Hydrophobic silicon wafer bonding

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Wafers prepared by an HF dip without a subsequent water rinse were bonded at room temperature and annealed at temperatures up to 1100 °C. Based on substantial differences between bonded hydrophilic and hydrophobic Si wafer pairs in the changes of the interface energy with respect to temperature, secondary ion mass spectrometry (SIMS) and transmission electron microscopy (TEM), we suggest that hydrogen bonding between Si-F and H-Si across two mating wafers is responsible for room temperature bonding of hydrophobic Si wafers. The interface energy of the bonded hydrophobic Si wafer pairs does not change appreciably with time up to 150 °C. This stability of the bonding interface makes reversible room-temperature hydrophobic wafer bonding attractive for the protection of silicon wafer surfaces.

Silicon wafers with hydrophilic surfaces can be bonded at room temperature (RT). This has been attributed to the presence of OH groups on the mating surfaces that form hydrogen bonds between the two wafers.[1,2] Hydrophobic Si wafers prepared by a dip in diluted HF without subsequent water rinse have shown a similar RT bonding performance.[3] Dispersion van der Waals forces have been suggested as the origin of the attraction force between the two hydrophobic wafers.[3] It has also been suggested[3] that the loss of the bondability of the wafers after a dip in concentrated HF is due to an increased surface roughness. However, the suggested model[3] is unable to explain the fact that the improved surface microroughness of hydrophobic (111) Si wafers prepared by etching in BHF solution [HF (49%):NH$_4$F (40%)=1:4][4] degrades the bondability. Moreover, no reason has been given why the contact wave velocity during RT bonding is not a monotonic function of HF concentration and is also not correlated to the resulting RT interface energy of the bonded wafer pairs. In the present letter, the mechanisms associated with hydrophobic wafer bonding will be examined and a new model will be proposed.

4 in., n-type, Czochralski-grown, 7.5–12.5 Ω cm, (100) Si wafers with thickness of 511–539 μm from one specific wafer supplier were used in all experiments to assure that the surface conditions of original wafers such as roughness and waviness are kept as constant as possible. In order to obtain a consistent surface hydrophilicity, prior to RT bonding the wafers were treated in standard RCA1 (NH$_4$OH:H$_2$O$_2$:H$_2$O=1:1:5) and RCA2 (HCl:H$_2$O$_2$:H$_2$O =1:1:5) solutions with a de-ionized (DI) water rinse in between. One group of RCA treated wafer pairs was then bonded at RT. Another group of the treated wafers was dipped in ~1% HF for 2–5 min to render the wafer surfaces perfectly hydrophobic. Without subsequent DI water rinse the wafers were spin-dried under an infrared lamp at 3000 rpm for 30 s using a microcleanroom setup.[5] Wafer pairs

were then brought into contact. The contact wave velocity during RT bonding was found to be similar to that of hydrophilic wafers. The interface bond energy was measured by the crack opening method in air.[6,7]

The interface energy of bonded Si wafer pairs increases with time at a given temperature and gradually approaches a saturated value: for bonded hydrophilic wafers such an increase has been observed from RT (23 °C) and for bonded hydrophobic wafers it becomes significant from ~150 °C. Therefore, for bonded Si wafers the effect of storage at a given temperature on interface energy must be taken into account for comparison purposes. In this study, the saturated values of the interface energy will be used in all discussions.

Figure 1 shows the saturated interface energy of bonded hydrophilic and hydrophobic Si/Si wafer pairs as a function of annealing temperature T. The interface energy data represent average values of at least three measurements for each storage temperature. As seen from Fig. 1, for bonded hydrophilic Si/Si wafers the salient features of the interface energy change with temperature are (1) a substantial increase of the interface energy from RT to 150 °C with a transition point
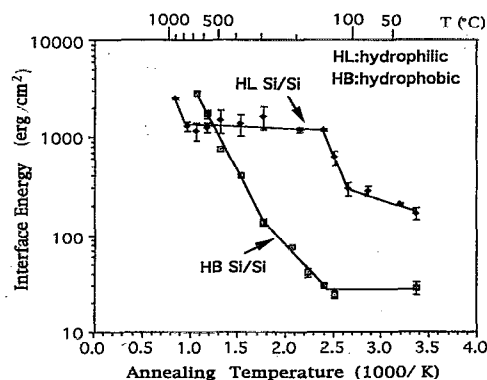

FIG. 1. Saturated interface energy of bonded hydrophilic and hydrophobic Si/Si wafers as a function of annealing temperature.

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around 110 °C; (2) a slow increase of the interface energy from 150–800 °C; (3) a drastic increase of the interface energy around 900 °C. Moreover, interface bubbles were developed in all samples which had been stored at temperatures between RT-900 °C.

The behavior of the interface energy of bonded hydrophobic Si/Si wafer pairs is significantly different: (1) the interface energy does not change appreciably with temperatures from RT to ~150 °C; (2) the interface energy increases in the temperature range of ~150–300 °C but no interface bubbles are generated; (3) starting at ~300 °C an increase of the interface energy with respect to temperature occurs accompanied by bubble generation at the bonding interface; (4) the interface energy reaches the fracture energy of bulk Si at ~700 °C.

The increase in interface energy and the generation of bubbles in bonded hydrophilic wafer pairs is attributed to the presence of water and OH groups at the interface.[8] Since very little water and OH groups are expected at the interface of RT bonded hydrophobic Si wafers—if at all present— some other mechanisms must be responsible for hydrophobic Si/Si wafer bonding. Among the three types of van der Waals intermolecular attraction forces, i.e., the dipole-dipole force between two polar molecules, the dipole-induced force between a polar and a nonpolar molecule and the dispersion force between two nonpolar molecules, the first one is the strongest. Moreover, hydrogen bonding is an especially strong form of dipole-dipole attraction in which the hydrogen atom in a polar molecule interacts with an electronegative atom of an adjacent molecule. It is the electrophilic hydrogen on one surface and the nonbonding electrons on the mating surface that are crucial for the formation of hydrogen bonding between two wafers.

After a dilute HF dip without DI water rinse, the silicon surface dangling bonds are mainly terminated by hydrogen but a significant amount of fluorine, about 0.12 of a monolayer, has also been found on the silicon surface.[9–12] The Si—H bond is weakly polarized, having dynamic effective charge of $0.1e$, where e is the charge of an electron.[4] The Si—F bond is strongly polarized and has an ionic nature.[11,13] Therefor, the formation of hydrogen bonding between two hydrophobic Si surfaces terminated by both hydrogen and fluorine is feasible:

$$\text{H-bond}$$
$$\text{Si—F}\cdots\text{H—Si}.$$
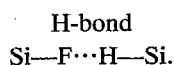
The number of Si—F bonds decreases drastically with time of DI water rinse.[13,14] Although the surface becomes slightly rougher after a water rinse,[13–15] the loss of Si—F bonds appears to be the main reason for the degraded bondability of the hydrophobic wafers. One of the supporting evidences is that Si (111) surfaces prepared by dipping in BHF with pH=9–10 become ideally smooth due to the preferential etching of the surface steps and defects by the BHF solution[4] but they do not bond well.[3] This bonding behavior can be understood by the recent finding that Si—F bonds are located mainly at chemical reactive sites such as atomic steps and surface defects.[15] We suggest that the lack of these sites on the BHF etched smooth (111)surface leads to the deple-

tion of Si—F bonds and results in a loss of bondability. Although *macroscopic* surface flatness may be slightly degraded due to the removal of the atomic steps, it is the *microscopic* roughness of mating surfaces which is crucial for the bondability. About 1–3 μm surface waviness over 4 in. commercial Si wafers does not pose an obstacle for wafer bonding at room temperature.[16]

The increase of the interface energy with temperature for the bonded hydrophobic Si pairs may be interpreted based on the fact that H is less stable in a dihydride (Si-H$_2$) structure than in an monohydride (Si-H) structure since both are simultaneously present on the HF dipped Si (100) surface.[4,12] The conversion of Si-H$_2$ to Si-H results in an increased polarity of the hydride and thus an increased bond energy via a possible rearrangement of the adsorbed species at the interface. Although the desorption of H from a HF treated Si surface was demonstrated to start at about 367 °C from dihydride and 446 °C from monohydride in ultrahigh vacuum,[17] our results on the formation of interface bubbles during storage of bonded hydrophobic Si wafers suggest that H desorption may start around 300 °C after sufficiently long times. Bubbles can be generated at the interface of RT bonded hydrophobic Si pairs during a 300 °C, ~14 h or a 400 °C, 0.5 h annealing. Some bubbles generated during the 300–400 °C annealing disappear after 3–19 days storage at RT in air. Hydrogen is known as a rapid diffusion species in silicon and its diffusivity can be as high as 2×10^{-13}–2×10^{-9} cm^2/s at RT.[18] Among the possible gases which can be expected in the bubbles, hydrogen is most likely to be able to diffuse through silicon, preferentially along the bonding seam with an even higher unknown diffusivity. Bubbles which do not disappear during RT storage probably contain desorbed hydrocarbons. Si—F bonds are believed to be stable up to 2000 °C annealing.[19] It is speculated that some Si—Si bonds can be formed at the bonding interface during annealing when hydrogen is released from monohydrides of the mating surfaces:

$$\text{Si-H}+\text{H-Si}\rightarrow\text{Si-Si}+\text{H}_2\uparrow.$$
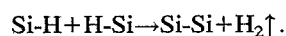
The almost constant fluorine coverage on the Si (100) surfaces dipped by 0.3%–30% HF[11] appears to be responsible for the almost constant interface energy of the RT bonded hydrophobic Si wafers treated by 1%–30% HF.[3] We have observed that for a constant surface preparation of the surfaces of two wafers, the contact wave velocity during RT bonding is mainly determined by the squeezing out of the trapped gas between the two wafers. We performed some experiments in which a razor blade was pulled out from the bonding seam at the edge of a RT bonded hydrophilic Si/Si pair under normal air pressure and under reduced air pressure. The crack which had been generated by inserting the blade rebonded (closed) again. The rebonding wave velocity increased drastically from 1.65 cm/s when the operation was performed in air at a pressure of 1 atm, to 12.3 cm/s when rebonding occurred in a chamber of reduced pressure of ~2.6×10^{-3} atm. When the HF concentration is above ~30%, in addition to almost unchanged H and F termination, significant adsorption of HF molecules on the HF dipped *Si* surface occurs.[15] It is likely that the vaporizing HF on the
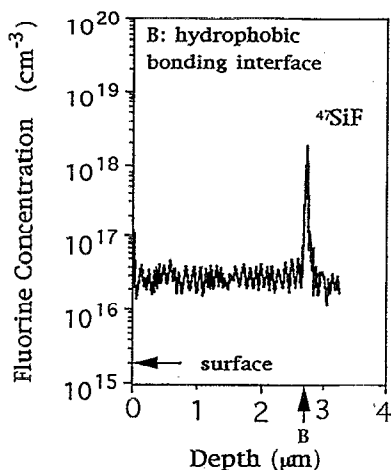
FIG. 2. SIMS profile of F concentration of a bonded hydrophobic Si wafer pair after annealing at 1100 °C for 2.5 h. The ^{47}SiF signal was recorded.

mating surfaces causes the even lower observed wave velocity during RT bonding compared to the case of wafers treated with lower concentrations of HF[3] while the unchanged RT interface energy is a result of the constant amount of Si—F bonds. In our experiments, the wafers dipped in 49% HF always show HF spots on the surfaces and do not bond after drying, due to severe surface roughening[20] as confirmed by our AFM (atomic force microscope) images. On the other hand, such physisorbed HF residues may also be present on the 1%–30% HF dipped Si surface[21] in much smaller amounts and their contribution to the attraction force between wafers during RT mating remains to be investigated.

Both the ^{19}F and the ^{47}SiF signals were measured in SIMS analyses and the F concentration at the interface of a bonded hydrophobic Si wafer pair annealed at 1100 °C for 2.5 h is about 2.4×10^{18} cm^{-3} (^{19}F) and 1.9×10^{18} cm^{-3}(^{47}SiF). Due to the possible interference of the ^{19}F signal by $^{19}H_3O$ the ^{47}SiF signal was used for measuring the F concentration (Fig. 2).[22] No ^{47}SiF signal was observed at the interface of bonded hydrophilic wafers after an analogous annealing. High resolution TEM images combined with spectroscopic ellipsometry measurements of the same samples clearly indicate that there is an intermediate layer with a thickness of ~20 Å with an optical density of about 27% less than Si at the bonding interface of the bonded hydrophobic wafer while there is an oxide layer of ~20 Å at the interface of the bonded hydrophilic wafer.

RT hydrophobic wafer bonding provides a stable bonding interface during storage at temperatures up to 150 °C. Neither an appreciable interface energy increase nor bubble formation were observed. Therefore, RT hydrophobic wafer

bonding is clearly more adequate than hydrophilic wafer bonding for surface protection against contamination and mechanical damage associated with wafer transportation which was suggested previously.[23] The bonded wafers have to be debonded before use in device processing. The fairly low RT interface energy of about 10 erg/cm^2 allows the debonding operation to be performed in a dry ambient rather than in water which would be required in the case of bonded hydrophilic wafers.[24] Thus, hydrophobic silicon wafer bonding can greatly simplify the debonding procedure and thus lower its cost.

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