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CHARACTERIZATION OF ZINC SELENIDE SINGLE CRYSTALS

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INTRODUCTION

ZnSe single crystals of high quality and low impurity levels are desired for use as substrates in optoelectronic devices. This is especially true when the device requires the formation of homoepitaxial layers[1]. While ZnSe is commercially available, it is at present extremely expensive due to the difficulty of growing single crystal boules with low impurity content and the resultant low yields. Many researchers[2-6] have found it necessary to heat treat the crystals in liquid Zn in order to remove the impurities, lower the resistivity and activate the photoluminescence at room temperature.

The physical vapor transport method (PVT) has been successfully used at MSFC to grow many single crystals of II-VI semiconducting materials including ZnSe[7]. The main goal at NASA has been to try to establish the effect of gravity on the growth parameters. To this effect, crystals have been grown vertically upwards or horizontally. Both (111) and (110) oriented ZnSe crystals have been obtained via unseeded PVT growth. Preliminary characterization of the horizontally grown crystals has revealed that Cu is a major impurity and that the low temperature photoluminescence spectra is dominated by the copper peak. The ratio of the copper peak to the free exciton peak is being used to determine variations in composition throughout the crystal[8].

It was the intent of this project to map the copper composition of various crystals via photoluminescence first, then measure their electrical resistivity and capacitance as a function of frequency before proceeding with a heat treatment designed to remove the copper impurities. However, equipment difficulties with the photoluminescence set up, having to establish a procedure for measuring the electrical properties of the as-grown crystals and time limitations made us re-evaluate the project goals. Vertically grown samples designated as ZnSe-25 were chosen to be measured electrically since they were not expected to show as much variation in their composition through their cross-section as the horizontally grown samples.

EXPERIMENTAL DETAILS

(1) Sample surface preparation

ZnSe crystals are very brittle and handling them requires much care. Samples were lapped manually on SiC paper, washed and then attached to glass platens using paraffin wax. Samples were then lapped on both sides using the Logitech Lapping and Polishing Equipment. Lapping was done with 9 micron alumina particles. Polishing was accomplished with 0.3 micron alumina particles suspended in 12.5% sodium hypochlorite solution diluted 50:50 with water. Chemomet Buehler paper was used for the polishing steps.

(2) Photoluminescence Measurements

The sample was placed in a cryostat and held at a temperature of $T=1.4$ K. An Ar ion laser from Coherent Inc. run at 364nm with 10mW was used to excite photoluminescence from the sample. A Spex spectrometer was used to collect the PL intensity data. The spectrometer was run at a voltage of 1730 and its slits were set at 0.18, 0.22 and 0.18.

(3) Electrical contacts

Electrical contacts were placed on the samples using 5/9 pure indium. The method employed does not require heating of the indium, instead it consists of depositing extremely thin sequential layers of indium until a good contact has been established. Gold wires were used to attach samples to the measuring equipment. At least 4 contacts were placed on each sample.

(4) Electrical resistivity measurements

Samples were placed in the Hall measurement cryostat set up. Van der Pauw[9] resistivity measurements of the as-grown crystals of ZnSe-25 using the established Keithley 220 Current Source and Keithley 181 Nanovoltmeter were not possible because their resistivity was beyond the capabilities of those instruments. Instead of the Keithley 181 Nanovoltmeter, a Keithley 617 Electrometer was used. Changes to the Hall measurements computer program were made in order to run the new configuration automatically. Many measurements were carried out manually in order to establish the correct waiting times and to be sure that measurements would be made in the ohmic regime.

(5) Capacitance measurements

Samples were measured as a function of frequency, ac voltage signal and superimposed dc bias voltage. The equipment used was a Hewlett-Packard LCR Meter Model 4275A. A short computer program was written in order to collect C-V measurements. The Keithley 617 was used as the dc bias voltage source in this case.

(6) Heat treatment of the samples

Samples were heat treated in closed quartz ampoules. Samples were originally surrounded by Zn powder and subsequently heated above the melting point of Zn and held at that temperature for 48 hours.

RESULTS AND DISCUSSION

The resistivity of the as-grown ZnSe-25 samples is so large that very long waiting times are required in order to let the sample reach equilibrium. The Keithley 617 is capable of giving resistance values directly using only two contacts. Values between individual contact pairs varied from 17 to 42 gigaohms. In order to make van der Pauw measurements, it was necessary to establish whether contacts were ohmic. Figure 1 displays the voltage vs. current curve obtained using the 220 current source and the 617 as a voltmeter. Waiting times between points shown were only 10 minutes. Under other circumstances, waiting periods needed to be as long as 45 minutes. The fairly linear behavior seen in this figure demonstrates that behavior of the sample is ohmic below 8 nanoamps. The deviations at higher currents may actually be due to limitations of the current source rather than non-ohmic behavior of the samples. Based on this information, a current of 3 nanoamps was used to measure the resistivity. The limitations of the current source were again noticeable when resistivity measurements as a function of temperature(200-400K) were taken. Values did not seem to change with temperature very much. The resistivity of the ZnSe-25 sample at 300K, using the van der Pauw method, was calculated to be 3.0×10^9 (ohm-cm).

Capacitance measurements were first made as a function of frequency. The frequencies of the LCR meter used range from 10 kHz to 10 MHz. This instrument is designed to measure samples with impedances of 10 megaohms or less, therefore obtaining data that can be ascribed to the sample itself is a challenging task. Nevertheless, since impedance of a capacitor in series is given by $1/\omega C$, some useful data may be obtained as the frequency of the measurement is increased. On the other hand, inductive losses may dominate at the highest frequencies. Figure 2 shows a capacitance vs. log frequency plot taken at a constant ac voltage of 0.1. As might be expected because of the length of the leads, the data above 1 MHz shows inductive behavior (showing a decreasing value of capacitance which reaches negative values at the highest frequencies). In order to make sure that these values are not genuinely due to the sample, capacitance measurements were taken at a fixed frequency of 4 MHz and the ac voltage was varied from 0.1 to 1.0 volts. Both capacitance and dissipation factor demonstrated that the inductive behavior nearly disappears at higher levels of ac voltages. In order to avoid short circuiting through the instrument at lower frequencies or being dominated by inductive losses at the higher frequencies, a frequency of 400 kHz was picked for conducting the C-V measurements. It should be mentioned that each pair of contacts was measured independently and that values of capacitance obtained ranged from 35 fF to 240 fF. Measurements were taken at temperatures ranging from 15K to 300K. Virtually no temperature dependence could be detected.

The C-V measurements were taken at room temperature with as low an ac signal as needed to prevent short circuiting through the LCR meter. The superimposed dc bias voltage was varied from -10 to +10 in 100 mV steps. As is expected for an insulating sample, no dependence upon dc bias voltage was found. Figure 3 displays the $1/C^2$ vs Bias voltage curve. The heat treated sample is expected to show a dependence on bias voltage which may then be used to calculate the number of carriers present[10].

Prior to subjecting the electrically measured sample to a heat treatment to lower its resistivity, photoluminescence measurements were taken. Figure 4 depicts the photoluminescence spectrum at wavenumbers between 22000 and 22700 cm^{-1} . Three major features are seen. They are the peaks at 22592.5, 22445.5 and 21900 cm^{-1} . The first peak is ascribed to the free exciton peak while the other two are presumably related to the copper impurities[11]. It should be noted that it has been observed that the sample surface condition affects the magnitude of the peaks, although it appears that it affects them all equally[12]. It is expected that the ratio of the first to the second peak will increase dramatically after the heat treatment.

CONCLUSIONS

This project provided this investigator with the opportunity to learn about some of the activities in the microgravity division and work with single crystals of technological importance for optoelectronics. In particular, the exposure to the photoluminescence and semiconductor polishing and etching will be very useful for this investigator's future research projects. At the same time, her expertise with insulating materials was crucial for

establishing the proper procedures for measurement of the electrical resistivity and capacitance measurements of the as grown ZnSe-25 crystals. The resistivity of these crystals at room temperature was determined to be 3×10^9 ohm-cm. CV measurements confirmed the highly insulating nature of these crystals by showing no bias voltage dependence. Since all data reported was obtained by borrowing equipment from other branches, it is recommended that the crystal growth and solidification branch purchase a Keithley 617 electrometer for both the resistivity as well as the C-V measurements. This equipment is versatile in that it can be used to measure resistance directly, as a voltage source, a voltmeter and also as a current meter (as low as 1×10^{-15} amps). It should be added that in order to use the 617 to its fullest capability and allow measurement of resistances higher than a few gigaohms, additional hardware changes will be needed. The LCR meter used to obtain the capacitance values (HP4275A) has to be used with care as discussed in the results section. A single frequency capacitance meter better capable of measuring higher impedance samples can be obtained from Boonton Electronics or Andeen-Hagerling. However, the HP4275A will work well with lower resistivity semiconducting crystals.

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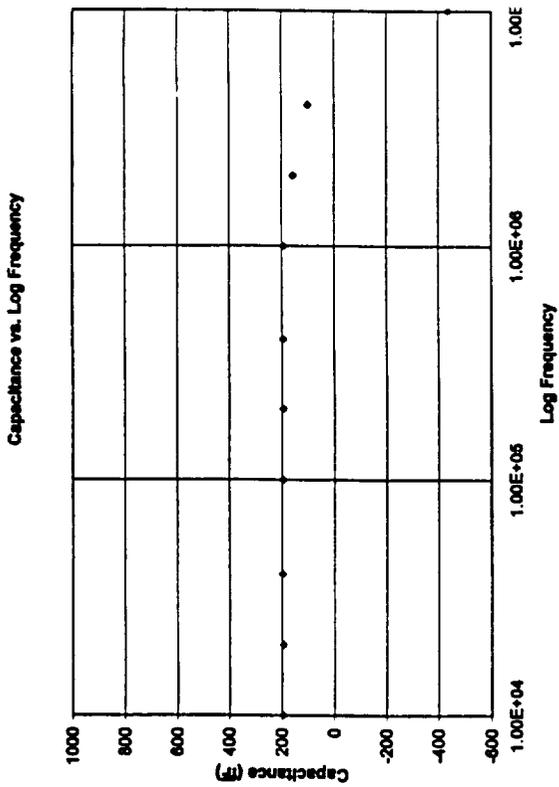


Figure 1

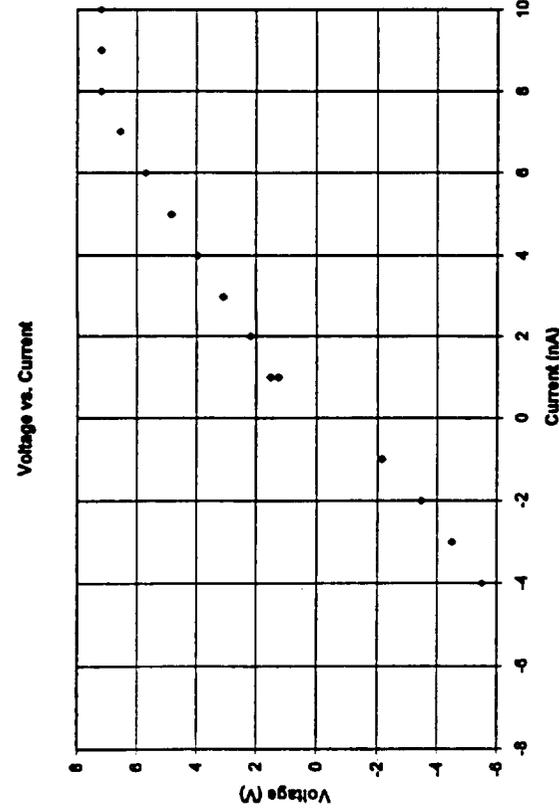


Figure 2

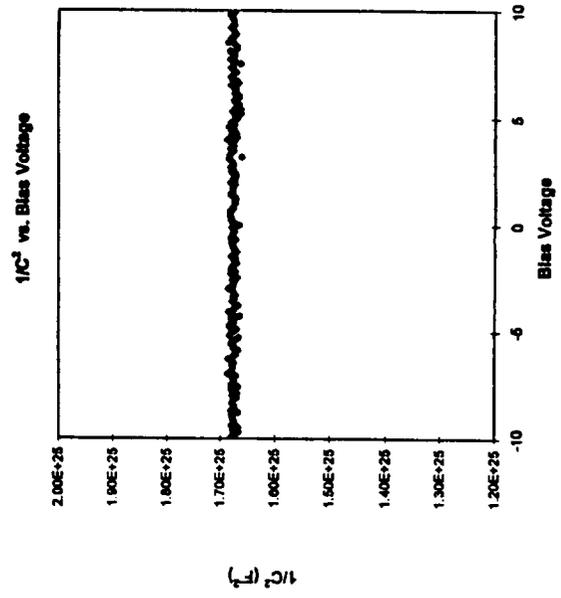


Figure 3

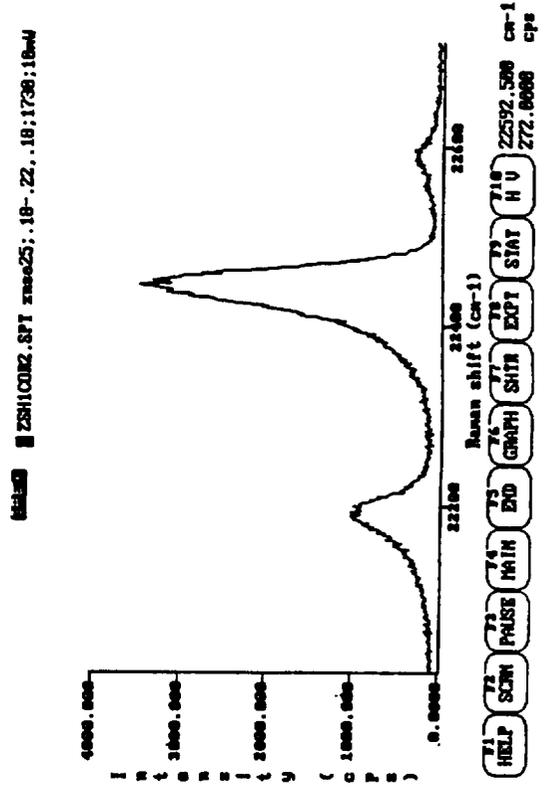


Figure 4

