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PHOTOELECTRONIC PROPERTIES OF ZINC PHOSPHIDE

CRYSTALS, FILMS, AND HETEROJUNCTIONS

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ABSTRACT

Variations in crystal growth techniques are continuing with the goal of (1) improving single crystal quality, and (2) producing variations in crystal properties by doping and post-growth variations of stoichiometry.

DLTS measurements using Mg/Zn₃P₂ Schottky diodes gave information on three deep levels between 0.55 and 0.66 eV above the valence band in sublimation grown crystals with densities in the 10¹⁵ to 10¹⁶ cm⁻³ range, and a shallower level at 0.12 eV with a density of 10¹⁵ cm⁻³ in an iodine-transport grown crystal. Rough correlations with previous Hall and DLTS analysis are indicated.

Investigation of surface properties of Zn₃P₂ indicate that a Br-MeOH etch leaves a Zn-rich surface (62 at. %) for both sublimation-grown and iodine-transport grown crystals.

Detailed measurements were made on thick Mg/Zn₃P₂ junctions on sublimation-grown and iodine-transport grown crystals of log J-V characteristics as a function of temperature, for crystal substrates as etched, and after heat treatment in hydrogen at several temperatures. A systematic change in the junction transport mechanism from tunneling at heat-treatment temperatures less than 300°C to recombination/generation for heat-treatment temperatures between 300°C and 500°C was found for Zn₃P₂ crystals grown by both growth techniques. A simple model involving a depletion of free carrier density near the surface as a result of heat treatment in hydrogen is proposed. Recombination/generation proceeds through a level lying about 0.45 eV above the valence band, where a level has been detected by previous Hall analysis and DLTS.

Thin film Mg/Zn₃P₂ cells showed log J-V characteristics that are strongly light dependent, indicating an increase in tunneling with illumination.

Evidence that the barrier height of the $\text{Mg}/\text{Zn}_3\text{P}_2$ junction is actually of the order of 0.9 - 1.0 eV was obtained from C-V measurements as a function of frequency, $1/C^2$ vs V curves obtained at all frequencies extrapolating to 0.95 V.

Attempts to prepare $\text{ITO}/\text{Zn}_3\text{P}_2$ junctions by electron-beam evaporation of ITO on single crystal substrates yielded poor diodes and negligible photovoltaic behavior. It is likely that a required air bake to produce desirable ITO properties after deposition was deleterious for the junction.

INTRODUCTION

The major topic described in this report is measurements on the junction transport properties of $\text{Mg}/\text{Zn}_3\text{P}_2$ junctions prepared on single crystals growth both by sublimation and by iodine chemical transport. Also included first are brief descriptions of additional crystal growth experiments, and of some DLTS measurements that were made on Zn_3P_2 crystals. Present research focusses on junctions formed on Zn_3P_2 using one of several possible deposition techniques and materials for the large bandgap window, and on fundamental investigation of the materials properties of Zn_3P_2 and how these can be varied through differences in preparation and post-preparation treatments.

CRYSTAL GROWTH

Two further approaches have been attempted to decrease the time and effort required for single crystal growth of Zn_3P_2 . In the first approach the growth ampoule was modified to a shape similar to that of the ampoule used for Bridgman growth from the melt. The idea was to add a capillary tube at the end of the normal ampoule (in this case, 3 mm inner diameter and 2 cm long) so that only one preferred growth direction could survive after the capillary section was filled. This approach was unfortunately unsuccessful because of the difficulty of transporting material deep into the capillary tube in our system.

The second approach involves growth from a Zn_3P_2 seed. A smaller tube containing a seed crystal was fixed to the regular growth tube in our horizontal system. In this case, it is necessary to control only the supersaturation in front of the growth interface to grow the crystal. We hope to report some result in the next Progress Report.

Because of inherent electrical differences between sublimation-grown and iodine-transport grown crystals, which also seem to affect junction properties formed on these two different types of crystals, variations of crystal growth by iodine transport will be tested. These will involve transport using ZnI_2 , ZnBr_2 and ZnCl_2 , with the additional possibility that incorporation of Br or Cl on P sites may lead to donor activity, of which only suggestions were seen with iodine transport. In addition a more careful investigation will be carried out of the effects of annealing under maximum phosphorus pressure, maximum zinc pressure, and vacuum.

DLTS MEASUREMENTS

In cooperation with the solid state laboratory of Hewlett-Packard in Palo Alto, we carried out DLTS characterization of several Zn_3P_2 single crystal samples.

The capacitance signal from a Schottky barrier ($\text{Mg}/\text{Zn}_3\text{P}_2$ in our case) is detected by a fast capacitance meter driven by an HP DLTS detector power supply. The output voltage signal is fed through a program filter, and then into a HP 3437A voltmeter with sensitivity of $20 \mu\text{V}/\text{pf}$. A bias pulse was generated by a HP 8007B pulse generator with $100 \mu\text{s}$ pulse width and up. The smallest capacitance transient could be detected $100 \mu\text{s}$ after the end of the bias pulse. A maximum of sixteen readings could be recorded by the computer between $100 \mu\text{s}$ and 1 sec. The sample was contained in an Air Products and Chemicals Model NT3=1103 Heli-Tran dewar with very good temperature stability. The temperature was normally varied from -80° to 110°C with a maximum of 256 values between. The whole system was controlled by an HP 9825B computer. Typically all data were recorded on a disc during a run and analysis was done by the same computer later.

For our measurements $\text{Mg}/\text{Zn}_3\text{P}_2$ Schottky barriers were used. Reverse bias from -2V to 0V with pulse width of 1 ms was applied to generate the capacitance transient, so that only hole traps (majority carrier traps) were investigated. The pulse width was selected to be long enough to ensure that all traps were filled. The maximum capability of the instrument in terms of pulse time intervals and temperature intervals was used in our measurements.

Figure 1 shows the capacitance transient spectrum for two $\text{Mg}/\text{Zn}_3\text{P}_2$ junctions. The solid curve indicates the spectrum for a sublimation-growth Zn_3P_2 crystal. Considerable structure is observed but with some uncertainty as to the exact trap parameters because of the overlap of several

Figure 1. DLTS spectrum for two $\text{Mg}/\text{Zn}_3\text{P}_2$ junctions. Solid curve is for junction prepared on sublimation-grown Zn_3P_2 single crystal; dashed curve is for iodine-transport grown Zn_3P_2 single crystal.

peaks. It is evident, however, that quite deep levels are present because of the response at higher temperatures. If we assume simply three superposed peaks and resolve the spectrum by step-wise decomposition, we are able to arrive at values for the energy level, capture cross section and density of the trap levels. These are summarized in Table I and Figure 2. It is evident from the relatively small range of temperatures available for the measurements that the ionization energy of the levels can be determined only to within about 20% and that the corresponding capture cross sections may be in error by as much as two orders of magnitude.

The dashed curve in Figure 1 indicates the DLTS spectrum for iodine-transport grown crystals. A well-defined peak corresponding to a relatively shallow level is observed. The trap parameters for this level are determined to somewhat greater accuracy than those for the sublimation-growth crystal.

As reported in Progress Report No. 8, the imperfection levels observed from the Hall effect and conductivity vs temperature measurements are different for sublimation-grown and iodine-transport grown crystals. Some correspondence is found between the electrical determination of 0.47 eV levels with a density of $5 \times 10^{18} \text{ cm}^{-3}$ in the sublimation-grown crystals, and of 0.14 eV levels with a density of $2 \times 10^{16} \text{ cm}^{-3}$ in the iodine-transport grown crystals, and the levels identified by DLTS.

TABLE I

Calculated Trap Parameters for Zn_3P_2 Crystals from DLTS Measurements

Trap Index	Hole Ionization Energy, eV	Hole Capture Cross Section, cm^2	Density, cm^{-3}
1 ^a	0.55	6×10^{-15}	1.4×10^{16}
2 ^a	0.58	2×10^{-11}	1.2×10^{15}
3 ^a	0.66	1×10^{-13}	5.0×10^{15}
I ^b	0.12	3×10^{-18}	1.1×10^{15}

^a Measured in sublimation-grown Zn_3P_2 single crystal.^b Measured in iodine-transport grown Zn_3P_2 single crystal.

SURFACE TREATMENTS OF Zn_3P_2

Surface phenomena were investigated in order to relate different surface treatments to device performance. It has been observed by optical microscopy (to 1000X) that surfaces were drastically changed from smooth to rough appearing after heat treatment in hydrogen above 500°C for a few minutes. Under the same treatment, the amount of surface change appears to be less for crystals grown by iodine-transport than for crystals grown from sublimation. For the same kind of heat treatment, but below 450°C , no apparent changes in the surface could be optically detected.

A series of samples, all etched with 5% Br-MeOH, but heat treated in hydrogen at different temperatures: no heat treatment, 300° , 400° and 500°C , were prepared for electron microprobe analysis. The sensitivity of this technique ($\pm 1\%$ by weight) was not sufficient to distinguish between differences conceivably caused by different heat treatments. There was a strong indication, however, that the Br-MeOH etch left a Zn-rich surface for both sublimation-grown and iodine-transport grown crystals: differences were observed between signals for a 15 kV electron accelerating voltage and a 20 kV voltage (expected to have about 30% more bulk sampling volume than the 15 kV case). Typical results indicate 62 atomic % of Zn at the surface rather than the expected 60% found in the bulk.

Mg/Zn₃P₂ JUNCTIONS

In Progress Report No. 10 we reported some initial results on the temperature dependence of J-V curves for Mg/Zn₃P₂ junctions, but without drawing any conclusions. We have subsequently devoted our attention to an understanding of the transport mechanism in these junctions, also as a function of different surface treatments before junction formation.

Mg/Zn₃P₂ Schottky diodes were fabricated by vacuum deposition of a thick film of Mg (0.5 to 1.0 micrometer) onto the Zn₃P₂ at a pressure of 4×10^{-8} Torr and an evaporation rate of about 100 Å/sec. Prior to the deposition Zn₃P₂ samples were heat treated between 20° and 500°C for a few minutes in hydrogen, and then were etched with 5% Br-MeOH to remove about 1 micrometer of material from the surface. Au back contacts were evaporated after heat treatment. The as-prepared junction was immediately measured: J-V characteristics between 80 and 300°K, and C-V characteristics at 295°K. If two mechanisms were observed to contribute to the transport, careful analysis based on two J₀ and A values were performed to ensure accurate representation of each mechanism. The results of these investigations are summarized in Table 2 and in Figures 3 and 4.

The transport mechanisms was investigated via the temperature dependence of the J-V characteristics. For simple cases, where a plot of log J vs V yields a single straight line, direct computation of J₀ and A can be readily accomplished. In other cases, where the log J-V characteristics indicate more than one transport mechanism active, the following expression was used as the basis for the analysis:

$$J = J_{01} [\exp(\alpha_1 (V - JR_s)) - 1] + J_{02} \{ \exp(\alpha_2 (V - JR_s)) - 1 \} + (V - JR_s) / R_p$$

where α_i are the slopes of the log J-V curves for the i^{th} mechanism,

TABLE II
SUMMARIZED TRANSPORT MECHANISMS FOR Mg/Zn₃P₂ JUNCTIONS

Zn ₃ P ₂ Growth Method	Sample Preparation ^a Prior to Mg Deposition	Junction Transport Mechanism	C-V (1 MHz) Analysis Extrapolated V _b (V)	Density (cm ⁻³)
PVT	5% Br-Meth as-etched	two-step tunneling	0.93	6.3x10 ¹⁵
CVT	"	"	0.78	1.0x10 ¹⁶
PVT	HT at 275°C and etched	two-step tunneling	0.95	6.5x10 ¹⁵
CVT	"	"	0.79	3.7x10 ¹⁵
PVT	HT at 400°C and etched	R/G with A=1.92 and E _{act} =0.453 eV	1.07	2.0x10 ¹⁶
CVT	"	R/G with A=2.35 and E _{act} =0.397 eV	0.57	4.0x10 ¹⁶
PVT	HT at 450°C and etched ^b	R/G with A=1.92 and E _{act} =0.456 eV	----	4.0x10 ¹⁶
CVT	"	R/G with A=2.0 and E _{act} =0.4 eV	1.28	3.5x10 ¹⁶
PVT	HT at 490°C and etched	tunneling	----	2.5x10 ¹⁶
CVT	"	thermally assisted tunneling with V _b =1.07 eV at T<180°K A _b =1.43 at T>180°K	0.78	1.0x10 ¹⁷

^a All heat treatment were performed in hydrogen environment. ^b Interfacial layer present.

PVT : physical vapor transport.

CVT : chemical vapor transport.

Figure 3. Slope of the log J-V curves, α , vs temperature for Mg/Zn₃P₂ junctions on sublimation-grown Zn₃P₂ single crystals after the heat treatments indicated on the figure. Also shown is the diode factor A for the case of hydrogen heat treatment at 400 $^{\circ}C$ for 6 min.

J_{oi} are the respective saturation currents, R_s is the series resistance, and R_p is the shunt resistance. Since the measured current is the result of superposition of the two contributing mechanisms, the actual J_{oi} and α_i cannot be determined from the recorded log J-V curves directly. In our analysis, the current at each voltage was carefully resolved into two components until it satisfied the above expression and was consistent with all other voltages.

A systematic change in the junction transport mechanism from tunneling at heat-treatment temperatures less than 300°C to recombination/generation for heat-treatment temperatures between 300°C and 500°C was determined for Zn_3P_2 crystals grown by both physical vapor transport and iodine chemical transport. Since the bulk free carrier concentration, as indicated by capacitance measurements, lies between 6×10^{15} and $1 \times 10^{17} \text{ cm}^{-3}$, direct tunneling through the potential barrier is unlikely. The fact that there is no temperature dependence for the observed tunneling indicates that it is unlikely that tunneling is occurring through surface or interface states.

In Figure 5 we propose a simple model that may explain the junction behavior. At low heat-treatment temperatures, the carriers tunnel through a trap center via two-step tunneling. For high enough heat-treatment temperatures, however, the free carriers are depleted from the surface region and the Fermi level near the surface moves toward the middle of the gap. The hole density has been measured by capacitance techniques at reverse bias as a function of depletion layer width; a much more rapid decrease in hole density toward the surface is observed for the higher heat-treatment temperatures. Recombination/generation becomes the dominant transport mechanism when the Fermi level crosses a particular active deep level. For this situation, the activation energy of a $\ln(J_o T^{-1/2})$ vs $1/T$ plot indicates the location of the level. Values of

(a)

(b)

Figure 5. Proposed schematic energy band configurations for (a) low heat-treatment temperatures and/or high hole densities near the surface, (b) high heat-treatment temperatures and/or low hole densities near the surface. Tunneling dominates in (a), recombination/generation in (b).

0.45 eV for the sublimation grown crystals, and of 0.40 eV for the iodine-transport grown crystals, agree with level locations independently found at 0.47 eV by Hall analysis and at 0.42 eV by DLTS analysis (by Dr. T. Suda in Japan using our samples).

For heat-treatment temperatures greater than 500°C, drastic physical changes in the Zn_3P_2 surface are visible, and simple descriptions of the junction transport processes are probably inadequate.

The actual log J-V curves described above are given in Figures 6 through 9 for completeness.

THIN FILM $\text{Mg}/\text{Zn}_3\text{P}_2$ SOLAR CELLS

Two thin film $\text{Mg}/\text{Zn}_3\text{P}_2$ junctions were prepared using the processing described above except that film thicknesses were about 150 to 200 Å. Figure 10 shows the dark and light J-V curves for the better of the two cells, with the spectral response in the insert. This cell yielded $J_{sc} = 6 \text{ mA/cm}^2$, $V_{oc} = 0.18 \text{ V}$ and a $ff = 0.61$ under AM1.5 illumination. The spectral response measurement indicates that only about 30% of the input energy has been collected, which suggests a J_{sc} of about 20 mA/cm^2 if correction is made for reflection and absorption losses due to the Mg film. The fill factor is typical for a 1 ohm/cm^2 series resistance. Tunneling is responsible for the low V_{oc} , as is indicated by the cross over of the dark and light J-V curves in Figure 10, which suggests a change of J_0 and diode factor A under illumination.

Figure 11 also illustrates the light effects on the junction transport by comparing the $\log J_{sc} - V_{oc}$ variation measured under illumination with the log J-V curve for the cell in the dark, and the log J-V curve for a typical thick $\text{Mg}/\text{Zn}_3\text{P}_2$ diode in the dark. Enhanced tunneling is evident for high illumination intensities. This result is consistent with the proposed model for the dark junction transport, since tunneling may be

Figure 6. Log J vs V characteristics of an as-etched $\text{Mg}/\text{Zn}_3\text{P}_2$ junction.

Figure 7. Log J vs V characteristics after heat-treatment in H_2 at 275°C for a $\text{Mg}/\text{Zn}_3\text{P}_2$ junction.

Figure 9. Log J vs V characteristics after heat treatment in H_2 at 490°C for a $\text{Mg}/\text{Zn}_3\text{P}_2$ junction.

Figure 10. Dark and light J-V curves for a thin film $\text{Mg/Zn}_3\text{P}_2$ solar cell. Insert shows the spectral response of this cell.

expected to dominate under high illumination as the Fermi level is closer to the band edge. A reduction of deep level density through variations in growth conditions should lead to an increase in V_{oc} and cell efficiency.

BARRIER HEIGHT OF Zn_3P_2 JUNCTIONS

In the previous Progress Report we reported a barrier height of 1.07 eV from log J-V vs temperature measurements. We have also investigated C-V behavior as a function of frequency between 10 KHz and 4 MHz; for a good junction in which capacitance of an insulating layer does not contribute and in which trapping effects are minimized, $1/C^2$ vs V plots extrapolate to 0.95 V for all frequencies. These results suggest that the barrier height may be larger than the normally believed value of about 0.8 V.

ITO/ Zn_3P_2 JUNCTIONS

Two ITO/ Zn_3P_2 junctions were prepared by electron-gun evaporation of ITO through collaboration with Jan Werthen and using the facilities of the Xerox Palo Alto Research Center. This is the technique that has yielded 9.7% efficiency for ITO/CdTe solar cells. ITO was evaporated under a reduced oxygen pressure of 1×10^{-6} Torr with an evaporation rate of 2 A/sec. Film thicknesses were between 1000 to 2000 Å. A heat-treatment of the junction at 230°C in air for 2 min is required in this method to make the ITO film transparent and conducting (presumably to convert it from amorphous to polycrystalline). Only poor diodes were produced, however, and only very small photovoltaic effects were observed. It is likely that the heat treatment in air step in this processing leads to oxidation of the Zn_3P_2 and diffusion of the oxide with deleterious effects on the junction.

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