The Role of Surface Chemistry in Bonding of Standard Silicon Wafers

Q.-Y. Tong,* T.-H. Lee, and U. Gösele[a]

Wafer Bonding Laboratory, Duke University, Durham, North Carolina 27708, USA

M. Reiche*

Max-Planck-Institute of Microstructure Physics, D06120, Halle, Germany

J. Ramm and E. Beck

Balzers Limited., FL-9496, Liechtenstein

ABSTRACT

Hydrophilic silicon surfaces become hydrophobic without microroughening after 200°C low energy hydrogen plasma cleaning. The fully hydrogen-terminated silicon surfaces do not bond to each other, not even by the application of external pressure. A subsequent 400 to 600°C, 4 min thermal treatment in ultrahigh vacuum converts the wafer surfaces to hydrophilic and bondable which can be attributed to desorption of hydrogen from the surfaces. Hydrophobic silicon surfaces prepared by a dip in HF (without subsequent water rinse) are terminated by H and a small amount of F, or by H and a small amount of OH (after subsequent water rinse). Hydrogen bonding of Si–F···(HF)···H–Si or Si–OH···(HOH)···OH–Si across the two mating surfaces appears to be responsible for room temperature spontaneous hydrophobic or hydrophilic wafer bonding, respectively.

Introduction

Wafer bonding without an adhesive is feasible and can be attributed to intermolecular or interatomic attraction forces between the mating surfaces.[1,2] For successful room temperature wafer bonding, the wafer surfaces must be sufficiently clean, flat, smooth, and able to induce attraction forces by an appropriate surface chemistry.

In order to avoid interface bubbles caused by surface contamination and to control the interface quality, a sufficient surface cleanliness is essential. Commercially available standard silicon wafers are not perfectly flat and smooth. The mating surfaces must be able to conform to each other through elastic deformation of the wafers by the attraction forces between the two surfaces during the room temperature bonding process. Therefore, the flatness variations of bonding surfaces have to be smaller than a critical value which is determined by the wafer thicknesses, Young's modulus, and the bond energy.[3] Since the surface attraction forces involve mainly short-range intermolecular forces and decrease drastically as the distance between the mating surfaces increases, for bonding to occur the two mating surfaces must be in sufficient proximity which requires an adequate surface smoothness. In principle, the surfaces of any materials with or without adsorbates or impurities can be attracted to each other since the dispersion van der Waals force originating from charge distribution fluctuations is ubiquitously present. This force is effective if the intermolecular distance falls below a critical value. It implies that if mating surfaces are perfectly clean such as in an ultrahigh vacuum (UHV) system, and are in intimate contact, bonding of almost all solids appears to be possible due to the adhesion forces provided by atoms or molecules of the mating surfaces themselves.

However, in an ambient other than UHV the mating surfaces are usually terminated by foreign species. In this study, we show that the surface chemistry plays a critical role in wafer direct bonding independent of whether the surfaces are hydrophilic or hydrophobic. Surface termination with desirable chemical groups permits commercial standard wafers to be bonded without the application of an external pressure.

* Electrochemical Society Active Member.
[a] Present address: Max-Plank-Institute of Microstructure Physics, Weinberg 2, D-06120, Halle/Saale, Germany.

Bonding Mechanisms

Even though atomic force microscope (AFM) measurement results have revealed that the mean surface roughness of prime grade commercial silicon wafers is around 1.5 Å and the maximum peak-valley height is in the range of 15 Å, it has been found that hydrophilic silicon wafers can be bonded together easily at room temperature. Hydrophilic silicon surfaces are usually realized by OH group termination. At relative humidities of 50% or greater, there is more than one monolayer of hydrogen-bonded molecular water on Si–OH groups of the hydrophilic Si surfaces.[4] During room temperature bonding, the two wafers bond to each other via hydrogen bonding between adsorbed water molecules on the two surfaces, Si–OH···(HOH)···OH–Si. Since water molecular triplets are more stable than three isolated water molecules or dimers,[5] the linkage of three or more water molecules can form a bridge across the two bonding surfaces. Because the size of an OH group is about 1.0 Å and the distance between two hydrogen-bonded oxygen atoms in ice is 2.76 Å, hydrophilic Si surfaces separated by up to about 10 Å can be bridged to adhere through clusters of three or more hydrogen-bonded water molecules at room temperature, as indicated in Fig. 1. This implies that with the aid of water bridging a mean surface microroughness of up to ~5 Å is tolerable for successful hydrophilic Si wafer bonding.

Commonly, hydrophobic silicon surfaces are produced by a dip in HF aqueous solution. After an HF dip without subsequent deionized (DI) water rinse the silicon surface is mainly terminated by hydrogen but also by a small amount of fluorine. The fluorine coverage may vary with the HF concentration, but their detailed functional relationship is still a subject of investigation. Sunada *et al.*[6] have reported that two-orders of magnitude variation in HF concentration results in very little change in the fluorine coverage. Their results indicate that there is about 0.12 of a monolayer of fluorine on the silicon surface if a HF concentration of less than 10% is used. Watanabe *et al.*[7] have also demonstrated that the fluorine concentration increases only by a factor of five when the HF concentration is increased 100-fold. Grundner *et al.*[8] have found the fluorine coverage changes with HF concentration with a minimum fluorine coverage at around 5% HF. Takahagi *et al.*[9] showed a continuous increase of the fluorine coverage with HF concentration. In this study, 4 in., p-type, Czochralski-grown, 4 to 6 Ω cm, (100) silicon lay-

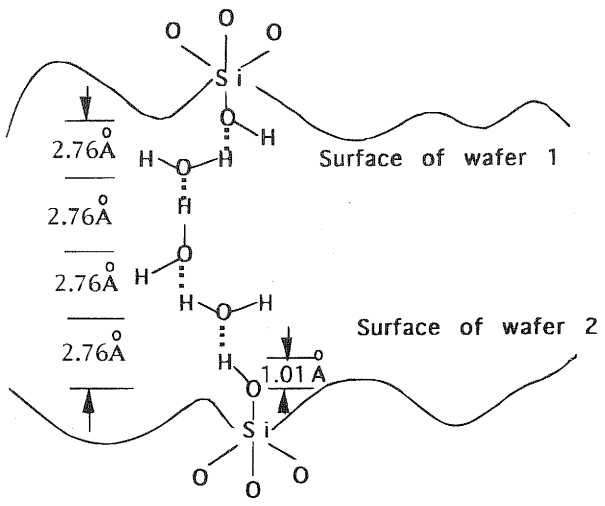

Fig. 1. Schematic illustration of a linkage of three water molecules between two hydrophilic mating surfaces to bridge a gap between wafers at room temperature.

ers of 2.5 μm thickness bonded to a 4 in., n-type, Czochralski-grown, 7.5 to 12.5 Ω cm, (100) silicon wafers with a thickness of 511 to 539 μm were used. The hydrophobic surfaces were realized by a 1% HF dip for ~1 to 2 min and the hydrophilic surfaces were formed by standard RCA cleaning solution with RCA-1 {NH_4OH-H_2O_2-H_2O (1:1:5)} and RCA-2 {HCl-H_2O_2-H_2O (1:1:5)}. Both hydrophilic and hydrophobic silicon pairs bonded spontaneously at room temperature. Figure 2 shows the secondary ion mass spectrometry (SIMS) profiles of fluorine (Fig. 2a) and oxygen (Fig. 2b) at the interface of bonded hydrophilic and hydrophobic silicon pairs after 1100°C annealing for 2.5 h. The ^{19}F concentration of 2.4×10^{18} cm^{-3} at the hydrophobic interface (HB) is much higher than the concentration of 4.0×10^{16} cm^{-3} at the hydrophilic interface (HL). On the other hand, the ^{16}O concentration of 5.4×10^{20} cm^{-3} at the hydrophobic interface (HB) is much lower than the 1.0×10^{22} cm^{-3} at the hydrophilic interface (HL). The SIMS results appear to be consistent with the speculation that hydrophilic bonding may be attributed to hydrogen bonding between Si–OH and HO–Si across two mating wafers while hydrogen bonding between Si–F and H–Si across two mating wafers is most likely to be responsible for room temperature bonding of hydrophobic Si wafers.[10]

It is known that various polymers $(HF)_n$ consisting of hydrogen bonded HF molecules with n equal to 3 or more are present in gaseous HF and the $(HF)_2$ dimer seems to be less stable than the higher polymers.[11] The distance of H···F in a hydrogen bonded polymer H–F···H–F···H–F··· is 2.55 Å.[11] Recent thermal-desorption spectroscopy results[12,13] show some physisorbed HF residual molecules on the Si surface after a HF dip without a subsequent DI water rinse. Crystal chemistry has indicated that F ions and OH ions are similar. They are not only of approximately the same size but they are also isoelectric.[14] It is therefore conceivable that similar to the hydrophilic wafer bonding via hydrogen-bonded water linkages, a cluster of three or more hydrogen-bonded HF molecules may bridge the two mating surfaces so that two surfaces which are separated by up to about 8 Å can still be bonded by hydrogen bonding, Si–F···(HF···HF···HF)···H–Si, see Fig. 3.

It is known that when hydrophilic silicon wafers are exposed to vacuum or high temperature and dry ambient they become increasingly less bondable.[15] Above 200°C the bonding process stops[16] which is attributed mainly to the loss of the hydrogen-bonded water molecules from the mating surfaces since there is only a minor change in the surface density of OH groups.[17] Similarly, our experiments show that heating to ~150°C of commercial silicon wafers with hydrophobic surfaces which are HF dipped without subsequent water rinse can also lead to a loss of their bondability. Since the surface roughness of the wafers and the surface density of Si–H and Si–F are unlikely to change at this low temperature,[10] the result appears to support the HF bridging bonding argument.

If hydrophobic silicon surfaces are realized by an HF dip followed by a DI water rinse the Si–F bonds can be replaced by Si–OH bonds due to an exchange reaction of Si–F with water[18]

$$\text{Si–F} + \text{HOH} \rightarrow \text{Si–OH} + \text{HF} \qquad [1]$$

The resulting silicon surfaces are terminated mostly by H and small percentage of OH groups. If the water rinse

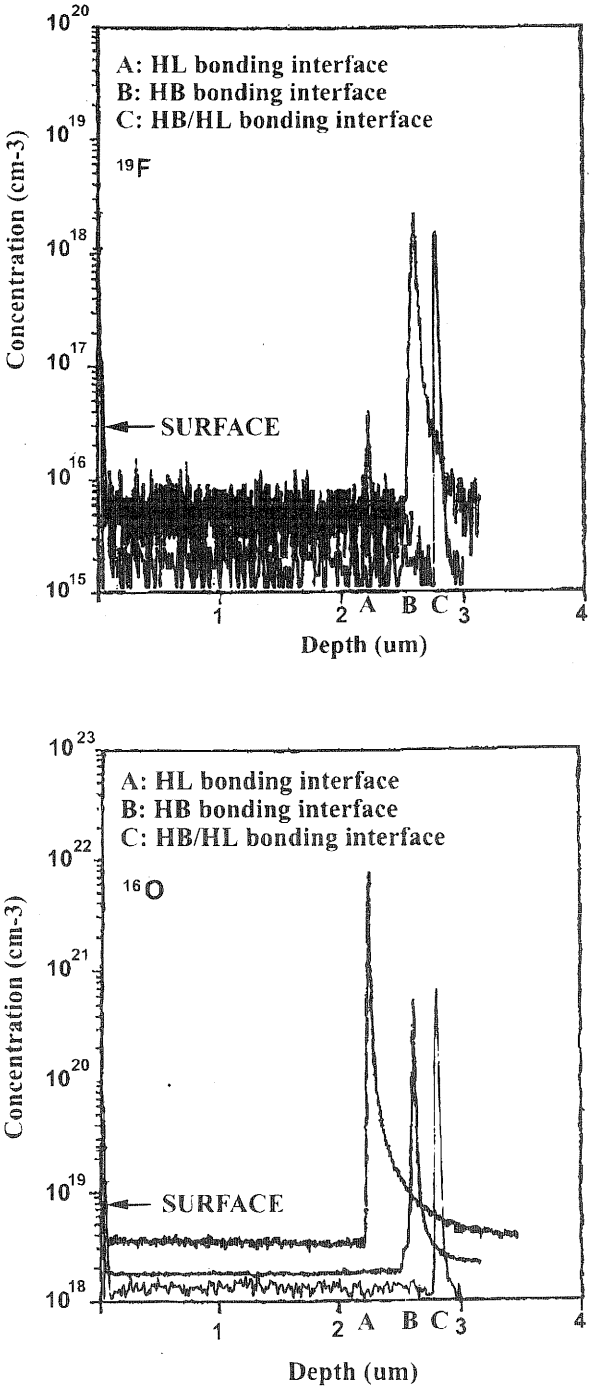

Fig. 2. SIMS profiles of F (a, top) and O (b, bottom) at the bonded interface of hydrophilic (HL), hydrophobic (HB) (1% HF dip without subsequent DI water rinse) and hydrophobic (HB/H_2O rinsed) (1% HF dip with subsequent DI water rinse) Si/Si pairs after 1100°C, 2.5 h annealing.

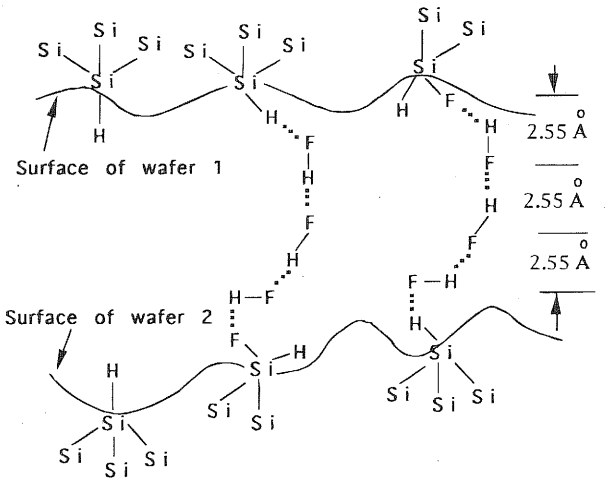

Fig. 3. Schematic diagram of HF bridging across the hydrophobic bonding surfaces at room temperature.

time is around ~1 to 2 min the OH surface coverage is about the value of the initial F coverage,[18] *i.e.*, about 0.12 of a monolayer. However, there is also a slow replacement of Si–H by Si–OH

$$Si\text{–}H + OH^- + H^+ \rightarrow Si\text{–}OH + H_2 \qquad [2]$$

It was reported that 3 to 5 h of water rinse may be required to render the silicon surface covered with one monolayer of OH groups.[18] Therefore, the bonding mechanism of hydrophobic silicon wafers which are HF dipped with subsequent water rinse appears to be Si–OH···(HOH)···HO–Si. The hydrogen bonding of Si–OH···(HOH)···H–Si is less likely as we see later on.

In order to check the change of surface microroughness during a HF dip and subsequent DI water rinse, AFM measurements were performed (Digital Instruments Nanoscope III in tapping mode with a measured area of 0.5 × 0.5 μm). Figure 4 shows the AFM images of silicon sample surfaces which were cut from the same 4 in. (100) silicon wafer: (a) an RCA-1 treated hydrophilic surface (HL), (b) a 5 min, 1% HF dipped hydrophobic surface (HB), and (c) a surface prepared by 5 min, 1% HF dip followed by a 5 min DI water rinse (HB/H_2O rinsed). Table I lists the values of microroughness parameters for the three samples: rms, maximum height R_{max} and mean roughness R_a. It is clear that the silicon surface roughness basically has not been changed by the 1% HF dip and by the subsequent DI water rinse.

To verify the above speculation of the bonding mechanism, the following experiment was carried out. Two 4 in., CZ, (100) commercial silicon wafers were dipped in 1% HF for 1 min without subsequent DI water rinse. They were bonded at room temperature. The bonding strength was estimated by measuring the surface energy γ of one of the wafers in the pair when they were partially debonded by

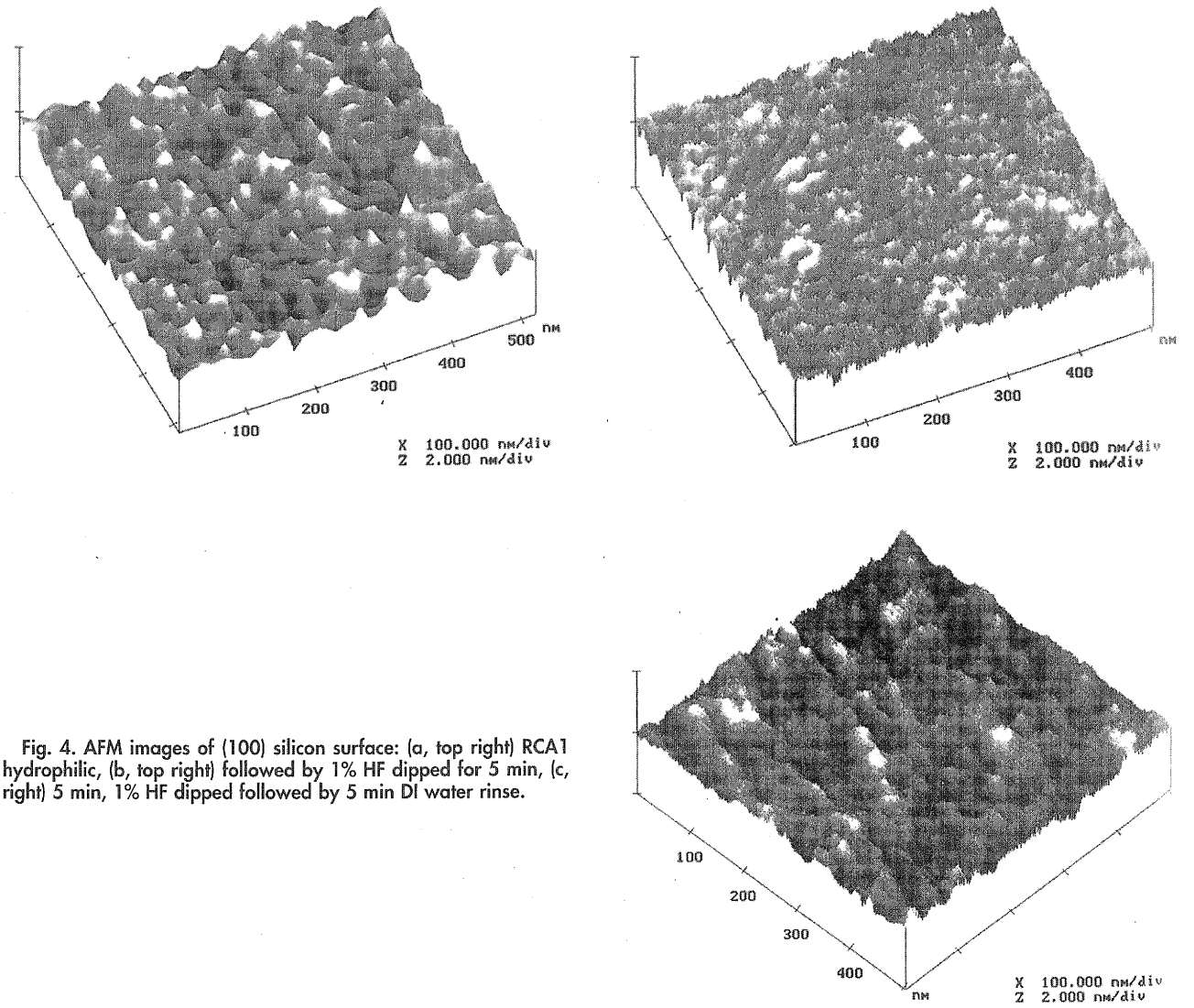

Fig. 4. AFM images of (100) silicon surface: (a, top right) RCA1 hydrophilic, (b, top right) followed by 1% HF dipped for 5 min, (c, right) 5 min, 1% HF dipped followed by 5 min DI water rinse.

Table I. AFM results of microroughness parameters.

Parameters	Original HL Si (RCA1)	1% HF 5 min	1% HF 5 min + 5 min H_2O
rms (Å)	1.44	1.38	1.44
R_{max} (Å)	12.63	14.49	13.27
R_a (Å) mean roughness	1.14	1.06	1.14

inserting a razor blade. The surface energy γ_o was obtained. The pair was then separated completely by a thicker razor blade. The two wafers were kept parallel and separated by a gap of about 1.5 mm in a special rack with three spacers. A DI water flushing through the gap was performed for ~1.5 min. The pair was spin dried and bonded again at room temperature. The surface energy becomes γ. Five pairs of bonded silicon wafers were measured, and an average increase of the surface energy of 50 ± 25% after DI water rinse was observed.

The change of the surface energy should be proportional to the difference in the energy of each hydrogen bond between F···HF and OH–HOH bonds which are 6.7 kcal/mol [11] and 10 kcal/mol (isolated OH groups), respectively.[19] We assume that one Si–F bond is replaced by one Si–OH bond and all SiF bonds have been replaced during the water rinse. We also assume that no Si–OH bonds were generated by reaction between Si–H and HOH. The ratio of the surface energies after and before DI water rinse should be

$$\gamma/\gamma_o = (10/6.7) = 149\% \quad [3]$$

which is in agreement with the experimental results.

One of the bonded pairs was stored in air at room temperature for 500 h following water rinse and room temperature bonding. The surface energy increased to 60 mJ/m^2. It may be attributed to a reaction between water and Si–H on both mating surfaces resulting in a slow replacement of Si–H by Si–OH leading to increased hydrogen bonded OH groups across the two wafers.

In addition to the SIMS profiles of fluorine and oxygen at the interface of the bonded silicon HB and HL pairs, in Fig. 2 the corresponding SIMS profiles of HB/H_2O rinsed pairs after 1100°C annealing for 2.5 h are also shown. It can be clearly seen that the following relations hold for the fluorine concentrations at the bonding interfaces

$$2.4 \times 10^{18}\ \text{cm}^{-3}\ (\text{HB}) > 1.5 \times 10^{18}\ \text{cm}^{-3}\ (\text{HB/H}_2\text{O rinsed}) > 4.0 \times 10^{16}\ \text{cm}^{-3}\ (\text{HL})$$

For the oxygen concentrations at the bonding interfaces we get

$$1.0 \times 10^{22}\ \text{cm}^{-3}\ (\text{HL}) > 6.5 \times 10^{20}\ \text{cm}^{-3}\ (\text{HB/H}_2\text{O rinsed}) > 5.4 \times 10^{20}\ \text{cm}^{-3}\ (\text{HB})$$

Figure 5 is a cross-sectional transmission electron microscope (TEM) image of the interface of the HB/H_2O rinsed pair after 1100°C annealing which shows that there are some randomly disturbed areas at the bonding interface. Although at some places small oxide precipitates are present, no noticeable oxide layer is observed. Similar results were also reported by other researchers.[20]

The SIMS results appear to be consistent with our speculations proposed above. It should be noted that although the peak concentration of fluorine in the HB/H_2O rinsed sample is only 27% lower, the total amount of fluorine in the bonding interface region is much lower for the HB/H_2O rinsed sample than for the HB sample which shows a much broader concentration distribution. Fluorine has a subsurface distribution in an HF-treated silicon (HB) sample.[21] When the HF-treated sample is oxidized (in our case when the polymerization of Si–OH groups across the mating surfaces takes place during annealing of the HB/H_2O rinsed sample) the residual fluorine atoms which were distributed in a subsurface layer and were not replaced by OH groups during the water rinse may pile up at the interface.

Bonding of Fully Hydrogen-Terminated Surfaces

In order to determine whether F or OH groups on commercial silicon wafer surfaces are essential for spontaneous bonding, the bonding behavior of completely hydrogen-terminated silicon surfaces was examined.

It has been demonstrated that excited or ionized hydrogen is able to remove native oxide as well as hydrocarbons on silicon wafer surfaces resulting in a pure hydrogen terminated surface.[22,23] In this work, 3 in., (111), floating zone (FZ) silicon wafers with resistivity of 5000 Ω cm and thickness of 381 ± 25 μm were used. The wafers were cleaned by a commonly used standard RCA solution. The wafers were boiled in both RCA-1 and RCA-2 for 10 min, a 5 min DI water rinse in between, and also at the end. A Balzers modular UHV multichamber system consisting of a load lock, a single-wafer plasma cleaning module, and a Si molecular beam epitaxial (MBE) growth chamber (ULS 630) was used in the experiments. Argon and hydrogen, both with the same flow rate of 20 cm^3/min, were fed into the cleaning chamber where the potential between filament and ground (chamber wall) was 40 V and the discharge current was 20 A. After pumping down of the load lock chamber, the wafer was pushed into the plasma cleaning chamber and immersed in the H_2/Ar plasma for 10 min. The wafer was held in a horizontal position with front surface down and was on a floating potential to avoid sputtering during the plasma cleaning. The pressure in the chamber was ~5.5×10^{-3} mbar, and the wafer temperature was about 200°C during cleaning. After 10 min, the plasma was turned off and the wafer was cooled down for 3 min before being transferred to the load lock and taken out. The native oxide was completely removed and the silicon wafer surface was strongly hydrophobic due to a fully hydrogen-terminated surface after H-plasma cleaning.[22]

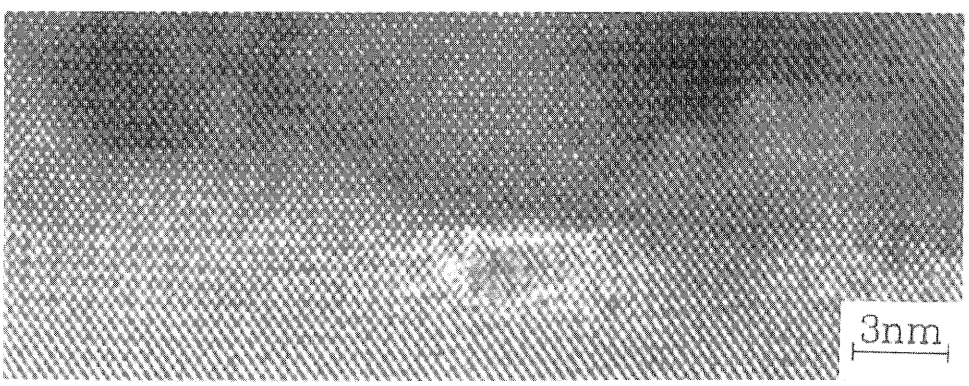

Fig. 5. TEM image of bonded interface of HB/H_2O rinsed pair after 1100°C, 2.5 h annealing.

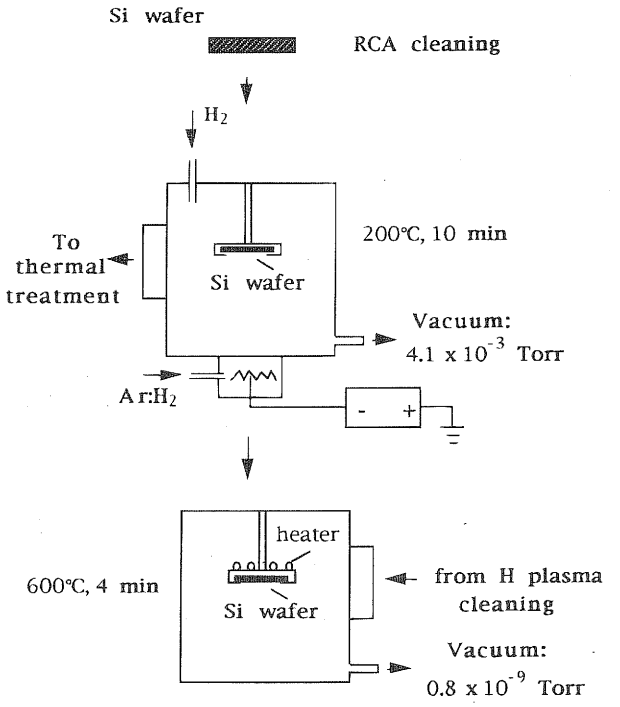

Fig. 6. Schematic diagram of hydrogen plasma cleaning process flow.

In contrast to the prediction of a recent study,[24] the fully H-terminated wafers did not bond to each other in air even when an external pressure was applied. This behavior is understandable since Si–H is very weakly polarized having only a dynamic effective charge of $0.1e$ where e is the charge of an electron.[25] The surface microroughness was not degraded by the low temperature H-plasma cleaning as determined by TEM images. These results suggest that the dispersion van der Waals forces between the two fully H-terminated commercial surfaces are not sufficiently high to bond them together even with the aid of a dipole-dipole force resulting from a dynamic effective charge of $0.1e$ of Si–H bonds.

In order to remove the hydrogen from the Si surfaces, in a separate experiment the wafers were transferred to a silicon MBE growth chamber in UHV of around 8×10^{-10} Torr *in situ* via a transport channel to be treated at 400, 500, or 600°C for 4 min after H-plasma cleaning. A schematic of the H-plasma cleaning and bonding process is shown in Fig. 6. The wafers were then cooled for 10 min before being taken out of the load lock. Two wafers of each of three pairs (six Si wafers) were treated at an identical annealing temperature. Each pair of wafers was then bonded at room temperature by DI water flushing and spin-drying procedures. It has been found that all silicon wafers after thermal treatment at 400 to 600°C became hydrophilic. However, the wafers annealed at 400°C still did not bond to each other well. The 500 or 600°C annealed wafers bonded spontaneously with only two small particle bubbles present in each pair. The surface energy of the room temperature bonded pair was 45 and 127 mJ/m^2 for the 500 and 600°C treated wafers pairs, respectively. The surface energy of the 600°C treated pair was about 86% of that of the same wafer pairs after RCA cleaning while that of the 500°C treated pairs was much lower (~30%). These results can be explained by previous observations[23] that the integrated hydrogen content on the wafer surface is reduced to 38 and 50% of that of the untreated wafers after 600 and 500°C thermal desorption treatment, respectively, while 75% of hydrogen still remains on the surfaces of 400°C treated wafers.

The fresh silicon surface resulting from the thermal desorption of hydrogen quickly formed Si–OH groups after being exposed to air and flushed by water. Therefore, similar to normal hydrophilic silicon wafer bonding, the hydrogen bonding between adsorbed water molecules on the bonding surfaces appears to be responsible for the spontaneous room temperature bonding of the H-plasma cleaned silicon wafers.

Figure 7 shows a cross-sectional TEM image of the bonded interface of a Si/Si pair which was H-plasma cleaned, 600°C thermal desorption treated, and 1100°C, 2.5 h annealed. Only about 2×10^5 per cm interface length of oxide islands (typically 25 Å thick and 300 Å wide) and related defects were present at the interface. The almost perfectly flat bonded interface indicates that the surface microroughness was not degraded during the processing.

Conclusions

1. For successful room temperature wafer direct bonding, wafer surfaces must be sufficiently clean, flat, smooth, and have an appropriate surface chemistry. Although dispersion van der Waals forces which are ubiquitously present on all solids would provide a sufficient attraction force for bonding of supersmooth surfaces, for commercial silicon wafers the introduction of appropriate monolayers on bonding surfaces is crucial for spontaneous room temperature bonding under ambient conditions. For completeness, we mention that recent experimental results have revealed that in ultrahigh vacuum, two clean surfaces of standard silicon wafers may be covalently bonded together at room temperature without such monolayers, with[26] or without[27] the application of an external force.

2. For hydrophilic silicon wafers with a native oxide on the surface the hydrogen bonding between adsorbed water molecules on mating surfaces, Si–OH···(HOH···HOH···HOH)···OH–Si is most likely responsible for spontaneous bonding of commercial silicon wafers.

3. For hydrophobic silicon wafers which are dipped in diluted HF without subsequent DI water rinse, spontaneous room temperature bonding of commercial silicon

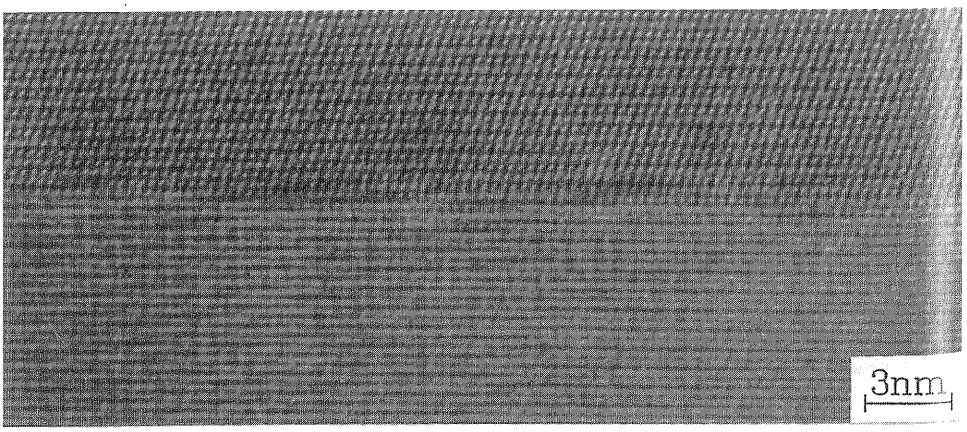

Fig. 7. High resolution TEM image of bonded interface of H-plasma cleaned and 600°C thermally desorbed Si/Si pair after 1100°C, 2.5 h annealing.

wafers appears to be due to Si–F···(HF···HF···HF)···H–Si hydrogen bonding.

4. Because Si–F is replaced by Si–OH during a DI water rinse, for hydrophobic silicon wafers which are dipped in diluted HF with subsequent DI water rinse, spontaneous room temperature bonding of commercial silicon wafers may be caused by Si–OH···(HOH···HOH···HOH)···OH–Si hydrogen bonding.

5. Fully hydrogen-terminated silicon surfaces can be realized by hydrogen plasma cleaning which are hydrophobic and do not bond to each other at room temperature in air in the case of commercially available silicon wafers. Whether an improvement in the smoothness of the silicon surfaces might enable bonding of fully hydrogen-terminated silicon surfaces is an open question.

Acknowledgment

The authors are grateful for material and financial support by SEH Company.

Manuscript submitted March 8, 1996; revised manuscript received Oct. 1, 1996.

Duke University assisted in meeting the publication costs of this article.

REFERENCES

1. M. Shimbo, K. Furukawa, K. Fukuda, and K. Tanzawa, *J. Appl. Phys.*, **60,** 2987 (1986).
2. Q.-Y. Tong and U. Gösele, *Mater. Chem. Phys.*, **37,** 101 (1994).
3. U. Gösele and Q.-Y. Tong, in *Proceedings of the Second International Symposium on Semiconductor Wafer Bonding: Science, Technology, and Applications,* M. A. Schmidt, T. Abe, C. E. Hunt, and H. Baumgart, Editors, PV 93-29, p. 395, The Electrochemical Society Proceedings Series, Pennington, NJ (1994).
4. J. W. Whalen, *J. Phys. Chem.*, **65,** 1676 (1961).
5. D. Hankins and J. Moskowitz, *Chem. Phys. Lett.*, **4,** 527 (1970).
6. T. Sunada, T. Yasaka, M. Takakura, T. Sugiyama, S. Miyazaki, and M. Hirose, *Jpn. J. Appl. Phys.*, **29,** L2408 (1990).
7. S. Watanabe and M. Shigeno, *ibid.*, **31,** 1702 (1992).
8. M. Grundner, D. Graf, P. Hahn, and A. Schnegg, *Solid State Technol.*, 69 (Feb. 1991).
9. T. Takahagi, I. Nagai, A. Ishitani, and H. Kuroda, *J. Appl. Phys.*, **64,** 3516 (1988).
10. Q.-Y. Tong, E. Schmidt, U. Gösele, and M. Reiche, *Appl. Phys. Lett.*, **64,** 625 (1994).
11. L. Pauling, *The Nature of The Chemical Bond,* 3rd ed., p. 461, Cornell University Press, Ithaca, NY (1960).
12. G. J. Pietsch, U. Köhler, and M. Henzler, Materials, Research Soc. Spring Meeting 1993, Y12.4, San Francisco, 1993, p. 459.
13. M. Hirose, T. Yasaka, K. Kanda, M. Takakura, and S. Miyazaki, in *Proceedings of the Second International Symposium on Cleaning Technology in Semiconductor Device Manufacturing,* J. Ruzyllo and R. E. Novak, Editors, PV 92-12, p. 1, The Electrochemical Society Proceedings Series, Pennington, NJ (1992).
14. T. Thomas, H. Elmer, I. D. Chapman, and M. E. Nordberg, *J. Chem. Phys.*, **62,** 2219 (1963).
15. W. P. Maszara, G. Goetz, A. Caviglia, and J. B. McKitterick, *J. Appl. Phys.*, **64,** 4943 (1988).
16. R. Stengl, K.-Y. Ahn, and U. Gösele, *Jpn. J. Appl. Phys.*, **27,** L2364 (1988)
17. L. Pauling, *The Nature of the Chemical Bond,* 3rd ed., p. 635, Cornell University Press, Ithaca, NY (1960).
18. D. Gräf, M. Grundner, and R. Schulz, *J. Vac. Sci. Technol.*, **A7,** 808 (1989).
19. R.K. Iler, *The Chemistry of Silica,* p. 630, Wiley, New York (1979).
20. H. Himi, M. Matsui, S. Fujino, and T. Hattori, *Jpn. J. Appl. Phys.*, **33,** 6 (1994).
21. S. Kasi, M. Liehr, and S. Cohen, *Appl. Phys. Lett.*, **58,** 2975 (1991).
22. B. Anthony, L. Breaux, T. Hsu, S. Banerjee, and A. Tasch, *J. Vac. Sci. Technol.*, **B7,** 621 (1989).
23. J. Ramm, E. Beck, A. Zueger, A. Dommann, and R. E. Pixley, *Thin Solid Films,* **228,** 23 (1993).
24. K. Ljungberg, Y. Bäcklund, A. Söderbärg, M. Bergh, M. Andersson, and S. Bengtsson, *This Journal,* **142,** 1297 (1995).
25. G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, *Appl. Phys. Lett.*, **56,** 656 (1990).
26. H. Takagi, K. Kikuchi, R. Maeda, T. R. Chung, and T. Suga, *ibid.*, **68,** 2222 (1996).
27. U. Gösele, H. Stenzel, T. Martini, J. Steinkrichner, D. Conrad, and K. Scheerschmidt, *ibid.*, **67,** 3614 (1995).