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Characterization of single crystalline ZnTe and ZnSe grown by vapor phase transport.

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Abstract. Tubular furnaces were designed and built to obtain single crystalline ZnTe and ZnSe ingots using respectively physical and chemical transport methods. Different temperature profiles and growth rates were analyzed in order to optimize the necessary crystalline quality for device development.

Optical and scanning electron micrographs of the corrosion figures produced by chemical etching were used to obtain the dislocation density and the misorientation between adjacent subgrains in ZnTe and ZnSe wafers. Structural quality of the single crystalline material was determined by transmission electronic microscopy. Optical transmittance was measured by infrared transmission spectrometry and the resulting values were compared to commercial samples.

1. Introduction

ZnTe is a useful II-VI compound for optical devices because of its wide energy gap (about 2.3 eV at room temperature) [1]. This semiconductor material has been found to become photorefractive when it is appropriately doped with V or with Mn and V. The combination of photorefractivity and semiconductivity make this material attractive for many applications as optical power shielding and holographic interferometry. Moreover, ZnTe:V have a superior photorefractive performance at wavelengths from 0.6 to 1.3 µm than other photorefractive materials. This semiconductor might also be used for windows due of its important optical transmission.

The structures based on ZnSe for laser emission in the blue-green range of the spectrum have been mainly grown on GaAs due to the high quality of these commercially available substrates. However ZnSe homoepitaxy is a promissory line of investigation with the aim of diminishing the density of structural defects [2]. As ZnSe transmits in a wide range of the infrared spectrum it is also used for lenses and windows.

In this paper we study the growth of single crystalline ZnTe and ZnSe [3] by vapor phase transport. These materials have notable electro-optical properties [4]; however, as the quality of detectors and optical devices are critically dependent on its crystalline properties, our aim was to determine the best growth conditions to obtain a high crystalline quality. The crystal quality was determined by chemical etching and transmission electron microscopy (TEM). The optical transmission under incident IR radiation was evaluated with the purpose of using ZnTe and ZnSe in the manufacturing of lenses and windows.
2. Experimental Procedure.

Electrical and optical properties of semiconductors are determined by their impurities, so it is important not only to diminish them but also to know which ones are present. The elements used in the synthesis of ZnTe and ZnSe can be obtained with a purity of 6N for Zn and Te, and 5N for Se. These elements were purified by dynamic vacuum distillation previous to their employment in the synthesis [5-7].

Tubular furnaces for single crystalline growth of semiconductor ingots of the II–VI family were designed, built and used several times with different temperature profiles to get the best conditions for each single crystalline compound synthesis. Vapor Phase Transport without and with gaseous carrier, molecular iodine in our case, was the chosen technique. It requires a particular temperature profile with the corresponding growth conditions control: A) growth speed in the first case for single crystalline ZnTe growth (figure 1a); and B) ampoule temperature gradient, growth time and amount of iodine in the latter case for single crystalline ZnSe growth (figure 1b).

![ZnTe ingot](image1)

**Figure 1:** a) ZnTe ingot grown by Physical Vapor Phase Transport. b) ZnSe ingot grown by Chemical Vapor Phase Transport with iodine as gas carrier.

Various reagents were used for the chemical etching of each one of the semiconductor compounds. The micrographic results for each material were compared to determine the relative advantages of the

![OM micrographs](image2)

**Figure 2:** a) OM micrograph of a chemically etched ZnTe wafer. b) OM micrograph of a chemically etched ZnSe wafer. c) SEM micrograph of the same ZnTe wafer of figure 2a. d) SEM micrograph of the same ZnSe wafer of figure 2b.
chemical solutions. Data analysis determined the following chemical selection: \( K_2Cr_2O_7 + HCl \) for ZnTe and \( KMnO_4 + H_2SO_4 \) for ZnSe. Figures 2a and 2b show micrographs obtained by optical microscopy (OM), and figures 2c and 2d correspond to micrographs respectively obtained by scanning electronic microscopy (SEM) of the same chemically etched wafers of ZnTe and ZnSe crystals.

A precision ion polishing system (PIPS), Model Gatan 691 (VAr+< 4 kV) was employed to get thin specimens from ZnTe and ZnSe in planar view geometry. The TEM examination of the samples was performed with a JEOL JEM 2000 FX (W termoionic filament) at 200 kV of operation. A JEOL JEM 3000 F (Field Emission Gun) at 300 kV of operation was used to obtain LRTEM and HRTEM images by means of a Gatan CCD camera.

Transmission spectra of ZnTe and ZnSe crystals, grown at our laboratory and commercial ones, were obtained using a Perkin-Elmer System 2000 Fourier transmission infrared equipment (FTIR).

### 3. Results and Discussion.

Table 1 shows the dislocation densities and adjacent subgrain misorientation obtained as a statistical average of different measurements in the same wafer with the chosen reagent for the semiconductor compound.

| Semiconductor Compound | Reagent         | \( \delta_{\perp} (\text{cm}^2) \) | \( \phi (\text{\textdegree}) \) |
|------------------------|-----------------|-----------------------------------|---------------------------------|
| ZnTe                   | \( K_2Cr_2O_7 + HCl \) | \( 2.31 \times 10^5 \)            | 11                              |
| ZnSe                   | \( KMnO_4 + H_2SO_4 \) | \( 6.2 \times 10^5 \)            | 22                              |

3.1. ZnTe TEM characterization

3.1.1. Jeol JEM 2000 FX.

Figure 3a shows the [1 1 0] zone axis of the transmission electron diffraction (TED) pattern of the ZnTe specimen. The TEM images corresponding to \( g = [0 0 -2], [0 0 2] \) and \( [-2 2 0] \) have shown no dislocations in the semiconductor material. As an example, the image for \( g = [0 0 -2] \) is illustrated in figure 3b.
3.1.2. Jeol JEM 3000 F

The high resolution TEM images were obtained with the [1 1 1] zone axis (figure 4a). In figure 4b no dislocations are present confirming a low dislocation density. It can also be observed the excellent structural crystalline order between dislocations whose etch pits were revealed by chemical reagents in the previous analysis.

3.2. ZnSe TEM characterization

3.2.1. Jeol JEM 2000 FX

Figure 3c is the transmission electron diffraction diagram with [1 1 0] zone axis. TEM images with \( g = [1 -1 1] \) and \( g = [2 -2 0] \) have shown no dislocations in the semiconductor material. Figure 3d is an example of this fact (\( g = [2 -2 0] \)).

3.2.2. Jeol JEM 3000 F

Dislocations presence have been analyzed by choosing the (1 1 1) zone axis in the TED diagram (figure 4c). High resolution TEM images were obtained with different magnifications. None of them show dislocations confirming the low dislocation density. Figure 4d corresponds to a larger TEM magnification and, as in the case of ZnTe, it can be observed the excellent structural crystalline order between dislocations revealed by chemical etching in the previous stage.

![Figure 4](image)

**Figure 4:** a) [1 1 1] TED pattern. b) HRTEM image with [1 1 1] zone axis. c) [1 1 1] TED pattern. d) HRTEM image with [1 1 1] zone axis.

3.3. ZnTe and ZnSe transmission spectra.

Figure 5a and 5b compare the transmission spectra obtained from one of the samples of ZnTe and ZnSe grown in the Solid State Materials Research Centre (CINSO), and one commercial sample of each type used for optical windows. Both spectra confirm that these materials can be used in manufacturing optical devices and in windows for IR detectors in a broad range of wavelengths, especially in the first and second atmospheric window (3-5 \( \mu m \) and 8-14 \( \mu m \) respectively). It was
determined that the polishing improvement of materials produced also an improvement of the transmittance values.

The spectral curves indicated undesirable oscillations in the H$_2$O and CO$_2$ absorption wavelengths due to the internal calculation of the FTIR program, since in these absorption bands the measurement error increases due to very small signal values.

4. Conclusions
Transmission electron microscopy micrographs confirmed the low dislocation density and the excellent crystalline quality of the grown materials between dislocations previously studied by chemical etching.

The semiconductor material grown at CINSO and the commercial wafers have comparable FTIR spectra, suggesting their possible use as IR transmission windows.

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