Germanium surface hydrophilicity and low-temperature Ge layer transfer by Ge–SiO₂ bonding

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Wafer bonding and layer transfer are two fundamental technologies in the fabrication of advanced microsystems. In the authors’ experiments, prior to Ge wafer bonding, the hydrophilicity of the germanium surface after wet chemical treatment and O₂/N₂ plasma activation is evaluated by contact angle measurement. The effects and mechanism of wet or dry treatments on the Ge surface roughness are also characterized. The results are used to tailor the Ge–SiO₂ direct bonding process. Finally, oxygen plasma activation for 10 s and B⁺/H⁺ coimplantation are employed to facilitate Ge–SiO₂ direct bonding and Ge layer transfer at a low temperature. In comparison with hydrogen only ion implantation using the same fluence, coimplantation of B⁺ and H⁺ decreases the layer transfer temperature from over 400–320 °C. © 2010 American Vacuum Society.

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I. INTRODUCTION

Silicon-on-insulator (SOI) substrates are used by the microelectronics industry for their improved circuit performance.1,2 Stress engineering and other techniques have propelled the technology in complementary metal-oxide semiconductor devices since the 90 nm technology node. However, device scaling in the sub-32 nm nodes necessitates materials innovation to achieve further mobility enhancement and increase the drive current of metal-oxide semiconductor field effect transistors. Recently, germanium-on-insulator (GeOI) has been proposed as a potential substrate for next-generation microelectronics technology because it combines the high carrier mobility of Ge along with the structural and electrical advantages rendered by SOI.3,4

Wafer bonding is an important technology to fabricate GeOI because of the flexibility in combining dissimilar materials.5 Proper cleaning and surface activation to obtain smooth hydrophilic surfaces are essential to achieving successful wafer bonding.6,7 However, processing of a Ge surface is a difficult task because the typical Si cleaning solutions etch roughen the Ge surface. Consequently, Ge–SiO₂ bonding at room temperature is difficult. Kim et al.8 characterized the high etching rates using standard cleaning solutions of SC1 and SC2 at room temperature and reported that high etching rates of over 100 nm/min are mostly accelerated by hydrogen peroxide (H₂O₂). Hence, the use of strong oxidants in the Ge surface treatment prior to wafer bonding is not recommended. Alternatively, GeOI can be produced by depositing a SiO₂ layer on Ge by chemical vapor deposition and subsequently bonding is conducted via the SiO₂/SiO₂ interface, for which reliable cleaning processes are available. Obviously, direct Ge–SiO₂ bonding is better and simpler, albeit more difficult. Chao et al.7 reported that a highly hydrophilic germanium surface obtained by an ammonium hydroxide (NH₄OH) treatment can lead to a high bonding strength after annealing at low temperature. However, the time of this wet chemical treatment must be carefully controlled; otherwise the root mean square (rms) surface roughness may go above 1 nm and the resulting materials are not suitable for room temperature bonding. The effects of different NH₄OH concentrations on Ge surface hydrophilicity are also unclear. Recently, Si and SiO₂ wafer prebonding treatment using plasma activation has been developed to obtain the maximum bonding strength after low temperature (<300 °C) annealing,9 but it is still not clear whether plasma activation can actually facilitate Ge–SiO₂ bonding.

By means of ion-cutting utilizing hydrogen ion implantation, many types of different thin films can be transferred onto different substrates after annealing at 400–600 °C.10 However, this high temperature process is not suitable for large area Ge thin film transfer. The bonded Ge/SiO₂ pair may separate or break into small pieces because of the large mismatch in the thermal expansion coefficients between Si

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and Ge (2.56 x 10^{-6} °C^{-1} for Si and 5.9 x 10^{-6} °C^{-1} for Ge). Therefore, a low-temperature Ge wafer bonding and layer transfer process is necessary for GeOI fabrication. Lin et al.\textsuperscript{16} transferred a single crystalline Ge film onto glass by hydrogen ion implantation with a fluence as high as 1.5 x 10^{17} cm^{-2}, which is much higher than the typical fluence of ~5 x 10^{16} cm^{-2}. This high ion implant introduces more damage to the crystal. Tong et al.\textsuperscript{12} reported another approach by using B^{+}/H^{+} coimplantation in low-temperature silicon layer transfer. Here, boron preimplantation enhances the exfoliation process by generating radiation-induced defects\textsuperscript{12} or changing the charge state of free hydrogen, which in turn alters the bubble nucleation and growth.\textsuperscript{13} So far, there have been few reports on B^{+} coimplantation in Ge and it is uncertain whether this method can be adopted for Ge layer transfer.

In this work, we investigate the Ge surface hydrophilicity systematically. Contact angles are determined from samples after undergoing seven different procedures and for each one, different dipping times are measured. These processes include a dry process under O_2/N_2 plasma and wet chemical processes involving diluted ammonium hydroxide (NH_4OH), hydrochloric acid (HCl), and hydrofluoric acid (HF). Based on the results, successful Ge–SiO_2 direct bonding is demonstrated after oxygen plasma activation. B^{+}/H^{+} coimplantation is subsequently employed to fabricate a GeOI structure at a temperature below 320 °C.

II. EXPERIMENT

Commercial φ100 mm (100) n-type Ge wafers with a resistivity of 0.02–0.2 Ω cm and (100) Si wafers covered with 1 μm thermal oxide layer were used. For surface hydrophilicity characterization, the Ge wafer was cut into 20 x 20 mm² strips, degreased, and cleaned with acetone and alcohol, rinsed in de-ionized (DI) water, and dried in a spin-dryer prior to surface treatment. Some of the Ge samples were exposed to O_2 and N_2 plasmas for 10–120 s using a dry approach by using B^{+} coimplantation in low-temperature Ge layer transfer. EVG810, the plasma and diluted NH_4OH. Afterwards, static contact angle measurements were performed on a Ramé-hart instrument using distilled water droplet (1 μl) as the medium at ambient humidity and temperature. Each sample was measured three times to determine average value and the maximum variation is less than ±10%.

In order to fabricate GeOI, the Ge wafers were implanted with 180 kV, 5 x 10^{15} cm^{-2} B^{+} and 55 kV, 6 x 10^{16}/cm^{-2} H^{+}. The implantation voltages were chosen to get similar implantation depths of B^{+} and H^{+} based on TRIM simulation. Because the implanted H^{+} ions diffuse slightly toward the damaged layer, the depth of the boron peak is a little bit shallower than that of the hydrogen peak. One of the implanted Ge samples was cut into small pieces and annealed between 200 and 450 °C for 30 min under N_2 to confirm the layer transfer temperature. Another coimplanted Ge wafer and SiO_2 wafer were cleaned and activated using O^{+} plasma for 10 s. Immediately thereafter, these two wafers were rinsed in DI water, dried, and bonded at room temperature. The bonded pair was further annealed at 200 °C for 2–3 h to enhance the bonding strength and finally annealed at 320 °C for 20 min to finish the Ge layer transfer. The cross section of the GeOI was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Raman spectroscopy and Hall-effect measurement were employed to characterize the transferred Ge film. The sample surface roughness was measured by atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

A. Ge surface hydrophilicity and roughness after dry and wet treatments

At room temperature, hydrophilic bonding is easier than hydrophobic bonding.\textsuperscript{5} There is a tendency that the more hydrophilic the surface, the stronger the bonding strength between the bonded wafers at room temperature. A straightforward method to determine the surface hydrophilicity is to measure the contact angle. It is obvious that the more hydrophilic the surface, the smaller the contact angle should be. Figure 1(a) shows the Ge wafer surface hydrophilicity after various surface treatments, with the most hydrophilic surface on the left. All the values given in the figure are mean values. Obviously, the most hydrophilic Ge surface is obtained after low-temperature O_2 plasma activation (the contact angle is 4.1° for only 10 s activation) whereas the most hydrophobic surface results after treatment in HCl (1:5). It is noted that the contact angles after all these treatments are time dependent. That is, the degree of surface hydrophilicity can be changed by varying the processing time. If the O_2 plasma activation time is more than 10 s, the Ge wafer surface will be so reactive that the water droplet completely spreads out and the contact angle will be close to the limit of detection (<3°). As shown in Fig. 1(a), both the plasma and diluted NH_4OH (1:5) are effective in facilitating surface hydrophilicity.

The mechanism of plasma activation of Si at low temperature consists of (a) the removal of contaminants on the surface and (b) the increase of the total surface area and consequently the amount of absorbed silanol groups (–OH).\textsuperscript{14} It is observed from our experiments that oxygen plasma activation has a larger effect on Ge than Si. This is because the calculated surface energy of Ge is always lower than that of Si.\textsuperscript{15} The common bond energies based on the Ge surface are always smaller than those based on Si. Thus, in the activation process, it is easier to break up bonds on the Ge surface and generate new dangling bonds to absorb electronegative atoms such as oxygen, nitrogen, or so on. After rinsing in DI water, the –OH groups can attack the surface and form the Ge–OH groups on the bare Ge surface or one with a native oxide. The polar OH groups also can form...
hydrogen bonds readily with water molecules. For silicon, a cluster consisting of two or three water molecules is energetically more favorable than an isolated water molecule. The improved hydrophilicity on the Ge surface can obviously enhance the spontaneous bondability between bare Ge and SiO₂. According to the contact angle results in Fig. 1(a), the diluted HCl process can yield a more hydrophobic Ge surface than diluted HF (even at higher HF concentrations). This may be attributed to that the acid has a removing selectivity of germanium oxides.

The phenomenon of wafer direct bonding originates from the intermolecular forces of attraction between two contacting surfaces. In order to conduct room temperature wafer bonding, the bonding surfaces should be sufficiently smooth and flat, with the rms surface roughness being less than 1 nm. Hence, we measure the sample surface roughness after each activation method and the results are shown in Fig. 1(b). For each sample, we choose three points as the scanned zones and the scanned size was 5×5 μm². For germanium, it is found that the rms surface roughness does not change evidently after N₂ plasma activation, diluted HF (1:4), and diluted HCl (1:10) treatment. Other treatment processes including O₂ plasma activation, diluted NH₄OH, and HCl (1:5) may lead to larger rms surface roughness, unless the processing time is controlled carefully. Using the O₂ plasma activation for 10 s, the rms surface roughness can be controlled to around 0.5 nm. Based on these results, we conduct successful Ge–SiO₂ direct bonding after O₂ plasma activation for 10 s. The bonding energy is enhanced after annealing at 200 °C for 2–3 h.

**B. Low-temperature Ge layer transfer**

Figure 2(a) shows the surface images of the Ge specimens after B⁺/H⁺ coimplantation and annealing at 340 °C for 30 min. Obviously, large bubbles and blisters emerge after annealing at this temperature. This is hardly an astonishing result by itself but it is interesting that no bubbles or exfoliated blisters are observed on samples after annealing at 330 °C for 30 min using optical microscopy. The results indicate that the threshold temperature for blister formation is around 330–340 °C. It is also worth noting that blisters are observed from Ge (implanted with hydrogen only) only after annealing at 400 °C or above. The size of these blisters in the coimplanted Ge is between 6 and 25 μm, which is much bigger than that in the Ge (implanted with hydrogen only) after annealing. This phenomenon suggests that the efficiency of transforming implanted H into H₂ increases greatly because of the presence of boron preimplantation.

In order to characterize the bubbles and blisters evolution process, AFM is used to measure the sample surface after annealing at 320, 330, and 340 °C, as shown in Figs. 2(c)–2(e). The results clearly reveal the evolution process of molecular hydrogen in the vacancies or platelets leading to a sufficiently high internal pressure to form microcracks or bubbles under the implanted layer. During annealing, the radius of small bubbles expands from ~0.5 μm to several micrometers. The relationship between the microcrack radius and annealing temperature/time model can be found elsewhere. Figure 2(b) depicts the cross-sectional TEM image of the Ge sample after annealing at 320 °C. Two main H-induced microcracks located on the (100) and (111) planes are observed. The surface roughness after splitting is determined by the length of the (111) microcracks that connect the two (100) microcracks.

Lee et al. reported that B preimplantation in Si can reduce the H-trap density, which in turn enhances H diffusion and the kinetics of blistering. In silicon, boron has been reported to facilitate blistering because less energy is required...
to break B–H bonds (2.04 eV) than Si–H bonds (2.5 eV).\(^{19}\) However, in Ge, the energy to break Ge–H bonds (1.9±0.2 eV) is not larger than that for B–H bonds.\(^{20}\) In silicon, each implanted H ion produces approximately ten Frenkel pairs (self-interstitials and vacancies) at implantation energies between 30 and 100 keV.\(^{16}\) For germanium, Monte Carlo simulation indicates that the generated vacancies are also around this value, but for each implanted B ion at 180 keV, ~550 vacancies and ~640 vacancies are generated in Si and Ge, respectively. Considering that most of the H atoms interact immediately with the implantation-induced vacancies or pre-existing dangling bonds, the minimum H fluence needed for Ge layer splitting may be a little higher than for Si.

Thus, we hypothesize that H atoms or ions play two roles: (1) passivation of the Ge dangling bonds in defects/vacancies created by ion implantation and (2) trapping and reaction with B atoms to form boron hydride.\(^{21}\) Those relatively concentrated H atoms or B–H bonds, upon annealing, can enhance \(\text{H}_2\) formation leading to complete exfoliation. In other words, both trapping mechanisms can increase the efficiency of the implanted H atoms in the splitting process.

Using oxygen plasma enhanced wafer bonding and B\(^+\)/H\(^+\) coimplantation, we are able to fabricate a GeOI substrate successfully at 320 °C. Figure 3(a) shows the SEM image of the GeOI structure. After layer transfer, the top Ge surface roughness measured by AFM and the rms roughness is about 11 nm, as shown in Figs. 3(b). The top Ge needs chemical mechanical polishing (CMP) to decrease the rms roughness. It can be reduced after etching in a SC1 solution (\(\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:7\)).\(^{11}\) Figure 3(c) shows the crystal quality of the transferred Ge film by TEM. In the bonding interface, the hydroxides may also be able to polymerize at low temperature to form a strong covalent bond:

\[
\text{Ge} - \text{OH} + \text{HO} - \text{Si} \rightarrow \text{Ge} - \text{O} - \text{Si} + \text{HOH}. \quad (1)
\]

In this process, the \(\text{GeO}_2\) or GeO may be generated as reaction byproducts in the interface and the solubility of \(\text{GeO}_2\) may lead to a rough bonding interface, also shown in Fig. 3(e).
Figure 4 shows two kinds of defects on the GeOI wafer surface. One type consists of regular round shape defects that can be enlarged after CMP or etching. These defects are probably induced by annealing the voids which always emerge in the weakly bonded interface. The other type of defects comes from unbounded points induced by particles. After oxygen plasma activation, the wafer surface is very active and it is easy to trap particles from the air. Both types of defects are fewer at the center of the GeOI wafer but have higher densities at the edge of the wafer. Improving the clean-room class can probably decrease the defect density.

Because GeOI has a good lattice match with III-V semiconductors such as GaAs, it is important to characterize the strain in the top Ge in GeOI. Figure 5 depicts the Raman spectra of GeOI excited by a 514 nm laser. The Ge–Ge mode peak \( \omega_{\text{Ge-Ge}} \) appears at 299.1 cm\(^{-1}\) in the GeOI structure, a little smaller than \( \omega_{\text{Ge-Ge}} (300.2 \text{ cm}^{-1}) \) in the bulk Ge. We can calculate the strain component \( \varepsilon_{xx} \) by using the dependence of the measured Ge–Ge mode:

\[
\omega_{\text{Ge-Ge}} = \omega_{\text{Ge-Ge}} + b_{\text{Ge-Ge}} \varepsilon_{xx},
\]

where the coefficient \( b_{\text{Ge-Ge}} = -400 \text{ cm}^{-1} \). Accordingly, we know that the top Ge in GeOI has 0.27% tensile strain. Since germanium has a larger thermal expansion coefficient than Si, the strain may be mainly introduced by the annealing process after bonding. We hope to mitigate the strain by optimizing the splitting conditions such as adjusting the rising and falling rates of the temperature.

The conductivity type and carrier mobility in the top Ge are monitored by Hall-effect measurement. For the as-split GeOI structure, the conductivity in the top Ge is \( p \)-type which is induced by boron implantation. The room temperature hole carrier mobility is around 150 cm\(^2\)/V s at a doping concentration of \( 6 \times 10^{18} \text{ cm}^{-3} \). This mobility is mainly reduced by the high doping concentration and high surface roughness. In order to activate the implanted boron, the GeOI substrate is annealed at 500 °C for 2 min in N\(_2\). Now the conductivity in the top Ge becomes \( n \)-type. In germanium, the boron ions are easily activated from its substitutional position to interstitial position. Thus, the top Ge in the GeOI regains its bulk doping type (\( n \)-type). The electron mobility is around 200 cm\(^2\)/V s and it is about 1.5 times higher than that in SOI fabricated by the same process (top silicon thickness is \( \sim 505 \text{ nm} \)). Based on the GeOI structure, the electron carrier mobility can be further improved by epilayer growth of other materials with higher mobility due to the good lattice match.
IV. CONCLUSION

In summary, the hydrophilicity of Ge is evaluated after various dry and wet surface treatments to obtain the optimal Ge wafer bonding conditions. Spontaneous bonding of the Ge–SiO2 pair is greatly improved after the O2 plasma activation. For the B+/H+ coimplanted Ge, 340 °C is a critical temperature for the formation of bubbles and subsequent blistering. Finally, the GeOI structure is fabricated at 320 °C, which is much lower than that for samples implanted only with hydrogen.

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