PUBLICATION A

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Effects of Plasma Activation on Hydrophilic Bonding of Si and SiO_2

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Low-temperature bonding of Si wafers has been studied utilizing reactive ion etching-mode plasma activation. The hydrophilic Si and thermally oxidized Si wafers were exposed to N_2, Ar, or O_2 plasma prior to bonding in air or vacuum. After plasma treatment the wafers were cleaned in RCA-1 solution and/or deionized water. Strong bonding was achieved at 200°C with all the investigated plasma gases, if proper bonding and cleaning procedures were used. Extended RCA-1 cleaning deteriorated the bond strength, but a short cleaning improved bonding. We found that the activation of the thermal oxide has a larger influence on the bond strength than the activation of the native oxide surface in Si/oxide wafer pairs. We suggest that the plasma treatment induces a highly disordered surface structure, which enhances the diffusion of the water from the bonded interface. As a result of the plasma exposure the number of the surface OH groups is greatly increased enabling strong bonding at a low temperature.
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Direct bonding of hydrophilic silicon wafers can be applied to the fabrication of silicon-on-insulator (SOI) structures and advanced microelectromechanical and optical devices. Wafer bonding usually requires high-temperature annealing above 1000°C to achieve strong bonding between the wafers. When bonding preprocessed wafers it is essential to restrict the annealing temperature in order to avoid undesirable changes and reactions in the substrate structures. In the case of materials with different thermal expansion coefficients excessive stresses may arise in the bonded wafer pair. Therefore, it is mandatory to find a low-temperature bonding process that results in strong bonding at temperatures below 400°C.

It has been reported that strong hydrophilic bonding with Si can be achieved at a low annealing temperature ($<400°C$) by exposing the wafers to a low pressure plasma prior to the bonding.[1-3] Alternatively, surfaces can also be activated with ion bombardment in vacuum.[4] The plasma of various gases, including O_2 and Ar, have been found to yield similar results.[1,3] Infrared spectroscopic measurements have confirmed that the bond strengthening in hydrophilic bonding of Si is due to the formation of covalent siloxane bonds (Si-O-Si) at the bonded interface.[3,5] This reaction which involves dissociation of silanol groups at the interface can take place even at room temperature. The resulting bond strength is limited by the number of silanol groups available for the bonding reaction. Further bonding only occurs at higher temperatures via plastic flow and distortion of the silica tetrahedra. Ion bombardment by plasma exposure or by incident ion beam is known to create structural defects on a Si surface.[6] The particles and ions impinging on a Si surface also have a charging effect.[6] It has been proposed that the disordered surface structure is responsible for the increased reactivity of the surface.[1] Farrens *et al.* have suggested that the increased oxidation rate (Si-O-Si bond formation) at the bonded interface is due to the plasma induced surface charge.[2] Amirfeiz *et al.* found no evidence to substantiate this hypothesis.[3] They suggested that plasma treatment creates a porous surface structure which enhances the diffusivity of water molecules from the bonded interface. In summary, a number of experiments with varying, sometimes conflicting, results have been published on plasma-activated Si wafer bonding. This suggests that the effects of plasma activation are not fully clarified yet.

We have studied the influence of various plasma and bonding parameters on the hydrophilic bonding of Si and SiO_2 using alternative surface treatment procedures prior to bonding. The bonded interface strength was measured with the crack-opening method,[1] and the voids at the bonded interface were studied with scanning acoustic microscopy (SAM).

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Experimental

In the experiments, ⟨100⟩ oriented p-type Czochralski grown silicon wafers with a diameter of 100 mm were used. The resistivity of the wafers was 1-10 Ω cm. A thermal wet oxide layer with a thickness of 500 nm was grown at 1050°C on part of the wafers to be used for hydrophilic Si to SiO_2 bonding (oxide/Si bonds) and SiO_2 to SiO_2 bonding (oxide/oxide bonds). Prior to bonding, the wafers were activated in a reactive ion etcher (RIE, Electrotech) using argon, oxygen, or nitrogen plasma. During the plasma exposure the chamber pressure was 50-150 mTorr with the gas flow set at 30 sccm. The rf power was varied between 50 and 150 W. With these parameters the bias voltage at the substrate electrode varied between 125 and 280 V. The duration of the plasma exposure was varied between 10 s and 10 min. After the plasma treatment the wafers were cleaned in an RCA-1 (NH_3:H_2O_2:H_2O, 70°C) solution and/or deionized water (DIW). To study the influence of the cleaning step on the bond strength, different cleaning times were used. After cleaning, the wafers were dried in a spin dryer. The wafers were subsequently bonded in a commercially available wafer bonder (Electronic Visions EV801). The bonding was carried out either in air or in vacuum usually at room temperature or in some cases at 150°C. The bonded wafer pairs were annealed for 2 h at 100°C. After this first annealing step the wafers were cut into rectangular slices using a dicing saw. The diced samples were annealed for 2-100 h at 100-500°C. The surface energies of the diced samples were measured in air using the crack-opening method.[1] The bonded wafer pairs were inspected for interfacial voids using IR transmission imaging and scanning acoustic microscopy (Sonix UHR2000). The surface roughness of the plasma-activated surface was measured with a Digital Instrument D3100 atomic force microscope (AFM) using silicon tips in the tapping mode.

Results and Discussion

The surface energy of SiO_2/Si bonds as a function of annealing temperature is shown in Fig. 1 for different surface activation treatments. For reference, the surface energy of the nonactivated oxide/Si bonds is depicted in Fig. 1b. For nonactivated oxide/oxide bonds we have measured approximately the same surface energy. The wafers were exposed to oxygen, argon, or nitrogen plasma and subsequently cleaned with RCA-1 and/or DI water before bonding in air. Strong bonding is observed for all plasma species investigated after annealing up to 300°C, if a proper cleaning procedure is used. For example, a short RCA-1 cleaning step for 45 s results in strong bonding whereas extended RCA-1 cleaning deteriorates the bond

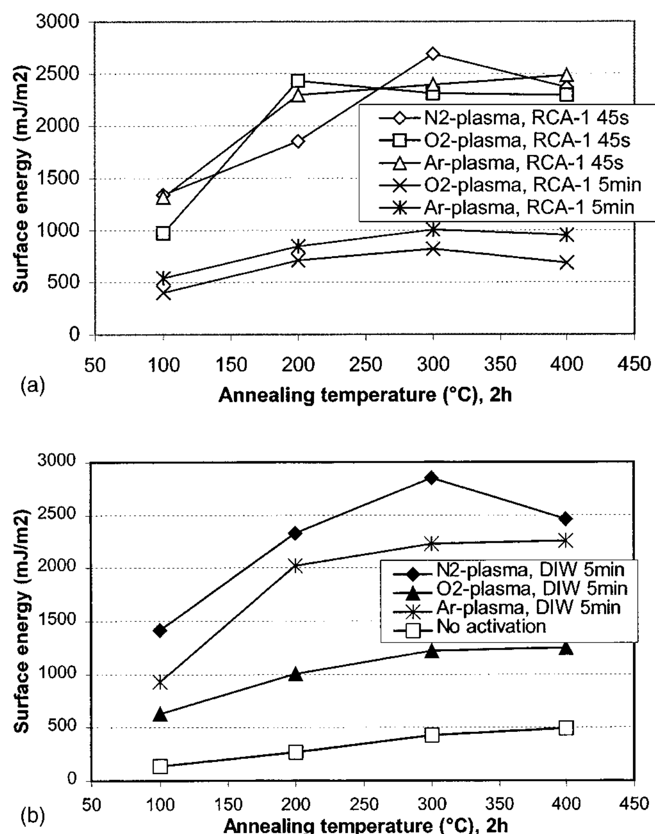

Figure 1. (a) The surface energy of oxide/Si bonds for different plasma gases and for different RCA-1 cleaning times. The bias voltage at the substrate electrode was ~200 V, and the plasma exposure time was 30 s. The wafers were bonded in air. The bond annealing time was 2 h. (b) The surface energy of oxide/Si bonds for different plasma gases. The subsequent cleaning was performed in DI water. The surface energy of the nonactivated oxide/Si wafer pair is shown as a reference. The bias voltage at the substrate electrode was ~200 V, and the plasma exposure time was 30 s. The wafers were bonded in air. The bond annealing time was 2 h.

strength. Our results also show that for wafers exposed to an oxygen plasma DIW rinse is not effective in bringing about strong bonding.

Bonding experiments using plasma activation with a varying bias voltage and exposure time were also carried out. A short plasma exposure up to 30 s was found to be more efficient than a treatment lasting several minutes. The AFM measurements show that an extended plasma exposure increases the surface roughness. A surface roughness of 2 Å was measured for a Si wafer activated with Ar plasma for 10 min, as compared to a roughness of 1 Å for an untreated sample. Plasma activation at a 200 V bias voltage lasting less than a minute was not found to have any effect on the surface roughness. Figure 2 shows the measured surface energy as a function of the bias voltage for a wafer pair exposed to an oxygen plasma for a constant time of 30 s. The bias voltage was controlled by adjusting the plasma pressure and power. When measured after a heat-treatment at 200°C the bond strength increases with an increasing bias voltage if the wafers are cleaned with an RCA-1 solution after the plasma exposure. When the cleaning is carried out in DIW, the influence of the ion energy is less pronounced. Our results suggest that the activation extends to a depth controlled by the average ion energy in the RIE process. Increasing the bias voltage results in ions penetrating deeper into the wafer.[6] Figure 3 shows simulated profiles of O_2, N_2, and Ar implanted at 200 eV into SiO_2.[7] The projected range of 200 eV O_2^+, N_2^+, and Ar^+ ions varies between 1 and 2 nm. This shallow surface layer is very reactive and readily adsorbs water from the cleaning solution. Measurements using optical ellipsometry show that RCA-1 cleaning for 5 min after plasma exposure removes a 5 nm layer from the surface of the activated oxide. Therefore, we conclude that in the RCA-1 bath the damaged layer induced by plasma is consumed and eventually the activation is lost, as we have observed for extended cleaning times. This etchback process is less effective when the bias voltage and penetration depth of the ions increase.

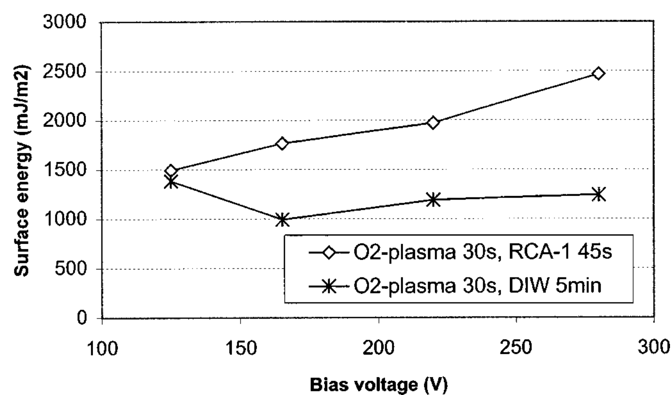

Figure 2. The influence of the bias voltage on the bond strength of oxide/Si bonds. The bonding was performed in air after which the bonded wafer pairs were annealed at 200°C for 2 h.

While a surface energy of >2000 mJ/m^2 was obtained for oxide/Si bonds, the surface energy of oxide/oxide bonds remained below 1500 mJ/m^2 with all the activation treatments (Fig. 4). The observation is consistent with earlier results on low temperature bonding of hydrophilic Si.[8] The silanol groups (Si-OH) of opposing surfaces can react and polymerize even at room temperature provided that they are in close proximity.[1] Therefore, the interface water trapped between the hydrophilic wafers has to be removed before the polymerization of the Si-OH groups can take place. If one of the wafers is covered with a thin native oxide layer, the water can diffuse to the oxide/Si interface and oxidize silicon, even at a low temperature. When both wafers are covered with a thick oxide layer, the diffusion of water to the oxide/Si interface is hampered at low temperatures.

A mass spectroscopic analysis of the wafer pairs bonded without plasma activation has proved that the interface water can oxidize Si generating molecular hydrogen at the bonded interface.[9] Hydrogen gas was also found to be the main constituent inside the cavities (voids) after annealing at <700°C. We carried out experiments where two unoxidized hydrophilic Si wafers were bonded (Si/Si

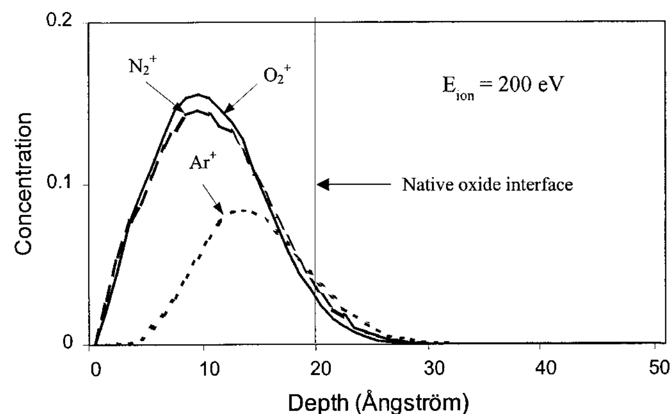

Figure 3. The distribution profiles of 200 eV O_2^+, N_2^+, and Ar^+ in SiO_2 simulated using the SRIM2000 code.[7] The approximate thickness of the native oxide is given as a guideline.

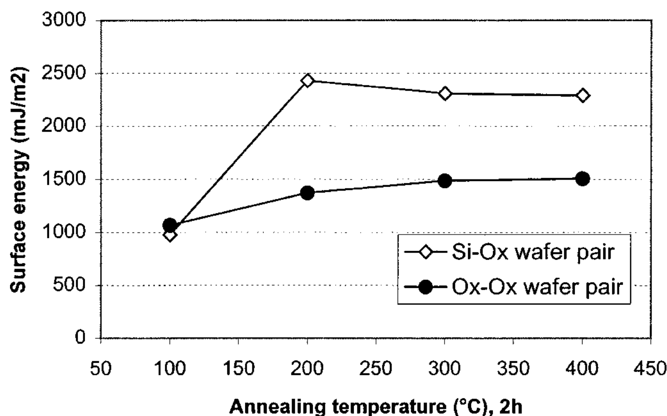

Figure 4. Comparison of Si/oxide and oxide/oxide bonds. The wafers were activated with oxygen plasma (30 s) followed with RCA-1 cleaning (45 s). The wafers were bonded in air. The bond annealing time was 2 h.

bonds) using different plasma activation treatments. A large number of presumably hydrogen-induced voids was observed by scanning acoustic microscopy (SAM) after annealing at 100-400°C (Fig. 5a). No hydrogen-induced voids were found in hydrophilic silicon-to-oxide and oxide-to-oxide wafer pairs (Fig. 5b). The result is in agreement with the reported behavior of the voids in wafer pairs bonded without plasma activation.[1] This suggests that the plasma-enhanced bonding process involves a similar oxidation reaction as the conventional hydrophilic Si wafer bonding.

The molecular water resulting from the polymerization of Si-OH groups may either out diffuse along the bonded interface or react with Si according to $2H_2O + Si \rightarrow SiO_2 + 2H_2$.[1] The difference in bond strength at 200°C between oxide/Si and oxide/oxide bonds and the behavior of the voids suggest that most of the interface water is consumed by oxidation reaction if at least one of the oxide layers is sufficiently thin.

Figure 6 presents the measured surface energy for oxide/Si wafer pairs bonded with the O_2 plasma activation but in different atmospheres. A reduced surface energy of 1000 mJ/m^2 was measured for the samples which had been bonded in vacuum or at 150°C in air in contrast to the values of >2000 mJ/m^2 obtained for the wafer pairs bonded in air at room temperature. The molecular water is known to desorb from a Si wafer surface at above 110°C.[1] It is then reasonable to assume that most of the water has desorbed from the surface held at 150°C or in vacuum. The observed difference in the surface energies corroborates the important role of water molecules in the early phase of hydrophilic bonding.

In comparison, no dependence of the bond strength on the bonding atmosphere was observed in the samples activated with nitrogen or argon gases. Both vacuum and air bonding resulted in strong bonding at 200°C, if argon or nitrogen RIE was used. Hence, the adsorption of the OH groups appears to produce a more stable surface coverage in this case. We simulated the surface sputtering process using the SRIM2000 Monte Carlo code.[7] For 200 eV Ar ions incident on a SiO_2 surface the average sputtering rates for Si and O are 0.041 and 0.227 atoms/ion, respectively. For real surfaces the sputtering yield changes during the ion bombardment due to variations in surface roughness and changes in the stoichiometry. The large relative difference in the atomic sputtering rates nevertheless suggests that the silica surface under Ar bombardment becomes enriched in Si. The hydroxyl groups link to the enriched silicon atoms and constitute a stable hydrated surface. For oxygen plasma exposure the surface remains saturated with oxygen and cannot bind to OH before a light etching step in RCA-1.

We also studied the influence of the plasma activation if only one of the two wafers is activated. The surface energy results for Si/oxide wafer pairs in Fig. 7 show that the activation of the thermal oxide has a larger effect on the bond strength than the activation of the native oxide surface. The same result was obtained both for argon and oxygen plasma. The result can be explained by the varying degree of hydrophilicity of the surfaces. The surface of native oxide can accommodate a higher density of silanol groups compared to the thermal oxide. The density of OH groups on the thermal oxide surface is $0.06/nm^2$ whereas the fully hydrated silica surface contains about 4.6 OH groups per nanometer squared.[1] Hence, the reduced density of the bonding sites available on the thermal oxide surface becomes the strength-limiting factor in bonding. The number of bonding sites is increased during the plasma treatment rendering the surface more reactive. The relative amount of this enhancement is more pronounced in the case of the thermal oxide. Figure 7 also shows that after annealing at 200°C, where the majority of Si-OH

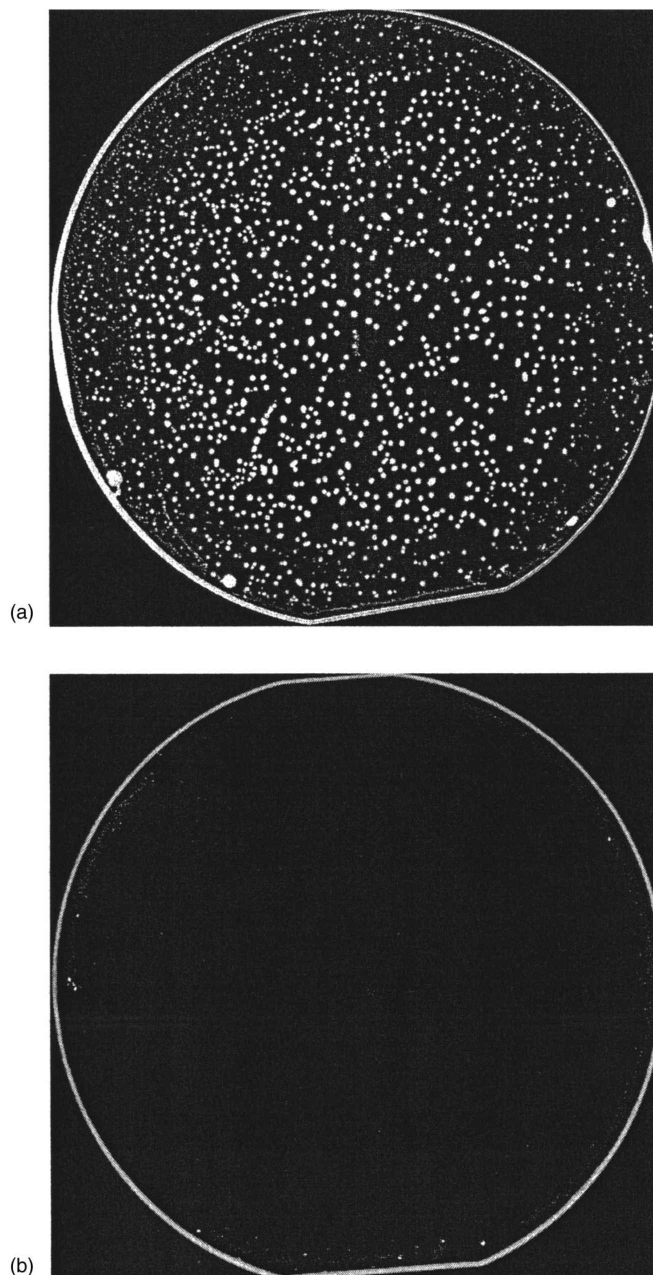

Figure 5. (a) A SAM image of a hydrophilic Si/Si wafer pair. The wafer pair was activated with argon plasma followed with DI water rinse. The bonding was carried out in air with the bond annealing at 200°C for 2 h. (b) A SAM image of Si/oxide wafer pair. The wafer pair was activated with argon plasma followed with DI water rinse. The bonding was carried out in air and the bond annealing at 200°C for 2 h.

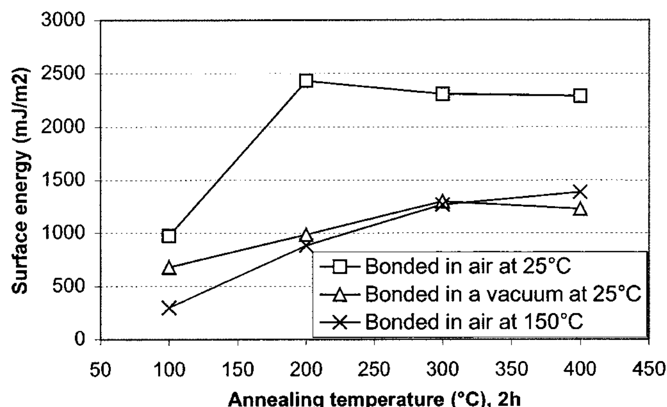

Figure 6. Surface energy as a function of annealing temperature for Si/oxide wafer pairs bonded in different atmospheres. The wafers were bonded after activation in oxygen plasma followed with RCA-1 cleaning.

groups should have reacted to form Si-O-Si bonds, the contributions of the two bonded wafers add almost linearly to the final bond strength.

We also measured the surface energy for argon-plasma-activated and DI water cleaned samples after annealing at 50-300°C for 67 h. The bonding was performed in air. The surface energy of 1200 mJ/m^2 was measured after 50°C, and the surface energy increased linearly as a function of temperature up to 200°C after which the saturated value of 2500 mJ/m^2 was reached. In hydrophilic bonding of Si without plasma treatment the surface energy of >1000 mJ/m^2 is obtained only at 150°C after the interface water has been removed.[1] Our result suggests that the interface water is removed at $<50°C$ if the wafers are exposed to plasma before bonding. We believe that the diffusivity of the water at the bonded interface is increased due to a highly disordered surface structure induced by plasma activation. After the water has been removed the OH groups can react and form siloxane bridges across the bonded interface. It is well documented that in hydrophilic Si wafer pairs the polymerization of surface Si-OH groups according to Si-OH + Si-OH → Si-O-Si + H_2O increases the bond strength.[1,5] To obtain strong bonding at a low annealing temperature, there should exist a high number of available bonding sites (Si-OH groups) on a wafer surface.[1] We suggest that plasma induces a surface structure, which can accommodate a much higher number of OH groups than the equilibrium density of 4.6/nm^2 reported for silica.[1,10] This equilibrium value corresponds to a surface energy of ~1600 mJ/m^2[1] if we assume that each silanol pair is converted to one siloxane bond. In contrast, the measured surface energy of 2500 mJ/m^2 would require 7.2 siloxane bonds per nanometer squared suggesting a high initial surface coverage by OH ions. Iler has calculated that the surface of fully hydrated silica holds about 7.85 hydroxyl groups per square nanometer. [11] This value is very close to the OH coverage required for surface energies measured in this experiment.

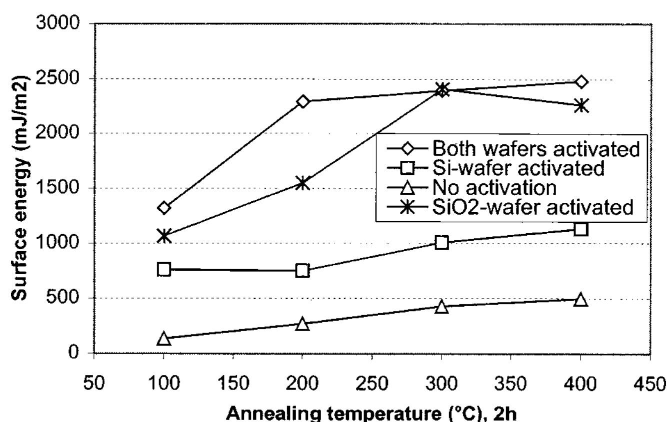

Figure 7. Surface energy of bonded Si/oxide wafer pairs activated by plasma exposure of the Si wafer or the oxide wafer or by exposure of both wafers. The nonactivated wafer pair is given as reference. The activation treatment was a 30 s argon plasma exposure followed with a 5 min DI water cleaning.

Conclusions

Our experiment demonstrates that strong hydrophilic Si-to-thermal-oxide bonds can be obtained at temperatures below 200°C by exposing the wafers to RIE-mode plasma prior to bonding. Both inert and reactive plasma gases result in strong bonding suggesting that the surface activation of hydrophilic Si wafers results from physical modification of the surface layer. This activation is lost under extended treatment in an RCA-1 solution suggesting that the modified surface layer is slowly consumed by chemical etching. Argon or nitrogen plasma activation yields stronger bonds than oxygen plasma, if the bonding is carried out in vacuum. This can be explained by a more stable surface configuration for OH groups on the oxide surface enriched in Si. Because plasma-assisted wafer bonding yields a high surface energy at $<100°C$, we suggest that the plasma activation creates a surface structure which enhances the escape velocity of water from the bonded interface. The damaged surface layer presumably accommodates a high concentration of OH groups resulting in high bond strength.

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