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2002 J. Phys.: Condens. Matter 14 12755

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J. Phys.: Condens. Matter **14** (2002) 12755–12759 PII: S0953-8984(02)54085-6

Study of induced structural defects on GaSb films grown on different substrates by the liquid phase epitaxy technique

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Received 27 September 2002
Published 22 November 2002
Online at stacks.iop.org/JPhysCM/14/12755

Abstract

Gallium antimonide is a promising material for semiconductor technology application. Its structural and electronic properties are very important in the fabrication of semiconductor-based devices working in the energy gap of 0.3–2.4 eV. One of the main advantages of gallium antimonide is that it can be grown as thin film which allows its use in integrated devices. Currently, the large number of studies of the material and developments in obtaining useful instruments are opening up interesting device possibilities—such as laser diodes, photodetectors and thermophotovoltaic cells. But the main factor as regards making useful devices compatible with actual technology is the requirement that these devices must have thicknesses in the region of 10 μm, which means that it is necessary to improve the thin-film fabrications processes.

In this work we study the formation of GaSb films over Si{1, 1, 1}, silica, sapphire and CdTe polycrystalline substrates using the liquid phase epitaxy technique. The substrates will induce dislocations, and the generation of polycrystalline and randomly oriented films strongly depends on the type and quality of the substrates used.

1. Introduction

Gallium antimonide (GaSb) is an interesting material due to its unusual characteristics [1] which may facilitate its use in semiconductor-based devices. First of all, is an interesting material to use in designing photonic devices such as laser diodes and photodetectors, due to its direct band gap at 0.7 eV matching with the 1.55 μm window in the silica fibres used in optical communications [2]. Moreover, it is also a very good substrate for semiconductor integrated devices, because of its lattice parameter (6.09 Å) being very near to the lattice parameter of other semiconductors such as InAs, GaAlAs and CdTe [3]. Finally, one of the

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most promising applications of GaSb is in the development of thermophotovoltaic cells based on GaSb materials, either in bulk or in thin-film configurations [4].

Liquid phase epitaxy (LPE) growth is a technique for growing thin films which uses a solution of the desired material. One of the semiconductor compounds acts as the solvent and the other as the solute. The solution is saturated and then heated to above the precipitation temperature of the compound; it is then gradually cooled using a step cooling or a supercooling procedure. When the solution reaches the precipitation temperature, the compound is formed and deposited over the substrate. With this technique, thin films of very good quality can be obtained with about 1 μm thickness [5, 6].

In this work, morphological defects on GaSb thin films grown over different substrates by the LPE technique are studied. Scanning electron and atomic force microscopies are used for topological characterization. The chemical analysis of the thin film obtained is performed with the energy-dispersive analysis of x-rays (EDAX) technique.

2. Experimental details

GaSb films have been grown using LPE growth equipment made in our laboratory. The growth is carried out inside a quartz tube, with a controlled Ar atmosphere. The source material is contained in a mobile graphite boat, which is displaced over several substrates. The system of thermocouples in the LPE equipment allows control of the temperature better than 0.5 °C.

Four different substrates were used: Si {1, 1, 1} (section 3.1), silica (section 3.2), sapphire (section 3.3) and polycrystalline CdTe (section 3.4). As the source material we used a Ga solution which was saturated with GaSb synthesized previously. For the thin-film growth we used a step cooling method. The III:V mass ratio was 3.5. On each run, the solution was heated up to 600 °C at a rate of 250 °C h^{-1} and maintained at this temperature for 2 h to homogenize the solution. Then we reduced the growth temperature to 570 °C at 50 °C h^{-1} and let the film grow for 18 min. After the thin-film growth the system was cooled at 150 °C h^{-1} to room temperature. All the growth processes were carried out under an Ar atmosphere with an initial pressure of 450 Torr [6].

3. Results

3.1. Si substrates

For the GaSb thin-film growth over Si, a commercial silicon substrate, {1, 1, 1} oriented, with a lattice parameter of 5.43 Å, was used. The dimensions of the substrate were 9 mm × 10 mm. Figure 1 shows the thin film obtained as observed with the SEM and AFM techniques. It is worth noting that a quite homogeneous film covering the substrate was obtained as observed in figure 1(a). Although the film is spread widely over the whole surface of the substrate, it was not fully crystalline and hexagonal microcrystals can be found with a metallic substance over the substrate. Figure 1(b) shows the typical hexagonal microcrystals grown. EDAX measurements have confirmed that the microcrystals are of crystalline GaSb, but that the rest of the material covering the substrate is an excess of Ga; this can be explained as due to the fact that the film was grown from a Ga solution. The GaSb hexagonal microcrystals have a preferential orientation parallel to the substrate, although they can also be observed in different orientations; this may be due to the growth over the Ga excess deposit, because when Ga is removed with hot water, these crystals disappear. The size of these crystals is homogeneous, about 5 μm, as shown in figure 1(b). The shape of the microcrystals corresponds to one of the possible forms that presents the {1, 1, 1} direction of the GaSb. We can also see that microcrystals grow independently of one another, so we can assume an island growth mechanism for the GaSb over a Si substrate.

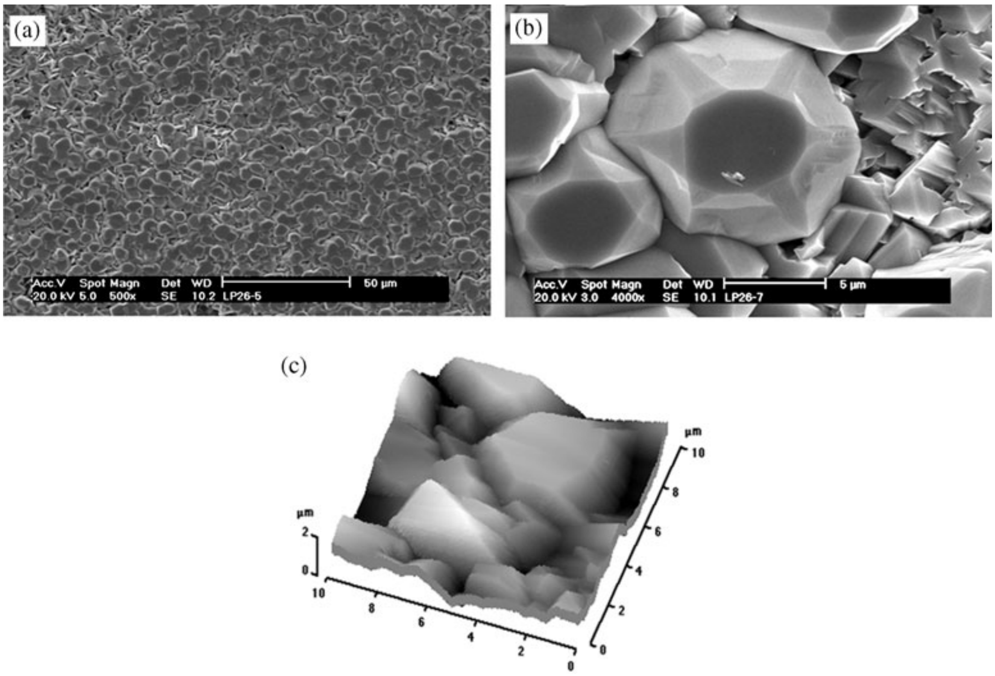

Figure 1. (a) A SEM image of a GaSb film grown over Si; (b) a SEM image of microcrystal over a Si substrate; (c) an AFM 3D mapping of film grown over a Si substrate.

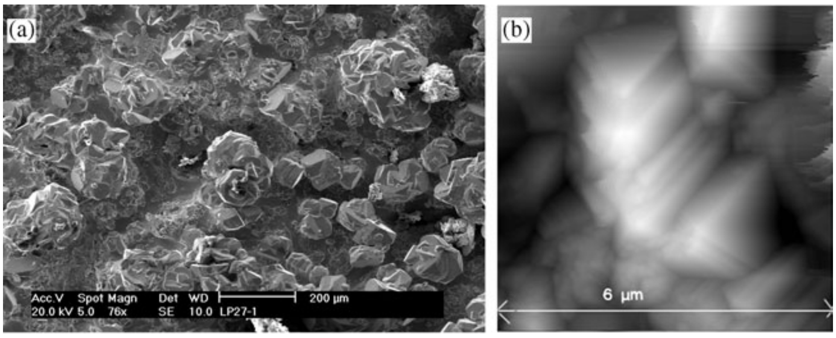

Figure 2. (a) A SEM image of a group of crystals over silica; (b) an AFM image of triangular microcrystals.

Figure 1(c) shows the microcrystals as observed with the AFM technique, which confirms that the crystal structure is hexagonal with an average size of 3–5 μm. In a three-dimensional map we can see irregularities of about 2 μm on the surface. These irregularities constitute a probe of the independent growth of the crystals.

3.2. Silica substrates

For the growth over silica substrates a commercial amorphous silica substrate was used. In figure 2 we can see that the crystals forming GaSb thin films over silica have grown forming different groups, while many parts of the substrate remain clean. EDAX measurements show that observed crystals are of GaSb. Crystal groups do not show a regular shape and they do not have

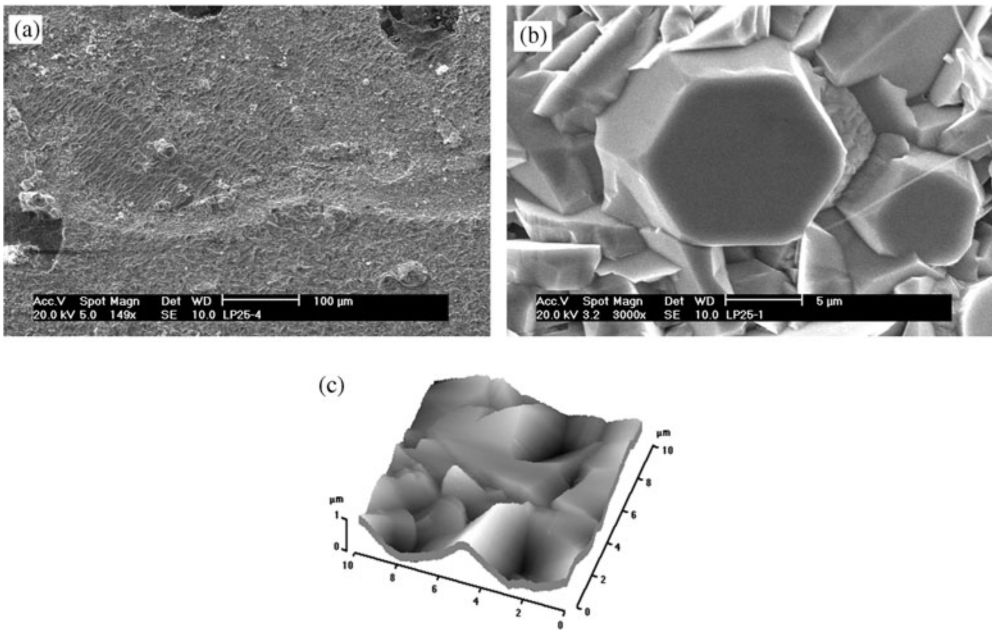

Figure 3. (a) A SEM image of GaSb film over sapphire; (b) SEM detail of a hexagonal microcrystal over sapphire; (c) an AFM 3D mapping of GaSb film grown over sapphire.

a preferential orientation. The sizes of these groups vary from 10 to 30 μm. In this way GaSb has grown around nucleation centres that have reproduced the groups that are present on the silica surface. We can see that an amorphous substrate has little influence on the GaSb growth.

Figure 2(b) shows the AFM details of the crystal groups, indicating that these groups are formed by microcrystals. These microcrystals present a preferential shape of crystallization, as has been observed: triangular crystals about 2 μm in size. This shape is consistent with the most common crystallization along the preferential plane of growth in GaSb, the $\{1, 1, 1\}$ plane.

3.3. Sapphire substrates

In this case a commercial monocrystalline sapphire $\{1, 0, 0, 0\}$-oriented substrate was used. In figure 3(a) it can be observed that the surface of the substrate is completely covered by microcrystals. We confirmed by means of EDAX that the crystals are of GaSb. These microcrystals have preferentially a hexagonal shape, as observed in figure 3(b), like that previously shown over the silicon surface. The sizes of these hexagons are between 5 and 10 μm, but the orientation is less uniform than that observed for the microcrystals grown over silicon. We can see in figure 3(a) that the film forms terraces over the substrate. These terraces are formed by the growth of hexagonal microcrystal layers with a slight misorientation with respect to the substrate. The hexagonal shape that seems to be preferred in the SEM pictures is not so clear in AFM images (shown in figure 3(c)) because of the misorientation of the crystals. But the three-dimensional mapping of the surface indicates that the size and the proximity of microcrystals make this film the smoothest one among all those considered in this work.

3.4. CdTe substrates

In this case a polycrystalline CdTe substrate synthesized in our laboratory with dimensions 8 mm $\times$ 9 mm was used.

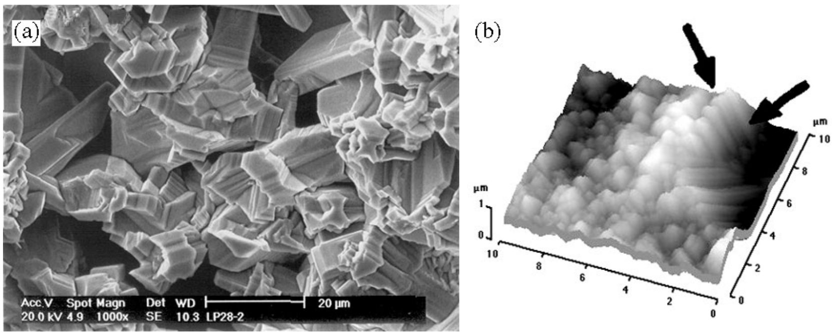

Figure 4. (a) A SEM image of a group of GaSb crystals over a CdTe substrate; (b) AFM detail of GaSb microcrystals.

A SEM image of thin films grown over CdTe substrates is shown in figure 4(a); it indicates that polycrystals have grown forming groups around a nucleation centre, while other zones of the substrate are clean, without films. The sizes of these groups vary from 5 μm in the less dense zone to about 20 μm in the most populated one. Also we can see that these groups do not present a preferential plane of crystallization. Like in the case of the silica substrate, the influence on the growth direction of the CdTe substrate is very slight. As regards the AFM measurements shown in figure 4(b), small microcrystals, about 0.5 μm, are present on the surface of the thin film. These microcrystals, as for the silica substrate, have a triangular shape that corresponds with the $\{1, 1, 1\}$ GaSb plane, but they do not have a preferential orientation; this might have been desirable if the substrate had any influence on the GaSb growth.

4. Conclusions

GaSb thin films have been grown over four different substrates by the LPE technique. Films grown over Si and sapphire monocrystalline substrates have proved to be the most homogeneous and smooth ones. Hexagonal microcrystals of 4–5 μm have grown covering almost all of the substrate in both cases. This hexagonal shape can be identified as the $\{1, 1, 1\}$ plane of GaSb. The influence of the substrate forces of the GaSb $\{1, 1, 1\}$ plane as regards growth in the hexagonal form instead of the triangular preferential shape has been demonstrated. Films grown over silica and polycrystalline CdTe show nucleation groups, while zones of the substrate remain free of GaSb. Microcrystals present a triangular shape and are randomly oriented. That shows us that GaSb has grown without any influence from the substrate as regards shape and as regards orientation of the growth. The crystal size is smaller than in films grown over monocrystalline substrates.

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