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Annealing Temperature-Dependent Interfacial Behavior of Sequentially Plasma-Activated Silicon Bonded Wafers

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***Abstract*—The annealing effects of voids, amorphous layer, and bonding strength in the sequentially plasma-activated silicon/silicon bonded interface were investigated. The interfacial silanol groups and water were condensed and removed, respectively, below and above annealing at 150 °C. About 400 °C, the bonding strength was reduced because of the increased void density associated with the plasma-induced surface defects and the increased thickness of interfacial silicon oxide. The increase of the interfacial thickness layer after annealing was confirmed by high-resolution transmission electron microscope and detected as silicon oxide using the electron energy loss spectroscopy. The surface roughness and contact angle were measured to explain the influence of plasma processing parameters on the interfacial behavior after annealing. While the water contact angle increased with the increase in the O_2 reactive ion etching (RIE) time, the surface roughness was initially decreased and then increased. The surface activation with 400-W O_2 RIE plasma induced defect sites such as nanopores and craters. This study indicates that the O_2 RIE plasma time and power have to be as low as possible to reduce surface roughness and defects but have to be high enough to properly activate the surface with enough surface energy to achieve high quality of Si/Si interface. [2010-0124]**

***Index Terms*—Annealing, electron energy loss spectroscopy (EELS), interfacial amorphous layer, sequentially plasma-activated bonding (SPAB), surface roughness, void density, water contact angle.**

A room temperature direct bonding method called sequentially plasma-activated bonding (SPAB) has been developed to address the challenges in high-temperature bonding [1], [2]. Examples of the challenges are fractures in materials due to coefficient of thermal expansion and lattice mismatch and also gas formation in the cavities between the wafers. In the SPAB, smooth surfaces are activated using oxygen (O_2) reactive ion etching (RIE) plasma followed by nitrogen (N_2) microwave (MW) radicals and bonded in a clean room with hand-applied pressure. The RIE plasma activation results in clean surfaces, with a large number of dangling bonds (free bond), which are free from native oxides, contaminations, and particles. Then, the N_2 MW radical treatment increases the reactivity of the surfaces. Unlike other typical plasma bonding technologies (i.e., O_2 RIE) that require heating at 200 °C–300 °C [3], the SPAB allows spontaneous bonding at room temperature and provides an interface with high bonding strength equivalent to the bulk materials without annealing. This is due to the strong adhesion between the highly reactive surfaces covered with sequential plasma-induced oxides and nitrides [1]. Therefore, it has a wide range of potential applications in the integration of temperature-sensitive microelectromechanical systems, such as resonators and accelerometers, and microfluidic devices.

One of the major issues in plasma-based bonding technologies is the interfacial voids (i.e., unbonded regions), which control the reliability such as bonding strength and hermeticity [4]. Voids mainly attribute to the presence of surface particles, contaminants, reaction by-products (i.e., H_2O and H_2), and plasma-induced defects. While plasma-induced voids can be controlled using optimized plasma parameters, nucleation of voids may accelerate during fabrication process flow at higher temperatures in some applications. For example, in the smart-cut process, bonded specimens go through up to a 600 °C heating step to fabricate silicon-on-insulator substrates [5]. It has been reported that the bonding strengths of the silicon (Si) bonded wafers in the SPAB were reduced after annealing in air [2]. This reduction was thought to be due to the formation of voids and brittle oxide layers across the interface. While the quality (i.e., tensile strength) of the bonded interface was investigated after annealing, the cause of the reduction of bonding strength after annealing was not investigated. This letter reports Si/Si interfacial behavior in terms of void density, bonding strength, and nanointerfacial thickness at different annealing temperatures. The water contact angle and roughness of silicon surface are also studied in order to gain insight into the characteristic behavior of the interface.

P-type single side mirror polished CZ grown (100) silicon wafers with a thickness of $525 \pm 25\ \mu$m were used for the experiments. A wafer level hybrid plasma bonding (HPB) system was used for SPAB. Details of the HPB system can be found elsewhere [1]. The wafer surfaces were sequentially activated at low vacuum pressure using a 13.56-MHz oxygen (O_2) radio-frequency RIE plasma followed by 2.45-GHz N_2 MW radicals at room temperature. Silicon was processed by a 200-W O_2 RIE plasma for 60 s at 100 Pa followed by 2000-W N_2 MW radicals for 30 s at 100 Pa unless otherwise mentioned. These plasma parameters were chosen from that of the best bonding results obtained in the previous studies of SPAB [1], [2]. Fig. 1 shows the infrared (IR) transmission images of Si/Si bonded wafers (a) before annealing and after annealing at (b) 400 °C, (c) 600 °C, and (d) 800 °C in air for 4 h. The ramping rate for annealing was 200 °C/h. The interfaces were observed after each annealing step. Plasma-induced voids, as well as thermal voids (caused by annealing), were observed at the interfaces. This is a typical example of reproducibility of void nucleation at the Si/Si bonded interface in the SPAB before and after annealing. While the plasma-induced voids were not significantly changed up to 400 °C annealing, the thermal voids were nucleated in between 400 °C and 600 °C. The plasma-induced voids were caused by surface defects (i.e., nanopores and craters) and increase in surface roughness during plasma activation [6]. These issues can be addressed through proper choice of plasma processing parameters and bonding in particle-free clean rooms. The thermal voids were grown preferentially at plasma-induced defect sites on the activated surfaces. The nucleation of thermal voids is attributed to the hydrogen gas generated from the oxidation of silicon by the following: 1) adsorbed water onto the plasma-activated silicon surfaces and 2) water produced at the bonded interface by silanol bond condensation [3]. Coalescence and disappearance of the thermal voids were observed (red arrows in Fig. 1) at 800 °C and then remain unchanged up to 900 °C (not shown). This accumulation of voids should not happen unless an oxide should flow in the microvoid across the interface. Consistent results of the viscous flow of silicon oxide have been reported above 800 °C for hydrophilic bonding [5].

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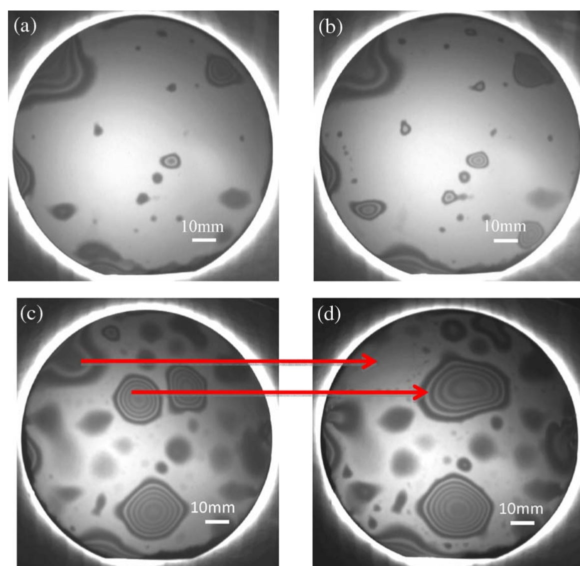

Fig. 1. IR transmission images of bonded Si/Si wafers (a) before annealing and after annealing at (b) 400 °C, (c) 600 °C, and (d) 800 °C.

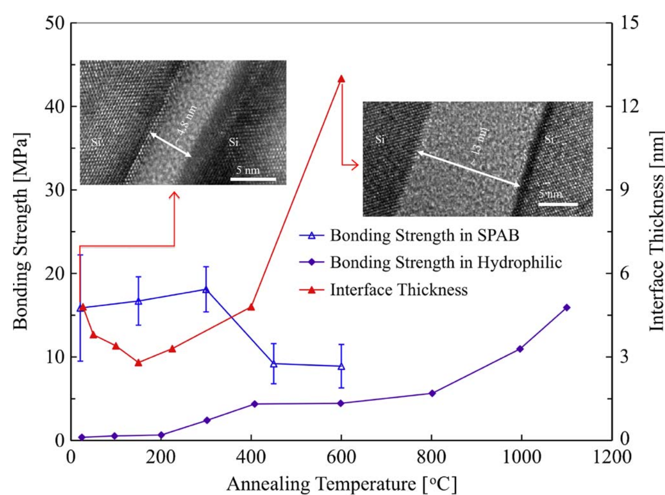

Fig. 2. Interfacial thickness (using HRTEM) and bonding strength of Si/Si in the SPAB compared with hydrophilic bonding strength [7] as a function of annealing temperature.

Fig. 2 shows the interfacial thickness and bonding strength of Si/Si in the SPAB compared with hydrophilic bonding strength (as reported in [7]) as a function of annealing temperature. To measure the bonding strength, specimens of 10×10 mm^2 sizes were glued with copper jigs and then pulled apart by using a tensile tester from Instron. The average bonding strengths for three specimens were plotted with the standard deviations. Since a considerable change in the macrovoid density was not detectable up to 400 °C from the IR images, the bonded interface was extensively investigated using high-resolution transmission electron microscopy (HRTEM) after precise annealing steps (at 50 °C, 100 °C, 150 °C, and 225 °C for 1 h in each step in air). In addition, it has been reported that the higher the O_2 RIE power, time, and pressure, the higher the surface defects [8]. Therefore, an O_2 RIE plasma with a low power of 50 W for 15 s at 60 Pa and 2500-W nitrogen radicals for 30 s at 60 Pa were used for the surface activation to reduce the plasma-induced surface damage. This reduction of surface damage allows insight into the influence of precise annealing on the interfacial behavior. A few-nanometer-thick amorphous layer was observed by HRTEM at different annealing steps as shown in Fig. 2. The interfacial thickness reduced with the increase in the annealing temperature up to 150 °C and then increased up to 600 °C. The decreased thickness of the amorphous layer up to 150 °C might be correlated to the condensation of silanol [Si–OH] to form siloxane bonds [Si–O–Si] across the interface. The increased thickness of the amorphous layer above 150 °C may be attributed to the diffusion of interface waters (both adsorbed and produced from condensation of silanol) to the bulk to oxidize silicon. These results are consistent with those observed by X-ray reflectivity and Fourier transform IR spectroscopy [9].

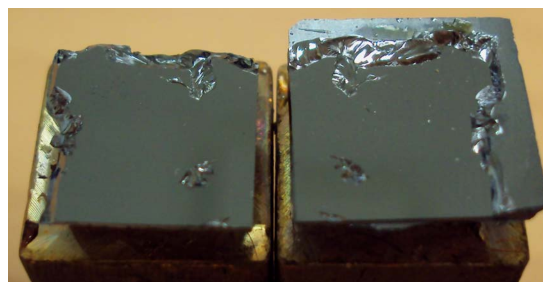

Fig. 3. Fracture images of Si/Si interface in the SPAB before annealing. Bulk fractures are evident.

The annealing temperature-dependent interfacial thickness is comparable with the bonding strength of Si/Si in the SPAB and that of the hydrophilic bonding method. The bonding strength in the SPAB before annealing was about the same as that in the hydrophilic bonding at 1100 °C [7], which was about 10–20 MPa. In the SPAB, from room temperature to 300 °C, the bonding strengths were varied in the range of 15–18 MPa and then decreased. The difference in the standard deviations of the bonding strength before and after annealing was due to the discrepant roles of the plasma-induced voids and nonreacted OH molecules at the interface and their rearrangements. The reduction in the bonding strength after 300 °C is attributed to the sudden increase in the void density, as shown in Fig. 1. Furthermore, the reduction in the bonding strength at higher annealing temperature was due to brittle nature of the thicker interfacial layer (Fig. 2). This phenomenon was investigated by the tensile pulling test of the bonded interface before and after annealing. While interfacial debonding was observed for the 600 °C annealed interface (not shown), bulk fractures were confirmed in Si before annealing (Fig. 3). On the other hand, in hydrophilic bonding, the bonding strength increased with the increase in annealing temperatures at different slopes. The hydrophilic bonding results from the interaction between silanol (Si–OH) groups formed on the surface and requires annealing at high temperatures in order to achieve a bonding strength equivalent to that in the SPAB. In the SPAB method, silicon wafers were spontaneously bonded due to the reaction between OH groups through highly reactive oxynitride (O_xN_y) layers on the activated surfaces without annealing.

In order to confirm the composition of the interface amorphous layer, a high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) were performed using a field-emission TEM (JEOL 2100F, $C_s = 0.50$ mm) in conjunction with a Gatan Enfina 1000 spectrometer, operating at 200 kV. The energy resolution was about 1.0 eV. The probe conditions for EELS were 1.0- and ~0.3-nm diameters, respectively, in TEM and STEM. A semiangle convergence in the STEM was 14 mrad. All spectra were calibrated to the zero-loss peak and deconvoluted to remove multiple scattering influences. This was the same specimen used for the HRTEM after 600 °C annealing, as shown in Fig. 2. Low-loss EELS profile was recorded as shown in

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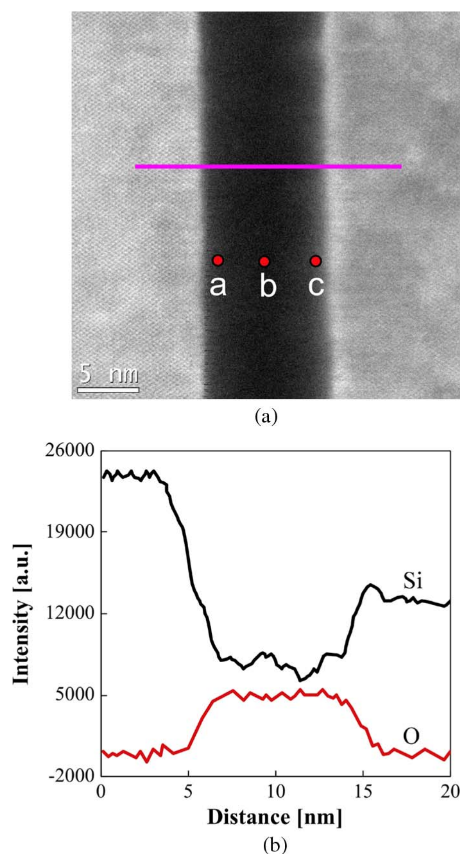

Fig. 4. (a) STEM image of Si/Si bonded interface recorded with an HAADF detector. Horizontal line indicates EELS line scan position. (b) STEM-EELS spectrum imaging line profile across the interface amorphous layer.

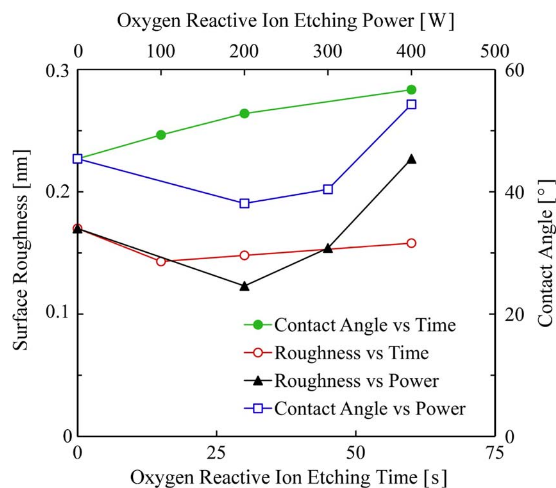

Fig. 5. Surface roughness and contact angle of silicon as a function of O_2 RIE time and power.

Fig. 4(b) at 0.5-nm intervals along the line trace shown in Fig. 4(a). The energy range for the spectra was 5–50 eV. In an earlier study [10], the presence of nitrogen was investigated in the locations a, b, and c of Fig. 4(a). This was critical because N_2 radicals enhanced surface reactivity of the activated surface (using O_2 RIE), resulting in improved bonding strength. No nitrogen was detected. However, the nitrogen concentration might be below the detection limit of EELS. While the spectrum of Si significantly reduced at the interface, the spectrum of oxygen increased. Thus, the presence of silicon oxide and, hence, the oxidation of silicon at the interface are confirmed.

In order to understand the influence of plasma processing parameters on the nucleation of voids, interfacial amorphous layers, and bonding strength, the dependence of surface roughness and contact angle of silicon on the O_2 RIE time and power in the sequential activation was investigated. The root-mean-square (rms) value of surface roughness was measured in tapping mode over a scanning area of 2×2 μm^2 using an atomic force microscope. Fig. 5 shows the surface roughness and contact angle of silicon as a function of O_2 RIE time and power. For O_2 RIE time, the specimens were activated by a 200-W O_2 RIE plasma at 100 Pa followed by 2000-W N_2 MW radicals for 30 s at 100 Pa. In the case of O_2 RIE power, the specimens were activated by O_2 RIE plasma for 60 s at 100 Pa followed by 2000-W N_2 MW radicals for 30 s at 100 Pa. While the water contact angle increased with the increase in the O_2 RIE time, the surface roughness was initially decreased and then increased. An increase in contact angle refers to a decrease in surface energy and, hence, a decrease in bonding strength [11]. On the other hand, both the contact angle and surface roughness were identically varied as a function of the O_2 RIE power. While activation with low-power O_2 RIE (i.e., 200 W) smoothened the surface (roughness of $\sim$0.12 nm), a high O_2 RIE power (i.e., 400 W) increased the surface roughness ($\sim$0.23 nm) considerably. In addition, the plasma-induced defect sites such as nanopores and craters were observed after activation with 400-W O_2 RIE power. The increased surface roughness associated with the nanopores (depth of $\sim$2.2 nm) increased the void nucleation as well as degraded the bonding strength after annealing. This study indicates that the O_2 RIE plasma time and power have to be as low as possible to reduce surface roughness and defects but have to be high enough to properly activate the surface with enough surface energy.

The influence of postbonding annealing temperature on void density, bonding strength, and thickness of Si/Si bonded interface in the SPAB has been investigated. Annealing of the bonded wafers condensed interfacial silanol groups and removed interfacial water below and above 150 °C, respectively. At 400 °C, the reduction of bonding strength was due to the increased void density and the increased thickness of interfacial silicon oxide. Voids were nucleated at plasma-induced defect sites. The contact angle and surface roughness measurements provide guidelines to achieve void-free Si/Si interface with high bonding strength in the SPAB. This indicates that the SPAB applies not only to low-temperature but also to high-temperature packaging applications.

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