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Procedia Materials Science 9 (2015) 444 – 449

Procedia Materials Science

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International Congress of Science and Technology of Metallurgy and Materials, SAM – CONAMET 2014

Crystalline quality of CdSe single crystalline commercial wafer

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Abstract

Cadmium selenide is a II-VI semiconductor compound with 1.67 eV energy gap (≈ 300 K) and high stopping power for nuclear radiation. Its crystalline structure is hexagonal (wurtzite) and it is used in solar cells, transistors, light emitting diodes, electroluminescent devices, nuclear radiation detectors at room temperature and nonlinear optical devices [Shan et al. (1994), Young et al. (1994), Van Calster et al. (1988), Chopra (1969), Bhargava (1997)]. It is also employed as substrate for epitaxial growth of HgCdSe [Korostelin et al. (1996)]. Qualities of devices are critically dependent on their material properties. Crystalline characterization of a CdSe commercial wafer was our main goal. The crystalline quality was evaluated by different techniques. Since it is used as an optical window in the IR spectrum, its optical transmittance was measured by FTIR (Perkin-Elmer System 2000). The etch pits distribution was determined by chemical etching. Dislocation density was obtained by counting on optical micrographs (Union Versamet 5279) meanwhile misorientation between adjacent subgrains by means of Shockley - Read approximation. The reliability of the techniques used in determining the crystalline quality was evaluated. The etching solution was sensitive in linear defects detection and crystalline quality was adequate for devices manufacture of this material. Transmission electron microscopy employment confirmed these result.

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Peer-review under responsibility of the Scientific Committee of SAM–CONAMET 2014

Keywords:CdSe, Fourier Transform Infrared Spectroscopy, Chemical Etching, TEM.

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doi:10.1016/j.mspro.2015.05.015

1. Introduction

Cadmium Selenide is a II-VI semiconductor employed in the manufacture of nuclear radiation detectors. Since devices of this material operate at room temperature [Burger et al. (1982)] it becomes a semiconductor compound of great importance. Its wide band gap is 1.67 eV at 300 K. This material has hexagonal close packed structure (wurtzite type) (SG: P63mc (186), a = 4.299 Å, c = 7.01 Å). As CdSe does not polarize by a difference of potential, it is a possible alternative to CdTe or HgI_2 detectors [Roth and Burger (1988)]. On the other hand in the case of HgI_2 it must be mentioned that CdSe is much more thermally, mechanically and chemically stable [Zhu et al. (2000)].

In this paper, the crystalline quality of a CdSe single crystalline commercial wafer is studied. In order that in the future a comparison can be made with the material grown in our laboratory different techniques were employed for the characterization such as chemical etching, from which by calculation, using micrographs obtained by optical microscopy, is obtained the dislocation density [Hirth and Lothe (1968)] and misorientation between adjacent subgrains [Cottrell (1956)]. The structural order of the material is also studied by transmission electron microscopy (TEM) to determine the material defects presence at the micrometer scale or at nanoscale. The CdSe optical transmission spectrum was also obtained due to its importance as IR window.

2. Experimental Procedure / Methodology

CdSe wafer (Fig. 1a) is [0001] oriented, which was verified by X-ray diffraction, by means of Laue technique, employing a Phillips diffractometerPW3710. This single crystalline commercial material was grown by the high-pressure Bridgman (BPH) method using an inert gas as it is mentioned in its commercial report. The main advantage of this method is that the crystallization rate can be controlled. The wafer is bright gray at the light incidence (Fig. 1a). It is square of 1 cm side with cut corners, and mirror like as the lamp signs are shown by reflection on the wafer surface (Fig. 1b). The unfocused wafer thickness (1.5 mm) is also observed in Fig. 1b.

The optical transmission of the wafer, which was mechanical polishing acquired (Fig. 1c), was measured employing an equipment of Fourier transform infrared spectroscopy (Perkin-Elmer System 2000). This measurement was carried out in the range 1 μm ≤λ≤ 25 μm (Fig. 2 in red). This spectrum is comparable to those obtained in the same range of wavelengths using the same wafer polished at the lab with 1 micron free of agglomerates alpha alumina (LECO Corporation). It was also compared with the spectra reported by the commercial company for this material (Fig. 2 in black).

Chemical etching was performed on the surface of the wafer (Fig. 3a) to observe the distribution of etch pits by means of a metallographic microscope (Versamet Union 5279). The chemical etching solution (1) was prepared employing [Warekois et al. (1962)]:

$$30\ HNO_2 + 0.1\ HCl + 10\ HAc(glacial) + 20\ H_2SO_4\ (9M) \tag{1}$$

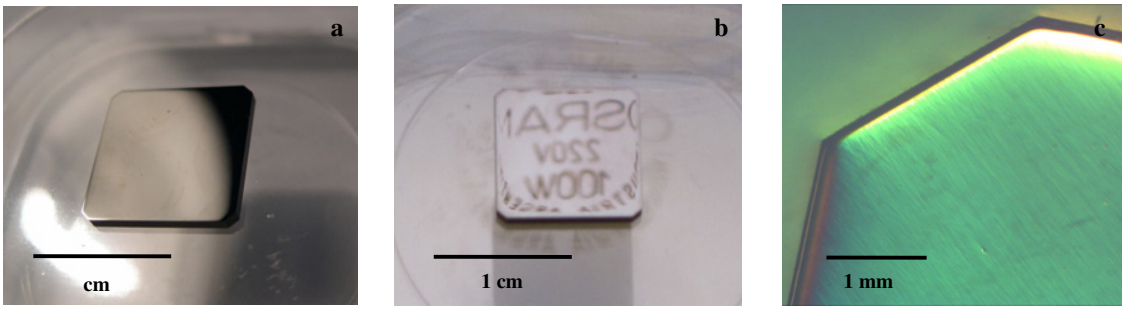

Fig. 1. (a) CdSe commercial wafer, (b) Lamp signs reflection on the surface of the CdSe wafer, (c) Cut corner in the wafer border where it can be observed the commercial mechanical polishing.

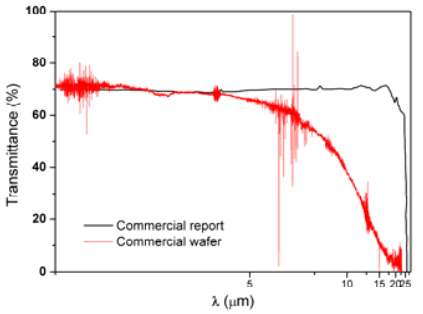

Fig. 2. Experimental values of the optical transmission of CdSe commercial wafer (in red) superposed to the graph commercially reported (in black).

This chemical solution was chosen among others, because present no over etching when the wafer immersion time is exceeded. Fig. 3b shows the over etched wafer surface produced by another chemical solution rejected due to this effect. The dislocation density values were determined by counting on micrographs of the etch pits distribution. Angular misorientation between the observed adjacent subgrains was calculated employing the Shockley-Read approximation (2):

$$\varphi \approx b/D \tag{2}$$

where b is the Burger vector module, which is approximately the CdSe lattice parameter value and D is the average distance between dislocations in the shared subgrain boundary.

The mean values of these magnitudes were obtained from micrographs that gave information of the etch pits distribution over the entire surface of the wafer.

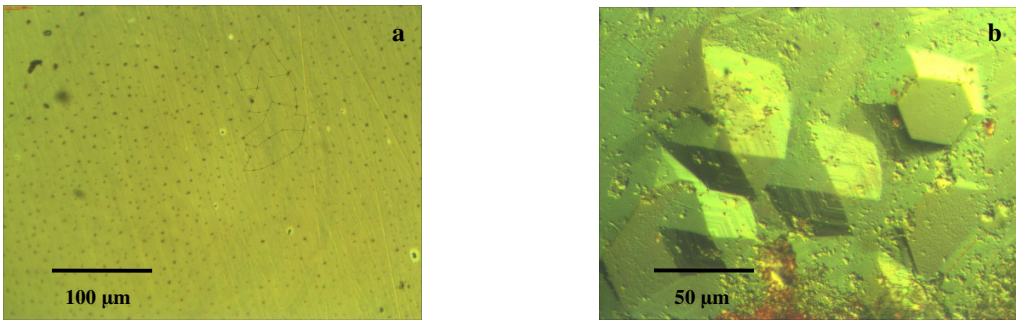

Fig. 3. (a) Chemical etching on the wafer surface. Some micrograph subgrains are delineated to favor observation, (b) Over etching of the CdSe commercial substrate.

Cadmiun Selenide thin films were obtained for subsequent TEM observation. These were obtained by combining techniques of mechanical grinding and ion thinning. This requires a SBT 590 tripod and a precision ionic polishing system (PIPS) model GATAN PIPS 691, operated with energy lower than 4 keV. Defects presence in CdSe was studied using a FEI Tecnai F20 microscope with field emission gun. The acceleration voltage was 200 kV and a camera GATAN 2k x 2k Ultrascan was used.

3. Results and discussion

According to the commercial report CdSe optical transmission is 70% (Fig. 2 in black). The commercially

acquired wafer measurements show values close to 70% up to a wavelength of 5 microns (Fig. 2 in red). The difference between the obtained values and those in the graphic shown in the report, corresponding to wavelengths greater than 5 microns, could be attributed to a higher density of crystal defects in the commercial wafer which usually occurs in its growth or to a higher impurities concentration in the material. The dislocation density of the commercial material is not listed in the report specifications of the acquired wafer, but the total impurities concentration is listed and at most is only 0.00111025 at. %. As it seems unreasonable that the material purity could have been altered by chance before growth, we attribute the difference in optical transmission at a higher concentration of crystal defects and not related to the purity with which the wafer was acquired. As shown in Fig. 2, the measured wafer spectrum decays asymptotically toward 0 from a wavelength of 5 to 22 microns. In our case the spectral curves show undesirable oscillations in the absorption wavelengths of H_2O and CO_2 due to the internal calculation program performing FTIR, since in these absorption bands the measurement error increases when signal values are divided by very small ones. In the case of the commercial report spectrum, there were no oscillations probably due that measurements were carried out under controlled atmosphere.

Chemical etching of the wafer surface allows to study the presence of crystalline defects (etch pits) by optical microscopy employing similar micrographs to Fig. 3a. The average value of the dislocation density performing counting on micrographs taken throughout the wafer surface is $\delta = 5.2 \times 10^5$ cm^{-2} and the average misorientation between adjacent subgrains is $\varphi = 9''$. It is notable the difficulty in observing the subgrain structure. Figure 3b shows the over etched wafer where the hexagonal symmetry in the basal orientation of semiconductor material can be observed.

Thin films have been employed to get high-resolution images (HRTEM) to determine the existence of dislocations at the local structural order. The electron diffraction pattern corresponding to the same region was obtained as well as it is shown in Fig. 4, along the zone axis $[1\bar{1}20]$. An excellent structural order could be observed with no dislocations presence at nanoscale.

TEM micrographs with lower magnifications were obtained as follows: Fig. 5b is the electron diffraction diagram of Fig. 5a, the zone axis is $[\bar{2}4\bar{2}3]$ (or $[021]$) and Fig. 6b is the electron diffraction pattern of Fig. 6a, the zone axis is $[2\bar{2}01]$ (or $[2\bar{2}1]$). Both Figs. 5a and 5b, such as 6a and 6b show the nonexistence of defects.

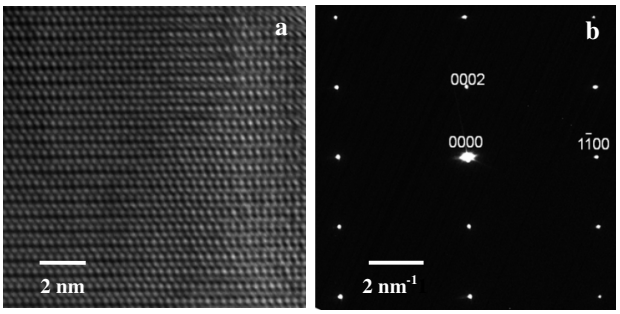

Fig. 4. (a) HRTEM micrograph of a CdSe thin foil, (b) Transmission electron diffraction diagram in the same region as before (Fig. 4 (a)) with zone axis $[1\bar{1}20]$.

Analysis results of the presence of dislocations, in low and mid resolution, might be different because in such cases the analyzed area is larger in many orders. No dislocations were detected in any sample of CdSe studied by TEM. The same result was observed in commercial ZnTe [Trigubó et al. (2010)] and commercial ZnSe, both are II-VI semiconductors grown by HPB [Núñez García et al. (2013)], although in the former were detected stacking faults and in the ZnSe case were observed twins.

Optical microscopy allowed observing a smooth surface without pores in both cases, CdSe and ZnSe [Núñez García et al. (2013)], meanwhile pores were frequently observed in ZnTe [Heredia et al. (2011)].

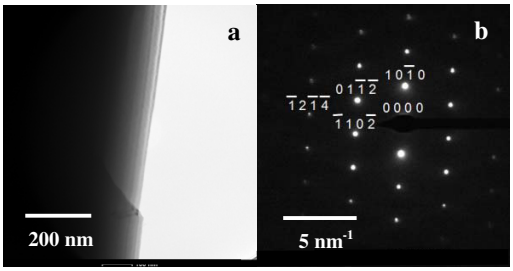

Fig. 5. (a) TEM micrograph of a CdSe thin film, (b) Transmission electron diffraction diagram in the same region as before (Fig. 5 (a)) with zone axis $[02\bar{1}1]$.

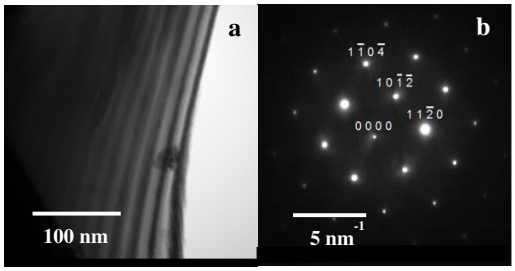

Fig. 6. (a) TEM micrograph of another region of the same sample of CdSe thin foil (Fig 5), (b) Transmission electron diffraction diagram in the same area as before (Fig. 6 (a)) with zone axis $[2\bar{2}1]$.

4. Conclusions

It was experimentally determined that the optical transmission of the material is not affected by the mechanical polishing previously done by the commercial company. Defects generated during CdSe ingot growth (HPB) in the region of the acquired wafer determined that the optical transmission spectrum of the commercial wafer does not match respect of which appears on the commercial report.

Chemical etching on the basal surface (0001), commercial wafer orientation, allowed its linear defects detection. The dislocation density is low and the angular misorientation between adjacent subgrains is negligible. Hexagonal symmetry present in the basal plane was determined by x-ray diffraction diagram (Laue technique), electron diffraction diagram and chemical etching.

Excellent structural order and absence of defects between dislocations was determined at nanoscale. Since the linear defects in the hexagonal crystal structure, most often occur in the basal plane (0001), in the future this orientation will be mainly studied [Aguirre et al. (2007)].

Acknowledgements

The authors thank CONICET and FRBA-UTN by the grants, respectively PIP 1122-00901-00355 and 25 / C116 which enabled this work. Also to Dr. J. Codnia of CEILAP-UNIDEF-CITEDEF for the Fourier transform infrared spectra.

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