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D. Fathy, C. W. White, and O. W. Holland

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Growth and characterization of epitaxial layers of Ge on Si substrates

D. Fathy, C. W. White, and O. W. Holland

Solid State Division, Oak Ridge National Laboratory, PO Box X, Oak Ridge, Tennessee 37831

Abstract

Thin single crystalline layers of Ge with atomically sharp boundaries have been formed epitaxially on (100) Si substrates. This was done by ^{74}Ge ion implantation into Si followed by steam oxidation. Using both Rutherford backscattering spectroscopy (RBS) and transmission electron microscopy (TEM), we have found that a Ge layer forms as a result of Ge segregated at the moving SiO_2 interface during steam oxidation. For a SiO_2 layer that has swept through the implanted region, essentially all of the Ge is snow-ploughed and no Ge is lost to the oxide layer.

The Ge layers and its two bounding interfaces, i.e., Ge/ SiO_2 and Ge/Si, have been characterized as a function of the implantation dose and energy. The thickness of the Ge layer formed is dependent on the implantation dose. Thicknesses from a fraction of a monolayer to greater than 50 monolayers of Ge can be formed on Si by this mechanism. Initially the Ge layer forms a coherent interface with the underlying Si with no misfit dislocations, and misfit dislocations only appear as the thickness of the film is increased.

Introduction

The pile-up and depletion effect of impurities in Si by a growing SiO_2 front have been studied for dopants such as P and As.^{1,2} The pile-up takes place when the impurity has a low solubility in SiO_2 and a slower diffusion rate in Si than the rate of oxide formation. In this case, the impurity is rejected from the SiO_2 and piles up at the Si- SiO_2 interface. The reverse of this situation leads to depletion and loss of impurities from the Si. Such segregation effects often lead to a change in the oxidation rate^{3,4,5} due to a change in oxidation kinetics at the Si/ SiO_2 interface.

The reflection of Ge atoms by SiO_2 has been used in this experiment to form an epitaxial layer of Ge-rich Si on the Si substrate. Different doses of Ge from 1×10^{14} to 1×10^{17} at/cm² were implanted in Si at different energies. Graded implants of Ge with energies of 35, 50, and 100 keV with total doses greater than 1×10^{17} at/cm² were also used. Following implantation, the samples were oxidized in a tube furnace at different oxidation times and temperatures. In the case of deep implants (160 keV), lower implantation doses lead to a laminar Ge-rich Si layer when irradiation doses equal or exceed 1×10^{17} at/cm². At high doses, polycrystalline Ge islands form at the SiO_2 /Si interface, often protruding into the SiO_2 . The results obtained so far indicate that shallow high-dose implants give a laminar layer provided that a high-energy low-dose implant is also used. However, as will be shown, the interfacial roughness is dependent on the dose used. No measurable difference was observed between the (100) and (111) implanted substrates, with the exception of the faster pile-up due to the faster oxidation rates in (111) Si. A similar effect was observed at high temperature (e.g., 1000°C). No pile-up was observed with dry oxidation of similar samples.

Experimental procedure

Single crystals of (100) and (111) orientation with resistivities (n-type) in the range of 1-15 ohm-cm were used in this work. The implantations were done at liquid nitrogen temperatures using $^{74}\text{Ge}^+$ ions with an average current density of 10 μA over the implanted area (5 cm²). The oxidation was done in a tube furnace at 900°C or 1000°C by passing steam or oxygen gas over the samples. In this way, oxide thicknesses in the range of 800-4000 Å were grown on the implanted samples. Transmission electron microscopy samples were prepared for high-resolution microscopy by a combination of mechanical polishing and Ar ion beam milling. The final ion beam milling was done at 2 keV. The RBS was done at 2 MeV using a scattering angle of 145°.

Observation

Rutherford backscattering data of Fig. 1a shows the random spectra for 100 keV implants to a dose of 1×10^{16} /cm² Ge ions. In the as-implanted samples, the position of arrows for Ge, Si, and oxygen refers to the energies associated with scattering from these elements at the surface. In this case, the top 1200 Å of the Si substrate is amorphized by the energetic Ge ions; this is measured from the TEM results. The Ge ions are distributed within this layer in a Gaussian profile with a mean projected range of ~ 720 Å.

Figures 1b and c show RBS random spectra after two different thicknesses of oxides have been formed on the 100 keV Ge-implanted samples. The oxide thicknesses are 210 and 350 nm respectively. The relation between the rate of SiO_2 growth and the consumption of Si is given approximately by $x_{\text{Si}} = 0.46x_{\text{oxide}}$.⁶ According to this relation for the sample in Fig. 1b, approximately 95 nm of Si is consumed. The thickness corresponds to an oxide layer roughly equivalent to the total range of the implanted Ge ions. In this case, a nearly total pile-up is visible. Figure 1c shows that by further growth of the oxide layer, the Ge is carried to greater depths within the Si matrix.

As shown in Fig. 1, Ge can be transplanted to substantial depths by oxidation. Also, the width of the Ge peak is resolution limited and suggests the formation of a Ge-rich layer of uniform thickness.

The effect of dose is shown in the micrographs of Fig. 2a,b,c. for the case of complete pileup. Up to 1×10^{16} , a laminar uniform layer of Ge is formed; see Fig. 2a. The thickness of Ge is roughly 30 Å (9 monolayer). For higher doses, the layer is no longer laminar; this is shown in Fig. 2b. The bounding interface between the Ge layer and the SiO_2 remains sharp, but more undulated. The Ge layer seems to form regularly spaced mismatch dislocations with the underlying Si substrate. A higher dose of 1×10^{17} is shown in Fig. 2c. The Ge layer is polycrystalline with Ge crystallites protruding in the SiO_2 layer. Only in such very high doses is Ge detected in the SiO_2 , presumably by the SiO_2 growing around the crystallites. High-resolution images for two doses shown in Fig. 2a and 2b are shown in Fig. 3a and b respectively.

Figure 1. 2 MeV, RBS random spectra of (a) as implanted with 100 keV Ge ions to a dose of 1×10^{16} at/cm²; (b,c) after steam oxidation in a tube furnace of 900°C. The pile-up of Ge and its push deeper into Si by the SiO_2 front is shown.

Figure 2. Cross-sectional micrograph showing the morphology of the Ge layer for different dose implants after oxidation and completed pile-up.

Figure 4a,b,c shows the result of graded implants. It was found that as a result of grading out the implantation at higher doses, a uniform thick layer of Ge can be formed. As shown in Fig. 4a, a planar layer of Ge is formed after a complete pile-up. The only defects observable from the transmission images are the misfit dislocations at the interface, lying in (110) plane parallel to the interface. A higher magnification image of this layer is shown in Fig. 4b. The extent of the Ge layer is indicated. Consecutive dislocations at the interface boundary are also encircled in this figure. Comparing Fig. 4b and 4c, with the images of Fig. 3a and b, it would appear that even though a much greater pile-up is obtained, the crystallinity and the flatness of the SiO_2/Ge remains the same. The occurrence of the misfit dislocations is increased. Measurements based on the distance between defects (encircled regions) indicates a 1 in 35 spacings (about 3% mismatch). RBS channeling results obtained from the sample shown in Fig. 4a gives a minimum yield of $\sim 35\%$ for the Ge layer. This is much higher than the results expected based on the number of defects observed in the TEM results. The inconsistency is thought to be due to inhomogeneous strain and the gradation of the lattice constant that exists across the film; similar observation was made for thin films of Ge on Si grown by molecular beam epitaxy.⁶

Figure 4. TEM images of the graded energy implants to a dose of 1×10^{17} at/cm². (a) Showing the uniformity of the epitaxial Ge layer. (b,c) High resolution image showing the presence of regularly spaced dislocation running parallel to the interface.

Summary

The pile up of Ge-implanted samples during thermal oxidation has been studied and it has been shown that:

- (a) Epitaxial layers of Ge-rich Si on Si, passivated with a thermal oxide, can be grown on Si using a technique that utilizes the segregation effect at an oxidizing interface.
- (b) The Ge layer and its two bounding interfaces, studied at high resolution, reveals a sharp transition between this layer and its two bounding SiO_2 and Si regions, with no evidence of an intermediate transition layer such as GeO_x .

In Fig. 3a, the extent of the Ge layer (30 Å) and its interface with the underlying Si are shown by the arrows. There is no evidence that any measurable thickness of GeO_x is formed between the Ge and SiO₂. This would have been detected in the TEM results as a change in the absorption contrast of the amorphous layer, due to a large difference that exists in the density of the SiO₂ to that of GeO_x (2.14 gr/cc for SiO₂ vs 4.3 gr/cc for GeO₂). In the Ge layer itself, there is no evidence of any faults, grain boundaries or precipitates associated with oxygen or Si agglomeration.

There is a small change in lattice parameters but no indication of mismatch dislocations in such very thin layers is evident. Figure 3b shows the results for thicker films (30 monolayers = 150 Å). In this case, the structure of the Ge/SiO₂ interface remains atomically sharp. At the Ge/Si interface, mismatch dislocations are visible. An estimate based on the spacing of visible dislocations shows a mismatch of the order of 2% (1 Si lattice mismatch in every 50 lattices of separation), which is half that expected between Si and Ge. The position of the mismatch dislocations, which are in the Si substrate, is indicated.

Figure. 3. High resolution images of two different doses (as indicated on the micrographs), showing the extent and orientation of the Ge layer.

- (a) The Ge layer is laminar with no observable defects and a coherent interface.
- (b) Misfit dislocations generated at the interface are indicated by letter D.

- (c) The layer itself is crystalline with the same orientation as that of the underlying Si.
- (d) The interface formed is completely coherent and the misfit dislocation density approaches the ~3% between Ge and Si for thicknesses of 20 nm.

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