High-quality Ge films on Si substrates using Sb surfactant-mediated graded SiGe buffers


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High-quality Ge films were grown on Si substrates by solid-source molecular beam epitaxy using SiGe graded layer and Sb surfactant-mediation technique. Transmission electron microscopy measurements show that samples grown using this method have a lower threading dislocation density than those grown by other typical methods, such as grading at high temperature (700 °C) only, grading at intermediate temperature (510 °C) only, and the use of low temperature Si buffer. A relaxed Ge film on a 4-μm-thick graded buffer was grown and shown to have a threading dislocation density of $5.4 \times 10^5$ cm$^{-2}$ and surface roughness of 35 Å. Ge $p-i-n$ diodes were fabricated and tested. Under a reverse bias of 1 V, the $p-i-n$ Ge mesa photodiodes exhibit a very low dark current density of 0.15 mA/cm$^2$. © 2001 American Institute of Physics. [DOI: 10.1063/1.1421092]

The rapid development of optical communications demands low cost optical components that operate in the near infrared windows of fiber optic transmission (1.3 and 1.55 μm). Pure Ge photodetector integrated on Si is one of the promising candidates for this purpose, owing to its band gap of 0.67 eV and full compatibility with modern Si technology. Nevertheless, the large-scale practical application of this kind of device is not yet realized due to the difficulty in the growth of high-quality pure Ge films on Si with a low threading dislocation density and smooth surface. One earlier attempt was done by Luryi, Katzalsky, and Bean1 in the early 1980s where only an 1800-Å-thick step-graded SiGe buffer layer was employed between the top $p-i-n$ Ge film and the underlying Si substrate. The leakage current of the diodes was very high ($\approx$ 200 mA/cm$^2$ at −1 V) due to the high density of dislocations. Samavedam et al.2 fabricated improved Ge photodiodes using a thick graded SiGe buffer ($\approx$ 10 μm) with an intermediate chemical mechanical polishing step. The leakage current was reduced to 0.2 mA/cm$^2$ under a reverse bias of 1 V. Another interesting approach was made by Sutter, Kafader, and Von Kanel3 and Colace et al.4,5 in which a pure Ge film was directly grown on Si by using a hydrogen-surfactant mediation step followed by a post-growth cyclic thermal annealing treatment. Recently, we have also shown high-quality relaxed SiGe buffers with a very low threading dislocation density and smooth surface by combining the use of a graded buffer and an Sb surfactant mediation technique.6 The high quality arises from the optimized relaxation of the structure, where not only threading dislocations but also Sb are used to relieve stress caused by the 4% mismatch between Si and Ge.

In this letter, we study systematically the Sb surfactant-mediated graded buffer layer growth technique, which leads eventually to the growth of high-quality Ge films on Si using SiGe buffers with steep grading rates. $p-i-n$ Ge diodes were fabricated on a 4-μm SiGe buffer and these diodes exhibited very low leakage current and a high external quantum efficiency.

A solid-source molecular beam epitaxy was used for sample growth. In order to show the effect of Sb surfactant mediation on the quality of the buffer, we compared with four samples having different growth conditions. All samples have the same top-layer Ge molar fraction of 0.5. Samples A, B, and C consist of a 2 μm graded SiGe with a grading rate of 25% Ge per 1 μm, followed by a 0.3 μm Si$_{0.5}$Ge$_{0.5}$ buffer. Sample A was grown at 510 °C. One ML Sb was also deposited and no Sb pre-deposition was used for samples B, C, and D. Samples B and C were grown at 700 and 510 °C, respectively. Sample D was simply a low-temperature SiGe assisted 200-nm-thick Si$_{0.5}$Ge$_{0.5}$ film. The growth temperature cycle used was the same as that in the literature.7 Figure 1 shows weak beam dark field transmission electron microscopy (TEM) images of the samples. For sample A, the dislocations occur near the bottom of the buffer and the top Si$_{0.5}$Ge$_{0.5}$ layer is dislocation free. For samples B, C, and D, however, there are high densities of threading dislocations penetrating to the top Si$_{0.5}$Ge$_{0.5}$ layer. A quantitative study of threading dislocations by the Schimmel etch pit method8 shows that the threading dislocation density of 1.5 × 10$^4$ cm$^{-2}$ is obtained for sample A, while samples B, C, and D have threading dislocation densities as high as 10$^5$ cm$^{-2}$. Surface roughness measurements on as-grown samples by AFM show that the root mean square (rms) roughness of 20, 161, 38, and 27 Å is obtained for samples A, B, C, and D, respectively.

In order to gain further insight into Sb mediation, we have investigated the grading rate dependence on the resulting threading dislocation density and surface roughness. A series of samples were grown at 510 °C by grading Ge from 0% to 50% Ge with a 0.2-μm-thick Si$_{0.5}$Ge$_{0.5}$ layer on top. An Sb layer 1 ML thick was predeposited. Figure 2(a) shows the threading dislocation density as a function of grading rate. The threading dislocation density decreases with the decrease of grading rate. For comparison, the threading dis-

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location densities of samples B and C are shown as well. Figure 2(b) shows the rms roughness as a function of grading rate. The surface becomes one order of magnitude smoother compared with those samples grown at higher temperatures. In addition, the lower grading rate is used, the smoother surface it becomes.

It is interesting to discuss why Sb surfactant improves the film quality markedly. For graded SiGe films grown at high temperature (≥700 °C), there are at least certain amounts of threading dislocations (10^6 cm^{-2}) to compensate misfit strain and relax the film. For relaxed SiGe films grown on low-temperature Si, the film relaxation relies on the termination of threading dislocations by point defects produced in the low temperature Si layer.

Thus to obtain low-dislocation-density film, a certain amount of point defects is needed in the low-temperature Si layer by optimizing the Si layer thickness and its growth temperature or by using other methods. For graded SiGe films grown only at intermediate temperature (∼500 °C), misfit dislocations cannot move effectively during film growth and once the film builds enough strain energy, it cracks abruptly by generating large amounts of threading dislocations. As the film continues to grow, thickness and Ge molar fraction increase and the strain builds up again. The relief of strain will take place by generating threading dislocations again at the upper layer. Graded SiGe films grown using Sb surfactant mediation at intermediate temperature (∼500 °C) are of high quality because Sb helps the motion of misfit dislocations during growth, eventually decreasing the threading dislocation density in the film.

Using the abovementioned method, two pure Ge samples were then grown on Sb-mediated graded SiGe buffers. The structures consist of the following layers: 100-nm-thick Si buffer, linearly graded Si_{1-x}Ge_x with x from 0 to 1 (the top 0.6-μm-thick buffer was doped with Sb of 0.7–1 ×10^{17} cm^{-3} to form n layer), 0.8-μm-thick undoped Ge and 0.1-μm-thick B-doped p^+ Ge with a doping density of 5×10^{18} cm^{-3}. The only difference between the two samples is the thickness of the linearly graded Si_{1-x}Ge_x buffer, which is 1 and 4 μm, respectively. Figure 3 shows the bright-field cross-sectional TEM image of the sample with the 4-μm-thick buffer. A large density of threading dislocations is clearly seen in the graded buffer region only. In other words, the top 0.9 μm pure Ge layer is of high quality with a very low threading dislocation density, beyond the ability of the TEM method.

In order to characterize the low dislocation density, Nomarski microscopy was used to observe a defect selectively etched pure Ge sample with the 4 μm graded buffer.
FIG. 4. Nomarski image of the etched Ge film with a 4 \( \mu m \) buffer indicating I-coated pits arising from threading dislocations. The threading dislocation density is estimated to be \( 5.4 \times 10^5 \) cm\(^{-2} \). The inset shows the as-grown sample surface. The surface roughness is determined to be 35 Å.

Figure 4 shows a typical result. The selective etchant used was a mixture of CH\(_3\)COOH, HNO\(_3\), HF, and I\(_2\).\(^{11}\) The threading dislocation density was obtained by counting the I-decorated pits on the surface which were determined to be \( 35 \) Å. These two samples were fabricated into Ge diodes 100 \( \mu m \times 200 \) \( \mu m \) in size. Plasma enhanced chemical vapor deposition SiO\(_2\) was used for passivation. Figure 5 shows \( I-V \) measurement results. The dark current density of 0.15 mA/cm\(^2\) based on our doping profile. Minor carrier lifetime \( \tau_p \) of \( 10^{-7} \) s was used in our calculation.

In summary, we have demonstrated the growth of high-quality steep graded SiGe layers and the fabrication of Ge \( p-i-n \) photodiodes by using both Sb surfactant mediation and graded buffer technique. By comparing with those samples using other methods, the Sb-mediated samples exhibit a lower threading dislocation density and smoother surface. Ge \( p-i-n \) diodes fabricated by this method show very low dark current density of 0.15 mA/cm\(^2\) at a reverse bias of 1 V. These results suggest the potential applications of integrated 1.55 \( \mu m \) Ge detectors on Si substrates.

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