HTML ABSTRACT + LINKS

Fluorine-enhanced low-temperature wafer bonding of native-oxide covered Si wafers

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The bonding energy of bonded native-oxide-covered silicon wafers treated in the $HNO_3/H_2O/HF$ or the HNO_3/HF solution prior to room-temperature contact is significantly higher than bonded standard RCA1 cleaned wafer pairs after low-temperature annealing. The bonding energy reaches over 2000 mJ/m^2 after annealing at 100 °C. The very slight etching and fluorine in the chemically grown oxide are believed to be the main contributors to the enhanced bonding energy. Transmission-electron-microscopic images have shown that the chemically formed native oxide at bonding interface is embedded with many flake-like cavities. The cavities can absorb the by-products of the interfacial reactions that result in covalent bond formation at low temperatures allowing the strong bond to be retained. © *2004 American Institute of Physics*.
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Direct bonding of native-oxide-covered silicon wafers (termed bare silicon wafers) has many applications, such as in the fabrication of sensors and actuators.[1] Commercially available silicon wafers are usually covered with a thin native oxide layer of ~10 Å in thickness with a smooth surface having a rms roughness of about 1 Å. These wafers are adequate for direct wafer bonding. The silicon wafers are usually cleaned in standard RCA1 ($NH_4OH:H_2O_2:H_2O$) and RCA2 ($HCl:H_2O_2:H_2O$), or concentrated HNO_3 or $H_2SO_4:H_2O_2$ solutions followed by rinsing in de-ionized (DI) water to form Si–OH groups on the surfaces. When two silicon wafers are brought into contact, they are readily bonded via the water molecules that are hydrogen bonded to the polar OH groups on the two mating surfaces.[2] Upon annealing at elevated temperatures, the interface water molecules diffuse out most likely through the native oxide to the bulk Si where they react to form SiO_2 and hydrogen:

$$Si + HOH \rightarrow SiO_2 + H_2. \quad (1)$$

Then, the polymerization reaction takes place between the silanol groups of the mating surfaces to form siloxane bonds by

$$Si\text{–}OH + HO\text{–}Si \leftrightarrow Si\text{–}O\text{–}Si + H_2O. \quad (2)$$

The bonding energy can reach about 1.2 J/cm^2 after annealing at 150 °C.[3] In order to obtain a stronger bond for applications such as leak-free sensors, usually annealing above 1000 °C is necessary. However, the high temperature treatment is not compatible with bonding of processed silicon wafers that are thermally sensitive. Therefore, it is highly desirable to develop methods to yield a strong bond at low temperatures.

Several different methods have been developed for low temperature bonding of bare silicon wafers. A surface treatment of plasma of oxygen or other gases in reactive ion etch mode prior to room temperature bonding can significantly increase the bonding energy at low temperatures.[4–6] It has been reported that an oxygen plasma treatment of native-oxide-covered silicon wafers can increase the bonding energy to about 1500 mJ/m^2 at room temperature.[6] However, the plasma treatment introduces a damage layer in the near surface region that may degrade the device performance.[7] Although a dip in concentrated 70% nitric acid can enhance the bonding energy of bonded bare silicon wafers at low temperatures,[8] many voids developed at the bonding interface upon annealing due to the release of the trapped gaseous nitrogen monoxide in the chemically grown oxide.[9]

In this letter, we report the use of the mixtures of an oxidizing agent (HNO_3) and an oxide-etching agent (HF) to treat bare silicon wafers prior to bonding. Bonding energy close to the bulk silicon fracture energy has been obtained after annealing at 100 °C.

HNO_3 and HF mixtures are well-known solutions for etching silicon wafers through oxidizing silicon by HNO_3 followed by etching the oxide off by HF simultaneously. Previously, it has been reported that low HF concentration (0.025%–0.1%) in concentrated (70%) HNO_3 can effectively clean silicon surfaces,[10] and has been used for wafer cleaning prior to DI water rinse and room temperature bonding.[11] Only a small improvement in bonding energy at low temperatures was observed.[11] In this study, a mixture of water-diluted HNO_3 and low concentration HF, termed as $HNO_3/H_2O/HF$, was employed to treat native-oxide-covered silicon wafers. For comparison, a solution of concentrated HNO_3 mixed with low concentration HF (termed HNO_3/HF) was also used. When bare silicon wafers were removed from either mixture, the chemical solution does not stick on the wafer surfaces. It is probably due to the Si–F termination on the chemically formed oxide surfaces.[11,12] However, the fluorine passivation is immediately lost by rinsing in water, and the surface becomes hydrophilic as a result of substituting Si–F groups with Si–OH groups in water.[13] To preserve the Si–F termination, the bare silicon

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wafers were immediately bonded without subsequent DI water rinse after the treatment.

Silicon wafers used in this study were (100), boron doped *p*-type with resistivity of 1–10 Ω cm. Semiconductor grade 70% HNO_3, 29% NH_4OH, and 49% HF were employed. All wafers were cleaned in a modified RCA1 solution ($H_2O:H_2O_2:NH_4OH=10:1:1$) for 15 min at 70–80 °C. After rinsing in DI water, they were dipped in $HNO_3/HF(HNO_3:HF=1:1\times10^{-3})$ or $HNO_3/H_2O/HF(HNO_3:H_2O:HF=1:20:2\times10^{-4})$ mixture at 70–80 °C for about 5 min. Without DI water rinse the wafers were bonded in air at room temperature after spin-drying. The bonding energy was measured using the crack-opening method. The bonding interfaces were studied by transmission electron microscopy (TEM) of cross sections in edge-on orientation and inclined to the electron beam. The surface roughness of treated bare silicon wafers was analyzed by a Nanoscope III atomic force microscope (AFM).

Bare silicon wafers treated in HNO_3/HF mixture did not bond to each other spontaneously. For bonding of these wafers an external pressure had to be applied and there were some trapped gas-bubbles at the bonding interface. In contrast, the bonding of wafers treated in the $HNO_3/H_2O/HF$ mixture was spontaneous when they were brought in contact.

The observed room temperature bonding behaviors may be explained by the change of wafer surface roughness during the surface treatment. AFM measurements over a $1\times1\ \mu m^2$ area for bare silicon wafers treated in $HNO_3/H_2O/HF$ and HNO_3/HF mixtures were performed. The $HNO_3/H_2O/HF$ treated sample shows a very smooth surface with a rms roughness of 1.5 Å indicating no change in surface roughness by the $HNO_3/H_2O/HF$ treatment. In contrast, a significant surface roughening of bare silicon wafers treated in HNO_3/HF mixture was observed. An island-like structure uniformly distributed over the whole silicon surface was observed, which resulted in a rms roughness of about 7.9 Å. The measured surface roughness results are consistent with the report of Messoussi *et al.*,[12] but different from Ljungberg's[11] and Takizawa's[10] that reported no roughening.

The differences of the surface roughness after the two treatments can be attributed to the different etch rates of bare silicon in the two solutions. Since the etch rate of thermal oxide in the two solutions is negligible, the etch rate of bare silicon was determined by measuring the step height of a thermal oxide window on a silicon wafer using AFM. The etch rate of the bare silicon wafers was ~26 Å/min in HNO_3/HF and only ~1 Å/min in $HNO_3/H_2O/HF$ solution. The small gas bubbles of gaseous nitrogen monoxide on the wafer surfaces and the significantly higher etch rate of silicon in HNO_3/HF solution can result in selective etching on silicon surface resulting in the surface roughening.

The bonding energy as a function of annealing temperature for $HNO_3/H_2O/HF$ treated wafers bonded in air is shown in Fig. 1. For comparison, the bonding energies of bare silicon wafers treated by standard RCA1 solution and by 70% HNO_3 solution are also shown. Compared with the standard bonded pair or 70% HNO_3 treated pair the bonding energy of the $HNO_3/H_2O/HF$ treated pair is significantly enhanced and is close to the bulk silicon fracture energy after annealing at 100 °C. A similar bonding energy was also observed for bonded wafer pairs that were HNO_3/HF treated prior to bonding. However, the rough surface of the silicon wafers after HNO_3/HF treatment makes bonding nonspontaneous and results in interface bubbles.

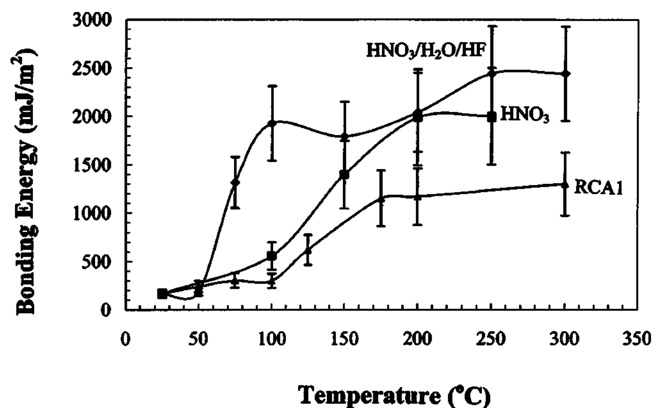

FIG. 1. Bonding energy as a function of annealing temperature for bonded wafers with $HNO_3/H_2O/HF$ treatment (diamonds), standard RCA1 clean (triangles), and 70% HNO_3 treatment (squares).

It is known that at a given annealing temperature, the bonding energy of a bonded hydrophilic silicon wafer pair reaches its saturation value after a certain period of time.[3] For the $HNO_3/H_2O/HF$ treated bonded pairs the bonding energy at 100 °C has reached over 1000 mJ/m^2 after annealing for 5 h and is strong enough for many applications. The bonding energy reaches its saturation value of ~2.4 J/m^2 in ~20 h, and the wafers were usually fractured when inserting a razor blade at the crack opening measurements.

The interfaces of bonded pairs were studied by cross-sectional TEM analysis. Figures 2(a) and 2(b) show the bonding interface for wafers treated in $HNO_3/H_2O/HF$ mixture and annealed at 350 °C for 45 h. As shown in Fig. 2(a) there is an amorphous oxide layer at the bonding interface with about 2 nm in thickness. Close inspections of the TEM

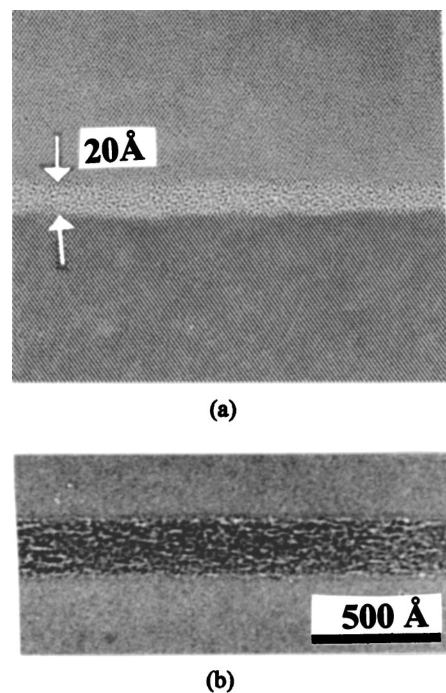

FIG. 2. TEM images of the bonding interface for wafers treated in $HNO_3/H_2O/HF$ mixture and after 350 °C, 45 h annealing. (a) High resolution electron microscopy (HREM) cross-section image; (b) image of the interface 10° inclined to the electron beam at underfocus.

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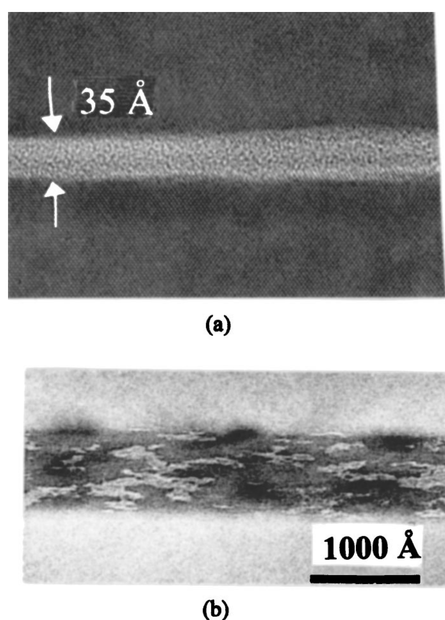

FIG. 3. TEM images of the bonding interface for wafers treated in HNO_3/HF mixture and after 300 °C, 45 h annealing. (a) HREM cross-section image; (b) image of the interface inclined 15° to the electron beam at underfocus.

images lead to the discovery of cavities in the chemically formed interface oxide layer. More detailed structures of the interface were detected by tilting the sample to different inclinations to the electron beam. Images showing the projections of interfaces inclined to the electron beam were taken at relative large underfocus values (0.5–1.3 μm) with cavity islands appearing bright in darker surroundings. Figure 2(b) is an image of the 10° tilted interface showing small cavity islands with lateral dimension in the order of 10 nm that is larger than the cavities (~3 nm) observed in the standard hydrophilic Si/Si bonded interface. The cavities lie across the whole interface layer rather than at the middle of the bonding interface. Similar observations were also obtained for bonding pairs with HNO_3/HF treatment and annealed at 300 °C for 45 h, see Fig. 3. However, as shown in Figs. 3(a) and 3(b), the interface layer is relatively thicker (about 3.5 nm) and the cavities are much larger (~100 nm) and flake-like than that observed in Fig. 2(b). This observation is contrary to Ljungberg's result of oxide-free on HNO_3/HF treated bare silicon surfaces from XPS analysis.[11]

Compared with 70% HNO_3 treated bonding pairs in Fig. 1, it appears that the existence of fluorine in the solutions and in the chemically formed oxide is essential in the significant enhancement of bonding energy at low temperatures. The simultaneous oxidation and etching on silicon surface to form oxide in $HNO_3/H_2O/HF$ solution continuously provides the very clean, fresh, and activated surfaces. We speculate that the fluorine promotes the formation of covalent bonds at the bonding interface during annealing at low temperatures of bonded bare silicon wafer treated by $HNO_3/H_2O/HF$ or HNO_3/HF. The polymerization reaction (2) shown above is reversible at temperatures less than ~425 °C. Therefore, most covalent Si–O–Si bonds will convert back to hydrogen bonding of Si–OH groups at temperatures lower than ~425 °C. If the water generated by the above reaction can be removed the covalent bonds can then be retained resulting in a covalent bonding.[3] It has been reported that fluorine incorporation in silicon oxide causes Si–O–Si ring breaking and changes of the silicon oxide network structure toward fluorinated silicon oxide with large size rings, lower density, facilitating a higher diffusion rate of impurities and enhanced moisture absorptivity.[14] This observation appears to be supported in this study by the formation of flake-like cavity islands in the interface oxide. By fluorinating the interface oxide prior to bonding, the by-products, water and hydrogen, of the above reactions (2) and (1), respectively, at the bonding interface can be absorbed effectively by the low-density fluorinated oxide leading to a covalent bonding.

Similar to the bonded wafers treated in concentrated (70%) HNO_3, small bubbles generated at bonding interface upon annealing at temperatures as low as 150 °C have also been observed in bonded pairs treated in HNO_3 diluted with water. In contrast, with the addition of small amount of HF, the $HNO_3/H_2O/HF$ treated bonded pairs are essentially bubble-free after annealing up to 300 °C. Considering that the bubbles are mainly formed by hydrogen and out-gassing of nitrogen monoxide in the silicon oxide during annealing, the addition of small amount of HF may significantly reduce the absorption of nitrogen monoxide and forms more open structured fluorinated silicon oxide thus preventing interfacial bubble generation.

In summary, the bonding energy of bonded bare silicon wafers treated in the $HNO_3/H_2O/HF$ or the HNO_3/HF solution prior to room-temperature contact reaches silicon fracture energy after annealing at 100 °C. The very slight etching and fluorine in the chemically grown oxide are believed to be the main contributors to the enhanced bonding energy. TEM images have shown that the chemically formed native oxide at bonding interface is embedded with many flake-like cavities. The cavities can absorb the by-products of the interfacial reactions that result in covalent bond formation at low temperatures allowing the strong bond to be retained.

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