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The Effects of HF Cleaning Prior to Silicon Wafer Bonding

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ABSTRACT

The effects of preparation of silicon surfaces in hydrofluoric acid (HF) solutions, prior to direct wafer bonding, is investigated. Surface analysis with atomic force microscopy, electron spectroscopy for chemical analysis, and estimation of the surface particle density is made. This is related to results from room temperature bonding experiments. A diluted (1-10%) HF solution is most favorable for hydrophobic silicon wafer bonding. The subsequent water rinse should be omitted, or performed in a careful way, to avoid particle contamination. HF:NH_4F solutions generally are not favorable for bonding. The initial room temperature bonding is attributed to the relatively weak van der Waals forces, which makes the bonding sensitive to the surface roughness and particle density. The surface chemistry appears to have a second order influence in hydrophobic bonding.

Introduction

Since the first report on silicon wafer bonding by Lasky and co-workers in 1985,[1] most bonding work published has dealt with hydrophilic surfaces, *i.e.*, the wafers are covered by a thin chemically grown oxide. It has been reported that hydrophilic surfaces are necessary for initial spontaneous bonding to occur, and that hydrophobic surfaces can be bonded only with the aid of an applied pressure.[2] In contrast, we have shown that spontaneous bonding also occurs for hydrophobic oxide-free surfaces.[3,4] Bonding of silicon wafers without any interfacial oxide is important, *e.g.*, for high power devices and as an alternative to epitaxial layers. Hydrophilic bonding always gives an interfacial oxide, resulting in an unacceptably high density of electron states at the interface.[5]

Since there are different opinions regarding the possibility of achieving spontaneous hydrophobic bonding, a closer investigation of how different cleaning processes affect the surfaces is essential. The initial room temperature bonding of hydrophobic surfaces has been attributed to van der Waals forces.[3,6] However, there are other authors arguing that the hydrophobic surface attraction is due to hydrogen bonds between fluorine or hydroxyl (OH) groups, coupled to the surface dangling bonds.[7,8] This should be compared to the initial bonding between hydrophilic surfaces, which has been attributed to hydrogen bonds between OH groups on the surfaces.[1,9]

Van der Waals interactions result from the charge distribution variations, causing temporary dipole moment in the molecules.[10] The forces are weak (5-20 kJ/mol) and the attraction energy decreases with the sixth power of the distance.[11] In case van der Waals forces are causing the attraction, the bonding process is very sensitive to the surface morphology. A somewhat stronger interaction is caused by so-called hydrogen bonds. These are formed when a hydrogen atom attracts two highly electronegative atoms, particularly N, O, and F, and the energies in this case reach values of 20-30 kJ/mol. If such bondings can be achieved between two mating surfaces, the initial, room temperature, bonding is stronger.

It has been observed that a water rinse after the HF etch has a negative effect on the room temperature bondability,[4] but the cause is still unclear. Different contact wave velocities for different concentrations of the HF etchant also were observed. The contact wave is observed as the movement of the border of the bonded area. It is observed by use of infrared light to which the silicon wafer is transparent. In this work we further investigate the effects on surface morphology, chemistry, and bondability after various pretreatments. We have cleaned silicon wafers in various HF solutions and characterized the cleaned surfaces with regard to surface roughness, chemical nature, and particle density. The roughness was measured with an atomic force microscope (AFM) and the chemical nature was measured using electron spectroscopy for chemical analysis (ESCA). The particle density was estimated using dark field microscopy. The results are then compared to results from bonding experiments.

Experimental

Room temperature bonding.—The silicon wafers used were 3 in. [100]- and [111]-oriented wafers, with a thickness of 380 ± 5 μm (Wacker, FZ, 10-12 Ω cm, n- and p-doped). All experiments were performed in a clean room environment. The wafers were etched for 1 to 10 min in aqueous HF solutions (aqHF), with concentrations between 1 and 50%, or buffered HF solutions (BHF), *i.e.*, HF(50%):NH_4F(40%) 1:7 or 1:20. All wafers were blown dry in N_2 after etching. When the wafers are contacted, the contact area spreads like a wave over the whole wafer. This wave was observed in transmitted infrared (IR) light, using an IR camera and a video setup. Normally, a slight pressure with the tweezers at the wafer edge was required to initiate the wave. If the contact area then grows without further help, the bonding is referred to as spontaneous.

AFM.—An atomic force microscope was used to characterize the silicon surfaces regarding topography and roughness. The AFM (Park Scientific Instruments Model SFM-BD2-210) operates at room temperature, under a flow of dry nitrogen gas. The instrument was used in the contacting mode, wherein the sample acts to deflect the Si_3N_4 tip and cantilever by a repulsive force. The topography of the sample is represented by the piezo driving voltage required to keep this deflection constant. The image processing be-

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hind the 3D topographies in this paper is kept at a minimum, so that the pictures represent the surface topographies as closely as possible. The tip is scanned laterally across a 200 × 200 nm area of the surface, and the tip radius is nominally less than 40 nm. Each cleaning procedure was performed as described above immediately prior to the AFM measurement.

ESCA.—Chemical analysis of the surfaces was performed in a sensitive ESCA instrument (Scienta, ESCA-300), using Al-K_α radiation.[12] The surfaces were again prepared as described above, and put into the vacuum chamber of the ESCA system within 30 s after being blown dry. In this instrument the signal from glancing angles can be used without losing sensitivity.[12] The information thus originates from the outermost atom layers only. In the measurements made here take-off angles of 8°, corresponding to an information depth of 5-10 Å, or 45°, corresponding to 35-70 Å, were used.

Particle contamination.—It has been shown that the amount of particles on a hydrophobic, HF-etched, silicon surface increases when the wafer passes an air/liquid interface,[13] *i.e.*, if the hydrophobic wafer is immersed in either the HF solution again, or in water. If so, repeated dipping is deleterious to the bondability. It has been shown that by using a layer of isopropyl alcohol (IPA) on top of the water surface, *i.e.*, the direct displacement technique, particle contamination can be avoided.[14,15] To verify this theory, we estimated the particle density on an HF-cleaned silicon surface, immersed one or several times in H_2O or H_2O/IPA. The liquid surface was contaminated with particles intentionally before immersing the wafers, to ensure a sufficient particle density. The estimation was made using the dark field mode of an optical microscope. Bonding experiments with HF-treated and H_2O/IPA-rinsed wafers were also made.

Some bonding experiments were performed inside a microclean room setup, similar to the one described by Stengl *et al.*[16] In this setup, the wafers to be bonded are placed over each other, with spacers in between, and then spin-rinsed, spin-dried, and bonded inside a chamber without opening it. Thereby the particle contamination is minimized.

Results

Room temperature bonding.—As mentioned before, aqHF-etched wafers have been observed to loose their bondability if they are water rinsed after the etch.[4] Therefore, in this investigation no subsequent rinse was made. The [100] wafers etched in aqHF all bonded spontaneously, although the higher concentration (50%) yields a somewhat slower bonding and more voids than the lower concentrations. This agrees with earlier observations.[4] The bond strength was measured by the razor blade method, first introduced by Maszara *et al.*[17] and was found to be independent of the aqHF concentration.[18]

After some experiments with buffered HF solutions, we observed that deposits (stains) were left on the BHF-etched surfaces if not rinsed in water after etching, possibly consisting of difficult-to-dissolve ammonia salts. Such a salt could be $(NH_4)_2SiF_6$, suggested by Yang *et al.*, who recently reported on observations of deposits from NH_4F solutions.[19] In the following experiments the BHF samples were all water rinsed 1 min after etching.

The [100] surface bondability after BHF etching depends on etching time and mixing rates. After etching for 1 min in BHF (1:20), the bonding is spontaneous, although slow. Wafers etched in BHF (1:7) appear to bond piecewise spontaneously. The contact wave proceeds a short distance and then stops, as if there was a particle preventing its movement. Applying some help, *i.e.*, pressing with the tweezers, makes the wave proceed, but a void is left. A longer etching time, in either of the mixtures, slows down or stops the contact wave.

[111] Wafers treated in BHF 1:7 and 1:20, bonded spontaneously, at a relatively high speed, even after 10 min etching. However some voids are left. After annealing in 1000°C for 30 min, most of these voids disappeared. Etching of [111] wafers in aqHF (10%) gives surfaces that bond piecewise spontaneously, similar to the case described above for [100] wafers in BHF.

AFM.—In Fig. 1 the AFM image of an Si surface treated in 10% HF can be compared with that of an as-received surface. The scale of the z-axis is greatly exaggerated. For convenience the rms value was chosen as a measure of the surface roughness. An as-received [100] surface has an rms value of 0.3-0.4 Å. In Fig. 2 are given the resulting rms values of the surface roughness for different mixing ratios of aqHF, after 1 min etching. The etched surfaces are all still smooth, with surface rms roughnesses below 1.5 Å. The surface roughness dependence on etching time is shown in Fig. 3, for 2, 10, and 50% aqHF. The differences are small, but as can be seen the surface roughness tends to increase with time for the lowest concentration, while the surface in the 50% solution has a constant and low roughness. This indicates that in the highly concentrated solution nothing happens to the surface after removal of the oxide.

In Fig. 4 are given the measured [100] and [111] surface rms roughnesses *vs.* etching time in BHF (1:7, 1:20). The [100] surface get rougher during etching in BHF (1:7), as compared to BHF (1:20). Included in the figure are data for [111] surfaces, etched for 5 min in the two solutions. The rms roughness of an as-received [111] surface was ~0.5 Å. The rms data show that a [111] surface is smoother after 5 min etching in either of the solutions, than a corresponding [100] surface.

ESCA.—Spectra obtained from surfaces treated in different HF solutions are shown in Fig. 5a-c. Correction for charge effects was made by using the C1S as internal reference peak at 284.8 eV. In agreement with other researchers[20] we find the fluorine peak (F1S) at 685 eV, the oxygen peak (O1S) at 532 eV, and the carbon peak (C1S) at 284.7 eV, for all concentrations. The concentrated (50%) HF solution (Fig. 5a) yields a somewhat larger fluorine signal than the more dilute (10%) solution, which agrees with other reports.[21,22] The carbon peak is believed to consist of signals from C-O, C-H, and C-C. Fluorine is mainly present as Si-F.

After a 2 min water rinse, the Si-F peak is shifted toward higher energies (686.2 eV). This can be seen in Fig. 6, where close-ups of the fluorine peaks are shown. The energy shift originates from the presence of oxygen.[21] Further, a new F component can be seen at ~688.6 eV. This peak most likely originates from physisorbed C-F, coming from Teflon in beakers, tweezers, etc.

Particle contamination.—Dark field micrographs of the surface cleaned in 10% HF before and after a water rinse, are shown in Fig. 7a and b. The particles were not spread homogeneously over the surface, so a representative part of the wafer area was chosen. Nevertheless, it gives a fairly good picture of what happens during the cleaning steps. Remember though, that these are artificial particle densities, due to the particle addition. It is clearly visible that immersing the hydrophobic wafer into the H_2O bath drastically increases the amount of surface particles. Covering the water surface with a thin layer of IPA reduced this effect substantially. After rinsing the HF-etched wafer in IPA/H_2O, the amount of particles was comparable to the nonrinsed hydrophobic surface. The surface is still hydrophobic after the rinse. A hydrophilic wafer was almost as particle-free after the rinse as before. These results are in agreement with other reports.[13-15] Wafers treated in HF, and rinsed in IPA/H_2O, bonded spontaneously at room temperature, and showed few voids. However, the wafer must be withdrawn slowly from the IPA-covered water bath to avoid inversion of the liquid meniscus at the wafer surface. This is also pointed out by Walter and McConnel.[15]

When using the micro clean-room setup, the rinsed (still hydrophobic) wafers bonded without visible voids. This indicates that particle contamination could be avoided inside the chamber, which was not possible in the previous exper-

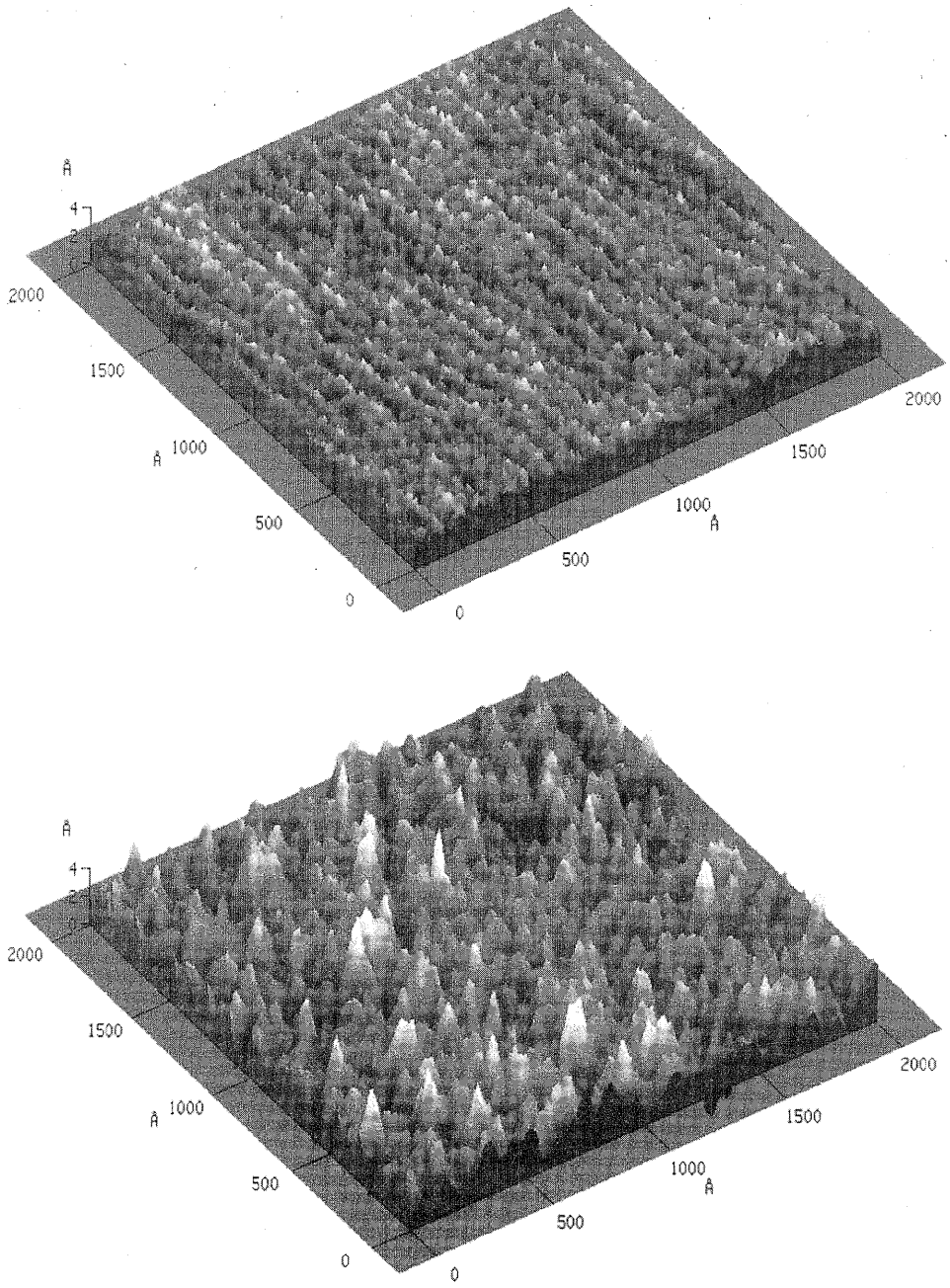

Fig. 1. AFM images of silicon [100] surface, (a, top) as received and (b, bottom) after 5 min etching in a 10% aqueous HF solution. The rms values are 0.39 and 1.29 Å, respectively.

ments. This result also shows that the particle contamination does not originate from the water itself.

Discussion

The etch rate of silicon in an HF solution is small, but measurable.[23] It has been found that the etch rate of silicon in a concentrated strongly acidic HF solution is so small that it is basically inert and only the native oxide is removed.[24,25] An explanation based on the etch mechanism is given: the etching proceeds in two steps, a slow oxidation of the hydrogen-terminated silicon surface by water molecules in the solution, and a fast removal of this oxide by the HF molecule.[25,26] Thus the etch rate is dependent on the OH^--concentration, and therefore higher in a more dilute, or less acidic, solution. This explains our observation: in a concentrated solution the etch rate of silicon is so small that the roughness of the original native oxide/silicon interface is maintained, and there is no further roughening of the surface, while in the more dilute solutions, the etching, and thus the roughening, of the surfaces proceeds. It may be expected that this should make the surfaces etched in low concentrations less bondable than ones etched in higher concentrations. Such dependence could not be seen in our investigation. However, as seen with this method, all the surfaces are extremely smooth, with rms roughness below 1.5 Å.

The effects of treatment in HF and BHF solutions on the silicon surface morphology have been studied by several researchers.[24,25] It has been found that an aqueous HF solution, with a pH between 1 and 2 (corresponding to concentrations of 50 down to 1% HF), probably etches silicon in an isotropic way, while buffering the solution with NH_4F results in an etching anisotropy, which increases with pH.[24,25] For more alkaline solutions, this results in atomically smooth [111] surfaces, and consequently [111] facets on a [100] surface.[25] This may explain the appearance in Fig. 4, where the rms roughness saturates after more than 5 min etching in the more alkaline solution (1:20), indicating that facets appear on the surface, which stops further etching. The number of contact points between the BHF treated [100] surfaces therefore becomes small, which may explain the low bondability of the surfaces treated for longer times in BHF. A major reason for the difficulties in bonding of BHF-etched surfaces are probably the observed deposits, which seem to be hard to dissolve. Remaining deposits could explain the observed piecewise spontaneous

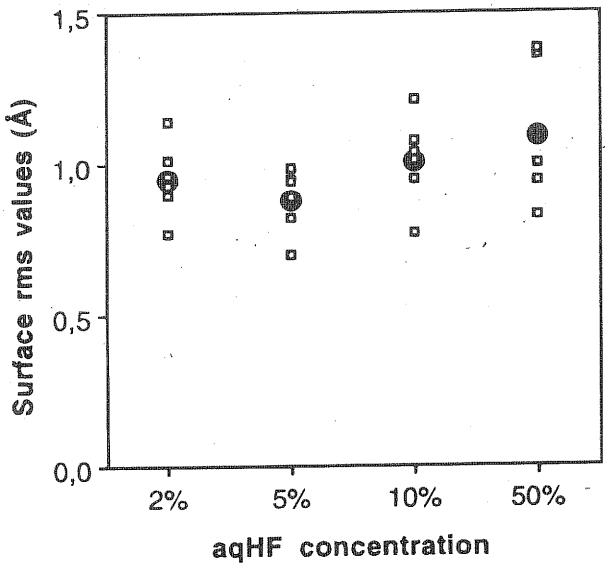

Fig. 2. RMS roughness of Si[100] surfaces after 1 min etching in 2, 5, 10, and 50% aqueous HF solutions. The circular markers are the mean values.

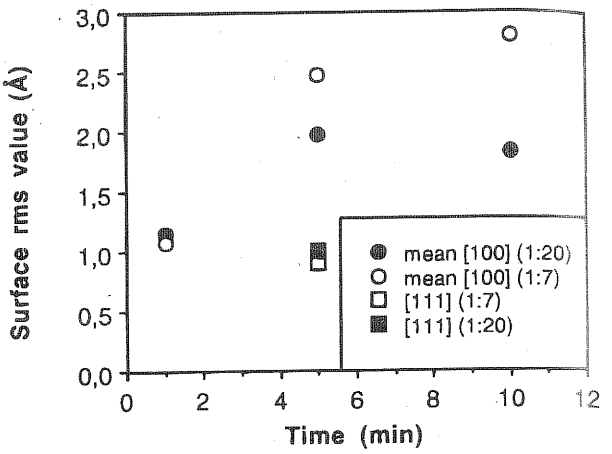

Fig. 4. RMS roughness of silicon [100] and [111] surfaces *vs.* etching time in buffered HF solutions [HF(50%):NH_4F(40%); 1:7 and 1:20]. The data for the [100] surfaces are mean values from six samples, while the [111] data are for one sample each.

bonding behavior. The water rinse that becomes necessary due to these deposits, also may cause particle contamination, in accordance with the observations for aqHF.

HF treated surfaces are believed to be covered to about 90% by hydrogen.[20,21] The mechanism of the initial bonding of hydrophobic surfaces has been discussed by several researchers.[3,6-8] The suggested attraction forces are: van der Waals forces,[3,6] hydrogen bonds between Si-F and H-Si on the mating surfaces,[7] and hydrogen bonds between mating OH groups.[8]

The first possibility includes different kinds of attraction between atoms coupled to the surface. These weak van der Waals forces act between nonpolar, as well as polar, molecules as briefly described above. Hence, if a completely hydrogen-terminated surface could be achieved, a surface attraction should be observed. However, this would probably be weaker than if, *e.g.*, F or OH are present, which is true when HF-etched surfaces with or without subsequent water rinse are used. Polar species would give rise to stronger dipole and hydrogen bonds, and thus increase the total bond strength.

Consider the second theory above, Si-F···H-Si. Our results show that an HF etch yields Si-F on the surfaces, and

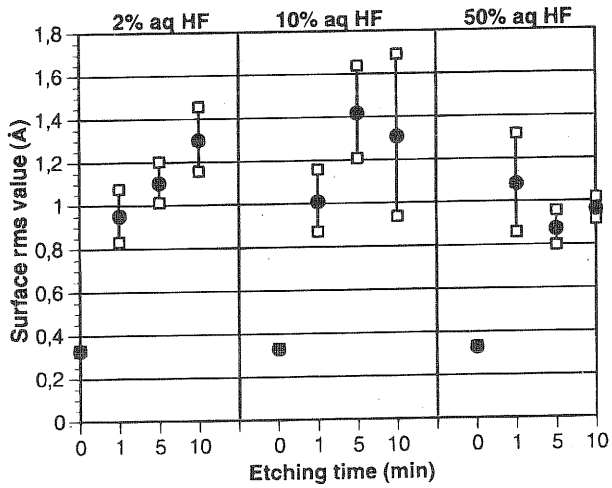

Fig. 3. Mean values (from six samples) of the measured rms roughnesses of silicon [100] surfaces *vs.* etching time in 2, 10, and 50% aqueous HF. The errors bars are based on the standard deviation (6 samples each).

also that a higher HF concentration increases the amount of these groups. This should, if F alone is responsible for the bonding, increase the surface bondability and the resulting bond strength. Further, a water rinse, removing the fluorine, should annihilate the bondability. We have seen that the surface bondability decreases for higher concentrations of aqHF, and that the room temperature bond strength is principally constant for concentrations of 1-50%.[18] This contradicts the above. Also, since the H_2O/IPA or micro-clean room rinsed surfaces were perfectly bondable, the surface fluorine cannot be necessary for initial room temperature bonding to appear, as was suggested by Tong *et al.*[7]

For the third possibility above, namely, hydrogen bonding between OH groups, hydroxyl groups must be present instead of fluorine. Himi *et al.*[8] suggest that, since a water rinse exchanges F into OH, a process including a highly concentrated HF etch followed by a water rinse should give a high density of hydroxyl groups, and consequently good bonding. Since the above results show that water rinsed surfaces can be bonded, although this was not believed in earlier reports,[4] this may be possible. We have seen that water rinsing introduces problems. In the ESCA spectra is seen that the amount of F and C actually increases on the water-rinsed surface, probably originating from physisorption of contaminants such as Teflon. To get rid of these, a slight heat-treatment (to ~200°C) can be made. Additionally, a water rinse, introducing oxygen on the surface, can influence the electrical behavior of the resultant bond.[18]

Water rinsing has earlier been reported to be deleterious for room temperature bonding.[4] We have shown that a careful rinsing procedure can eliminate this problem. The rinsing step is observed to introduce particles on the hydrophobic surfaces. Direct displacement processing, *i.e.*, a thin IPA layer on top of the water surface, prevents this particle contamination, and even removes particles from the wafer surface.[13-15] Our results confirm the prevention of particle addition, and the wafers were perfectly bondable after an IPA/water rinse. Conclusively, the earlier observed nonspontaneous bonding of water rinsed wafers is explained by particle contamination, rather than by modification of the surface chemistry.

It was shown that the use of a bonding chamber like the one presented by Stengl *et al.*,[16] in which the wafers to be bonded are rinsed and spin-dried in a micro clean-room, is another solution to the particle problem. The surfaces bond spontaneously, and there are almost no presence of voids, which was observed in conventional water rinsing. This again leads to the conclusion that the main reason for the earlier observed nonspontaneous bonding of water-rinsed wafers is due to surface particles.

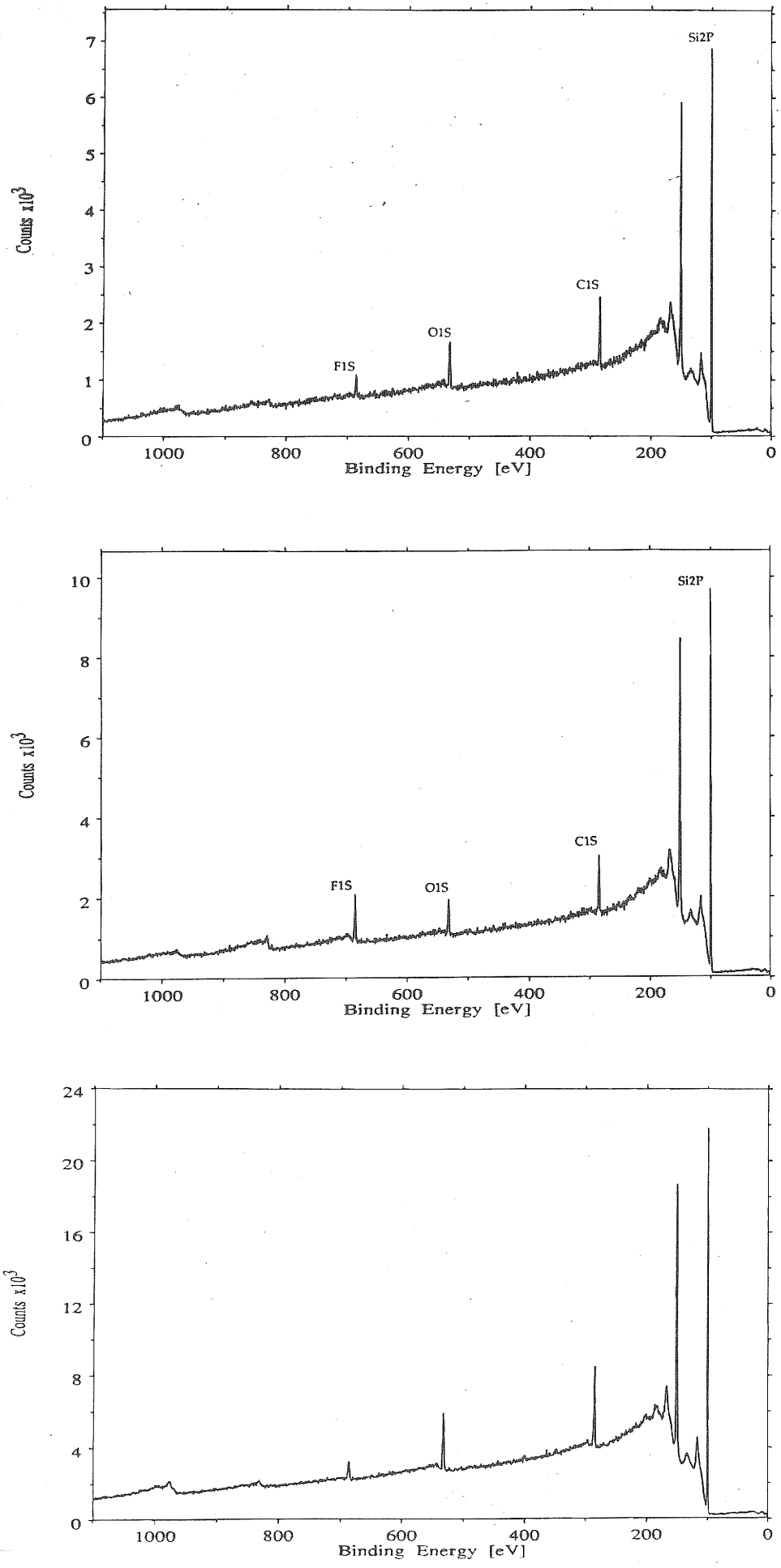

Fig. 5. ESCA surveys from silicon [100] surfaces treated in (a, top) 10% aqueous HF, (b, center) 50% aqueous HF, and (c, bottom) HF(50%):NH_4F(40%), 1:7. Take-off angle 8°.

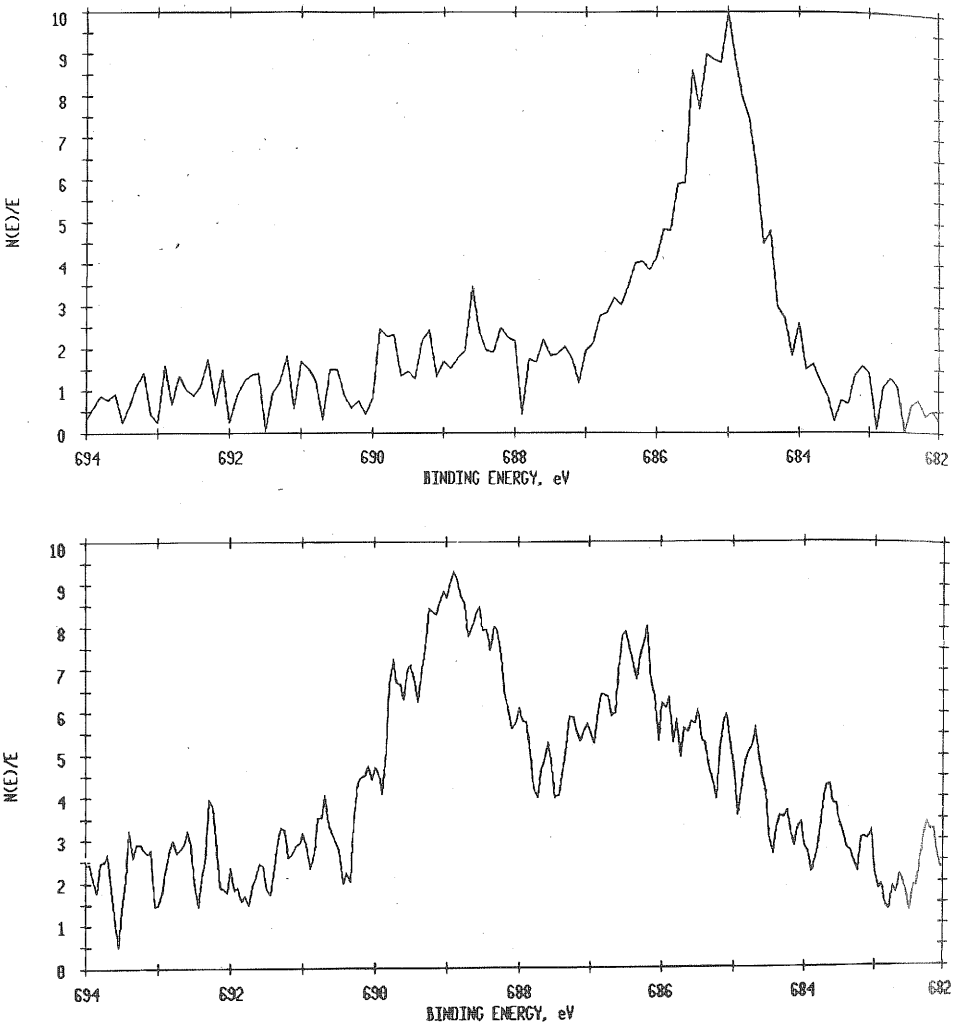

Fig. 6. Close-up of the fluorine (F1S) peaks in the ESCA spectra from silicon [100] surfaces etched in 10% aqueous HF, (a, top) with and (b, bottom) without rinsing in DI water. Take-off angle 45°.

Summary

Based on our results, the following can be concluded regarding hydrophobic bonding of silicon surfaces: if hydrophobic bonding is to be accomplished, an aqueous solution of HF with concentrations between 1 and 10% appear to be the most appropriate pretreatment. Water rinsing should be omitted, unless a careful rinsing process can be done where particle contamination is avoided. Such processes could for instance be the direct displacement technique,[14] or rinse/dry in a micro clean-room.[16] The application should be taken into account, though, since the electrical properties can be affected.

Etching in HF:NH_4F solutions generally is not recommended for bonding. The etching anisotropy increases with the increasing amount of NH_4F. This gives rise to [111] faceting of a [100] surface, which is not favorable for bonding. Smooth [111] surfaces, which bond spontaneously, can be achieved. However, difficult-to-dissolve deposits were observed on the surfaces after BHF treatment. This makes rinsing necessary, which in turn may introduce particles.

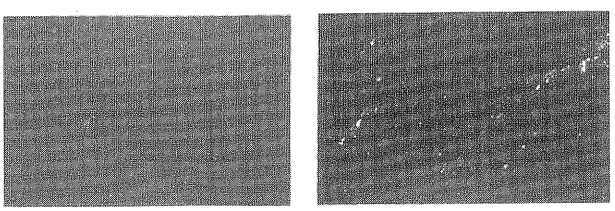

Fig. 7. Dark field micrographs of a silicon surface after etching in 10% aqueous HF (a, left) before and (b, right) after water rinsing. Both liquid surfaces were intentionally contaminated with particles.

The above results show that the main parameters affecting the bondability are the surface roughness and the particle density. The surface chemistry is also important, but appears to be of second order dependence, at least in hydrophobic bonding. If it has not been assured that the surfaces are sufficiently smooth and clean, the surface chemistry makes no difference.

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Effects of Si—C Bond Content on Film Properties of Organic Spin-on Glass

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ABSTRACT

Spin-on glass (SOG) coating solutions containing various amount of Si—CH_3 were synthesized by hydrolytic polymerization from monomers of tetramethoxysilane and methyltrimethoxysilane. Film properties of the SOG film formed from the synthesized coating solutions were evaluated as a function of Si—CH_3 concentration. The film shrinkage linearly decreased with the Si—CH_3 content, and it became zero when the Si—CH_3 concentration was 100%. Water absorption as well as dielectric constant of the film decreased with increasing Si—CH_3 content. Fourier transform infrared spectroscopy showed that this tendency can be attributed to the decrease of Si—OH content, which decreased with an increase of Si—CH_3 content. Si—OH in SOG film causes a high shrinkage of the film due to its heat-induced polycondensation. Si—OH is also the origin of a high dielectric constant and water absorption because of its high polarization. Therefore, SOG with a high organic content is preferred.

Spin-on glass (SOG) has been widely used for an interlevel dielectric material of ultralarge scale integrated circuit (ULSI) for its good step planarizing property.[1-14] Inorganic SOG, which is a solution of slightly polymerized alkoxysiloxane oligomer, was used for this purpose in earlier times.[15-18] Inorganic SOG is synthesized by the hydrolysis of tetraalkoxysilane monomer, and it contains no direct bonds of Si—C in its molecule. Usually, coated SOG film is subject to heat-treatment around 400°C during a curing process. The alkoxysiloxane oligomer undergoes its polymerization accompanied with volume shrinking during the cure process by polycondensation of silanol (Si—OH) included in its molecule.[19-22] However, shrinkage of the inorganic SOG is so large that the film is liable to cause cracking.[19,23] Thus the film thickness of inorganic SOG is restricted to approximately 150 nm. In order to improve the step planarization on patterned interconnection, several iterations of overlapping coating are required.[17,18] Inorganic SOG, however, does not have the capability of forming thick film even by multiple coating because of its poor crack resistance. Namely, inorganic SOG no longer satisfies the requirements of recent progress in ULSI manufacturing.

In order to solve the above mentioned requirements, inorganic SOG material has been developed.[19,24,25] Organic SOG contains direct Si—C bonds in its chemical structure. Organic SOG has been proved to have an excellent crack resistance and a capability to form thick film.[23,24,26] A number of studies have been made to reveal properties of organic SOG film. These studies, however, have been restricted in view of their practical uses, so that a guideline to design the properties of the organic SOG has not been fully understood.

In this study, organic SOG solutions containing various amounts of organic (Si—C) content were synthesized by copolymerization of the monomers. Our own synthesis was essential because SOG solution consisted of some compositions which could not be obtained from market. The composition of the SOG solutions were adjusted as closely as possible to that of commercial products. The film properties of the synthesized SOG were evaluated as a function of the organic content. In addition, the mechanism which explains the film property was presented with respect to the chemical structure of SOG.

Experimental

Synthesis of organic SOG.—The method for the synthesis of organic SOG coating solution is illustrated in Fig. 1. Tetramethoxysilane (LS-8114) and methyltrimethoxysilane (LS-8113) were obtained from Toshiba Silicone Corporation; their purities were 99.9% up. These two raw materials and deionized water were mixed together in a conical flask in the molar ratio indicated in Table I. As for samples 1 and 2, the indicated amount of methanol was added to the mixture in order to retard the polymerization. Except for sample 1, quantities of added water were equiv-

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