Various methods of surface treatment for hydrophilic direct bonding have been investigated. The void formation has been systematically examined in low and high temperature in SiO2-SiO2 direct bonding. The effect of surface pretreatments, annealing time, temperature and pressure on voids formation and removal have been observed. H2SO4-H2O2 mixed solution, nitric acid, acetone followed by isopropanol cleaning and finally O2 plasma as surface pretreatments were considered and compared. Long annealing time were chosen in order to saturate the reactions at the interface. It was observed that the optimized O2 plasma in terms of exposure time leads to void free high energy wafer bonding. The effect of oxide thickness in dissolving the voids has been investigated. Using the proper cleaning methods and subsequent low temperature long time annealing step, leads to high bonding energy of the order of bulk Si fracture energy with low density of voids.
Introduction

Direct wafer bonding has been used extensively in semiconductor industry in order to stack materials with different crystalline relationship to one another [1]. Semiconductors on insulator (SOI) is the most well-known application of direct bonding. Nowadays direct bonding has made promising opportunities to achieve innovative stacked structures [2]–[4]. Direct bonding has enabled new applications of semiconductor devices such monolithic three dimensional (M3D) integration of complementary metal oxide semiconductor (CMOS) transistors [2], [3]. Conventional 2D integrated circuits (ICs) have transistors formed on the top surface of the semiconductor wafer. In order to build 3D ICs, additional semiconductor layers are needed on top of the existing devices and interconnect layers [2], [3]. There are some crucial requirements for this 3D layer formation. The first one is defect free single crystalline semiconductor layer. The second one is low temperature processing in order to avoid disturbance of existing devices and interconnect lines underneath the forming 3D layer [2]–[4]. Therefore, a low temperature wafer bonding process possessing a high bonding strength is required to fulfill the 3D integration of CMOS transistors. By employing low temperature wafer bonding integration of other materials (III-V, Ge) in monolithic 3D stacks have become possible [4].

In this paper we have examined the interfacial voids origins in the hydrophilic SiO₂-SiO₂ direct bonding. Various methods have been employed as surface pretreatment before bonding. The voids have been systematically observed at low and high temperatures for long and short times; since it is reported that by long time annealing at low temperature the bonding reactions will saturate and tiny thermal voids can appear after very long time annealing [5]. The effect of the SiO₂ thickness on the void formation and removal has also been investigated.

Hydrophilic direct bonding

Q. Y. Tong and U. Gösele have summarized the hydrophilic bonding process into three steps base on annealing temperature (Fig. 1) [6], [7]:

1) From room temperature to 110 °C. The bonding is dominated by hydrogen bonding between one or more monolayers of water molecules adsorbed on both surfaces prior to bonding. The stable adsorbed water molecules, which are in the form of triplets, produce a hydrogen bonding with a separation of 1.1 nm between surfaces. Considering the total number OH groups with different types, the calculated theoretical maximum bonding strength can be 0.165 J/m².

2) 110 °C - 150 °C: the adsorbed water molecules become mobile and have been removed from the interface. Oxygen covalent bonds can be formed at some location at the interface and the distance between two surfaces is shrunk from 1.1 nm to 0.6 nm. By similar calculation the theoretical maximum bonding strength can be 1.674 J/m².

3) 150 °C - 800 °C: The stable covalent bonds between two surfaces are formed. But the bonding strength changed slightly by annealing in this range. In the case of SiO₂-SiO₂ bonding the trapped water diffuse into the SiO₂ lattice and hydrolyses the SiO₂ and in the case of Si-Si bonding the trapped water diffuses into the Si lattice and oxidizes the Si. That leads to hydrogen
release from the reaction, which agglomerate as annealing void at the interface. At this stage the separation distance between two surfaces is ~ 0.3 nm.

4) Above 800 °C: The bonding strength has reached its maximum by the aid of oxide flow at the interface which closes the micro gaps. The annealing will shrink the size of the voids by prolonging the time or increasing the temperature of annealing. It is reported that highly strained oxide layer start to flow at 800 °C, but less dense and more inert layers such as thermal SiO₂ layers require a higher temperature annealing > 1100 °C. By similar calculation the theoretical maximum bonding strength at this stage, is 4.932 J/m².

![Diagram](image)

Figure 1. The chemical bonds at the interface of bonded hydrophilic silicon wafers at different temperatures: (a) room temperature to 110°C, (b) 110°C to 150 °C, (c) 150 °C to 800 °C and (d) higher than 800 °C.

If we exclude the circular shape voids which appear due to the particle on the surface after the bonding, the other main sources of the voids in the low temperature direct bonding can be categorized into three different types: 1) trapped air which are visible immediately after the bonding; 2) voids due to the thermal decomposition of the hydrocarbon contaminants remained at the surface which are called, thermal voids; 3) released water from the O-H groups or the
hydrogen byproducts of the oxidation reactions [5], [8]. However, it has been reported that the presence of even a thin thermal oxide layer at the surface prevents the diffusion of water molecules from the bonding interface to the bulk Si; consequently the Si oxidation is hindered and the H₂ outgassing is avoided resulting in fewer voids at the interface [9].

Experiment

In these experiments bonded surfaces were thermally oxidized SiO₂ layers on (100) n-type Si wafers. Four different surface pretreatment before bonding were considered in our experiments including 1) H₂SO₄ and H₂O₂ mixture called the Piranha solution, 2) Acetone and Isopropanol alcohol, 3) warm nitric acid and 4) O₂ plasma in a Reactive Ion Etching (RIE) tool. Direct bonding after pretreatments were manually conducted in a clean atmospheric ambient. The bonded pairs were inspected by a FLIR E6 infrared (IR) camera with the detector resolution of 160*120 pixels, on a hot plate immediately after bonding and after annealing processes. The dark areas in the blue regions represent the voids at the interface. Due to the limitation in the resolution of infrared images and reflections from surrounding objects, blurry dark surroundings around the voids in the images were observed; that causes a difficulty in exact measurement of the voids sizes.

Maszara or dual cantilever bending (DCB) test methodology was used to measure the bonding strength (Fig. 2). A well-known formula, showing the relationship between the crack length and the surface energy was used to approximately calculate the bonding strength. \[ \gamma = \frac{3Eu^2w^3}{32l^4} \] where E is the Young modulus of the (0 0 1) Si material, u is the thickness the razor tip, w is the thickness of one wafer, and l is the crack length. Diced samples with a thickness of (10mm) from the bonded pairs were prepared for the bonding strength measurement. The bonding strength measurement for each bonded pair was performed on at least four identical samples. The blade was inserted manually in the interface; therefore, our calculation is an approximation of the bonding energy. Accurate calculation of the bonding strength can be achieved by controlling: the blade insertion speed, the inserted force and the environment, besides using a high resolution IR sensor for picturing.

Figure 2. Schematic figure of the razor blade technique employed for bonding strength measurement.
Results and Discussions

Various Methods for Surface Treatment

In these set of experiments thermally oxidized SiO$_2$ surface, were prepared for bonding using various surface treatment processes. In all of these experiments, the bonded wafers were consisted of two sets of wafers: a 100 nm and a 20 nm thermal oxide films grown on n-type Si wafers. First, voids formation was examined when SiO$_2$ surfaces were treated by Piranha and HNO$_3$ solutions which are effective in hydrocarbon removal. The Piranha solution is being used extensively as a standard cleaning in semiconductor fabrication processes.

a) Surface treatment by Piranha (110 °C, 10 min) and HNO$_3$ solution (80 °C, 5 min)

After cleaning the surfaces with solutions, the wafers were rinsed and dried then manually bonded at atmospheric (atm) pressure and room temperature. Figure 3, depicts the IR images of the bonded SiO$_2$-SiO$_2$ films treated by Piranha and HNO$_3$ solutions. The images were taken immediately after bonding.

![Figure 3](image)

(a) (b) (c)

(d) (e) (f)

Figure 3. Infrared pictures of the bonded SiO$_2$-SiO$_2$ wafers treated by Piranha prior to bonding: (a), (b) and (c), and treated by warm HNO$_3$ before bonding: (d), (e) and (f)
The IR pictures shown in Fig. 3. show that, both cleaning methods are effective in contamination removal. After bonding few voids appeared at the interface which could be due the trap voids or air at the surface (type 1). In Fig. 3. (b) and (d) almost void free bonding were achieved. Then all bonded wafers were annealed at 400 °C for 100h in air filled furnace and atmospheric pressure. Figure 4. shows the IR images of the bonded wafers as the same order shown in Fig. 3.

Comparing Fig. 3. and Fig. 4. it is clear that after annealing at 400 °C for a long time (100 h) the size of the already existing voids was increased and new voids have also appeared at the interface. It has been reported that the size and the density of the void depends on the annealing time and temperature [10]. The increase in the void size indicates the blister of the bonded area due to the pressure of the trapped gas in sounding area of the void. The increase in the number of voids can be attributed to the hydrocarbons, which were remained on the surfaces after
treatments, and can be polymerized during the annealing [10]. The bonded pair shown in Fig. 3 and 4.(b) was further annealed at 800 °C in N2 and atmospheric pressure for 2 h. The infrared image is shown in Fig. 5.(a). shows an increase in size for one void and rest remained unchanged. After that when the pair was further annealed for 2 h more in N2 and atmospheric pressure but at 1100 °C, two of the voids are significantly reduced in size; the infrared image is shown in Fig. 5.(b). The observed limitation in voids reduction even after the very high temperature annealing (1100 °C) can be related to the thermal oxide thickness. It is reported that there is a critical oxide thickness for the absorption of the byproducts, which below that thickness the gas byproducts cannot be dissolved completely into the oxide lattice [7], [10]. In the next experiment the bonded pair shown in Fig. 3 and 4.(c) was further annealed for 2 h more filled with H2, at 800 °C; the IR image is depicted in Fig. 5 (c). Infrared picture of the in a reduced pressure (20 Torr) reactor bonded wafers (Fig. 5.c) shows a clear change in the size of one void, but the other voids show a slight change in their shape or size, which can be due the limitation in the image resolution as mentioned earlier.

The bonded pair in Fig. 5.(c) was then annealed for 2 h more in a reduced pressure (20 Torr) reactor filled with H2 at a higher temperature of 1100 °C; the IR image is shown in Fig. 5.(d). Some trapped voids after bonding showed an increase in size. In Fig. 5.(e) the same pair was further annealed with the same conditions as Fig. 5.(d) for two hours more (total 4h at 1100 °C). As can be seen from the Fig. 5.(e) the voids remained unchanged after two hour more annealing at 1100 °C in the low pressure reactor. Then the bonded pair was annealed again at 1100 °C but this time in N2 filled furnace and atm pressure; IR image is presented in Fig. 5.(f). Most of the voids were completely disappeared after annealing at 1100 °C in N2 environment. Therefore, it can be concluded that at high temperatures N2 and atmospheric pressure are more effective in voids removal than H2 and low pressure. Some groups have reported that the vacuum annealing after bonding at high temperatures postpones the appearance of the voids and is not effective in removing the voids [5].
Figure 5. Infrared images of the bonded wafers which were shown in Fig. 2 and 3 (b), here after further annealing at 800 °C for 2 h in N₂ and atmospheric pressure (a), and after annealing for 2 h more but at 1100 °C in N₂ and atmospheric pressure. IR images of the bonded pair shown in Fig. 2 and 3 (c), here underwent another annealing at 800 °C for 2 h in H₂ and 20 Torr (c), after another annealing at 1100 °C for 2 h, in H₂ and 20 Torr (d), after more annealing for 2 h the total of 4 h at 1100 °C, in H₂ and 20 Torr (e), the final annealing of the bonded pair at 1100 °C for 2 h more but this time N₂ and atm pressure (f).

b) Surface treatment by O₂ plasma and acetone-isopropanol

In order to bond and transfer layers with temperature sensitive strained epitaxial SiGe or Ge layers, a high bonding strength is required to keep the strain in the layer; at the same time the highest temperature limit of the process is at temperatures lower than the epitaxial growth temperature (<500 °C); plasma activation is utilized to achieve high bonding strength at low temperature [7], [9]. Mechanism responsible for the improved bonding strength due to plasma activations are still debated [7]. It has been shown that plasma activation can modify the physical and chemical properties of the surfaces and the sub-surfaces; that can be beneficial in changing the topology of the surface and increasing the density of OH groups [7], [9], [11]. That results in a higher number of available sites for bonding, and it causes an increase in the bond strength by condensation of hydrogen bonded OH groups into covalent bonds [9], [12]. In the next experiments thermal SiO₂ surfaces (20 nm and 100 nm) were activated and treated by RIE O₂ plasma. Plasma activation using RIE can be considered as ion bombardment, since the ions are accelerated toward the substrate using a potential gradient. It has been reported that the plasma activation by RIE produces a low density, highly active oxide layer which is covered with a high density of OH groups. Low temperature annealing plastically deforms this oxide layer to fills micro voids; that results in a very high bond strength more than 2.5 J/m² [7]. It has also been shown that the RIE plasma reduced the surface roughness in spite of ambient plasma [14]–[16]. Other groups have examined the effect of the plasma parameters on voids formation [17], in these experiments we have investigated the effect of plasma exposure time in annealing void formation. The wafers were treated by O₂ plasma for 5 sec, 10 sec and 20 seconds, and then they were rinsed, dried and bonded at room temperature. Other bonded pairs were treated by dipping in Acetone (5 min), and then Isopropanol Alcohol (5 min), followed by rinsing and drying and direct bonding. One pair was cleaned by H₂SO₄-H₂O₂ solution as a control sample, in order to
evaluate the effect of environment contamination on the process and reproducibility of process. Infrared images of the bonded pairs immediately after bonding are shown in Fig. 6.

Figure 6. IR images of SiO$_2$-SiO$_2$ (100 nm-10 nm) bonded wafers immediately after bonding which were treated by: Piranha (a), acetone + isopropanol 1st sample (b), acetone + isopropanol 2nd sample (c), O$_2$ plasma for 5 sec (d), O$_2$ plasma for 10 sec (e), and O$_2$ plasma for 20 sec (f).

All bonded wafers show a small number of aggregated voids after bonding as presented in Fig. 6. Then all the bonded pairs were annealed at 400 °C for 100 h in air and atmospheric pressure (Fig. 7).
Figure 7. IR pictures of the bonded wafers shown in Fig. 6, after annealing at 400 °C for 100 h, in air and atmospheric pressure: Piranha (a), acetone+ isopropanol 1st sample (b), acetone+ isopropanol 2nd sample (c), O$_2$ plasma for 5 sec (d), O$_2$ plasma for 10 sec (e), and O$_2$ plasma for 20 sec (f).

Thermal voids and annealing voids start to appear in all pairs; but more bubbles have emerged in Fig. 7 (f) which was activated for 20 sec by O$_2$. Figure 8. illustrates the infrared image of the plasma activated sample by O$_2$ for 20 s (Fig. 7.f), which has been annealed at 1100 °C for 2 h, in N$_2$ and atmospheric pressure.

Figure 8. IR picture of the bonded pair shown in Fig. 7. (f), after further annealing at 1100 °C for 2 h, in N$_2$ and atm pressure.

From these set of experiments it can be observed that 1) the number of voids after annealing increases with the plasma exposure time. 2) The size and the number of voids in plasma activated wafers (20 s) increases with increasing annealing time and temperature, similar to the
previous reports [5]. Contrary to the wafers treated by Piranha shown in Fig. 5.(f), the voids in Fig. 8. did not decrease in size or density after 1100 °C annealing in N₂. This can be attributed to a very high bonding strength value achieved by O₂ plasma, which inhibits the diffusion of interface gas byproducts along the interface and blocks their movement [5] and/or it is due to the limitation in thermal oxide thickness as mentioned earlier. It is reported that after O₂ plasma, the hydrophilicity of the surface increases due to an increase in the number of OH groups at the surface [7], [9]. The larger number of OH groups results in more bonding sites and consequently more byproducts such as water and hydrogen [5], [7]. Similar to the previous reports we have observed that voids in plasma treated surfaces do not arise from the remaining hydrocarbon decomposition on the surface; but they are due the large number of interface reaction byproducts at the interface and the presence of micro defects. These voids can be called annealing voids to discern them with thermal voids [5].

**The Effect of Thermal Oxide Thickness in Voids Removal**

In the next experiments the effect thermal oxide thickness in voids formation and voids removal was investigated. Si wafers with various thermal oxide thicknesses (50 nm, 220 nm, 500 nm) were bonded to Si wafers with 20 nm thermal SiO₂ grown on top of them. All wafers were cleaned before bonding in a same cassette using Piranha for 10 min. Figure 9. presents the infrared images of the bonded wafers immediately after bonding.

![Figure 9. IR images of SiO₂-SiO₂ bonded wafers with different thermal oxide thicknesses immediately after bonding: 50 nm-20 nm first pair (a), 220 nm-20 nm first pair (b), 500 nm-20 nm first pair (c), 50 nm-20 nm second pair (d), 220 nm-20 nm second pair (e), 500 nm-20 nm second pair (f). All bonded wafers were cleaned by Piranha for 10 min prior to bonding.](image-url)
As it is shown in Fig. 9, few voids due to the particles or trapped air have appeared after the bonding. All of the bonded wafers in Fig. 9 were then annealed at 400 °C for 100 h, in air and atmospheric pressure; the infrared images after annealing are shown in Fig. 10.

![Figure 10. IR images of SiO$_2$-SiO$_2$ bonded wafers shown in Fig. 9. after annealing at 400 °C for 100 h, in air and atm pressure: 50 nm-20 nm first pair (a), 220 nm-20 nm first pair (b), 500 nm-20 nm first pair (c), 50 nm-20 nm second pair (d), 220 nm-20 nm second pair (e), and 500 nm-20 nm second pair (f).](image)

From the IR images shown in Fig. 10, one can observe that the number of voids for the bonded pair shown Fig. 10(d) have increased slightly but in other pairs the number of voids have remained unchanged. However, the size of the voids have increased for all bonded wafers. This can be due to a low bonding strength at the interface which allows the trapped gases to diffuse along the interface, combine together and increase in size. In order to examine the influence of thermal oxide thickness in voids removal, the bonded wafers in Fig. 10. (d), (e) and (f) were further annealed at an elevated temperature of 1100 °C for 2h, in N$_2$ and atmospheric pressure; the IR images after this annealing step are presented in Fig. 11.
Figure 11. IR images of SiO$_2$-SiO$_2$ bonded wafers shown in Fig. 11 (d), (e) and (f), after annealing at 1100 °C for 2h, in N$_2$ and atm pressure: 50 nm-20 nm second pair (a), 220 nm-20 nm second pair (b), and 500 nm-20 nm second pair (c).

Figure 11. depicts that for all of the bonded wafers the appeared thermal voids have been removed after a high temperature annealing at 1100 °C. The remaining voids are the trapped voids after the bonding which increased in size as it was shown in Fig. 10, and did not disappeared even after 1100 °C annealing (Fig. 11). It can be concluded that all of the thermal oxide thicknesses above 50 nm were effective in thermal voids removal and we did not see a difference among the chosen oxide thickness range. The bonded pair shown in Fig. 11. (c). was further annealed for two hours more under the same conditions mentioned for Fig. 11, but the voids remained unchanged. Therefore, in this case the longer annealing time at high temperature (1100 °C) was not effective in voids removal. After that the effect of thermal oxide thickness on annealing voids, which appear after plasma activation, was examined. A bonded pair was prepared by bonding a 20-nm thermal SiO$_2$ to a 500-nm thermal SiO$_2$ wafer. Both surfaces were exposed to O$_2$ plasma for 20 sec, followed by rinsing and drying before bonding. Figure 12. represents the infrared images of the bonded pair immediately after the bonding. There are small numbers of trapped voids at the interface after the bonding (see Fig 12.a). Then, the bonded pair was annealed at 400 °C for 100 h, in air and atmospheric pressure (see Fig 12.b). Thermal voids were emerged at the interface after the annealing step. After that, the bonded pair underwent another annealing step at 800 °C for two hours, in N$_2$ and atmospheric pressure; the IR image taken after this step is shown in Fig. 12. (c). The number and the size of the voids were remained almost unchanged after the annealing at 800 °C for two hours. Finally the bonded pair was annealed at 1100 °C for two hours, in N$_2$ and atmospheric pressure, as depicted in Fig 12 (d). After this step all the annealing voids were disappeared.
Comparing the bonded pair shown Fig 12. (d), with the one shown in Fig. 8, which both were annealed under the same condition, it can be observed that contrary to Fig. 8, all the annealing voids in Fig. 12 (d). were removed. The only difference between these samples was the thermal oxide thickness of one of the bonded wafers, a 100-nm in Fig. 8, and a 500-nm in Fig. 12 (d). Therefore, as it has been discussed in [5], [6] we observed that, the thermal oxide thickness has a direct effect in dissolving the annealing voids.

**Bonding Strength Measurement**

As explained earlier a razor blade test was used for the bonding strength measurement. A blade with a tip thickness of 0.22 mm was manually inserted into the 10 mm diced samples. Then the crack length or the broken part was measured to approximately calculate the bonding strength. For the samples which were annealed at 1100 °C despite their surface treatment a bonding strength energy higher than the bulk Si fracture energy was achieved. Optical image of the de-bonded samples (Fig. 13. a) shows a pull out of material of one sample to the other due to the very high bonding energy. The same results was observed for the samples treated by piranha, isopropanol-acetone, and O₂ plasma, which had annealed at 400 °C for 100 h. However, the
HNO$_3$ treated samples annealed at 400 °C for 100 h, exhibited a bonding strength in the range of 1-1.5 J/mm.

**Conclusion**

Different methods for surface treatment of SiO$_2$ films prior to direct bonding were examined in terms of voids formation. The treatment methods included Piranha solution (110 °C, 10 min), warm HNO$_3$ (80 °C, 5 min), dipping in acetone (5 min) followed by isopropanol dip (5 min) and finally O$_2$ plasma (5 sec, 10 sec and 20 sec). The voids formation was studied in terms of annealing time, temperature, pressure and SiO$_2$ thickness. It was observed that all cleaning methods are effective in hydrocarbon removal. The O$_2$ plasma treated samples exhibited higher bonding strength compare to the other methods, due to the higher density of OH groups on the surface created by O$_2$ plasma. However, the plasma time needed to be adjusted in order to control the amount of gaseous by-products, which accumulate as voids at the interface. The thermal oxide thickness had an effect in removing annealing voids created by O$_2$ plasma. The 500-nm thermal SiO$_2$ was effective in removing all the annealing voids. Employing the proper treatment method and subsequent low temperature long time annealing step (400 °C, 100 h), a high bonding energy of the order of bulk Si fracture energy with low density of voids can be achieved. Finally, it will possible to bond and transfer highly strain epitaxial SiGe and Ge layers using SiO$_2$ films and employing the proper treatment and annealing methods.

**References**


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