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Ammonium Hydroxide Effect on Low-Temperature Wafer Bonding Energy Enhancement

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A wafer prebonding treatment by ammonium hydroxide (NH_4OH) leading to a high bonding strength at low temperatures is presented in three material systems. After 200°C annealing, a surface energy of about 700 mJ/m^2 for thermal silicon-oxide bonding and of 1300 mJ/m^2 for plasma-enhanced chemical vapor deposition oxide bonding is realized. It is suggested that the lower ability of ammonia, the by-product of a polymerization reaction, to break the siloxane (Si-O-Si) bridging bonds appears to be responsible for the increase in surface energy in both silicon oxide bonding cases. NH_4OH treatment is also effective on bare germanium/silicon-oxide bonding with a surface energy of 800 mJ/m^2. A highly hydrophilic germanium surface obtained by this treatment accounts for the high bonding energy.
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As transistors are continuously scaled down, new materials and novel device/circuit structures have been suggested for further improvement of their electronic performance. Germanium on insulator (GeOI)[1-4] and three-dimensional integrated circuits[5,6] are among the most frequently discussed ones. GeOI has drawn much attention for its enhanced low field electron and hole mobility and minimization of parasitic capacitance compared to its conventional bulk silicon counterpart. However, the poor properties of germanium oxide make it unsuitable as buried insulator compared to silicon oxide. The cost of germanium and its brittleness also suggests silicon as the ideal substrate for GeOI wafers. Wafer bonding is one of the promising technologies for achieving this Ge/SiO_2/Si structure because of its flexibility in combining dissimilar materials. To avoid de-bonding in later processes such as Smart-Cut or chemical mechanical planarization (CMP), proper cleaning to obtain hydrophilic surfaces and high-temperature annealing are essential to achieve a high bonding energy. Germanium is known for its sensitivity to chemical solutions. The mismatch of thermal expansion coefficients between Si and Ge also complicates any subsequent thermal annealing processes. All these limitations make new approaches to the bonding of bare Ge/thermally oxidized Si highly desirable.

Chemical vapor deposited (CVD) oxides offer an alternative route to the fabrication of GeOI. With CVD oxide deposition on Ge, the bonding interface would be SiO_2/SiO_2 for which reliable cleaning processes are available. SiO_2/SiO_2 bonding is also of technological importance because silicon oxide is widely used for planarization in integrated circuits or as a masking material in the lithography process. Bonding of fully processed wafers is becoming a field of interest especially in the area of system-on-a-chip (SOC).[7] It is well known that SiO_2/SiO_2 bonding yields a substantially lower bonding energy than bare silicon bonding because of the difficulty of removing water existing at the bonding interface. The existing water molecules attack newly formed siloxane bonds and decrease the bonding energy.[8] Though higher temperature annealing achieves a high bonding energy, low-temperature annealing is still required for a number of bonding applications, such as dissimilar material bonding or 3D integrated circuits. Therefore, obtaining a sufficiently high bonding strength of the SiO_2/SiO_2 bonding wafer pairs at low temperatures for further processing is crucial.

A number of attempts have been reported for SiO_2/SiO_2 bonding. Plasma treatment prior to bonding has been reported to lead to a high bonding energy at moderate temperatures. Charged bonding surfaces and increased number of bonding sites have been suggested to be responsible for the increased bonding energy.[9,10] One drawback of plasma activation is that it may potentially be not suitable for fully processed wafers due to the antenna effect.[11,12] Conditioning wafer surfaces with chemical solutions prior to bonding has also been attempted. Nakanishi[13] studied SiO_2/SiO_2 bonding with hydrofluoric acid (HF) sprayed onto the bonding interfaces followed by applying high pressure. A bonding strength of up to 4.5 MPa was achieved at room temperature. It was speculated that an interlayer formed between the bonded SiO_2/SiO_2 is responsible for the high bonding strength. The bond strength strongly depends on the applied pressure, and applying high pressure might be undesirable for thin wafers, brittle materials (such as Ge), or sensitive MEMS devices. Considering the importance of SiO_2/SiO_2 bonding and increasing interest in GeOI substrates, we investigated the effect of ammonium hydroxide (NH_4OH) surface treatment on the bonding energy for thermal silicon oxide bonding, Plasma-enhanced chemical vapor deposition (PECVD) oxide bonding, and bare Ge/SiO_2 bonding. A possible mechanism for the observed enhancement in bonding energy will also be discussed.

Experimental

The experiments were performed with standard 4 in. p-type silicon wafers, and 4 in. n-type germanium wafers. On these silicon wafers, a thermal oxide layer of 100 or 300 nm thickness was grown. On some of the bare silicon wafers, a 350 nm thick PECVD oxide layer was deposited. To meet bonding requirements, the wafers with deposited PECVD oxide received a further CMP treatment in order to obtain a smooth, bondable surface.

Prior to bonding, the germanium wafers were cleaned with acetone and methanol for de-greasing, and the oxidized silicon wafers were cleaned with RCA solutions to remove metallic and organic contaminations and to obtain a hydrophilic surface. After rinsing in deionized water, some of the Si and Ge wafers were further treated with 29% NH_4OH diluted with deionized water at various ratios. Immediately following cleaning bonding in a micro-cleanroom setup[14] was performed. The wafer pairs were then annealed at 200°C or various other temperatures. Subsequently, the bonding energy was measured by the crack opening method[15] at room temperature.

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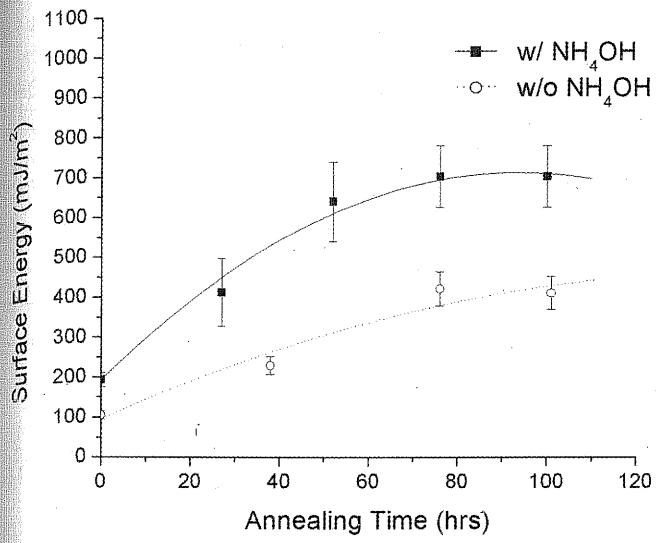

Figure 1. Comparison of the surface energy between NH_4OH treated thermal oxide bonding pairs and no NH_4OH treated ones. The annealing temperature was 200°C.

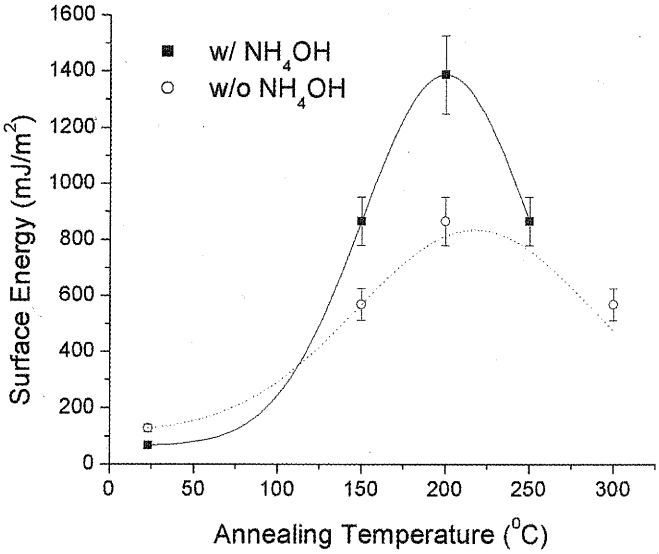

Figure 3. Surface energy of PECVD oxide capped silicon bonding pairs with and without NH_4OH treatment. The annealing time was 40 h.

Characterization of some bonded samples was performed by transmission electron microscopy (TEM) and secondary ion mass spectroscopy (SIMS). For facilitation of the SIMS detection, thinning one side of the bonded pair was performed after hydrogen and boron co-implantation before bonding.[16,17] Layer splitting took place under the identical thermal annealing cycle as for the other wafer pairs investigated.

Results and Discussion

The influence of NH_4OH cleaning on the surface energy is pronounced in these three systems. Figure 1 shows the surface energy of a thermal oxide bonding pair as a function of annealing time. The surface energy is increased from 425 to 700 mJ/m^2, which is high enough to allow further thinning processes involving CMP or Smart-Cut. After 250°C annealing, cross-sectional TEM (XTEM) samples could be prepared successfully for NH_4OH treated thermal oxide bonding wafers, as shown in Fig. 2. To the best of our knowledge, it is the first demonstration of a bonding interface of thermal oxide bonding pairs ever being prepared for TEM cross-sections at such low temperatures. The absence of interface voids in the picture is a result of voids disappearing under the TEM electron beam. A similar phenomenon was also observed in standard RCA cleaned bonding pairs and high temperature (500 or 900°C) annealed samples. The major difference of voids disappearing among these samples was the slower rate of disappearance for high temperature annealed wafer pairs, and the interface voids could therefore be captured during exposure (not shown). A deeper understanding of this sensitivity to the electron beam has not yet been developed.

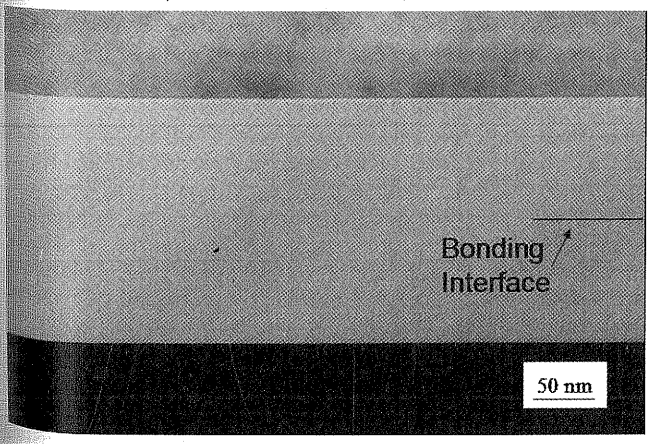

Figure 2. XTEM of thermal oxide bonding pair. The bonding interface is invisible and its position is indicated by the dark line.

Based on the success of thermal oxide silicon bonding, the ammonium hydroxide treatment was also applied to PECVD oxide bonding. The positive result is shown in Fig. 3 as a function of annealing temperature for an annealing time of 40 h. Generally, PECVD oxide bonding pairs with RCA cleaning as the only treatment showed higher surface energy than thermal oxides. This improvement was not due to a likely smoother surface obtained via the CMP process. Atomic force microscopy (AFM) measurements showed that the polished PECVD oxide wafer had a surface roughness of 5.9 Å, compared to 5.1 Å of a thermal silicon oxide wafer. Moreover, CMP polished thermal oxides showed similar bonding energies as the samples without CMP processing. The open structure of PECVD oxides is suggested to be responsible for the observed increase, and an in-depth discussion follows. Ammonium hydroxide treatment caused an even further enhancement in surface energy. Surface energies as high as 1300 mJ/m^2 were achieved after 200°C annealing for NH_4OH treated PECVD-oxide/PECVD-oxide bonding wafer pairs. A noticeable phenomenon was that the surface energy increased with increasing annealing temperature up to a maximum and then started to decrease as the temperature continued to rise. The effect appears to be associated with the accumulation of hydrogen diffusing out from the deposited PECVD oxide film degrading the bonding quality. The hydrogen gas formed big bubbles at the interface when these wafers were heated to higher temperatures. To avoid this problem, careful deposition and proper de-gas annealing prior to bonding is suggested.[18]

The improvement of bonding energy by NH_4OH treatment can be clearly visualized in the case of bare Ge/SiO_2 bonding case. Figure 4 shows infrared pictures of bare Ge/SiO_2 bonding pairs after annealing at 200°C for 16 h. The pair without NH_4OH treatment was mostly unbonded. Therefore, the surface energy was only measured on the NH_4OH treated pair, as shown in Fig. 5. A surface energy of 800 mJ/m^2 can be achieved after 100 h annealing at 200°C.

To understand the bonding mechanism associated with the NH_4OH treatment, SIMS measurements were performed on both thermally oxidized silicon bonding pairs and bare Ge/SiO_2 bonding

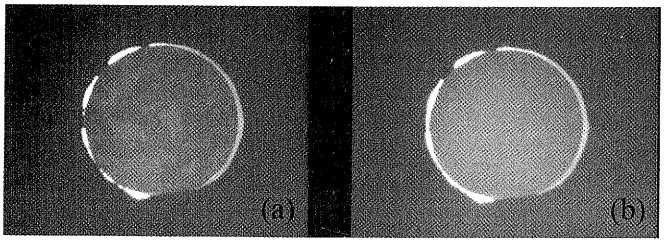

Figure 4. Infrared images of bare Ge/SiO_2 bonding pairs after annealing at 200°C for 16 h. (a) Pairs without NH_4OH treatment. (b) Pairs with NH_4OH treatment.

pairs. Figure 6 shows the nitrogen distribution in the thermal oxide bonding pairs. A substantial amount of nitrogen is observed in the top silicon layer of the NH_4OH treated sample. This high nitrogen density decreases with increasing distance away from the Si/SiO_2 interface. It is believed that the NH_4OH treatment introduces nitrogen atoms which then diffuse from the bonding interface to the top silicon wafer (but not to the bottom silicon wafer). These results indicate that formation of Si-N bonds does not occur nor account for the observed increase in the bonding energy in contrast to the case of Si_3N_4/Si_3N_4 bonding,[19] as nitrogen was mainly detected in the top silicon layer, instead of at the bonding interface.

The following mechanism for the improvement of the surface energy by ammonium hydroxide treatment in thermal oxide bonding is proposed. Ammonium hydroxide treatment leads to bonding surfaces terminated by amine $-NH_2$ and -OH groups. The electron-rich amine is a good acceptor for hydrogen bonds, and the basic character of amine causes proton transfer from acid groups, together with siloxane bond formation.[20] The reaction can be expressed as[21]

$$\text{Si-NH}_2 + \text{Si-OH} \rightarrow \text{Si-O-Si} + \text{NH}_3 \qquad [1]$$

This polymerization could be accelerated in high pH environment.[22] Ammonia would increase the pH of the surface-adsorbed water film,[23,24] and a faster polymerization reaction may be expected. The ammonium hydroxide treated thermal oxide sample required only 30 h to arrive at a saturated bonding energy value, while the RCA treated one needed almost 100 h.

In the above reaction, NH_3 is the reaction product instead of water as in the usual bonding mechanisms for hydrophilic silicon wafers. NH_3 can lower the energy required to rupture the siloxane

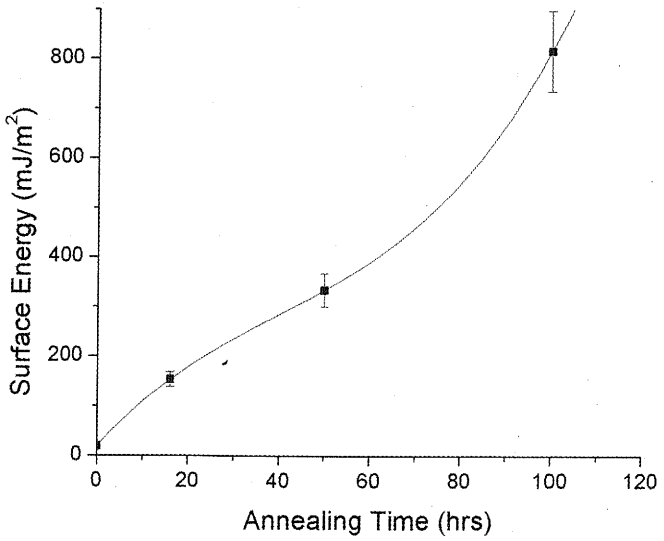

Figure 5. The surface energy of NH_4OH treated bare Ge/SiO_2 bonding pairs annealed at 200°C as a function of annealing time.

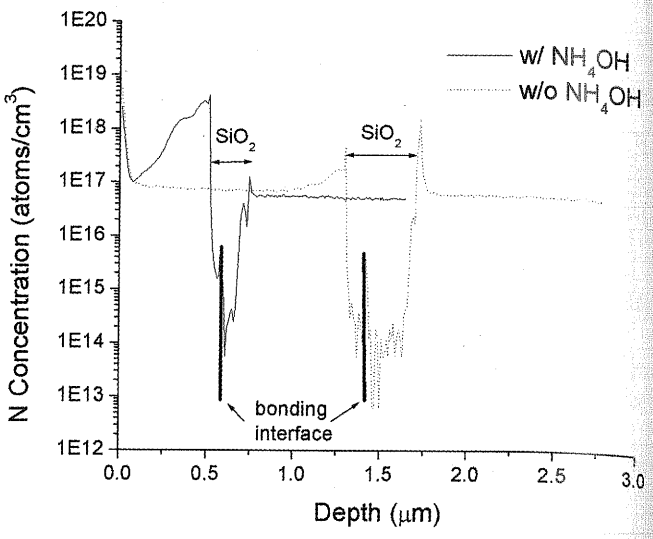

Figure 6. Nitrogen distribution in both NH_4OH treated and no NH_4OH treated thermal oxide bonding pairs by SIMS measurement.

bridging as water can, but has less tendency to do so than water molecules.[24] This means that NH_4OH soaked samples should have stronger bonds than RCA cleaned ones. The tetrahedral structure of ammonia inhibits diffusion into a silicon wafer. These large molecules would occupy some space at the interface retarding the formation of more siloxane bonds; thus the bonding energy of a NH_4OH treated oxide bonding pair is still lower than that of normal RCA-treated bare silicon wafer pairs. These ammonia molecules though can diffuse into the oxide layer. This occurs especially easily if the layer has a fairly open structure, as in the case of PECVD oxides. The strained bonds in PECVD oxide are also more easily attacked by ammonia and water molecules. The vacated space originally occupied by ammonia will then allow more siloxane bond formation, and a higher bonding energy can be obtained. SIMS measurement demonstrated a high nitrogen content in the top silicon wafer which was implanted with hydrogen for SIMS sample preparation, but no equivalent peak was observed in the mating bonded wafers. This unexpected observation is most likely associated with the implantation-induced damage in the hydrogen-implanted wafer, allowing ammonia molecules to move into the vacant spaces.

In bare Ge/SiO_2 bonding samples, no abundant nitrogen concentration was detected in the SIMS analysis, in contrast to the SiO_2/SiO_2 case. The high surface energy of Ge/SiO_2 system is attributed to a highly hydrophilic surface as a result of NH_4OH treatment. The highly hydrophilic surface could be visually observed after cleaning, especially in contrast to the hydrophobic surface of hydrogen-implanted Ge wafers. How ammonium hydroxide alters the surface chemistry of germanium will require further detailed chemical analysis.

With the suggested ammonium hydroxide chemical surface cleaning, a high surface energy can be obtained in thermal oxide, PECVD oxide, and bare Ge/SiO_2 bonding systems, and their various applications had been realized. Given a sufficient bonding energy by NH_4OH treatment, successful layer transfer at low temperatures has been demonstrated on bare germanium on oxidized Si (GeOI),[4] silicon on quartz[25] and InP on silicon with PECVD oxide as interlayer.[26] These results verified that an ammonium hydroxide treatment is a viable approach for low temperature wafer bonding for various applications requiring a sufficiently high bonding energy.

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