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On the structured imperfections of bulk GaSb using high resolution transmission electron microscopy

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Abstract

GaSb is a promising III–V direct band gap semiconductor with sphalerite type FCC structure. Its band gap value has made it an excellent candidate for the conversion of infrared radiation to electricity. The wafers of GaSb, that were studied, originated from ingots grown with the Liquid Encapsulated Chochralski method. In all cases, Energy Dispersive X-ray Spectroscopy and Particle Induced X-ray Emission measurements demonstrated an excess of Sb. In the present work conventional transmission electron microscopy (CTEM) and high resolution electron microscopy (HRTEM) were used in order to determine the effect of the Sb excess in the structural characteristics of the material, mainly after thermal treatment. A structure model based on the ordering of the Sb antisites (Sb_{Ga}) rather than the Ga vacancies (V_{Ga}) is proposed for the observed modulation in small areas of the material.

Keywords: GaSb; Modulated structure; High resolution electron microscopy; Deviation of stoichiometry

1. Introduction

The III–V family of semiconductors has produced materials over the years that have aided the advancement of science and technology. One of these materials is GaSb and the based ternary and quartenary compound giving the possibility for band gap engineering and thus offering a variety of uses. From the device point of view, GaSb's based structures have shown among others potentiality for applications in high efficiency thermophotovoltaic (TPV) cells. GaSb itself was proposed as a candidate for the conversion of infrared radiation to electricity and it was studied as a thermophotovoltaic material (Bet and Sulima, 2003). Nowadays many scientific groups have proposed it mainly as the best substrate, due to its good lattice matching with all the above mentioned ternary (with the addition of In) and quaternary (with the addition of In and As) compounds (Udayashankar and Bhat, 2001).

Also concerning its use as an electronic material, undoped GaSb is always found to be p-type with a hole concentration of the order of 10^{17} cm^{-3}. This type of conductivity is explained by the existence of doubly ionisable native defects, having the structure $V_{Ga}Ga_{Sb}$ (Dutta et al., 1996).

In a previous study (Zoulis et al., 2006) the material under investigation was found to have a slight deviation from its nominal stoichiometry presenting an excess of antimony in its concentration. Simultaneously all the samples prepared for TEM by ion milling show a well defined clustering in all their images.

The referred microstructural defects combined with the strong influence of any imperfection on the electrical properties of the material, were the driving force of this detailed study, focusing on the analysis of the high resolution TEM images.

2. Experimental

The studied GaSb wafers originated from ingots grown with the Liquid Encapsulated Chochralski method. The melt is stochiometric, with atomic weight percentages 50% Ga and 50% Sb. A seed is dipped into the melt of the stoichiometric alloy, close to its freezing point, and slowly pulled out, allowing a boule to grow at the end. The melt is encapsulated in a suitable liquid to protect it from oxidation during the process.

Samples for transmission electron microscopy (TEM) were prepared from different ingots. After their initial mechanical

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thinning, either ion milling or electrochemical polishing was used as a final stage. The TEM observations were performed on a JEOL 100CX conventional TEM having 100 kV operating voltage and a JEOL 2010 high resolution microscope working at 200 kV.

3. Conventional electron microscopy characterization

The aim of the present work is the study of the micro structural imperfections through the use of high resolution electron microscopy (HRTEM) for the determination of the specific point defects which lead to the detected Sb excess. In all cases, EDS and PIXE measurements demonstrated an excess of Sb, suggesting the presence of Ga vacancy (V_{Ga}) and/or Sb antisite defects (Sb_{Ga}).

The ion thinned samples that were studied with conventional transmission electron microscopy (CTEM) exhibited clusters while the samples that were prepared with electrochemical etching showed no clustering. Electron diffraction of the GaSb samples, which were studied with CTEM, portrayed very good crystal quality. Only in some cases extra spots occurred that were hardly visible. With greater time exposure the extra spots appeared in almost all the samples. The clusters in the ion thinned samples in several cases displayed Moiré patterns, suggesting that the crystal structure of the clusters is the same with the crystal structure of the matrix material with a small difference in the lattice constants. Also in the majority of the clusters a small rotation between the lattices was observed. Image in Fig. 1 shows one such cluster with Moiré fringes along the diffraction pattern of the same sample. The Moiré lines are perpendicular to the [0 2 2] crystallographic direction of the matrix material while in the same direction an extra spot appears in the diffraction pattern. The lattice constant of the crystal structure of the clusters can be calculated using the well known equation for the Moiré fringes distance (Hirsch et al., 1971).

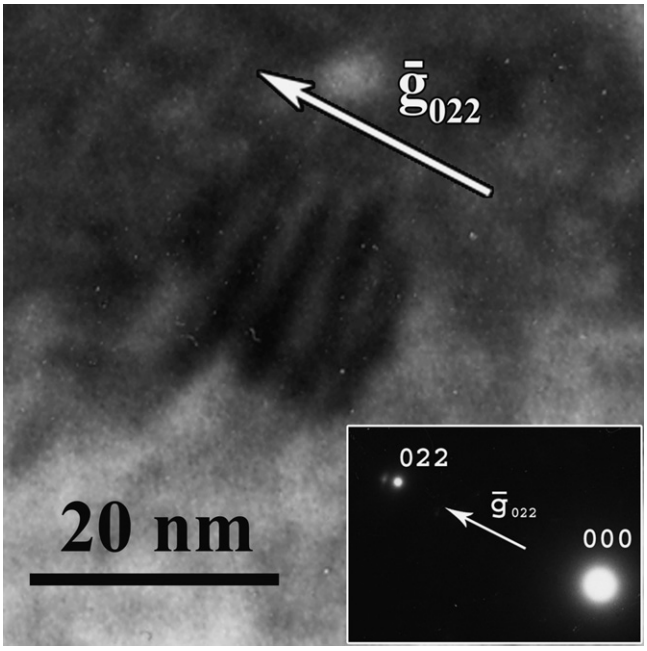

Fig. 1. An CTEM image of GaSb cluster with the electron beam along the $[1\,0\,0]_c$ crystallographic direction. Moiré fringes appeared in the cluster are perpendicular to the $[0\,2\,2]_c$ direction. The corresponding diffraction pattern with the extra spot of the Moiré fringes is depicted as inset.

For this particular case the calculated lattice constant of the clusters is approximately 0.576 nm, which is equal to a lattice difference of ~5.5% between the cluster and the matrix material, taking into account that the matrix material is pure GaSb having a sphalerite type FCC structure with lattice parameter $a_c = 0.61$ nm.

Measurements from various clusters of the material can be seen in Table 1. The results indicate that all the clusters are not the same. Small differences were observed in the cluster's lattice constant and angle with the matrix. Since these clusters do not appear in samples prepared with electrochemical etching it is evident that the clusters are induced from the ion thinning process. The Ga vacancies and Sb antisite defects produce the clustering with the help of ion thinning. This being a thermodynamic process, the clusters are not uniform and differences occur. For a better understanding of the clustering mechanisms the samples were annealed and studied in the electron microscope with CTEM and HRTEM.

4. High resolution electron microscopy study

A different case is observed in the case of in situ thermally treated samples prepared by electrochemical polishing in order to avoid the clustering introduced by the ion milling procedure. A typical electron diffraction pattern with the electron beam along the $[0\,0\,1]_c$ cubic direction of is shown in Fig. 2. More or less intense extra spots appeared along the {2 2 0} directions revealing an ordering of the material. Furthermore, tilting experiments suggest that the ordering is restricted in one of the {2 2 0} directions.

Fig. 3 shows an HRTEM image with the electron beam along the $[0\,0\,1]_c$ axis. It is clear that the material is ordered in small areas with a mean size of 20 nm. Insets (a) and (b) in Fig. 3 represent the Fourier Transform of the corresponding areas. The small arrows indicate the extra spots excited from the ordering of the material confirming that the observed ED patterns are the result of the overlapping of the diffraction from several discrete areas. Consequently the modulated structure can be described on the basis of an orthorhombic one with lattice parameters $a_o = n\sqrt{2}/2a_c, b_o = \sqrt{2}/2a_c$ and $c_o = a_c$, where a_c is the lattice parameter of the FCC GaSb.

The reconstruction of digitized HRTEM micrographs, via inverse FFT, using only the extra spots, reveals the arrangement of the positions that are responsible for the ordering. A typical example is illustrated in Fig. 4. The inset (a) shows the computer calculated Fourier Transform from the original image where the open black circles indicate the filtered spots used for the IFFT. The imaging code obviously represented in the filtered image, consists of characteristic rhomboid configuration of intense white dots displaced over the $[0\,1\,0]_o$ direction. The unit cell parameters deduced from this arrangement are $a_o = 13\sqrt{2}/2a_c, b_o = \sqrt{2}/2a_c$ and $c_o = a_c$.