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A surfactant-mediated relaxed $Si_{0.5}Ge_{0.5}$ graded layer with a very low threading dislocation density and smooth surface

J. L. Liu[a)]
Device Research Laboratory, Department of Electrical Engineering, University of California at Los Angeles, Los Angeles, California 90095-1594

C. D. Moore and G. D. U'Ren
Department of Materials Science, University of California at Los Angeles, Los Angeles, California 90095-1594

Y. H. Luo, Y. Lu, G. Jin, and S. G. Thomas
Device Research Laboratory, Department of Electrical Engineering, University of California at Los Angeles, Los Angeles, California 90095-1594

M. S. Goorsky
Department of Materials Science, University of California at Los Angeles, Los Angeles, California 90095-1594

K. L. Wang
Device Research Laboratory, Department of Electrical Engineering, University of California at Los Angeles, Los Angeles, California 90095-1594

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A method to grow a relaxed $Si_{0.5}Ge_{0.5}$ graded layer with a very smooth surface and a very low threading dislocation density using solid-source molecular-beam epitaxy is reported. This method included the use of Sb as a surfactant for the growth of a 2 μm compositionally graded SiGe buffer with the Ge concentration linearly graded from 0% to 50% followed by a 0.3 μm constant $Si_{0.5}Ge_{0.5}$ layer. The substrate temperature was kept at 510 °C during the growth. Both Raman scattering and x-ray diffraction were used to determine the Ge mole fraction and the degree of strain relaxation. Both x-ray reflectivity and atomic force microscopy measurements show a surface root mean square roughness of only 20 Å. The threading dislocation density was determined to be as low as $1.5 \times 10^4\ \mathrm{cm}^{-2}$ as obtained by the Schimmel etch method. This study shows that the use of a Sb surfactant and low temperature growth is an effective method to fabricate high-quality graded buffer layers. © *1999 American Institute of Physics.* [S0003-6951(99)03837-1]

SiGe has become an important material for electronic applications. Recently, thermoelectric properties in SiGe superlattices have attracted much attention because the figures of merit for these superlattices were found to be much higher than that estimated from the bulk values of their constituent materials and their equivalent composition alloy layers.[1,2] Several reports on type-I SiGe superlattices indicated a large decrease in thermoconductivity and an increase in thermopower.[3] Similar results are expected for type-II SiGe superlattices. In order to grow type-II SiGe superlattices, relaxed SiGe buffer layers are needed to allow tensile strain in the Si wells and to provide compressive strain in the SiGe barriers. For thermoelectric applications, one desires a thin buffer layer in order to minimize its thermoelectric contribution. However, a thin buffer leads to a large number of threading dislocations propagating into the superlattice thereby degrading the quality of the superlattice.

To date, strain-relaxed SiGe buffers have been successfully realized by at least three methods. One is to grow compositionally graded SiGe layers at high temperatures (typically at 700–900 °C) with a typical grading rate of 10% Ge per 1 μm.[4,5] The second is to use a low temperature Si buffer (typically grown at 400 °C) underneath a SiGe layer of constant composition grown at about 550 °C.[6] Another is to introduce impurities, such as carbon,[7] in SiGe layers to adjust the strain. These techniques have disadvantages of long growth times, thick buffer layers, rough surfaces, high residual strain degree, and/or high threading dislocation densities. For example, M. T. Currie[5] recently reported that a graded buffer with a final Ge concentration of 50% grown at 750 °C had a root mean square (rms) roughness of 373 Å and a threading dislocation density of $6.3\times10^6\ \mathrm{cm}^{-2}$. Devices grown on these buffers will likely perform poorly as a result of the high threading dislocation density and surface roughness. Previously, it was found that a segregating species, a surfactant, can be used to inhibit island formation in strain layer heteroepitaxy, and hence, to promote two-dimensional growth for the development of high-quality electron devices.[8] In this letter, we use Sb as a surfactant to fabricate a $Si_{0.5}Ge_{0.5}$ graded buffer. Our main purpose is to provide a relatively thin SiGe buffer with a very smooth surface and a very low threading dislocation density so that the Si/Ge superlattices grown on top of the relaxed buffer will be of high quality for thermoelectric and other applications.

The growth was carried out using a solid source molecular-beam epitaxy system. A *n*-type Si (100) wafer with a resistivity of 1–30 Ω cm was cleaned by a standard

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[a)] Electronic mail: jliu@ee.ucla.edu

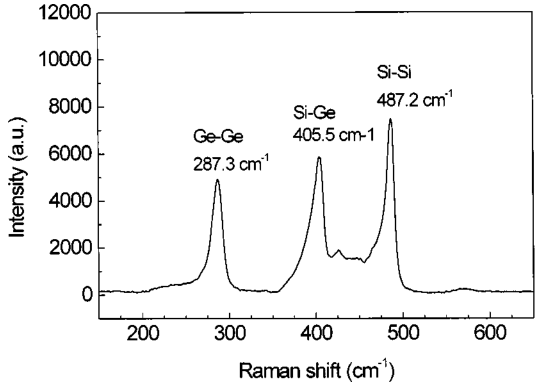

FIG. 1. Typical Raman spectrum of the sample. Three main Raman lines at 287.3, 405.5, and 487.2 cm^{-1} are Ge–Ge, Si–Ge, and Si–Si first-order optical phonons, respectively.

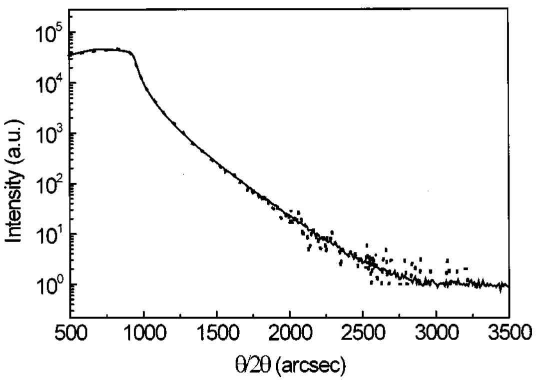

FIG. 3. X-ray reflectivity of the sample. The dotted data are the experimental points, while the solid line is a simulation results, giving the rms surface roughness to be 20 Å.

Sharaki cleaning method followed by an *in situ* thermal cleaning at 930 °C for 15 min. Then, the substrate temperature was decreased and maintained at 510 °C during the growth. The nominal Si growth rate was kept at 1 Å/s while the Ge growth rate was linearly changed from 0 to 1 Å/s. Under these conditions, a 1000 Å Si buffer was first grown followed by the deposition of 1 ML of Sb. Subsequently, a 2 μm graded SiGe with the Ge mole fraction varying from 0 to 0.5 was grown. The grading rate was 25% Ge per 1 μm. Finally a 0.3 μm constant $\mathrm{Si_{0.5}Ge_{0.5}}$ buffer was grown.

The ability to measure buffer layer composition and relaxation is essential for the calibration of growth process and control of the thermoelectric and other behaviors of the material. In this experiment, Raman scattering was first used to characterize the sample. Figure 1 is a typical Raman spectrum of the sample. The spectrum was taken at room temperature and excited by the 514 nm line of an Ar ion laser in the backscattering configuration. Three strong first-order lines in this spectrum are due to Ge–Ge ($287.3\,\mathrm{cm}^{-1}$), Si–Ge ($405.5\,\mathrm{cm}^{-1}$), and Si–Si ($487.2\,\mathrm{cm}^{-1}$) atomic vibrations. By using the frequencies of Si–Si and Si–Ge,[9] we obtained the Ge mole fraction in the top constant buffer of 0.49 with a residual strain of 5%. The use of the relative intensities between Si–Si and Ge–Ge peaks also gave a similar result.[9]

The Ge concentration and epilayer relaxation have also been measured using double axis x-ray diffraction. Figure 2 shows the symmetric (004) and asymmetric (224) rocking curves. In the absence of substrate tilt, the position of the layer peak intensity with respect to the substrate peak gives both the Ge concentration and film relaxation.[10] The layer peak position in these scans corresponds to a Ge mole fraction of 0.48 and a relaxation of 92%, in agreement with the results from Raman scattering. In addition, the intensity of the layer peak is fairly uniform out to $x = 0.48$, indicating a well-controlled linear grade.

Surface roughness is usually a problem when growing relaxed SiGe buffer layers with a high final Ge concentration. In order to estimate the surface roughness of our sample, x-ray reflectivity was performed and the results are shown in Fig. 3. The dotted data are the experimental points, while the solid line is a simulation results, giving the rms surface roughness to be 20 Å. The surface morphology associated with the surface roughness can be clearly seen from the atomic force microscopy (AFM) measurement and is shown in Fig. 4. A crosshatch pattern occurs along two inplane ⟨110⟩ directions and indicates the formation of misfit dislocations. Surface roughness was mainly due to crosshatch undulations and was estimated from a number of $20 \times 20\,\mu\mathrm{m}^2$ AFM images to be approximately 20 Å, in close agreement with that obtained by the x-ray reflectivity measurements. As seen from Fig. 4, the crosshatch lines are straight and long, indicating long misfit dislocations and potentially few threading dislocations in the sample. Since the surface roughness is related to the large strain fields near the

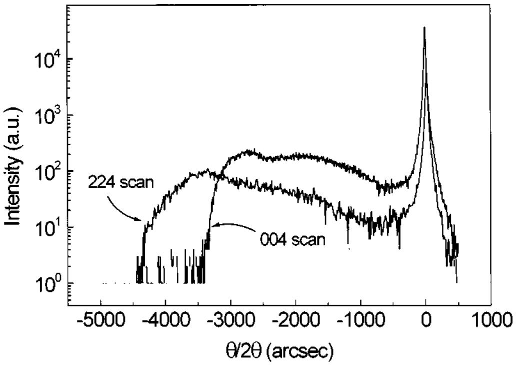

FIG. 2. X-ray (004) and (224) rocking curves of the sample. A Ge mole fraction of 48% and a relaxation of 92% can be obtained from these scans.

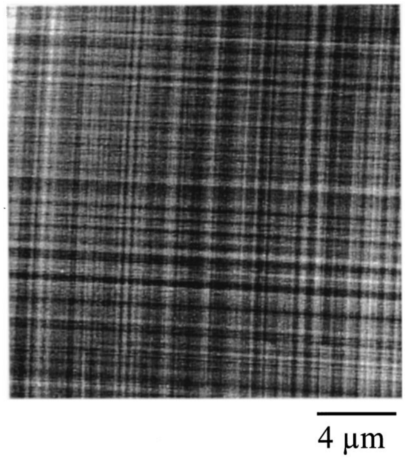

FIG. 4. AFM image of the sample. Crosshatch pattern related to misfit dislocations can be easily seen.

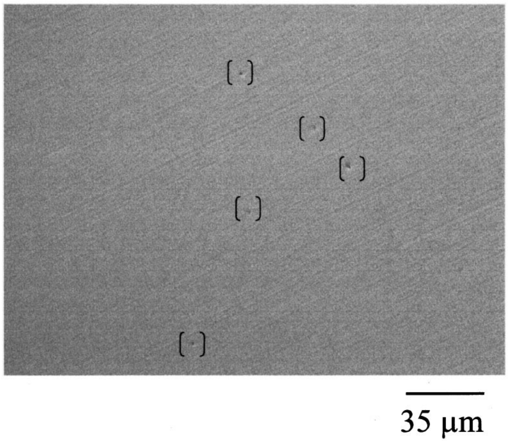

FIG. 5. Nomarski image of an etched sample depicting etched pits in the double brackets. The threading dislocation density is estimated to be $1.5 \times 10^4\ \mathrm{cm}^{-2}$.

dislocations and the smaller the critical thickness, the closer the surface is to the large strain fields, thus, the system trades strain energy for surface energy and the surface roughens.[4] The use of Sb as surfactant and low temperature growth can increase the critical thickness of SiGe on Si,[8] thus smoothening the surface.

The threading dislocation density was obtained by using a Schimmel defect etch[11] and then by counting the etched pits by Nomarski interference microscopy.[12] The solution used consisted of one part 75 g CrO_3 in 1000 ml H_2O to two parts 48% HF. The etch rate for Si in such a solution is 1 μm/min at room temperature. The etching was carried out at room temperature by dipping the sample in the solution for 30 s. Figure 5 is a typical image of the as-etched sample. The threading dislocation density in the upper graded layer (roughly estimated by Alpha-step measurements) was determined to be $1.5\times 10^4\ \mathrm{cm}^{-2}$. In fact, with several shorter etches $(<20\ \mathrm{s})$, one could see fewer etch pits within the same surface area, which suggests a lower threading dislocation density in the upper uniform buffer than in the graded buffer. The number obtained here is at least two orders of magnitude lower than previously reported graded buffer layers grown at high temperatures, where about $10^6\ \mathrm{cm}^{-2}$ threading dislocation densities were found for achieving strain relaxation.[4]

Although a detailed impurity depth analysis was not yet performed, it is likely that there is still some Sb remained in the buffer. This buffer, with its low dislocation density and low rms roughness, can be used for thermoelectric applications where phonon contributions are predominant. Additionally, this technique could also have potential applications in fabricating high mobility structures and other related devices if a flash-off step is used between the graded buffer and constant composition buffer to remove the Sb surfactant layer.[13] Related work is in progress.

In summary, we have fabricated a high-quality $Si_{0.5}Ge_{0.5}$ buffer with a steep grading of 25% Ge per 1 μm using Sb as a surfactant. The surface rms roughness is only 20 Å and the threading dislocation density is as low as $1.5\times 10^4\ \mathrm{cm}^{-2}$. This study shows that the use of surfactant mediation and low temperature growth result in high-quality graded SiGe buffer layers and may open up many new thermoelectric, electronic, and optoelectronic applications.

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