Growth of heteroepitaxial GaSb thin films on Si(100) substrates

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(Received 10 February 2004; accepted 12 April 2004)

The heteroepitaxial growth of GaSb thin films on Si(100) and GaAs(100) substrates is presented. The growth technique involves the use of atomic Ga and Sb species, which are provided by thermal effusion and radio frequency sputtering, respectively. The crystalline quality of the heteroepitaxial GaSb film on the Si substrate is high despite the larger lattice mismatch. Epitaxial quality is determined by high-resolution x-ray diffraction and Rutherford backscatter spectrometry channeling. Atomic-force microscopy is used to monitor the evolution of surface morphology with increasing film thickness. Transmission electron microscopy shows the formation of stacking faults at the Si/GaSb interface and their eventual annihilation with increasing GaSb film thickness. Annihilation of stacking faults occurs when two next-neighbor mounds meet during the overgrowth of a common adjacent mound.

I. INTRODUCTION

The "6.1 Å family" of semiconductor materials, GaSb, InAs, and AlSb, continues to attract considerable attention due to the prospects of producing both novel high-speed electronic and opto-electronic devices.[1,2,3] Current thinking is that devices will be fabricated on either GaSb or GaAs wafers. Small-diameter wafers of GaSb are available but naturally conductive as a result of an intrinsic p-type defect. Larger-diameter GaAs wafers are available; but thick buffer layers are required as a result of the large lattice mismatch of 7.8 % between the two materials. The purpose of this investigation is to consider the growth of GaSb on Si wafer substrates. The principal advantage of this marriage is the potential of combining the unique properties of the "6.1 Å family" of semiconductor materials with the highly developed technology for information handling in Si. The existence of silicon-on-insulator (SOI) or high-resistivity Si substrates can potentially solve the device-isolation problem. Some additional advantages of Si are substrate cost; the availability of large diameter, high-quality substrates; and a highly developed processing technology. Additionally Si has excellent mechanical properties in terms of strength and thermal conductivity relative to GaAs or GaSb.

The growth of III-V materials on Si has been a long-term goal of many because of the possibility of increased device performance by joining materials of these two families on a single chip. The object of practically all these research efforts has involved the growth of GaAs on a Si wafer.[4,5] The typically recognized problems of this effort includes a large lattice mismatch, difference in surface bonding (polar versus non-polar), and differences in the thermal expansion coefficient. Investigations have involved schemes such as strain-layer super lattices,[6] thermal annealing,[7] graphoepitaxy,[8] and most recently growth on a heteroepitaxial buffer layer.[9] No successful attempts have been made to grow GaSb on Si. Previous investigations have used GaSb as a stress relieving buffer layer for the growth of GaAs films on Si.[10] This suggests that GaSb yields more readily to an applied stress than GaAs. Another advantage that suggests the easier growth of GaSb on Si (as compared to that of GaAs on Si) is the required growth temperature. The optimum growth temperature for epitaxial GaSb is in the neighborhood of 430 °C as opposed to that of GaAs, which is in the range of 600 °C.[2] The higher temperature exacerbates the problem of unmatched thermal expansion coefficients.

Beyond crystallographic concerns with the growth of GaSb on Si, there are other potential problems of a semiconductor doping nature. Gallium is a p-type and Sb an n-type dopant in the Si. Further, Si is a potential p-type dopant in the GaSb-deposited thin-film material. These problems can potentially be avoided through the use of a properly designed low-temperature growth process. This level of complication will not be addressed at this time; the goal here is merely to prove that heteroepitaxial GaSb

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DOI: 10.1557/JMR.2004.0307

thin films of good crystalline quality can be obtained on Si(100) substrates.

II. EXPERIMENTAL

In this study, a stainless steel, cold-wall hybrid plasma-enhanced chemical vapor deposition reactor was used to grow epitaxial GaSb films. A turbo molecular pump backed by a Roots blower and a mechanical pump were used to maintain a base pressure of <5 × 10^{-8} Torr. Further, a load-lock was used to prevent the regular exposure of the growth chamber to atmosphere. The system contains a 3-in diameter radio frequency sputter gun that supplied the atomic Sb flux to the substrate. Also installed is a downward-facing effusion cell used to deliver Ga atoms to the substrate surface. A simple diagram of the hybrid reactor can be found in Fig. 1. This epitaxial growth technique represents a novel approach in the deposition of III-V compounds, in that both reactant species are exclusively atomic. It is typically the case that the group-V element, Sb in this case, is delivered by thermal effusion, and thus represents a flux of a variety of atomic species.

After considerable experimentation with the growth process, a standard procedure was established which consistently produced thin-film GaSb samples of high epitaxial quality on Si(100) substrates. This growth procedure is described in the following text. The substrates used were cleaved 2.5-cm × 3.75-cm rectangular pieces

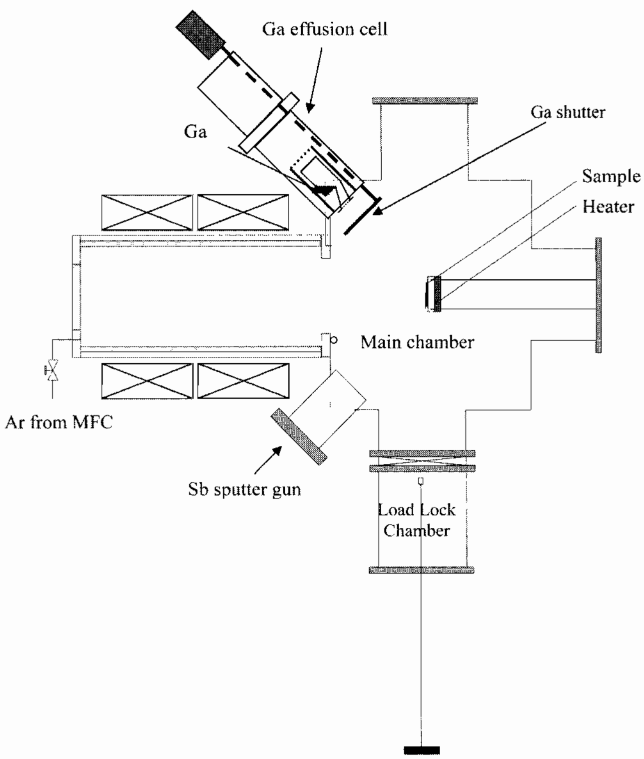

FIG. 1. Hybrid PE-CVD reactor with a thermal effusion cell for Ga, and a RF sputter gun for Sb deposition.

cut from test quality (100) Cz-Si and GaAs wafers. The substrate pieces were cleaned in an ex situ procedure that consisted of a degrease for 2 min in acetone under ultrasonic agitation, a rinse in reagent-grade methanol, and then a rinse of ultra-high purity (UHP) water. Finally the samples were subjected to a 60 s dip in a 5% HF solution with UHP-water.

Once the ex situ process was completed, the sample was fixed to an Nb susceptor and placed into the load-lock chamber. When the load-lock vacuum level reached approximately 10^{-6} Torr, the wafer was heated to 350 °C for five minutes to remove any volatile contaminants from the previous wet process. With a positive Ar flow from inside the main chamber, the load-lock door was opened and the sample was transferred into the main chamber by a magnetically coupled loading arm. The wafer was radiatively heated in vacuum by a boron-nitride coated pyrolitic graphite heater to a growth temperature of 290 °C < T_s < 550 °C.

The parameters used to grow the GaSb thin-film materials were a 0.67-mTorr reactor pressure maintained by a flow of 10-sccm Ar. These conditions were required for the steady-state operation of the Sb sputtering gun. The film quality was sensitive to the flux of both the Ga and Sb constituents on the substrate. The growth rates under these conditions was 30 Å/min. and was primarily determined by the Ga effusion cell temperature, as Ga flux was the limiting factor for this range of growth rates.

The effusion cell temperature was set in the temperature range from 970 to 1000 °C depending on the volume of Ga in the cell. The effusion cell temperature had to be increased over the life of a Ga charge to maintain a constant atomic flux. The Ga flux that produced the best material quality was estimated to be (1.4 × 10^{14}) atoms/cm^2-sec. The optimization of the entire process was based on the material quality measured by x-ray diffraction at the center location on the substrate surface. All other characterization data was obtained from material located near to the center location. This estimate was made by measuring the deposited thickness on an unheated substrate through Rutherford backscatter spectrometry (RBS) analysis. The Sb flux with an RF power level of 16.5 W was estimated to be (1.4 × 10^{14} atoms/cm^2-sec) by a similar technique. The atom-flux density across the substrate surface was not uniform as a result of the spatial separation between the two atomic sources. The profile of the measured atomic fluxes impinging on the substrate surface is shown in Fig. 2. All films were characterized by their (002) high-resolution x-ray diffraction HR-XRD signature. Interesting samples were sent out for further characterization by RBS, secondary ion-mass spectrometry (SIMS), and field-emission transmission electron microscopy (FE-TEM). These analysis techniques were performed at the IBM Microelectronics Fabrication Facility in Essex Junction, VT.

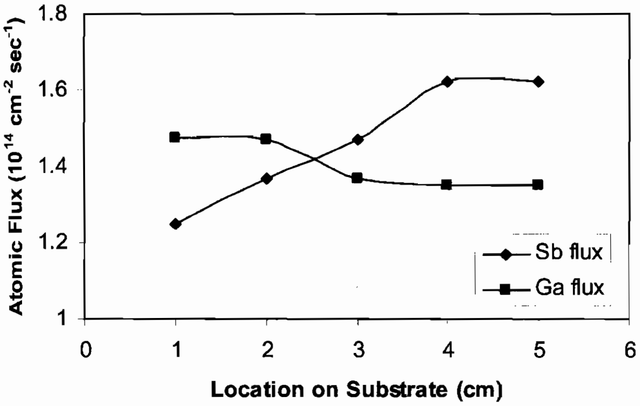

FIG. 2. Atomic flux of Ga and Sb species, calculated across the substrate surface from data obtained by the RBS analysis of single-component films deposited on an unheated substrate surface.

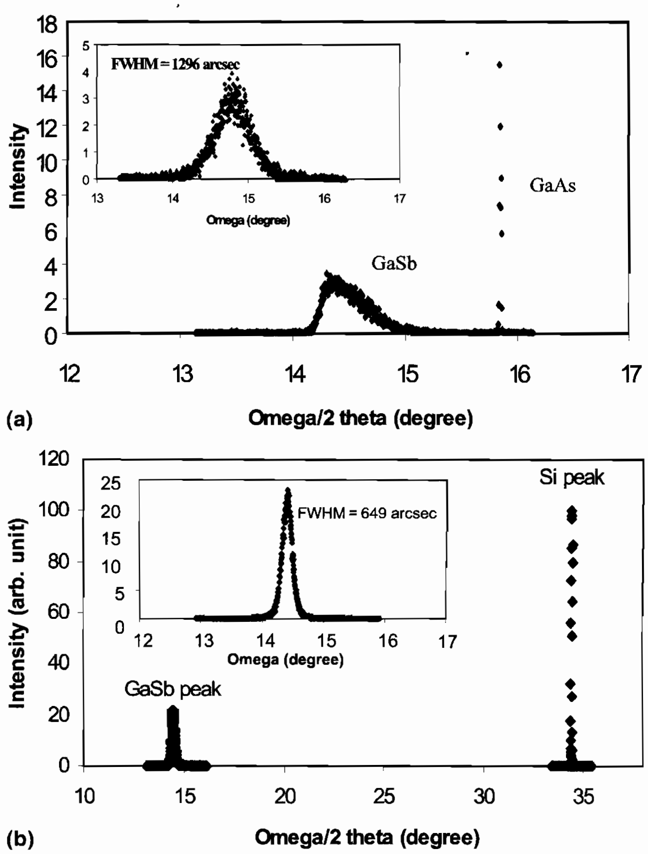

FIG. 3. (a) X-ray diffraction spectra of GaSb thin-film grown on a GaAs (100) substrate. The inset is the rocking curve of the thin film in the omega direction. (b) X-ray diffraction spectra of a GaSb thin film grown on a Si (100) substrate. The inset is the rocking curve of the thin film in the omega direction

III. RESULTS AND DISCUSSION

The standard procedure as previously described was developed to consistently produce thin-film GaSb samples of high epitaxial quality on Si (100) substrates. The majority of the thin-film samples were grown for a 40-min duration, which resulted in a film thickness of 120 nm. This process was developed by a continuous feedback loop that included the characterization of all materials by high-resolution x-ray diffraction. The omega/2 theta x-ray diffraction spectra for GaSb thin-film samples grown with the standard 40-min process are shown in Figs. 3(a) and 3(b) for both GaAs (100) and Si (100) substrates. These spectra show both the GaSb thin film and the Si and GaAs substrate peaks. As an indication of thin film quality, an inset showing the rocking curve for a scan in the omega direction is included. The full width at half maximum (FWHM) for material grown on Si(100) substrates was consistently better than those grown on GaAs substrates. One should not make too much of this result however, as the wafer cleaning and preparation technique have been optimized through the years in this laboratory for the use of Si wafers.

Another indication of epitaxial quality was obtained from RBS. The RBS channeling spectra for GaSb grown on a GaAs(100) and a Si(100) wafer substrate can be found in [Figs. 4(a) and 4(b)] . The ratio of channeled to random backscattered intensity, known as the chi-min value, is a direct indication of epitaxial quality. This value is observed to drop monotonically with increasing film thickness for both samples. The interpretation of this is that the epitaxial quality is improving as the film thickness is increasing. This interpretation suggests that the defect density in the crystal structure in both cases is decreasing with increasing film thickness. The film thickness for the two samples shown in these figures is different; the sample on the GaAs substrate is 120-nm thick and the one on the Si substrate is greater than 1000 nm. A chi-min value of approximately 7.5% is observed near the top surface for the thick sample grown on the Si substrate. These spectra both exhibit an artifact produced by the thin epitaxial films that is known as a "surface peak". The surface peak is only obtained for materials of very good crystallographic quality. Ions impinging on the surface are scattered more by the first few atomic layers than by the underlying atoms, because the underlying atoms are shadowed, or are in the "shadow cone" of the surface atoms. The surface-scattering generates a surface peak in the channeled spectrum.

The RBS results indicate that epitaxial quality improves with increasing film thickness. A cross-sectional TEM image of a 120-nm thick GaSb film grown on a Si (100) substrate further confirms this result; see Fig. 5. Stacking faults are clearly present across the film's cross-section, with the origin of the faults being the Si/GaSb interface. The stacking faults that propagate from the initial-growth surface are seen to annihilate with those that are propagating at a 90° angle relative to the first.

A further indication of epitaxial quality can be obtained from a measure of the etch-pit density. Results

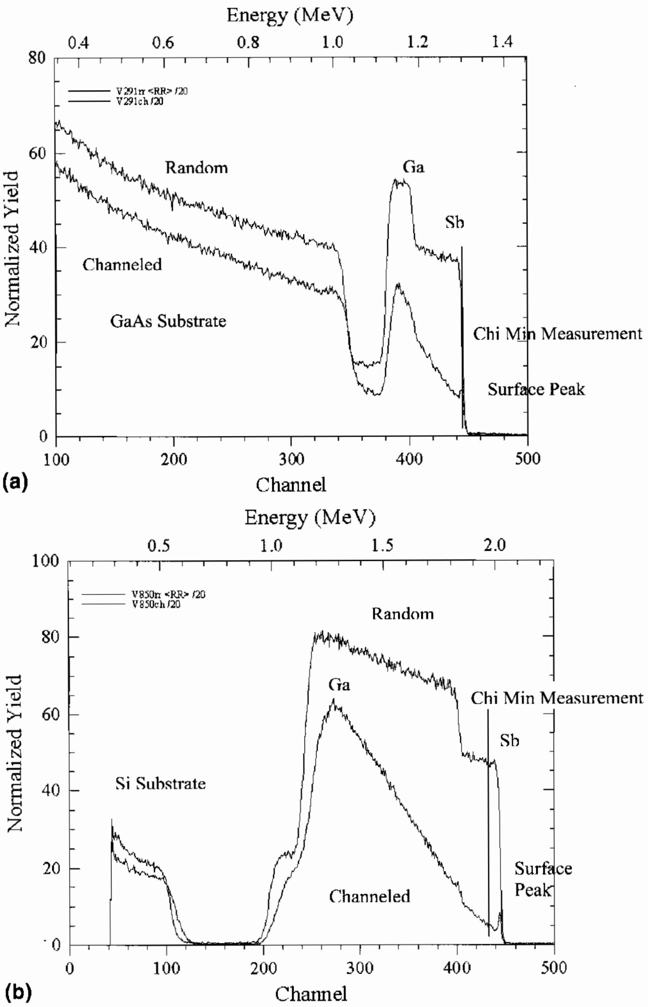

FIG. 4. (a) The RBS channeling spectrum for a 120-nm thick GaSb film grown on a GaAs(100) wafer substrate. The spectrum indicates that the crystalline quality of the film is increasing monotonically with increasing film thickness. (b) The RBS channeling spectrum for a 1000-nm thick GaSb film grown on a Si(100) wafer substrate. The spectrum indicates that the crystalline quality of the film is increasing monotonically with increasing film thickness.

are given for the films grown on the different material substrates and for different thin-film thickness. The etching solution used to delineate the crystal defects in the GaSb material was made of a dilute solution of H_2O_2:HF:HNO_3:H_2O. This technique is very subjective as a result of the experimenter's judgment of what constitutes an etch pit. One attempt to standardize this process was to make a similar measurement on a polished GaSb wafer piece that was obtained commercially. The EPD results for a variety of samples measured is presented in Table I.

The range of measured EPD values for the four different samples do not indicate significant differences in material quality. The fact that little difference is observed between that of a polished GaSb wafer and those of the

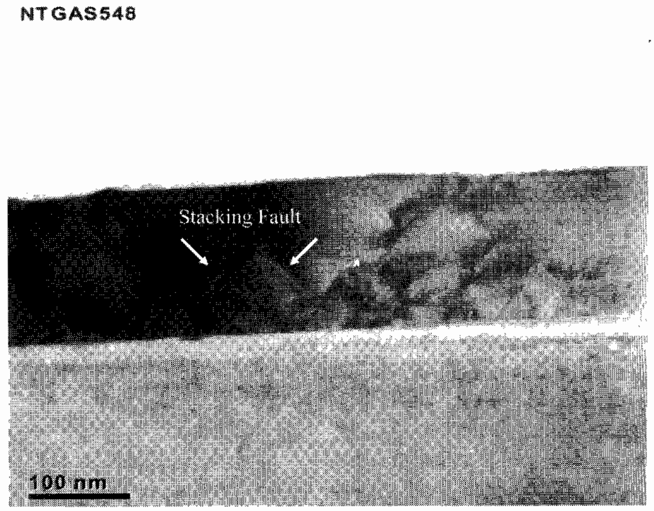

FIG. 5. Transmission electron microscopic image of a 120-nm thick GaSb film grown on a Si (100) substrate, using the standard process.

TABLE I. Measured Etch Pit Density for GaSb Materials.

Sample description	EPD
GaSb (100) wafer	1.1×10^4 cm^{-2}
GaSb film on a Si (100) wafer 1-micron thick	1.0×10^5 cm^{-2}
GaSb film on a Si (100) wafer 120-nm thick	2.3×10^4 cm^{-2}
GaSb film on a GaAs (100) wafer 120-nm thick	5.8×10^4 cm^{-2}

grown materials suggests that all of the thin-film materials were of good crystal quality with a minimum of defects. One unexpected result is that the EPD for the 1-μ thick film was higher than that for the 120-nm film. This result most likely derives from the fact that the sites delineated by the etch on the 1-μ thick sample were more visible than those on the thin samples.

The growth of high crystalline quality GaSb thin films on Si substrates was obtained only when the deposition process began with a flux of Sb directed at the Si substrate surface. Poorer quality material resulted if either Ga and Sb were started simultaneously, or if the initial species flux consisted of only Ga atoms. Previous investigations into the growth of GaAs on Si have been able to develop a process that was initiated with a flux of either species,[4] but this required special wafer temperature considerations. Initially it was thought that the growth of an epitaxial Sb layer would lead to improved GaSb film quality.[11] An Sb film of measurable thickness could not be formed on the substrate surface for temperatures greater than 250 °C. An Sb layer could be formed on the substrate at a temperature below 250 °C and its temperature could be raised without loss from the substrate. Attempts to grow on this Sb buffer layer, however, failed to produce the desired result and crystal quality declined as determined by the FWHM of the omega scans.

Next a series of experiments was performed in which an initial Sb flux was directed at the substrate surface for temperatures at or below those used to grow GaSb. These results are presented in Fig. 6, where the subsequent top GaSb film was grown at the optimum temperature of 480 °C. Several attempts were made to vary the temperature and duration of the initial Sb-only deposition; and although no appreciable Sb film was deposited beyond what is assumed to be a monolayer, good quality material was obtained. Several successful GaSb films, grown with extended Sb flux applications, were analyzed by SIMS to investigate the existence of an Sb layer. An example of this SIMS analysis can be found in Fig. 7, yet no change in the profile was observed for a variety of process schemes that included extended periods of Sb-only exposure. It is concluded that a monolayer of Sb on the Si surface is required for the successful growth of GaSb films on a Si(100) substrate. It is not possible to state with certainty that there is one and not two mono-layers of Sb deposited on the Si surface; but extended periods of growth failed to produce an Sb layer of thickness measurable by SIMS, between the GaSb layer and the Si substrate. It therefore can be assumed that the growth of a layer beyond one monolayer in thickness is limited by a low sticking-probability of Sb, on an Sb-covered surface.

Although in theory the choice of Si(100) as a substrate for GaSb growth appeared to initially be the wrong answer, current results suggests that it is possible to grow GaSb on a Si(100) substrate. The growth of GaSb on GaAs has also attracted considerable attention for its ability to form self-assembled quantum dots or three-dimensional islands. The large lattice mismatch between the two materials causes the initial thin-film growth to proceed by the Stranski-Krastanov mode, which results in the formation of three-dimensional islands. A comparison is made between the AFM image obtained for GaSb growth on a GaAs substrate (Fig. 8.) and that on a

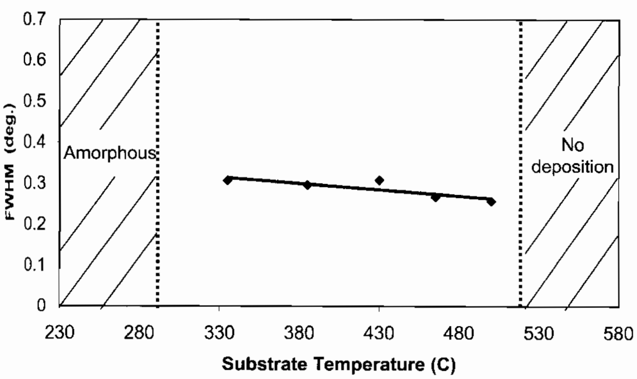

FIG. 6. Epitaxial quality of the GaSb layer on the Si(100) surface as a function of the substrate temperature used to deposit the initial Sb layer. The epitaxial quality was determined by the x-ray rocking curve width in the omega direction. The GaSb film thickness was 120 nm.

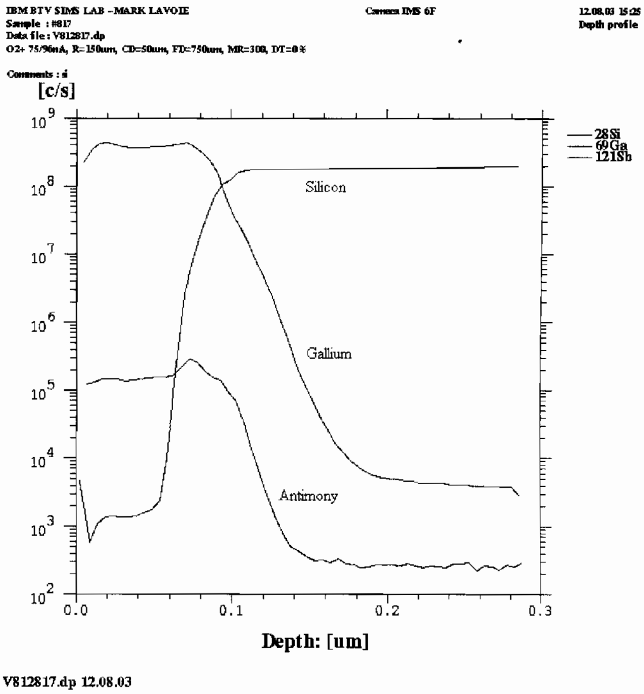

FIG. 7. Secondary ion mass spectrometry profile for a GaSb film grown on a Si substrate. The growth was initiated after a 20-min exposure of the surface to a Sb atomic flux at a substrate temperature of 350 °C.

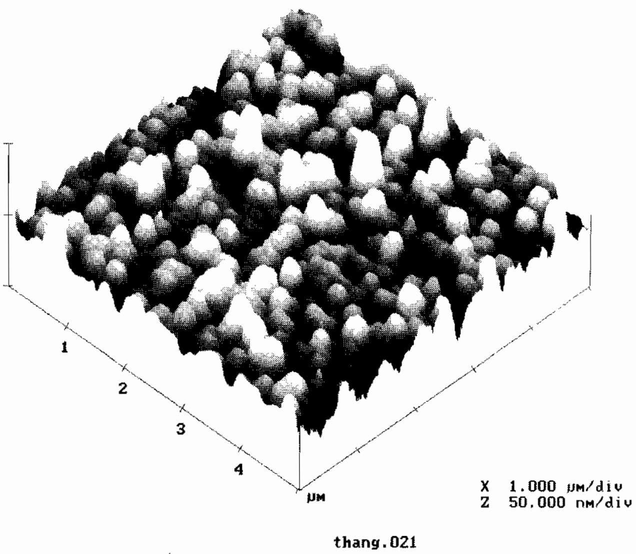

FIG. 8. AFM picture of surface of GaSb grown on GaAs (100) for 40 min. Note that the vertical scale is in increments of 50 nm/div.

Si (100) (Fig. 9.b) after 40 min of growth. The density of mounds on the GaAs substrate is higher (5.4 μm^{-2}) compared to (3.3 μm^{-2}) for Si (100). The mounds on the Si substrate are larger than those on the GaAs substrate, but fewer in number. The lower mound-density can potentially lead to a lower density of crystal defects; but mound density is very sensitive to the process conditions

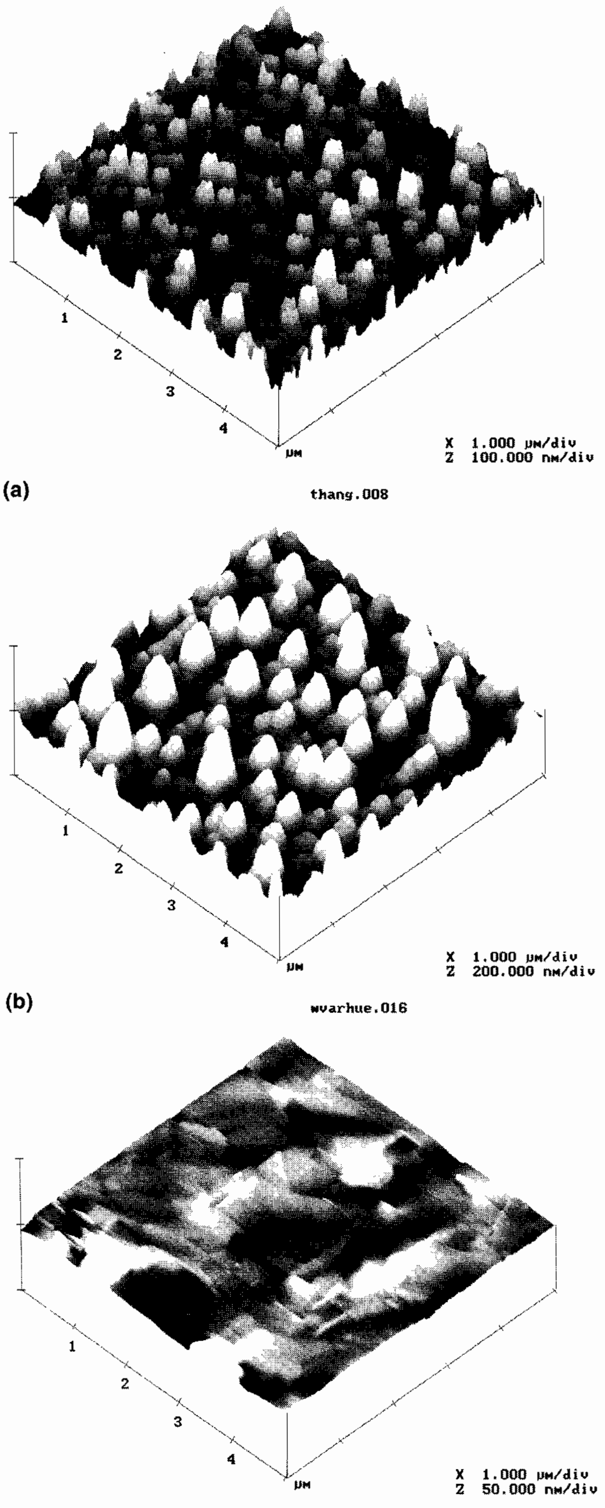

FIG. 9. (a) Atomic-force microscope image of a GaSb surface grown on a Si (100) surface after a period of 40 s. Note that the vertical scale is in increments of 100 nm/div. (b) Atomic-force microscope image of a GaSb surface grown on a Si (100) surface after a period of 40 min. Note that the vertical scale is in increments of 200 nm/div. (c) Atomic-force microscope image of a GaSb surface grown on a Si (100) surface after a period of 300 min. Note that the vertical scale is in increments of 50 nm/div.

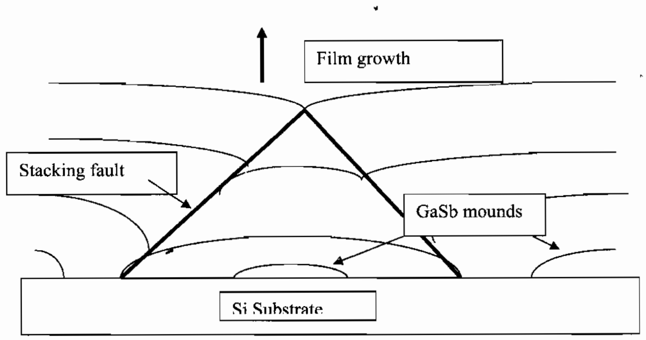

FIG. 10. Coalescence of neighboring GaSb islands with the formation and annihilation of stacking faults.

used to grow the materials, which has not been optimized here for growth on GaAs.

To understand this process further, a series of atomic-force microscopy AFM images were taken at different time intervals during the growth of the GaSb on the Si(100) substrate surface to reveal the evolution of the surface morphology. The atomic force microscopy image of the GaSb growth surface taken after three different periods of growth are shown consecutively in Figs. 9(a), 9(b), and 9(c) after 40 s, 40 min, and 300 min, respectively.

The surface after 40 s of growth reveals a mound structure with a density of (6 μm^{-2}) and a height of (35 nm). Continued growth after 40 min (or 120 nm of film thickness) finds the coalesces of mounds and an increase in the size of individual mounds. Finally after 300 min (or 1050 nm) of growth, the surface is extremely flat and growth proceeds via a layer-by-layer mechanism. The coalescence of the original islands potentially leads to the creation of crystalline defects. This problem is most likely the cause of the stacking faults observed in the TEM images shown in Fig. 5. The density of stacking faults and the presence of surface mounds coincide with one another. The annihilation of stacking faults is proposed to coincide with the overgrowth of two adjacent mounds over a common neighbor. A simple sketch depicting this process is shown in Fig. 10. It is interesting to note that in the case of GaSb growth on a Si(100) substrate, that the high stacking fault-density decreases rapidly away from the interface with the substrate and that good epitaxial quality can be established after 500 nm of growth.

IV. CONCLUSIONS

High-quality single-crystal, heteroepitaxial GaSb films have been grown on Si (100) substrates. The process uses a thermal effusion cell as the source of Ga and RF sputter gun as the source of atomic Sb. Although there is a significant difference in lattice constant between the substrate and the GaSb epi-layer, good crystalline quality films have been grown. Successful growth required the initial deposition of Sb on the Si substrate surface. The growth of GaSb on (100) Si began with the formation of 3-D islands similar to those previously found for growth on GaAs(100) substrates. The mounds are found to reduce in density with increasing film thickness as a result of overgrowth. The coalescence of islands coincides with the annihilation of stacking faults.

ACKNOWLEDGMENT

This work was made possible by a grant received from the Air Force Office of Scientific Research, for which we are grateful.

REFERENCES

1. C-H. Chang, R. Ludeke, L.I. Chang, and L. Esaki: Molecular-beam epitaxy (MBE) of $In_{1-x}Ga_xAs$ and $GaSb_{1-x}As_y$. *Appl. Phys. Lett.* **31,** 759 (1977).
2. B.V. Shanabrook, W. Bravos-Carter, R. Bass, B.R. Bennett, J.B. Boos, W.W. Bewley, A.S. Bracker, J.C. Culbertson, E.R. Glaser, W. Kruppa, R. Magno, W.J. Moore, J.R. Meyer, B.Z. Nosho, D. Park, P.M. Thibado, M.E. Twigg, R.J. Wagner, J.R. Waterman, L.J. Whitman, and M.J. Yang: Engineered heterostructures of 6.1 A III-V semiconductors for advanced electronic and optoelectronic applications in Engineered Nanostructural Films and Materials, edited by A. Lakhtakia and R.F. Messier. In SPIE Proceedings 3790, (1999). pp. 13–22.
3. P.M. Thibado, B.R. Bennett, M.E. Twigg, B.V. Shanabrook, and L.J. Whitman: Evolution of GaSb epitaxy on GaAs(001)-c(4x4). *J. Vac. Sci. Technol. A* **14,** 885 (1996).
4. S.F. Fang, K. Adomi, S. Iyer, H. Morkoc, H. Zabel, C. Choi, and N. Otsuka: GaAs and other compound semiconductors on Si. *J. Appl. Phys.* **68,** R31 (1990).
5. H. Kawanami: Heteropitaxial technologies of III-V on Si. *Solar Energy Mater. Sol. Cells* **66,** 479 (2001).
6. K. Nozawa and Y. Horikoshi: Low threading dislocation density GaAs on Si(100) with InGaAs/GaAs strained-layer superlattice-grown by migration-enhanced epitaxy. *Jpn. J. Appl. Phys.* **30,** L668 (1991).
7. Y. Takagi, H. Yonezu, Y. Hachiya, and K. Pak: Reduction mechanism of threading dislocation density in GaAs epilayer grown on Si substrate by high temperature annealing. *Jpn. J. Appl. Phys.* **33,** 3368 (1994).
8. J.Y. Cheng, C.A. Ross, E.L. Thomas, H.I. Smith, and G.J. Vancso: Fabrication of nanostructures with long-range order using block copolymer lithography. *Appl. Phys. Lett.* **81,** 3657 (2002).
9. M. Meyer: Motorola and IQE grow GaAs on large-area Si substrates (features: epitaxial growth). *Compound Semiconductor* Oct (2001).
10. H. Uchida, T. Soga, H. Nishikawa, T. Jimbo, and M. Umeno: Reduction of dislocation density by thermal annealing for GaAs/GaSb/Si heterostructures. *J. Cryst. Growth* **150,** 681 (1995).
11. J.A. Dura, A. Vigliante, T.D. Golding, and S.C. Moss: Epitaxial growth of Sb/GaSb structures: An example of V/III-V heteroepitaxy. *J. Appl. Phys.* **77,** 21 (1995).