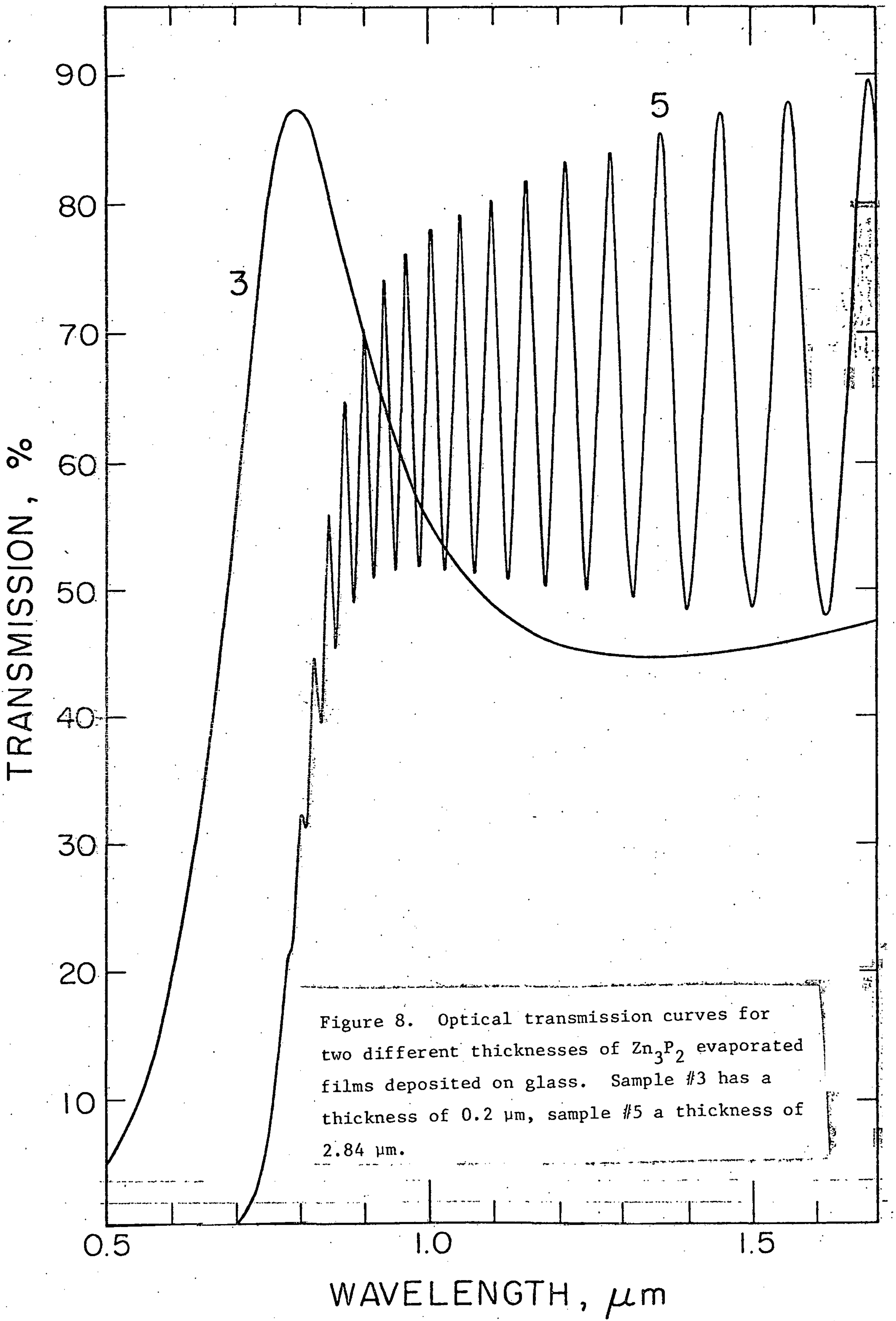

Figure 8. Optical transmission curves for two different thicknesses of Zn_3P_2 evaporated films deposited on glass. Sample #3 has a thickness of 0.2 μm, sample #5 a thickness of 2.84 μm.

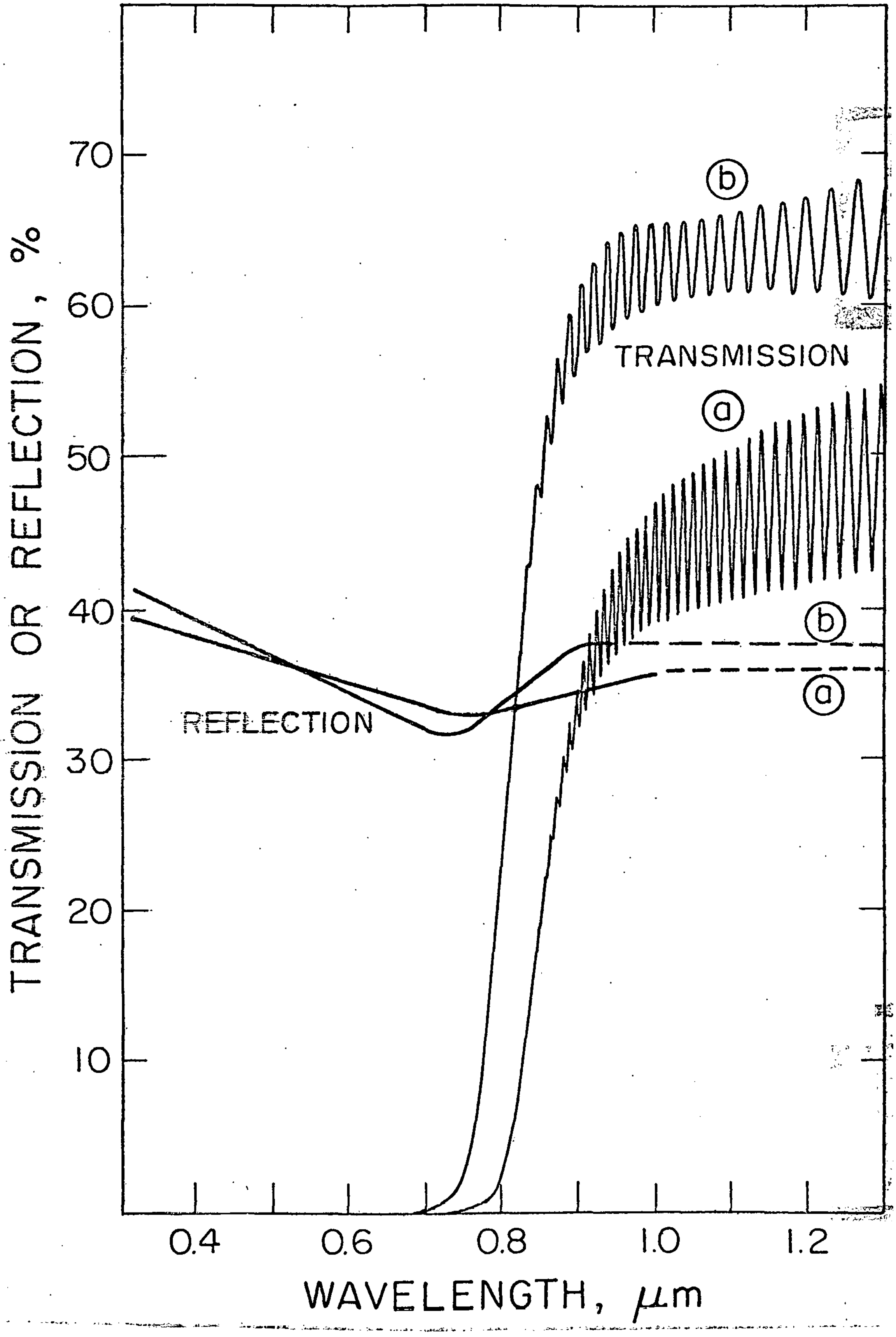

Figure 9. Transmission and reflection spectra for two films of Zn_3P_2 deposited at different substrate temperatures. Curves (a) for substrate temperature of 30°C; curves (b) for substrate temperature of 305°C.

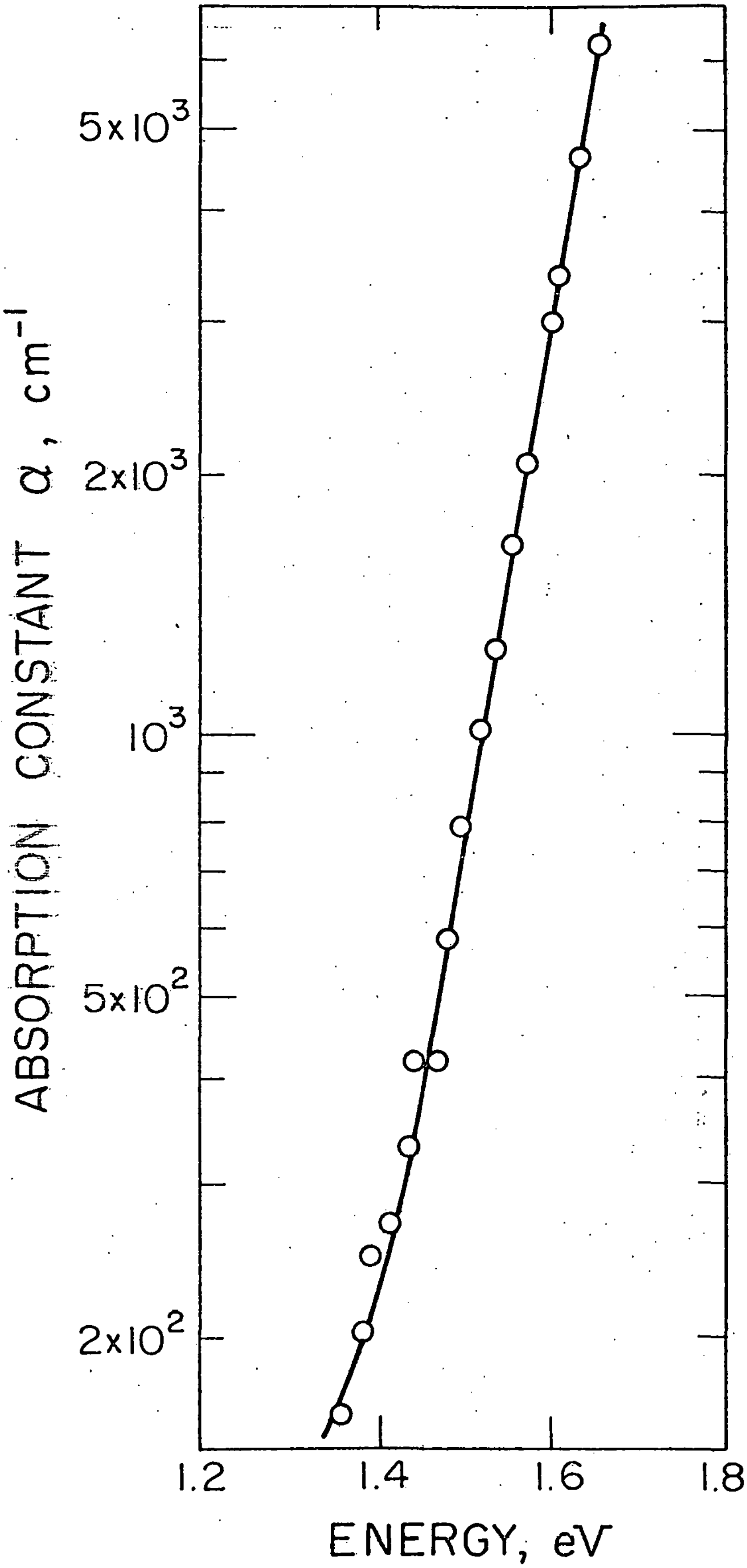

Figure 10. Energy dependence of the optical absorption coefficient for evaporated Zn_3P_2 film # 15.

direct bandgap, we have plotted α^2 vs photon energy to obtain a bandgap of 1.56 eV, which is compatible with values found in the literature.

Photoconductivity spectral response curves were measured for two films as shown in Figure 11. Assuming that the maximum of the photconductivity curve occurs at a photon energy for which the penetration depth ($1/\alpha$) is about equal to the film thickness (since lower energy photons will not be effective absorbed, and higher energy photons will be absorbed near the surface where the lifetime is lower), one would predict a maximum at 1.64 eV for sample #2 and at 1.61 eV for sample #5, using the data of Table I and Figure 10. The photoconductivity maxima are within at least a few hundredths of an eV of these values. The photoconductivity would be expected to fall off at lower photon energies in the same way as the optical absorption as long as there were no large change in carrier lifetime with photon energy, as indicated by the dashed line in Figure 11. The measured photoconductivity, however, is large at considerably lower photon energies, corresponding to a threshold about 0.4 eV smaller than the bandgap. This large extrinsic photoconductivity suggests a much larger lifetime for extrinsic photoexcitation, but the effect is not fully understood at this time.

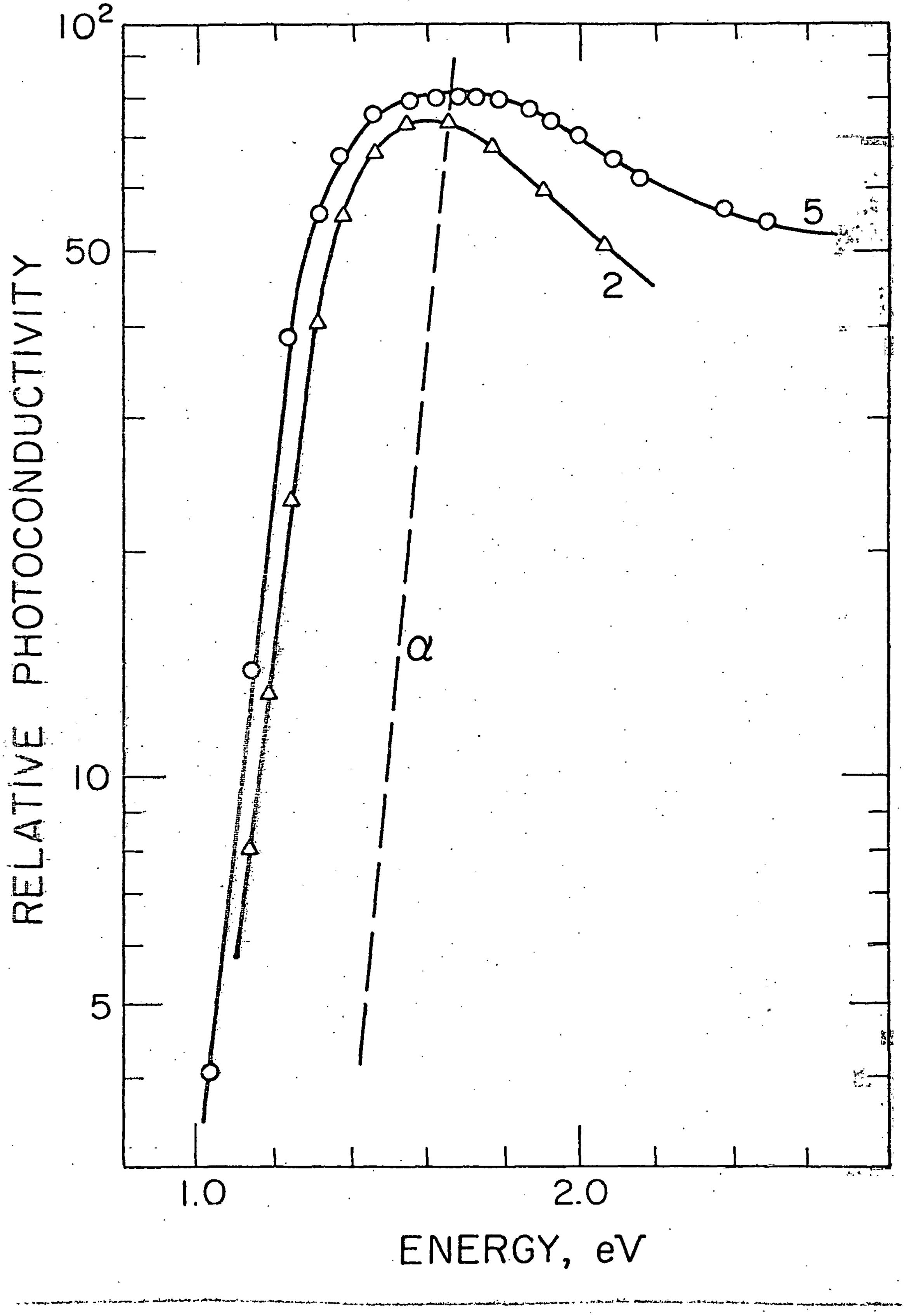

Figure 11. Spectral response of photoconductivity for evaporated Zn_3P_2 films #2 and #5. The dashed curve indicates the variation of the absorption coefficient.

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