Thin film germanium on silicon created via ion implantation and oxide trapping

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Abstract. We present a novel process for integrating germanium with silicon-on-insulator (SOI) wafers. Germanium is implanted into SOI which is then oxidized, trapping the germanium between the two oxide layers (the grown oxide and the buried oxide). With careful control of the implantation and oxidation conditions this process creates a thin layer (current experiments indicate up to 20-30nm) of almost pure germanium. The layer can be used potentially for fabrication of integrated photo-detectors sensitive to infrared wavelengths, or may serve as a seed for further germanium growth. Results are presented from electron microscopy and Rutherford back-scattering analysis, as well as preliminary modelling using an analytical description of the process.

1. Introduction

Silicon photonics is seen as the best platform to solve current connectivity issues associated with copper interconnects [1]. Silicon is transparent at optical communication wavelengths, and is ubiquitous throughout the semiconductor industry. Silicon photonic devices require on-chip photodetection which is usually achieved by integrating germanium onto the chip. In principle, germanium deposition is a scalable and low cost solution providing a high absorption coefficient for infrared wavelengths. All germanium photodetectors are grown currently via Molecular Beam Epitaxy [2], reduced pressure or ultra-high vacuum Chemical Vapour Deposition [3], or low-energy Plasma-Enhanced Chemical Vapour Deposition [4]. However, due to a 4% lattice mismatch between silicon and germanium, these processes require precise control to avoid excessive defects at the silicon/germanium interface and unacceptable dark current in subsequently fabricated photo-detectors [5]. Another method for introducing germanium into silicon is ion implantation. Previous work done on the oxidation of deposited silicon-germanium and pure germanium implanted into silicon has demonstrated that silicon is oxidized preferentially over germanium [6, 7]. Further, if the rate of oxidation exceeds the rate of germanium diffusion, the oxidation process leads to a “pile-up” of germanium at the surface. In this work we describe a novel method for germanium integration with silicon where implanted germanium is trapped between the growing and buried oxide layers on an SOI substrate. The process is shown schematically in Figure 1. We show experimentally that the germanium concentration is highly dependent on the oxidation process used, and that germanium concentrations as high as 87% can be achieved.
2. Experimental

Samples of single crystal 2.5 µm, or 220nm, silicon thin film thick SOI were implanted using Ge\(^+\) ions with fluences of \(3\times10^{16}\) cm\(^{-2}\), \(7\times10^{16}\) cm\(^{-2}\), or \(10^{17}\) cm\(^{-2}\). All samples were implanted at 33 KeV.

Subsequent to implantation, thermal oxidation was performed in a tube furnace. The length of oxidation was determined by consideration of the Deal-Grove Model [8]. This allowed us to produce samples with approximately equal oxide thickness despite the variation in oxidation temperature. For the 2.5 µm SOI samples were initially oxidized at 900°C for ninety minutes, 1000°C for 24 minutes or 1100°C for 9 minutes. The samples were then etched using buffered HF to remove the grown oxide. The etched samples were oxidized a second time at 900°C, 1000°C or 1100°C for 90 minutes (with each second oxidation temperature matching that from the first). The 220 nm samples were also oxidized twice and due to their initial and relative thin silicon thickness, the majority of the silicon was removed through these oxidations processes. This provides for a significantly increased germanium concentration compared to the thicker samples.

Confirmation of germanium “pile-up” was obtained via Transmission Electron Microscopy (TEM). Cross-sectional samples were prepared by mechanical polishing and argon ion milling. The germanium concentration of the samples was measured using Rutherford backscattering (RBS) with 1.5 MeV He\(^+\) atoms. RBS was performed after each oxidation step.

3. Results and Discussion

Figure 2a shows an example of a TEM image of a 2.5 µm sample implanted with a fluency of \(7\times10^{16}\) after an initial oxidation of 90 minutes at 900°C, while Figure 2b shows an example TEM image of a 220 nm sample implanted with a fluency of \(7\times10^{16}\) after a 45 minute oxidation at 1000°C. Figure 2a shows the “pile-up” of germanium whereas Figure 2b shows the trapping of germanium between the two oxide layers.

**Figure 1.** Schematic diagram showing the process resulting in germanium “pile-up”.

**Figure 2a.** TEM image of 2.5 µm sample

**Figure 2b.** TEM image of a 220 nm sample.
Figure 3 presents the experimental RBS data for a 2.5 µm sample after implantation with $1 \times 10^{17}$ cm$^{-2}$ Ge$^+$ ions and subsequently oxidized at 900 °C. The data was fit using a layer stack model similar to that shown in the right panel of Figure 1. Analysis of the RBS data after the initial oxidation for samples oxidized at 900 °C showed that they had the highest concentration of germanium in the SiGe layer, ranging from 72% to 80%. The samples oxidized at 1000 °C had germanium concentrations ranging from 45% to 53% and the samples oxidized at 1100 °C had the lowest germanium concentrations, ranging from 29% to 35%. These results demonstrate the sensitivity of the process to the balance between oxidation rate and Ge diffusion.

Figure 4 presents the RBS data of the same sample as in Figure 3, but after a second oxidation. As can be seen in the figure there is a much smaller silicon-germanium peak indicating a loss of germanium and the formation of a film of Si$_x$Ge$_y$O$_z$. The Si$_x$Ge$_y$O$_z$ is due to a high initial flux of oxygen which is normally reduced by the growing oxide layer [9], whereas the loss of germanium in the silicon germanium region is due to evaporation. These features are not apparent after only one oxidation due to the presence of a thin layer of silicon above the implanted germanium layer which acts as an initial oxide barrier. This barrier decreases the flux of oxygen to the oxidizing Ge-interface and prevents evaporation.

Analysis of the RBS data of the 220 nm samples indicated that the majority of the silicon was removed for the sample implanted with a fluency of $7 \times 10^{16}$ cm$^{-2}$ after the second oxidation at 1000°C. The peak concentration of the germanium in this sample was found to be 87%.

RBS data also indicated that the grown oxide on all samples in this study was thicker than that predicted from the Deal-Grove Model. This is due to a combination of three effects: the weakness of the silicon-germanium bond compared to the silicon-silicon bond, the lack of a stable germanium oxide as the germanium atom in the GeO that is formed is replaced by a silicon, and the suppression of interstitial injection [6, 9].

4. Preliminary Analytical Model

An analytical model is under development in order to offer a physical description for the thin film formation. The model uses finite differences to solve the diffusion equation with the boundary conditions being set so that there is zero flux of germanium out of the film. The initial condition is that of the solution to the diffusion equation in an infinite medium with an initial implantation fluency $Q$ and an effective diffusion coefficient for Ge of $D(T)$, where $T$ is the temperature of oxidation, and $C$ is the concentration of germanium at a point $x$ in the film at time $t$. The model is described by equation (1):
During the simulation the x-position of one boundary is moved to simulate the growing of the oxide layer. The movement of the boundary is based on a modified Deal Grove Model (to account for increased oxidation rates). This modification is used to describe the effect of the germanium at the oxide interface specifically the difference in the binding energies of silicon-silicon and silicon-germanium [3].

Results of the model of peak germanium concentration and film thicknesses for a 1.5 hour oxidation at 900°C are given in Table I. The model assumes $D$ is the only temperature dependent parameter, in Table I fixed for 900°C at $4.5 \times 10^{-18}$ cm$^2$s$^{-1}$.

$$C(x,t) = \frac{Q}{2\pi D(T)t} e^{-\frac{x^2}{4Dt}}$$

(1)

| Dose (cm$^2$) | Peak Germanium Concentration (%) | Film Thickness (nm) | D(cm$^2$s$^{-1}$) | Experimental Peak Concentration (%) |
|-------------|-------------------------------|--------------------|------------------|------------------------------------|
| 3x10$^{16}$ | 86                            | 15                 | 4.5x10$^{-18}$   | 80                                 |
| 7x10$^{16}$ | 90                            | 33                 | 4.5x10$^{-18}$   | 74                                 |
| 1x10$^{17}$ | 93                            | 50                 | 4.5x10$^{-18}$   | 77                                 |

As can be seen from the table the peak concentrations calculated from the model are greater than that of the experimentally determined concentrations. This is due to the effective rate of diffusion which according to this model is dependent only on the temperature. In reality the effective rate of diffusion is also concentration dependent meaning higher concentrations will lead a larger effective rate of diffusion. Further plans to improve the model will require incorporating this effect.

5. Conclusion and future work
The trapping of germanium between a growing and buried oxide layer has been demonstrated. The germanium has been found to be crystalline in nature and has concentrations greater for 220 nm SOI than for 2.5 µm SOI samples. Future work will involve developing a more rigorous model that will predict oxide growth rate as a function of germanium concentration at the interface as well indicating processing conditions which will provide for the maximum germanium concentration.

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