Oriented crystallization of GaSb on a patterned, amorphous Si substrate

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(Received 4 January 2000; accepted for publication 3 January 2001)

Oriented crystallization of GaSb on patterned, oxidized Si substrates was achieved by metalorganic chemical vapor deposition. The Si substrate was formed by patterning an array of inverted square pyramids having {111} sidewall facets, using lithography and anisotropic etching in KOH. The orientation and structure of GaSb crystals, at various stages of the growth, were examined by scanning electron microscopy and x-ray diffraction. X-ray diffraction pole figure analysis shows that {111} planes of GaSb are predominantly parallel to the {111} planes of the inverted pyramids. Extra (111) spots observed in the x-ray diffraction pole figure are interpreted in terms of multiple twinning of GaSb. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1352657]

Graphoepitaxy refers to the use of surface patterning to achieve orientation in overlayer films.[1] Several mechanisms of producing orientation via patterning have been described, ranging from induced nucleation, attachment of mobile crystallites,[2] and guided recrystallization.[3] Graphoepitaxy may have important application in the preparation of multilayer microstructures where single crystalline films of active materials with different properties are separated by amorphous, passive intermediate layers. The major problem in graphoepitaxy is the achievement of crystallographic perfection comparable to that achieved by conventional epitaxial methods.

GaSb-based compound semiconductors are of great interest for infrared optoelectronic devices over the spectral range from 1.24 μm for AlGaAsSb to 4.4 μm for GaInAsSb, as well as for high-speed electronic devices.[4] Since a semi-insulating substrate is not available in GaSb, semi-insulating GaAs is normally used for electronic applications. A principal concern in the growth of GaSb on GaAs substrates is the large, 8% lattice mismatch, which leads to a high density of threading dislocations. The dislocation density can be reduced by growing an appropriate thin, low temperature GaSb buffer layer.[5,6] However, the optimal growth condition for such an initial buffer layer has not yet been well established. Graphoepitaxy of GaSb may provide an alternative way of growing GaSb films on insulating materials such as SiO_2. In this letter, we present an investigation of graphoepitaxy of GaSb on a patterned, amorphous substrate by metalorganic chemical vapor deposition.

GaSb films were grown in a vertical quartz reactor operated at 76 Torr. A graphite susceptor was heated by a rf coil, to a growth temperature of 550–650 °C. Trimethylgallium (TMGa) and trimethylantimony (TMSb) in a Pd-diffused H_2 carrier gas were used as Ga and Sb precursors, respectively. TMGa and TMSb mole fractions within the reactor were 3×10^{-4} and 4×10^{-4}, respectively.

Silicon (100) substrates were patterned using electron beam lithography and anisotropic etching in KOH to form a hexagonal-close-packed array of inverted square pyramids, measuring 10×10 μm at the base, on 16 μm centers. The {111} facets of the inverted pyramids are close to atomically smooth. After patterning, the Si substrates were degreased in trichloroethylene, acetone, and isopropanol, and rinsed in deionized (DI) water. To eliminate carbon contaminants on the surface, the substrates were boiled in HNO_3 for 10 min, followed by a dip in HF for 15 s, and a rinse in DI water. The substrates were then oxidized in a boiling solution of $HCl:H_2O_2:H_2O$ (3:1:1) for 10 min to form a thin amorphous SiO_2 film (~5–8 Å) on the surface.[7] Since the SiO_2 layer is completely amorphous, the crystal structure of underlying Si is not seen by the growing GaSb layer. After rinsing in DI water, the substrates were blown dry with N_2. The grown layers were characterized by Nomarski differential interference contrast microscopy, scanning electron microscopy (SEM), and x-ray diffraction (XRD).

Figure 1 is a SEM micrograph of GaSb grown at 600 °C on a patterned Si substrate for 15 min. In the early stage of growth, the film consists of discrete crystals. Preferential nucleation of GaSb crystallites at the apexes and the corners of inverted square pyramids is evident. However, there is also some nucleation on plateaus and facets. Decreasing the gas-phase supersaturation by lowering the growth temperature to 550 °C did not greatly reduce nucleation on plateaus. Growth at 650 °C resulted in many of the inverted square pyramids remaining empty. The growth temperature is close to the melting point of GaSb (712 °C) and rapid surface dif-

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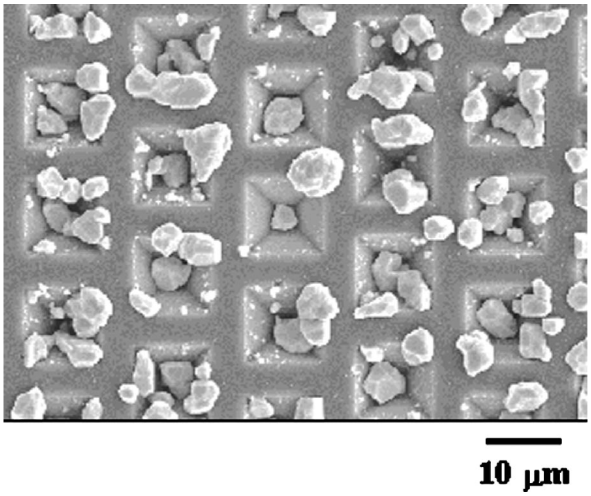

FIG. 1. SEM micrograph of GaSb grown at 600 °C for 15 min on a patterned, oxidized Si substrate. Preferential nucleation of GaSb crystallites at the apexes and the corners of inverted square pyramids is evident.

fusion could lead to the formation of a few crystallites being fed by a large surface region.

As the growth proceeds, large-grained GaSb crystals grow out of inverted square pyramids. Figure 2 is a SEM micrograph of the sample grown at 600 °C for 60 min. Electron probe x-ray microanalysis indicates that these large-grained crystals are composed of 50% Ga and 50% Sb. Double-crystal (004) XRD exhibits a strong diffraction peak with full width half maximum (FWHM) of ~1400 arc sec, indicating that a (100) plane of GaSb is parallel to the Si (100) substrate. This FWHM is comparable to that from GaSb grown on a GaAs substrate without an initial buffer layer.[8]

Figure 3 is an XRD pole figure using the (111) diffraction. There are eight high intensity, evenly spaced spots: four spots at ~55° and four spots at ~16° from the surface normal. Since the angle between the {100} and {111} crystallographic planes is 54.7° in cubic crystals such as Si and GaSb, this result indicates that GaSb crystals grown on the patterned Si substrate have GaSb {100} planes parallel to the Si {100} planes and GaSb {111} planes parallel to Si {111} planes, i.e., epitaxy. In addition, there are four pairs of spots at ~34°, and four pairs of spots at ~45°. The diffraction intensity of these spots are ~4 times weaker that that of the eight spots. The XRD pole figure measured from the film grown at 550 °C was found to be identical to that from the film grown at 600 °C.

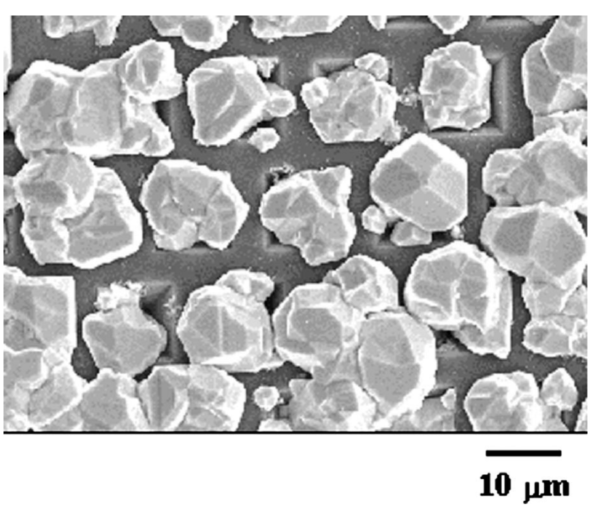

FIG. 2. SEM micrograph of a GaSb film grown at 600 °C for 60 min on a patterned, oxidized Si substrate.

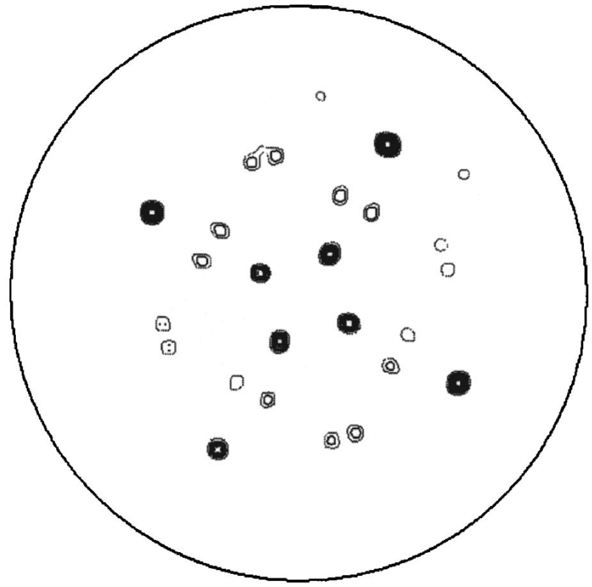

FIG. 3. (111) XRD pole figure of a GaSb film grown at 600 °C for 60 min.

Multiple twinning of GaSb is most likely responsible for the extra spots in the pole figure. Ino[9] used a multiply twinned particle model to explain 24 abnormal (111) spots observed in electron diffraction patterns in the gold films evaporated onto cleaved halide substrates. Twinning in GaSb crystals is commonly reported in liquid encapsulated Czochraski growth and is sensitive to the direction of growth and the melt composition.[10–12] Figure 4 is a schematic of multiply twinned GaSb particles, which are composed of five ideal octahedrons. In this structure, four octahedrons are joined to the four {111} faces of a primary octahedron. The primary octahedron is assumed to be congruent with the inverted square pyramids in the patterned Si substrate. Considering that the angle between a (111) plane in a secondary octahedron (marked as S in Fig. 4) and a (100) substrate plane is 15.8°, four {111} planes in secondary octahedrons are presumably responsible for the four spots observed at ~16°. Although the origin of eight pairs of spots, four at ~34° and four at ~45°, is not fully understood at this time, it is likely that different multiple twins having multiple positions on the substrate contribute to the extra pairs of (111) spots observed in the pole figure.

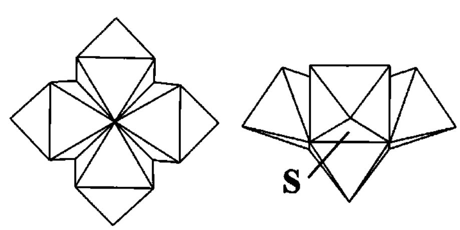

FIG. 4. Top and side schematic view of multiply twinned GaSb particles. Four octahedrons are joined to the {111} faces of a primary octahedron.

It is important to determine whether the orientation observed could be due to growth through pinholes present in the thin SiO_2 grown over the Si substrate. The same question applied to the experiments on GaAs growth over sawtooth-patterned Si, in which case the issue was left unresolved.[13] Although growth through pinholes cannot be ruled out absolutely, it is noteworthy that GaSb films were grown on plain (100) and (111) Si substrates covered with SiO_2 films prepared in the same way as on the patterned substrate. XRD pole figure analysis on these samples did not show any (111) texture, indicating that pinholes are probably not responsible for the oriented crystallization observed in this study.

A variety of mechanisms can induce oriented crystallization in graphoepitaxy. In the growth of ZnS on a patterned amorphous (111) Si substrate, the mobility of ZnS crystallites on the substrate was found to be critical in producing oriented crystallization.[3] In this case, an ultrathin ($\leqslant$100 Å) Cu film and a thin (1–2 μm) CdS film were evaporated onto the substrate to enhance the mobility of ZnS crystallites since CdS and ZnS form eutectic solutions with Cu that are liquid at temperatures higher than 700–800 °C. Assuming that GaSb nuclei on the SiO_2 surface are not highly mobile to facilitate oriented crystallization, the question becomes one of whether orientation occurs at nucleation or during film growth. To obtain more information on the mechanism of oriented crystallization, a GaSb film was grown on a patterned Si substrate consisting of smaller inverted square pyramids, measuring $0.1\times0.1\,\mu$m at the base, on 0.2 μm centers. Interestingly, the film grown on a smaller pattern did not show any (111) texture. This result suggests that there is an interplay of the surface diffusion length, the pattern size, and the local supersaturation for oriented crystallization. Systematic investigation of oriented crystallization as a function of the pattern size would reveal the role of surface supersaturation, diffusion, and surface energy.

This work was supported by the DARPA program on crystal growth (W. S. Coblenz). Facilities support by the NSF UW-MRSEC is gratefully acknowledged.

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