

Article

Exploring Chemical Catalytic Mechanisms for Enhancing Bonding Energy in Direct Silicon Dioxide Wafer Bonding

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Featured Application: It is a generic surface treatment for any wafer bonding using direct bonding of silicon dioxide layers such as SOI elaboration, hybrid bonding for 3D application, and CFET using bonding technology.

Abstract: The influence of pH on silicon dioxide direct bonding is studied, unveiling its role in bonding energy enhancement. We show that the deposition of basic salt or molecules consistently increases the silicon dioxide adherence energy. The underlying mechanisms, including silica hydrolysis and catalysis of siloxane bond formation, are explored. The results offer valuable insights into optimized direct bonding processes for microelectronics and related applications.

Keywords: direct molecular bonding; silicon dioxide bonding; bonding energy; adherence energy

1. Introduction

Direct bonding is a well-established technique with a wide range of applications, attracting significant interest due to its spontaneous bonding nature and the absence of intermediate materials. It is particularly relevant for microelectronics, microelectromechanical systems (MEMS), and biomedical devices [1–5]. In direct bonding, two types of energy are involved: adhesion and adherence [6–8]. Adhesion refers to the energy developed during bonding that enables mechanical deformation of the substrates [9–12], while adherence is the classical bonding energy required to separate the wafers after bonding [13–17]. Enhancing adherence, i.e., mechanical strength, at low post-bonding annealing (PBA) temperatures (<500 °C) is a key challenge in direct bonding. Many applications, particularly those involving CMOS devices on at least one of the wafers, cannot tolerate PBA temperatures above 400 °C. This is especially true for hybrid bonding, which enables advanced 3D applications. In this context, a PBA temperature of 400 °C is typically used for the copper/SiO₂ hybrid interface. Moreover, for certain applications, such as memory devices, PBA temperatures of 200 °C or lower are required [18–22]. Achieving high bonding energy at low PBA temperatures is therefore crucial.

Another prominent application that justifies this research is photonic integration on silicon, which has gained considerable interest. This application involves bonding III/V components to silicon wafers, where the coefficient of thermal expansion (CTE) mismatch between the materials restricts the use of high PBA temperatures. For example, direct bonding of indium phosphide (InP) to silicon is typically not annealed above 300 °C to avoid exceeding the brittle–ductile transition temperature (BDT) of InP, which is approximately



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350 °C [23,24]. Again, achieving high adherence after low-temperature PBA (below 500 °C) is highly desirable.

Methods such as plasma treatments and chemical mechanical polishing (CMP) are known to improve bonding adherence at low temperatures [25,26]. However, plasma treatments often require expensive equipment and may introduce drawbacks. For example, in hybrid bonding, plasma treatment can cause copper to sputter onto the dielectric surface, potentially leading to electrical leakage, particularly for future ultra-high-density interconnections with small pitch [27]. Additionally, plasma treatment can significantly increase the amount of interfacial water, as surface modifications at the nanoscale enhance hydration as shown by Larrey et al. [28]. This excess water could contribute to oxidation during PBA, potentially inducing bonding defects. CMP, on the other hand, does not always enhance bonding energy, as its effectiveness depends on the type of slurry used. The slurry may not always be compatible with the surface preparation needed to improve roughness and planarity. It may be beneficial to use CMP for its primary function while exploring other surface preparation techniques to enhance bonding energy.

Recently, N,N-diethylethanolamine (DEAE), an organic molecule, has been shown to enhance adherence at temperatures below 500 °C [29,30]. This is an exciting development, as DEAE is a low-cost solution that performs similarly to plasma treatment without causing morphological changes to the surface (such as sputtering or subsurface modification). This new technique for enhancing direct bonding energy could enable plasma-free surface preparation, even for applications requiring low PBA. In this study, we further explore this technology by testing other acidic and basic molecules, as well as salts, to identify the most promising candidates. We selected molecules with low vapor pressure to ensure they remain on the surface after drying. This is why some salts, which have no vapor pressure, were included in the study. Additionally, we chose acidic molecules to confirm whether the basic character is essential for enhancing bonding energy. By varying the pKa values, we aim to gain a deeper understanding of the direct bonding mechanisms associated with these molecules and salts.

2. Materials and Methods

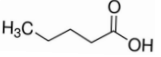
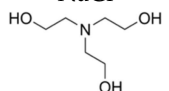
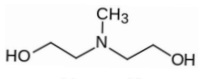
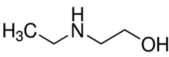
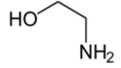
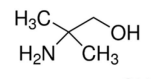
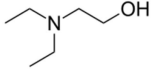
2.1. Adsorption of Chemical Species and Wafer Bonding

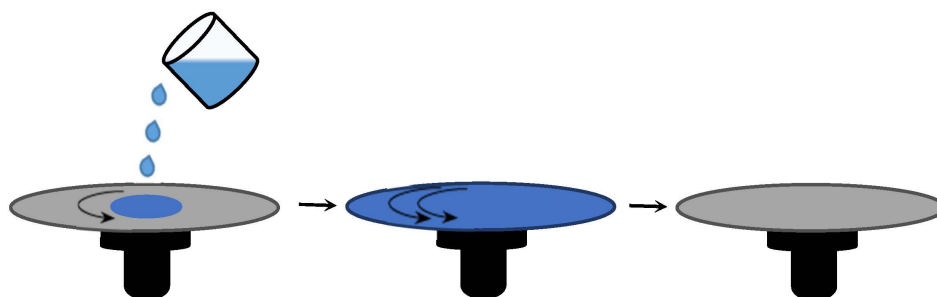
For this study, 200 mm (001) silicon wafers are used. A 100 nm thick thermal silicon dioxide (SiO₂) layer is grown on each wafer at 950 °C under a steam atmosphere. Wafers are, in the first step, cleaned using a standard DiO₃ and RCA (Radio Corporation of America) SC1/SC2 chemical treatment. They are dried using a Marangoni dryer.

Various chemical species (salts or organic molecules) with different acid dissociation constants are then applied to silicon dioxide wafer surfaces by spreading aqueous solutions (refer to Table 1). The chosen molecular solution (at a concentration of a few 10^{−4} g/cm³ in water) is poured onto the wafer surface and spread by rotating the wafer at 200 rotations per minute (rpm) for 45 s. The surface is then spin-dried at 2000 rpm for an additional 45 s (see Figure 1). Reference wafers are treated with pure DiW (deionized water) instead of the various chemical species.

Wafers exposed to the same solutions are bonded manually at room temperature within 5 min, in a clean room air atmosphere, following the drying step. After bonding, annealing is conducted at 100 °C for 2 h. The annealed structures are then cut into 20 mm wide beams and stored in a low-humidity atmosphere (<5% relative humidity, RH). This low-humidity storage will prevent the bonding interface from being filled by water and prevent any impact on direct bonding energy [31,32]. As soon as possible (<2 days), each beam undergoes annealing at desired temperatures (<500 °C) for two hours prior to bonding energy measurements.

Table 1. Table of the different evaluated molecules and salts with their partial vapor pressure (P_{vap}), acidic constant (pKa), topological formula, and molecular weight (g/mol).

Molecule Name	P_{vap} (Pa)	pKa	Formula	Molecular Weight	Supplier Merck
Hydrochloric acid	0		HCl	36	1.09057
Pentanoic acid	23	4.84		102	8.00821
Deionized water (DiW)	2340			18	
Sodium chloride	<1		NaCl	58	59222C
Triethanolamine	1	7.76		149	90279
N-Methyldiethanolamine (MDEA)	<1	8.52		119	471828
Ammoniac	860×10^3	9.23		17	09859
2-ethylamino-ethanol	<1	9.47		89	471461
Ethanolamine	50	9.5		61	15014
2-amino-2-methyl-1-propanol	<1	9.7		89	08578
N,N-Diethylethanolamine (DEAE)	190	9.87		117	471321
Sodium hydroxide	0		NaOH	40	1.09137

**Figure 1.** Experimental liquid solution spreading process.

Different tools are used in this study: a GC2441M infrared camera from Framos; a SAM_501_HD² acoustic microscope from PVA TEPLA (Westhausen, Germany); an SP2 from KLA Tencor (Milpitas, CA, USA) for the diffusion light scattering characterization; a Dimension FastScan AFM from Brücker (Palaiseau, France); and a VPD300A Rigaku (Neu-Isenburg, Germany) for the TXRF measurement. For the WOS/ATDGCMS, this measurement is outsourced to Tera Environment (Crolles, France). In order to avoid any transportation issues, we sent Tera Environment bonded wafers with trapped molecules at the bonding interface. The bonded are not annealed and Tera Environment debonds the wafer just before entering inside their measurement tool.

2.2. Bonding Energy Measurement

Bonding energy (adherence) is assessed using the Double Cantilever Beam technique (DCB) under prescribed displacement. A blade is inserted at the bonding interface, and the debonded length is measured. Transparency of silicon to infrared (IR) light facilitates mea-

surement using an IR camera. Bonding energy (G) is evaluated using El-Zein's formula [16] (Equation (1)).

$$G = \frac{3\delta^2 t^3}{16\beta_{11} a^4} \cdot \frac{1}{1 - \frac{t^3 \beta_{26}}{8\beta_{11} a^4}} \quad \text{with } \beta_{ij} = S_{ij} \frac{S_{13} S_{33}}{S_{33}} \quad (1)$$

where δ represents blade thickness, t the wafer thickness, and S_{ij} denotes compliance tensor factors. The crack length, a , is the sum of the debonded length measured by the IR camera (X_m), the blade bevel length (X_b), and a calculated length (X_λ) which is the distance between the first IR optical interference and the crack tip (Figure 2) [33]. To avoid water stress corrosion coming from the clean room atmosphere humidity, all bonding energy measurements are performed in an anhydrous atmosphere with a water concentration in nitrogen below 1 ppm. Indeed, it is important to remove any impact on bonding energy of the well-known silica water stress corrosion (WSC) [34,35]. This WSC impact the DCB bonding energy measurement has seen with DCB performed in vacuum [36], during steady-state DCB as shown by Bertholet et al. [37] or in anhydrous nitrogen [38]. The DCB measurement method using anhydrous atmosphere has been previously developed in our laboratory (cf. Figure 3) [33]. Even if the DCB is performed under anhydrous nitrogen, the bonding energy is taken after 5 min in order to take into account the internal water stress corrosion coming from the water trapped at the bonding interface [39–43]. Indeed, as it is the water of the bonding interface itself that is important, this time, we must take into account the WSC due to this specific amount of water.

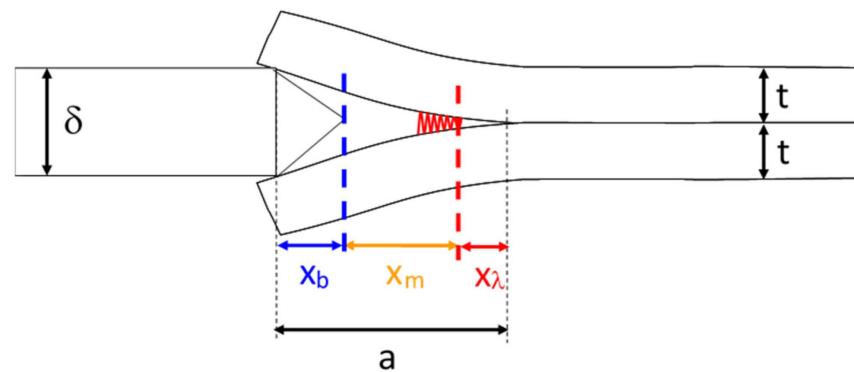


Figure 2. Principle of the DCB under prescribed displacement for direct wafer bonding energy measurement. δ is the blade thickness, t the wafer thickness, and a the crack length, which is the sum of the blade bevel X_b , the IR debonded length measurement X_m , and the calculated post IR debonded length X_λ [33].

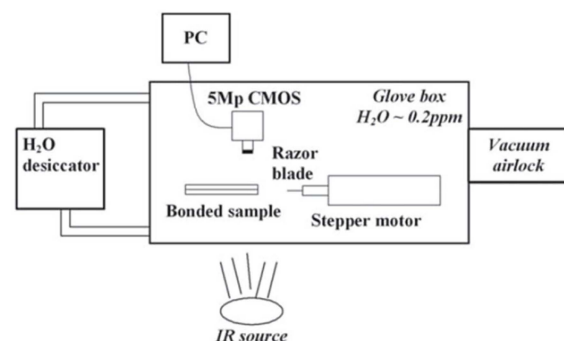


Figure 3. Experimental setup for anhydrous DCB bonding energy characterization [33].

3. Results

As shown in Figure 4a, the bonding waves for the different samples are smooth, with a nearly constant velocity of approximately 20 mm/s, which is typical of standard

hydrophilic bonding. This suggests that the adhesion energy is not affected by the different surface treatments. No bonding defects are detected, even when using scanning acoustic microscopy (see Figure 4b).

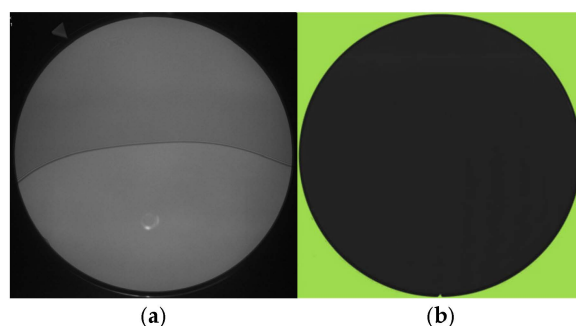


Figure 4. (a) Infrared characterization of the bonding wave, taken midway through its propagation. The white spot in the middle of the first half of the image corresponds to the infrared camera's image and is not a bonding defect. (b) Typical scanning acoustic microscopy image of the bonding studied. No bonding defects are detected. The pixel size is 10 μm .

Figure 5 shows the evolution of anhydrous direct bonding energies as a function of annealing temperature for various acidic and basic molecules. The concentrations were chosen to remain below the threshold for inducing particle contamination after spin drying. Although ammonia could have been used at a higher concentration, a similar concentration to the other molecules was chosen for comparative purposes. Regardless of the annealing temperature, the bonding energies increase in the presence of basic molecules.

Expanding on this finding, the influence of the pH of the spin-dried solution is examined using strong base NaOH solutions at concentrations ranging from 10^{-8} g/cm³ to 10^{-5} g/cm³. A NaOH solution of 10^{-5} g/cm³ represents the maximum concentration enabling spontaneous bonding. Indeed, with a NaOH solution of 10^{-4} g/cm³, bonding does not occur due to excessive NaOH “particles” (Figure 6), detected using diffusion light scattering with a size threshold of 1000 nm.

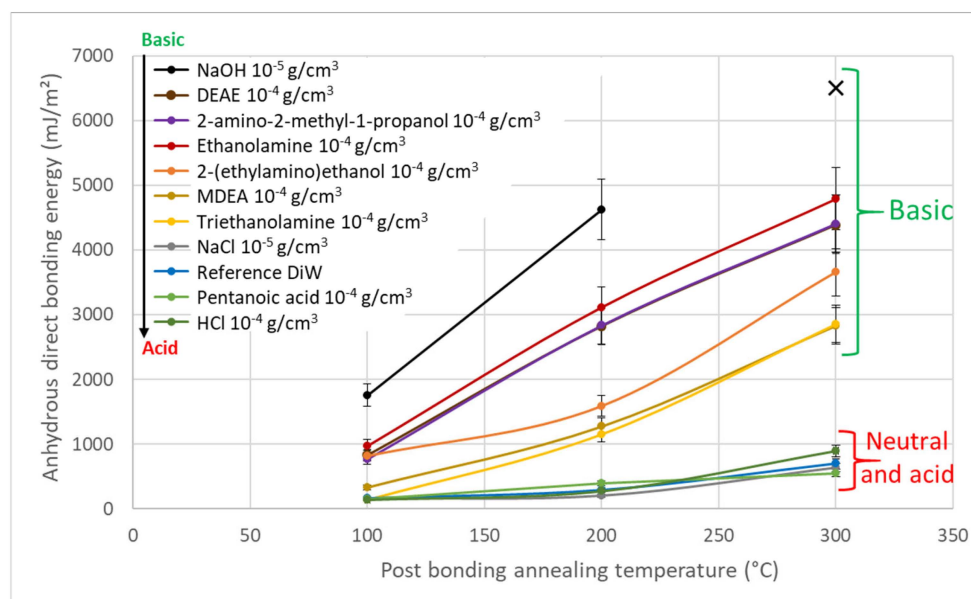


Figure 5. Influence of various acidic and basic molecules on anhydrous direct bonding energy as a function of the annealing temperature. The cross represents the sample breakage, meaning that the bonding energy is higher than Si bulk material fracture energy (We have chosen arbitrarily to put the cross at 6.5 J/m²).

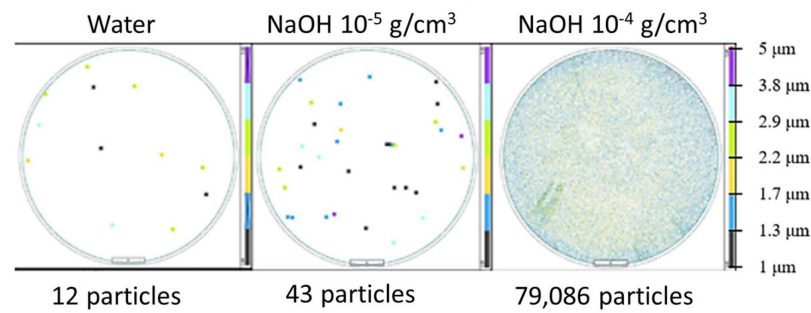


Figure 6. Diffusion light scattering images @1000 nm of Si wafers after water or NaOH solution dispense at two different concentrations.

These “particles” are probably sodium hydroxide crystals. Indeed, atomic force microscopy (AFM) did not reveal any changes in roughness (see Figure 7), and after DiW rinsing (Figure 8), fewer and smaller “particles” were otherwise detected on the wafer surface.

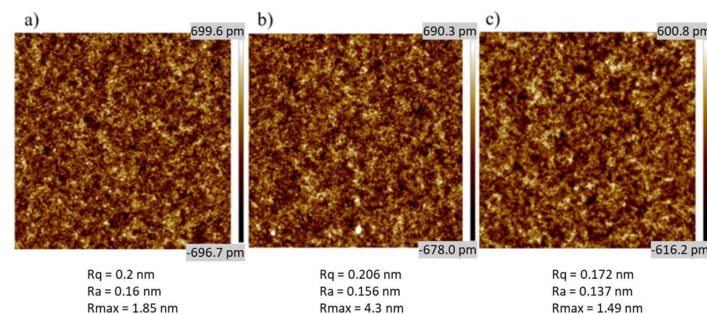


Figure 7. AFM (atomic force microscopy) images (scan size = 1 μm) of SiO_2 surfaces after spreading of: (a) deionized water, (b) $\text{NaOH } 10^{-5} \text{ g/cm}^3$ solution, and (c) $\text{NaOH } 10^{-4} \text{ g/cm}^3$ solution.

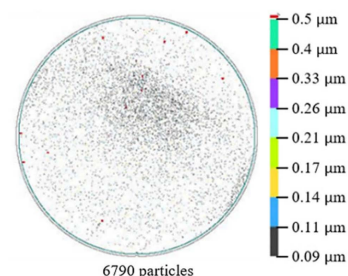


Figure 8. Diffusion light scattering images @90 nm of Si wafers after $\text{NaOH } 10^{-4} \text{ g/cm}^3$ solution dispense and DiW rinse.

Figure 9 shows that, at concentrations below 10^{-5} g/cm^3 , higher NaOH concentrations result in higher bonding energies whatever the annealing temperature. High pH thus yields high direct bonding energies, given the calculated spreading pH solution for each NaOH mass concentration (refer to Table 2). The influence of cations will be discussed later.

Table 2. Calculated pH of NaOH solutions that are spread on wafers prior to bonding.

NaOH Solution Concentration	Calculated pH
10^{-5} g/cm^3	10.4
10^{-6} g/cm^3	9.4
10^{-7} g/cm^3	8.4
10^{-8} g/cm^3	7.4

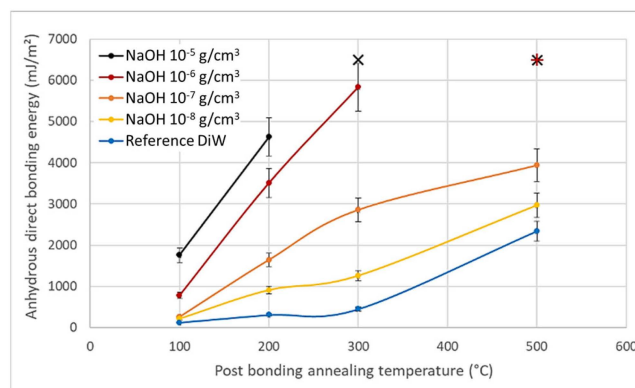


Figure 9. Influence of NaOH concentration in DIW on the anhydrous direct bonding energy for various annealing temperatures. Crosses represent sample breakage, meaning that the bonding energy is higher than Si bulk material fracture energy (we have chosen arbitrarily to put the cross at 6.5 J/m^2).

Bonding energies obtained after annealing at 300°C for 2 h with different chemical species are plotted in Figure 10 for various pHs. From these experiments, we deduce that increasing the amount of deposited hydroxide ions enhances silicon dioxide's direct bonding energies. A notable exception is ammonia ($4.5 \times 10^{-4} \text{ g/cm}^3$), yielding the same bonding energy as neutral or acidic molecules. This may be attributed to its high vapor pressure; this molecule likely evaporates from wafer surfaces prior to bonding, thus no longer being present at the bonding interface in our experiment conditions. However, if a solution were found to retain ammonia at the bonding interface, an enhancement in bonding energy should be measurable.

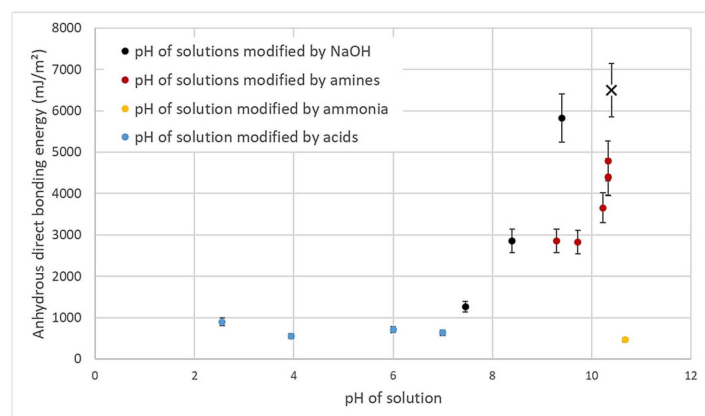


Figure 10. Anhydrous direct bonding energy of SiO_2 bonding as a function of pH of the dispensed solution, for a 300°C annealing during 2 h. The cross represents the sample breakage.

Noteworthy, the pH value of Figure 10 is only the pH value of the solution poured on the surface, not the pH of the bonding interface water itself. In order to investigate the link between adherence and deposited salts or molecules, we first tried to measure the number of species trapped at the interface. Direct measurements after wafer debonding and prior to annealing seem the most effective way of quantifying surface concentrations of molecules. For NaOH, total reflection X-ray fluorescence (TXRF) can be used to detect sodium atoms (refer to Table 3). Indeed, the Na^+ ionic concentrations vary depending on the concentration of the solution spread. As far as organic molecules are concerned, a wafer outgassing system (WOS) coupled with an automated thermal desorber–gas chromatography–mass spectrometer (ATD–GC–MS) can be used to quantify DEAE concentrations on wafer surfaces (just after wafer debonding). DEAE surface concentrations are comparable to Na

concentrations (refer to Tables 3 and 4), confirming the effective embedding of this specific molecule at the bonding interface. Of course, all these measurements could have been performed directly after the solution pouring. Especially for organic molecules, their vapor pressure is imposed to perform the measurement as soon as possible after the deposition, which is not easy to put in place. The bonding is then used here as a convenient path to protect the surface waiting for the measurement to be ready.

Table 3. Na⁺ concentrations on wafer surfaces from TXRF. 2×10^{11} at/cm² is the TXRF detection limit for Na⁺.

Dispense Solution	Na ⁺ Concentration on Wafer Surface (at/cm ²)
H ₂ O	$<2 \times 10^{11}$
NaOH 10^{-8} g/cm ³	$<2 \times 10^{11}$
NaOH 10^{-7} g/cm ³	2.8×10^{11}
NaOH 10^{-6} g/cm ³	1.8×10^{12}
NaOH 10^{-5} g/cm ³	1.2×10^{13}
NaOH 10^{-4} g/cm ³	8.4×10^{13}

Table 4. DEAE concentration on wafer surfaces measured by WOS/ATDGCMs.

Dispense Solution	DEAE Concentration on Wafer Surface (molecule/cm ²)
H ₂ O	ND
DEAE 10^{-6} g/cm ³	ND
DEAE 10^{-5} g/cm ³	9.74×10^{12}
DEAE 10^{-4} g/cm ³	8.14×10^{13}

Clearly, the molecule concentration on the silicon surface is not easily deduced from its bulk spreading solution concentration. Indeed, from the last value, theoretical NaOH and DEAE surface concentrations can be calculated for a 1 cm² surface, assuming 0.8 monolayers of adsorbed solution [44]. This would yield concentrations four orders of magnitude lower than actually measured surface concentrations, indicating a substantial concentration effect during drying, with water molecules evaporating more rapidly than added molecules (except for ions). However, evaporation kinetic differences are not high enough to explain such surface concentrations of molecules. High ion concentrations at the surface suggest the presence of electrostatic interactions (double layer effect) at the charged silica surface [45]. Calculations of surface concentration have been performed using Poisson Boltzmann equations. They are, however, beyond the scope of this article.

The pH value of the deposited solution is the key parameter in explaining the increase in bonding energy in this study. However, just as the concentration of molecules at the surface cannot be directly inferred from that of the solution, the pH at the bonding interface (if such a concept is meaningful) cannot be straightforwardly deduced from the pH of the spreading solution. Furthermore, knowing the molecular concentration at the surface provides limited insight, as the amount of water at the bonding interface depends on numerous factors, making it difficult to estimate an “interfacial pH” value.

Indeed, firstly, the humidity of the bonding atmosphere affects the amount of water adsorbed on the surfaces. Additionally, the propagation of the bonding wave itself could alter the water content at the interface. For example, gas compression between wafers during bonding increases its temperature, influencing the equilibrium between the surface and the atmosphere. It is the opposite of the edge bonding void generation mechanism, which is driven by gas decompression, lowering the temperature and causing water droplet condensation at the wafer edges [46–48]. The compression associated with bonding wave propagation explains why using dry gases like nitrogen or argon alone is insufficient to

prevent voids [46], as these gases can remove water from the wafer surface. Moreover, the water quantity at the interface may vary during the queue time before annealing. As demonstrated by Tedjini et al. [44], the water content at a hydrophilic silicon dioxide bonding interface can range from 1.6 to 3.4 monolayers, partially filling surface roughness gaps.

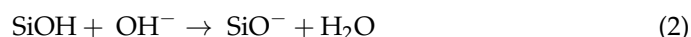
Given these complexities, it is difficult to determine the exact water content at the bonding interface, which is thus challenging to calculate concentrations. Additionally, at an interface width of only 1 nm, water ceases to behave like a liquid and exhibits properties more akin to ice, significantly reducing atomic mobility. Even if the concentration, acid-base equilibrium, and pH value could be determined, their physical interpretation under such interfacial confinement would differ markedly from conventional conditions. Therefore, focusing on the quantity of molecules may offer more practical and meaningful insights.

4. Discussion

The lattice parameter of the (001) silicon surface is 0.543 nm with two atoms per lattice cell, resulting in a silicon surface density of about 7 atoms/nm². A fully hydrophilic silicon dioxide has, according to Iler, a maximum silanol concentration of 5 to 8 nm⁻² [49]. Even with the highest surface concentrations of molecules or cations, the wafer surface is covered by less than 1/10 of a monolayer of DEAE or NaOH. A small quantity of active molecules significantly enhances the bonding energy, suggesting that molecules act more as catalysts than directly participating to the adherence mechanism.

Three mechanisms can be proposed to elucidate the bonding energy enhancement.

1. According to the model of Rieutord et al., direct bonding relies heavily on the contact of asperities [50]. For hydrophilic bonding, at room temperature, wafer adhesion primarily results from capillary bridges, hydrogen bonds and van der Waals forces [6]. Even at room temperature, occasional covalent bonds may also form at contact points (asperity summits), accounting for the observed increase in bonding energy under specific circumstances at room temperature [39]. OH⁻ ions are known to speed up the dynamics of siloxane bond formation by condensation of silanols, as observed e.g., in silica gel formation processes [49]. In silanol condensation, OH⁻ play the role of nucleophilic agent. Increasing the pH will then increase the silanol condensation kinetics. It is indeed widely recognized that OH⁻ ions can initiate nucleophilic attacks on surface Si atoms, resulting in the formation of siloxane bonds [51], as shown in Equations (2) and (3).



In presence of SiO⁻, the formation of siloxanes bonds is favored (Equation (6)).



As obvious from the equilibrium between Equations (5) and (6), OH⁻ ions directly catalyze the condensation reaction of silanols into covalent siloxane bonds, resulting in a bonding energy increase.

2. Based on the mechanism proposed by Fournel et al. [39], during annealing, water molecules trapped at the bonding interface hydrolyze silicon dioxide asperities. As the annealing progresses, water molecules infiltrate the oxide asperities volume and break certain silanol bonds. Consequently, asperities become more viscoplastic and are flattened, enabling the formation of new interfacial covalent bonds and thereby increasing the bonding energy (see Figure 11).

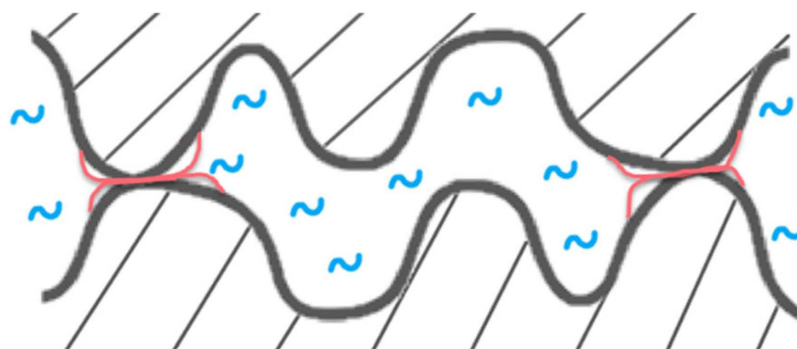
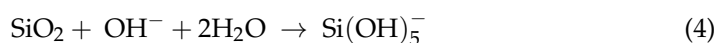


Figure 11. Asperity contact model with flattened asperities through silica volume hydrolysis.

Extensive research has been conducted on the exacerbation of silica and quartz hydrolysis under alkaline conditions [52,53]. Hydrolysis even intensifies with higher temperatures. The incorporation of basic molecules, which change the pH of interfacial water, increases hydrolysis mechanism described above and explains the bonding energy enhancement. This influence becomes even more pronounced during post-bonding anneals. Notably, the impact of alkaline ions on silica hydrolysis has also been extensively explored [54,55]. In addition to pH influence, Na^+ ions could also enhance the silica hydrolysis. However, as shown by Callagon La Plante et al. [56], the influence of a high pH (≥ 10) predominates over the type of cation influence. The cation influence might then be neglected for the moment.

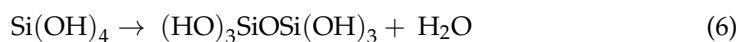
3. Another mechanism could be proposed suggesting that bonding energy enhancement can be attributed to silica dissolution and immediate condensation on the bonded asperity surface. It is well-established that OH^- ions attack and dissolve silica surface, as described in Equation (4) [57]:



A portion of the silica is dissolved increasing $\text{Si}(\text{OH})_5^-$ species in the interfacial water. These silicate ions subsequently form $\text{Si}(\text{OH})_4$ (Equation (5)):



Subsequently, $\text{Si}(\text{OH})_4$ can change into siloxane chains, as described in Equation (6):



Given that the bonding interface is a confined system (interface width ≈ 1 nm), the silicate compound could condense elsewhere at the interface [58]. In our context, it is conceivable that condensation is more efficient around contact points, potentially due to an increased number of binding sites, thereby resulting in higher bonding energies (see Figure 12). These contact points experience compression (approximately 100 bars [50]), which could explain the localization of condensation to mitigate elastic energy. Enlarging the contact point will reduce the compression pressure inside the asperities induced by van der Waals. This will reduce the interfacial elastic mechanical energy.

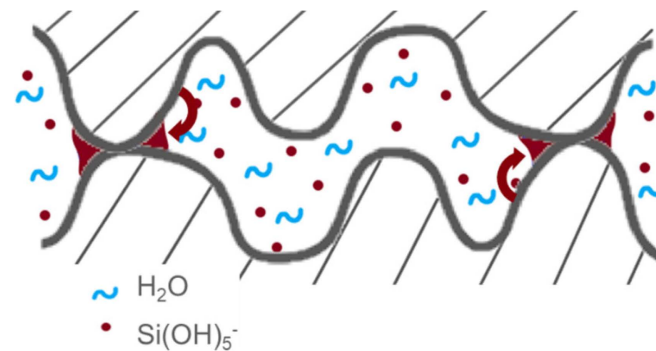


Figure 12. Asperity contact model with surface hydrolysis condensation.

However, this third model should no longer be considered. As demonstrated by P. Noël et al. [59], certain specific molecules can boost adhesion to the same extent without etching the SiO_2 layer. Obviously, without silica dissolution phenomenon, no silicates condensation could appear. P. Noël evaluated the impact of CsF, CsOH, and NaOH on bonding energy evolution during post-bonding annealing treatment.

As shown in Figure 13, all three salts have the same effect on adherence, with the fluoride ion (F^-) exhibiting the same impact as the hydroxide ion (OH^-).

However, as depicted in Figure 14, CsF does not etch silica more than deionized water (DiW), whereas NaOH shows a significantly higher etching rate.

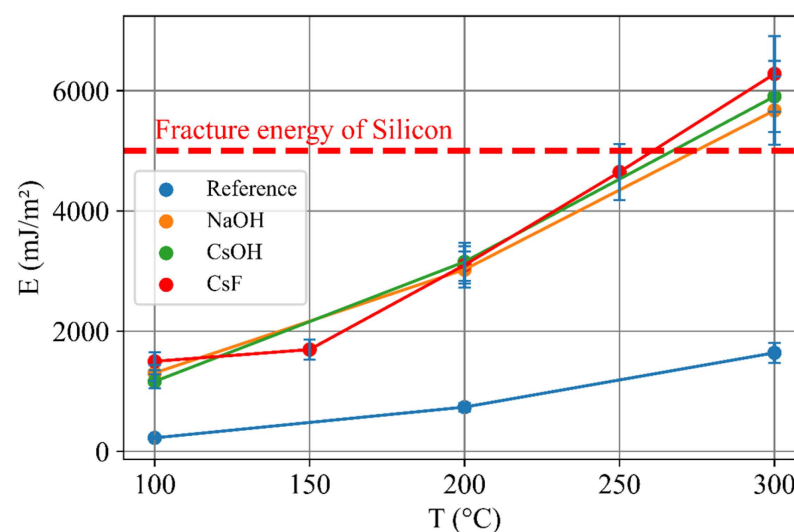


Figure 13. Bonding energy as a function of annealing temperature for the Reference (no catalysts), NaOH, CsOH, and CsF samples for 2 h annealing [59].

Therefore, the primary mechanism for bonding energy enhancement does not appear to depend on silica dissolution into silicates and condensation of these silicates on contact points.

To differentiate between the two first models, a comparison with plasma effects at room temperature has been performed (see Figure 15). Indeed, a reactive ion etching (RIE) plasma surface treatment prior to bonding is known to increase direct bonding energy at room temperature while waiting in clean room environments [39]. As shown in Figure 15, an increase by a factor of 11 could be obtained after two months with bonding energy reaching 1.1 J/m^2 . In contrast, the addition of DEAE at the bonding interface, without plasma pre-treatment, does not yield such a bonding energy increase at room temperature. An increase by a factor of just three is obtained, with bonding energy remaining below 400 mJ/m^2 .

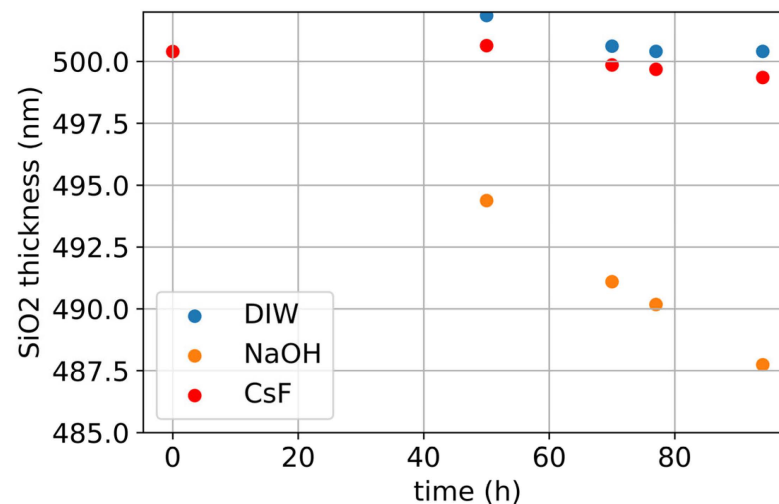


Figure 14. Silicon dioxide thickness measured by ellipsometry as a function of etching time in different solutions [59].

Regarding the first model—silanol condensation enhancement—our silica surfaces are cleaned using chemical treatments, particularly SC1 cleaning, which, as shown by Iler [49], fully hydrolyzes the silica surface, resulting in the maximum concentration of silanol groups. Neither plasma treatment nor the application of basic molecules alters the silanol density. Perhaps it could decrease this density, but it could not increase as it is already fully hydrolyzed due to the chemical SC1 precleaning. Now, if we consider that silanol condensation alone is responsible for the bonding energy enhancement, the lack of bonding improvement at room temperature with the basic molecule treatment suggests it would similarly fail with plasma treatment as both surfaces have the same silanol density. This implies that another mechanism must be responsible for the observed adherence increase.

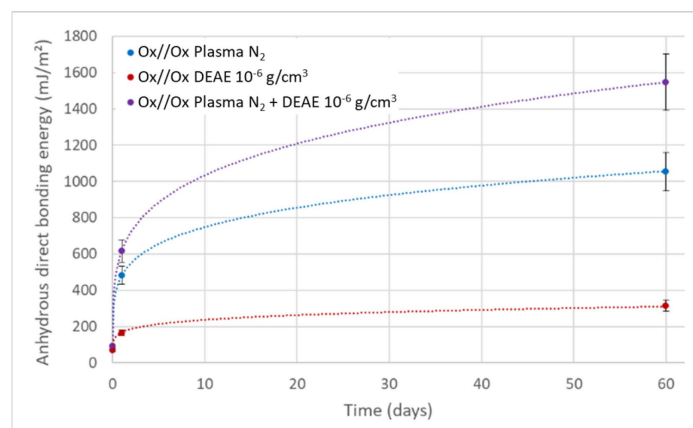


Figure 15. Comparison of plasma and DEAE effects on silicon dioxide direct bonding energy at room temperature aging the bonding in the clean room environment.

On a chemically precleaned surface, the effect of plasma treatment occurs at the subsurface level. Plasma treatment modifies the surface structure over a depth of approximately three to five nanometers through ion bombardment [60]. This modification of the subsurface silica atomic order likely facilitates water penetration and enhances silica–water hydrolysis kinetics, even at room temperature. This effect is further amplified in the presence of increased pH. For instance, the addition of DEAE immediately after plasma treatment and just before bonding leads to an even more rapid increase in bonding energy at room temperature over time (see Figure 15). In the absence of plasma treatment,

merely increasing the pH at room temperature is insufficient to achieve a tenfold increase in adherence. This suggests that additional energy is required for water to penetrate the asperity volume when the asperities have not been exposed to plasma treatment. Thermal annealing, in the absence of plasma treatment, could supply this energy.

The mechanism of asperity volume hydrolysis aligns most consistently with the observed results. At present, asperity hydrolysis—referred to as the second mechanism—offers the most straightforward and coherent physical explanation for these phenomena. In conclusion, based on the plasma treatment results, the second mechanism appears to be the correct one.

An additional argument supporting the asperity hydrolysis phenomenon can be drawn from the work of Lomonaco et al. on the SAB bonding mechanism [61]. In their study, the authors demonstrated that surface dangling bonds alone are insufficient to achieve high bonding energy. They used hydrophobic silicon surfaces and soft SAB activation to highlight the role of the amorphous silicon layer in the SAB mechanism. The soft SAB activation was sufficient to remove all silane bonds from the silicon surface, leaving reactive dangling bonds without producing a thick amorphous layer. One of the hydrophobic surfaces studied featured atomic terraces obtained through silicon epitaxial layer deposition, resulting in extremely low roughness.

Lomonaco et al. showed that only this exceptionally smooth surface could achieve high bonding energy, whereas a standard silicon surface with typical roughness (approximately 0.13 nm RMS) could not, even in the presence of reactive dangling bonds. If the roughness asperities of the silicon surface are not softened by the amorphization induced by SAB activation (which happened with a longer activation time), the dangling bonds remain too far apart to react effectively. Of course, for the extremely low roughness surface, the need for a soft amorphous layer is less pronounced, and a good bonding energy is obtained even after a soft SAB activation.

With a surface having a standard roughness, the presence of a soft amorphous silicon layer is therefore essential, in addition to the dangling bonds. This layer facilitates the widening of asperities and enables dangling bonds to form covalent linkages across the bonding interface.

Consequently, for the hydrophilic bonding of this study (which has similar roughness as Lomonaco's standard silicon surface), the enhancement of adherence is not primarily dependent on the catalysis of silanol condensation. Indeed, taking as a reasonable hypothesis that the surface density of dangling bonds and silanol one is roughly equal, even if silanol condensation were as energetically favorable as the recombination of dangling bonds, the atoms from both surfaces would still need to be in close proximity to react, as observed in the Lomonaco study. Surface asperities must be softened to allow silanol condensation, even if the condensation kinetics are very fast.

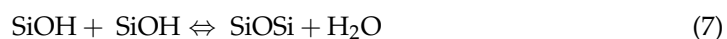
Thus, silanol condensation kinetics do not appear to play the primary role. Just the catalysis of silanol condensation is not enough to explain the bonding energy enhancement. Instead, asperity softening mechanisms seem to be much more significant. The asperity hydrolysis mechanism emerges as the most plausible explanation for the enhancement of direct bonding energy.

This hydrolysis is driven by water itself, but elevated temperatures are necessary to facilitate water penetration into the roughness asperities. In this context, the addition of basic molecules catalyzes the hydrolysis, which explains the results observed during post-bonding annealing: the adherence increases more rapidly with chemical booster molecule. When plasma treatment is applied, the asperities are preemptively modified by ion bombardment, enabling water hydrolysis to occur effectively even at room temperature. This last phenomenon could be even amplified by adding chemical booster molecule.

Naturally, if plasma treatment reduces the energy barrier for water to penetrate asperities at room temperature, the effect becomes even more pronounced during annealing. This explains the remarkable efficiency of plasma treatments, even at relatively low post-bonding annealing temperatures. It is not shown in this article, but we suspect to have an amplification of this effect adding chemical booster molecule after the plasma activation and post bonding annealing.

The primary effect of plasma is to facilitate water penetration into the roughness asperities, enabling their hydrolysis. This is further supported by the observation that no enhancement in bonding energy occurs when plasma-treated surfaces are bonded within the plasma chamber without introducing water at the bonding interface, as demonstrated by Fournel et al. [39].

The system, therefore, requires water to improve silica adherence. A high concentration of water at the bonding interface and in the subsurface is beneficial for this purpose. However, excessive water concentration can weaken siloxane bonds between the wafers, shifting the equilibrium of Equation (7) to the left:



It is also noteworthy that, if all the bonding energy enhancement techniques (temperature, plasma, chemical molecule) is to enable the water penetration inside the roughness asperity to hydrolyze them, this will reduce water at the bonding interface, pushing the equilibrium of Equation (7) to the right and favoring covalent bonding between the wafers. While removing water from the bonding interface increases bonding energy, it is a side effect of the primary mechanism—the need to soften the roughness asperities through silica hydrolysis.

Thus, it can be hypothesized that an optimal water amount exists that is sufficient to enable the mechanical softening of asperities but not excessive, and to minimize residual water at the bonding interface and maximize silanol condensation between the bonded surfaces.

5. Conclusions

Numerous basic amino–alcohol molecules and ions can be adsorbed onto SiO₂ surfaces, increasing direct bonding energy. This likely stems from OH[−] catalyzing silicon dioxide hydrolysis by trapped water at the bonding interface, increasing the flattening of bonding interface roughness asperities. Larger and closer contact surfaces of asperities promote then additional covalent bond formation. The introduction of such molecules after plasma treatments boosts the bonding energy even more as the plasma reduces the energy barrier for water to penetrate asperities. The influence of OH[−] anions is clearly demonstrated. However, further and more precise experiments are needed to assess the influence of cations, particularly multivalent cations or those with varying radii.

Even if the silica asperities hydrolysis seems to be the predominant mechanism, more experiments deserve also to be performed in order to fully describe the mechanism behind this chemical bonding energy enhancement of hydrophilic silica direct bonding.

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