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Structural characterization of doped GaSb single crystals by x-ray topography

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We characterized GaSb single crystals containing different dopants (Al, Cd and Te), grown by the Czochralski method, by x-ray topography and high angular resolution x-ray diffraction. Lang topography revealed dislocations parallel and perpendicular to the crystal's surface. Double-crystal GaSb 333 x-ray topography shows dislocations and vertical stripes than can be associated with circular growth bands. We compared our high-angular resolution x-ray diffraction measurements (rocking curves) with the findings predicted by the dynamical theory of x-ray diffraction. These measurements show that our GaSb single crystals have a relative variation in the lattice parameter ($\Delta d/d$) on the order of 10^{-5}. This means that they can be used as electronic devices (detectors, for example) and as x-ray monochromators.

Keywords: x-ray imaging; x-ray topography; Lang topography; double crystal topography

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1. Introduction

GaSb single crystals are group III-V semiconductors. They possess suitable properties for electronic devices (viz., transistors, detectors, infrared sources, and high-efficiency thermo-photovoltaic cells) especially due to their high electron-mobility and small band gap (~ 0.82 eV).[1-2] Further, the combination of band offsets and lattice matching with other semiconductor materials makes GaSb very valuable as a substrate for different electronic devices that are based on epitaxial thin-layer films. However, defects that can be present in its crystalline structure reduce electron mobility and can introduce stress/strain, and even defects, in the epitaxial film. The Czochralski technique, usually is employed to grow GaSb crystals.[1,3-7] Imperfections are expected (e.g., swirls, inclusions and dislocations) during growth that affect the crystal's structure and its electronic properties. Intrinsic GaSb single-crystals are always p-type. Dopants like Al and Cd retain its p-type conductivity, while Te at concentrations over 10^{17} atoms/cm^3 changes its conductivity to the n-type. The advantage of Al and Cd dopants is that they reduce anti-site defects.[8]

X-ray topography[9] is a technique well-suited to study structural defects in single crystals; it is sensitive to variations in the lattice parameter ($\Delta d/d$) because it is based on the x-ray diffraction imaging of a single crystal. Variant techniques are reported in the literature: Berg-Barrett, Lang, and double-crystal topography (or plane wave topography). More recently, synchrotron-based x-ray topography techniques (white beam topography and monochromatic beam topography) have been widely used.[10-14] The differences between these approaches are their sensitivity to $\Delta d/d$ and the type of defect to be detected.

High-angular resolution x-ray diffraction is a complementary measurement that can help to determine the crystal's quality. Such measurements are taken by the fine angular rotation of the crystal around the diffraction condition, the so-called rocking curve measurement. These assessments can be made using conventional x-ray sources or synchrotron sources. Different setups are employed for rocking curve measurements:[15] a) A dispersive setup using a 4-crystal

monochromator (conventional sources)[16] or a monochromatic beam of a synchrotron source; and, b) a highly sensitive non-dispersive setup based on high diffraction order.

In the present work, we used Lang topography, x-ray double-crystal topography, and rocking curve measurements to characterize GaSb single crystals with different dopants [Al (p-type), Cd and Te (n-type)], grown by liquid encapsulated Czochralski (LEC) in the [111] direction. We evaluated the quality of those crystals in relation to their practical application as electronic devices and x-ray monochromators, and discuss our findings here.

2. Experiment

Thin- (300 μm thick) and thick-crystals (2 mm thick) from GaSb ingots were oriented, cut, polished, and etched for analysis by Lang topography, double-crystal topography, and rocking curve measurements. Four samples were used: a) Two (samples 1 and 2) oriented and cut in the [111] direction [300 μm thick, both Al doped (10^{17} atoms/cm^3)]; and, b) two (samples 3 and 4) oriented and cut in the [110] direction [2 mm thick, one Cd doped (10^{17} atoms/cm^3) and the other Te doped (10^{18} atoms/cm^3)]. All were etched (HF : HNO_3 : CH_3COOH, 1:20:1) for 1 minute three times. We establish this procedure to remove the damaged layer due to cutting and polishing.

Lang topography, in the horizontal scattering plane, was carried out using a conventional x-ray source (Long Fine Focus Mo target) (Fig. 1a). The x-ray tube was set in the line focus geometry, so that the source's horizontal width was 40 μm (for a takeoff angle of 6º) and vertically it was 12 mm long. A 1.1 m long collimator with a slit of 150 μm allowed us to select, by the crystal diffraction, the energy of MoKα_1 (17.48 keV). The crystal was mounted on a Lang camera based on elastic translation.[17-18] The images were acquired with high-spatial-resolution Kodak Industrex M5 films.

We also carried out high-resolution double crystal x-ray topography (Fig. 1b) to better characterize these crystals. The x-ray tube (long fine focus) also was set in the line focus geometry.

We employed the same 1.1 m long collimator, but with a slit of 0.5 mm. As the first crystal, we employed an asymmetrically cut monochromator Si 333 (floating zone, b = - 0.04, magnification m = 25) at 8.05 keV (CuKα_1). The second crystal was the GaSb single crystal in different orientations [111] and [110]. The images again were acquired with high-spatial-resolution Kodak Industrex M5 films.

The rocking curve measurements were taken with the two different setups. For low-order reflections (111 and 220), a Ge 220 4-crystal monochromator was employed (Fig. 1c) at 8.05 keV. For high-order reflections (333 and 440) we chose an ultra-high resolution non-dispersive setup more sensitive to $\Delta d/d$ (Fig. 1d), also at 8.05 keV.

3. X-ray topography and rocking curve measurements

The Lang topography (Fig. 2a) was obtained from the thin GaSb 111 single crystals (samples 1 and 2, initially a single piece); however, for the 220 diffraction on transmission geometry (Laue case, Fig. 1a) at 17.48 keV. The resulting image shows several lines and small spots that, respectively, could reflect dislocations parallel or almost parallel to the surface, and normal or almost normal to the surface. The features resembling "holes" in the image might be dislocations or even other defects, such as precipitates. However, most of the spots and stripes are diffuse, an appearance that could be caused by insufficient etching during removal of the disturbed layer, or even the vertical divergence of the current setup that might blur the image. More comprehensive studies are needed to clarify the origins of this effect.

To better characterize the sample, we undertook double crystal x-ray topography (Fig. 1b) on the selected dashed area of the Fig. 2a, at 8.05 keV for the GaSb 333 diffraction in reflection geometry (Bragg case). Such topography (Fig. 2b) does not show images of dislocations or any other defects in the crystal's bulk. However, it is strongly sensitive to weak deformations near the crystal's surface. Dislocations, precipitates, or even structures caused by insufficiently etching when removing the disturbed layer are apparent in the image as big dark areas. Also, the image displays

narrow vertical stripes that can be associated with circular growth bands. Double-crystal topography of samples 3 and 4 (Cd doped and Te doped, respectively) taken with the 440 diffraction, not shown here, did not show such striations. Their absence might be due to the different orientation of the crystal, since all were grown under the same conditions (pulling velocity of 5.2 mm/h and with a seed rotating at 5 rpm). The striations almost always appear in GaSb crystals grown in the [111] direction via the Czochralski technique. This occurs because the method encompasses a substantial non-stationary growth process due to intense convective flows, misalignment of the axis of the crystal's rotation respect to the axis of the thermal symmetry, concentration overcooling, and other issues.[7] Together, these factors cause fluctuations in growth rate that are responsible for variations in the crystal's composition, entailing the formation of growth striations.[7] A solution for that is try to re-grow the crystal by the vertical Bridgman method.[7]

We can consider the topography shown in Fig. 2b as plane wave x-ray topography due to the experimental setup we described in the section 2. Accordingly, we can extract a $\Delta d/d$ map from the image. To obtain this map, we acquired the topography on the maximum slope at the high-angle side of the rocking curve. By considering the rocking curve of the GaSb 333 single crystal as a Gaussian profile with the same full width of half maximum (FWHM) of the diffraction curve predicted by the dynamical theory of x-ray diffraction (FWHM = 19.7 μrad), we can employ the following expression to determine the angular deviation ($\Delta\theta$) of the different points (a pixel-by-pixel approach) on the image:

$$\Delta\theta = \sigma\sqrt{\ln(I) + \ln(I_{\max})} + \omega \qquad (1)$$

where σ is the width of the Gaussian profile, I is the intensity on the different points on the image (pixels), I_{max} is the maximum intensity of the image, and ω is the angular position on the rocking curve where the image was acquired. With the different values for ($\Delta\theta$) we can determine the relative variations in the lattice parameter ($\Delta d/d$):

$$\frac{\Delta d}{d} = -\cot(\theta)\Delta\theta \qquad (2)$$

where θ is the diffraction angle.

The two dimensional (2D) and a tri-dimensional (3D) map of *Δd/d* is shown in Figs. 3a and 3b. Variations within $\Delta d/d \sim 10^{-5}$ are very apparent. The extinction depth (that is the depth to which x-rays penetrate during diffraction)[19-21] has values varying from 1 μm to 50 μm. So, the detected *Δd/d*, caused by dislocations, precipitates or even structures due to the insufficient etching, lies very close to the surface. Such variations were not detected by rocking curve measurements; we did not identify any differences in comparing the experimental- and the theoretical rocking curves [predicted by the dynamical theory of x-ray diffraction (Fig. 4)]. Also, high-order diffraction rocking curve measurements (based on the non-dispersive setup, more sensitive to *Δd/d*) showed no significant differences (Table I) for the FWHMs of the measured and theoretically predicted rocking curves. We anticipated both results. For the diffraction planes and the x-ray energy employed, the rocking curve measurements are not sensitive to *Δd/d* smaller than 10^{-5}, while topography is sensitive. This difference already was proven by several authors by strain mapping and *Δd/d* mapping acquired with a rocking curve imaging technique.[13-14]

4. Conclusions

We characterized GaSb single crystals with different dopants grown by the liquid encapsulated Czochralski technique via x-ray topography and high-resolution rocking curves.

Dislocations, precipitates, and growth bands were observed on different topographies. However, relative variations in the lattice parameter of about $\Delta d/d \sim 10^{-5}$ and the measured rocking curves matched with the theoretical predicted ones, give good reason to try to use those crystals for electronic devices (detectors, for example, Te-doped), and for x-ray monochromators (Al- and Cd-doped) in experiments that do not require high-energy resolution. The crystal quality was found to be compatible with other GaSb single crystals reported in the literature. However, we were not able

to detect that different dopants could help improve the crystal quality, as already described in the literature.[1] The detected growth striations can affect the electronic properties because, in these cases, the dislocation density can reach values of $10^2/cm^2$. For non-high energy resolution monochromator applications this is not a serious problem. Finally, there are no significant variations between the measured and theoretical predicted rocking curves.

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Table I. Full width at half maximum (FWHM) of the rocking curves measured with the non-dispersive setup (Fig. 1d).

Sample	Diffraction plane	Experimental vs. theoretical FWHM (μrad)
1 x 2 (GaSb 111)	333	34 vs. 30
3 x 4 (GaSb 110)	440	37 vs. 37

Figure captions

Figure 1. Experimental setups for structurally characterizing GaSb single crystals. a) Lang topography (transmission geometry - Laue case); b) Double-crystal topography; c) High-resolution x-ray diffraction based on 4-crystal Ge 220 monochromator; d) Ultra-high resolution x-ray diffraction for high-order reflections.

Figure 2. a) Lang topography (transmission geometry) of a 300 μm thick GaSb 2-20 single crystal (Al doped). Long fine focus MoKα_1 (40 kV x 20 mA). Exposure time 30h. b) Double-crystal topography of the dashed area of the GaSb -3-3-3 single crystal shown in fig. 2a. Long fine focus, CuKα_1 (40kV x 20mA). Exposure time 6h.

Figure 3. a) 2D map of the relative variations in the lattice parameter ($\Delta d/d$) based on the topography shown in Fig. 2b. b) 3D map of the relative variations in the lattice parameter ($\Delta d/d$) also from the topography in Fig. 2b.

Figure 4. a) High-resolution x-ray diffraction measurement (rocking curve) on the GaSb 111 single crystal using the 4-crystal Ge 220 monochromator (fig. 1c). Solid line: Theoretical rocking curve based on the dynamical theory of x-ray diffraction; open circles represent the experimental data. b) Rocking curve measurement on the GaSb 220 single crystal using the 4-crystal Ge 220 monochromator (fig. 1c). Solid line: Theoretical rocking curve based on the dynamical theory of x-ray diffraction; open circles represent the experimental data.