# Low-temperature hydrophobic silicon wafer bonding

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By introducing a nanometer-scale H trapping defective silicon layer on bonding surfaces, the bonding surface energy of bonded oxide-free, HF dipped, hydrophobic silicon wafers can reach a silicon fracture surface energy of 2500 mJ/m$^2$ at 300 to 400 °C compared with 700 °C conventionally achieved. Adding boron atoms on bonding surfaces can reduce the surface hydrogen release temperature but would not increase the bonding energy unless a defective layer is also formed. This indicates that, in order to achieve high bonding energy, the released hydrogen must be removed from the bonding interface. Many prebonding treatments are available for low-temperature hydrophobic wafer bonding including the formation of an amorphous silicon layer by $As^+$ implantation, by $B_2H_6$ or Ar plasma treatment, or by sputter deposition, followed by an HF dip and room temperature bonding in air. The interface amorphous layer may be recrystallized by annealing at elevated temperatures, e.g., at 450 °C for $As^+$-implanted samples. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1632032]

Many device and materials applications require interfaces of bonded silicon wafer pairs to be covalently bonded, oxide free, electrically as well as thermally conductive, and optically loss free.[1] Conventionally, this has been achieved by forming hydrophobic silicon surfaces using an HF dip to remove the native oxide followed by room-temperature bonding and high-temperature annealing (>700 °C) to enhance the bond. However, the high-temperature annealing prevents the bonding applications involving processed device wafers. Moreover, in order to use H-implantation-induced layer splitting (Smart cut method)[2] for thinning and layer transfer, the bonding energy of the bonded silicon wafer pairs must be higher than the fracture energy of the H-implanted region at the splitting temperature. Otherwise, the bond will fail and only blistering on the H-implanted wafer surface will take place. For conventional HF dipped hydrophobic bonded wafer pairs, layer transfer cannot be achieved because the bonding energy is too low at the splitting temperature of ~450 °C. Therefore, it is highly desirable to develop a low-temperature hydrophobic silicon wafer bonding technology.

Room-temperature covalent bonding of oxide-free silicon wafers was reported.[3,4] However, the use of high-temperature (>600 °C) preannealing[3] or of small wafers[4] in an ultrahigh vacuum (UHV) is required.

In order for bonded hydrophobic silicon wafer pairs to reach bulk fracture energy, the hydrogen from HF dipped, mainly Si—$H_2$ and Si—H terminated hydrophobic silicon surfaces at the bonding interface must be removed so that Si—Si covalent bonds across the mating surfaces can be formed:[5]

$$\mathrm{Si{-}H}_x + \mathrm{H}_x\mathrm{{-}Si} \rightarrow \mathrm{Si{-}Si} + 2x\mathrm{H}, \qquad (1)$$

where $x=1$ or 2.

The release of hydrogen from a stand-alone silicon wafer dipped in HF was shown to start at ~367 °C from Si—$H_2$ and ~447 °C from Si—H in UHV.[6] At bonded interfaces of hydrophobic silicon wafers, hydrogen desorption was demonstrated to start at ~300 °C.[5] However, the bonding energy of HF dipped silicon wafer pairs is still low at 300–500 °C (~200 mJ/m$^2$ at 300 °C and ~650 mJ/m$^2$ at 500 °C) even after 45 h annealing.[5] For bonding energy to achieve silicon fracture energy (2500 mJ/m$^2$), annealing at >700 °C is required. In this work, we show that removal of the released H from the bonding interface is the key to achieve high bonding energy at low temperatures.

Si (100) wafers with 3 in. diameter, 1–10 ohm cm, *p* type were used in this study ($p^-$ Si). $As^+$-ion implantation was performed at energy of 180 keV with a dose of $9\times10^{14}$ cm$^{-2}$ on silicon wafers covered with a native oxide. After cleaning in Radio Corporation of America (RCA) 1 solution, a dip in 2% HF aqueous solution to completely remove the native oxide, the $As^+$-implanted wafers were immediately bonded in air at room temperature ($As^+/As^+$). The $As^+$-implanted wafer was also bonded to HF dipped silicon wafer ($As^+/p^-$). The bonded $As^+/As^+$ and $As^+/p^-$ pairs were annealed at elevated temperatures. The bonding energy as a function of annealing temperature is shown in Fig. 1. For comparison, that of a bonded pair of conventional HF-dipped silicon wafers ($p^-/p^-$) is also presented. The bonding energy of $As^+/As^+$ and $As^+/p^-$ pairs was almost identical to $p^-/p^-$ pairs below 300 °C but increases rapidly at temperatures >300 °C and reaches silicon fracture energy of 2500 mJ/m$^2$ at 400 °C. No interface bubbles were observed at these temperatures by an infrared imaging system.

An amorphous layer at the bonding interface of the bonded $As^+/As^+$ pairs was observed by cross-sectional

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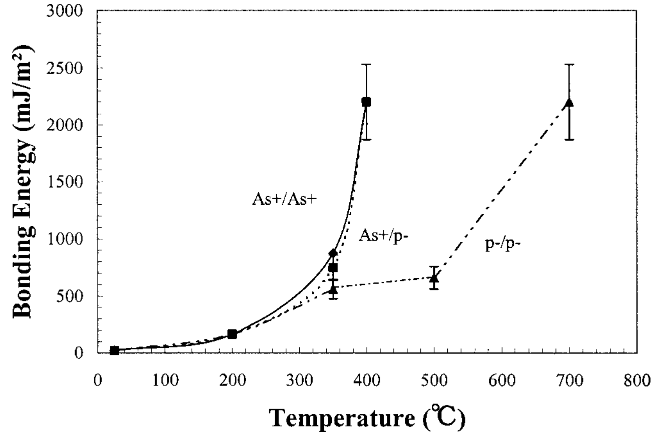


FIG. 1. Bonding energy as a function of annealing temperature of bonded $As^+$-implanted, HF-dipped, silicon wafer $As^+/As^+$ pair and $As^+/p^-$ pair. $As^+$-implantation conditions: Dose: $9\times10^{14}$ $cm^{-3}$ and energy: 180 keV. For comparison, that of bonded pair of conventional HF-dipped silicon wafers ($p^-/p^-$) is also presented.

transmission electron microscopy (TEM) images. The TEM image in Fig. 2(a) shows that an amorphous layer of 1650 Å in thickness was formed on both bonding surfaces after 400 °C annealing. This observation was in agreement with a SRIM2000 vacancy simulation[7] that predicts that an amorphous layer of ~1500 Å in thickness with peak vacancy concentration of $\sim2\times10^{23}$ $cm^{-3}$ can form by using these $As^+$-implantation conditions, see Fig. 2(b). The peak $As^+$ concentration of $\sim8\times10^{19}$ $cm^{-3}$ is estimated at depth of ~1200 Å from wafer surface. The interface amorphous layer can be completely recrystallized after annealing at 450 °C for 28 h. Figure 2(c) is the TEM image of the interface amorphous layer after annealing at 450 °C for 24 h just before the completion of recrystallization. The amorphous layer thickness was reduced from 1650 Å to 100 Å. Similar results were obtained by using only one $As^+$-implanted silicon wafer to bond to a conventional HF-dipped silicon wafer. However, when the $As^+$-implanted wafers were annealed at 900 °C for 20 min to completely recrystallize the amorphous layer prior to bonding, the bonding energy enhancement at low temperatures was no longer observed. This result indicates that the $As^+$ doping was not the reason for the bonding energy enhancement at low temperatures.

To confirm that removal of the released H from the bonding interface is the key to achieve high bonding energy at low temperatures, an amorphous silicon layer ($a$-Si) of 1.5 $\mu$m thick was sputter deposited on HF-dipped silicon wafer surfaces. Chemical–mechanical polish to remove 0.5 $\mu$m of surface $a$-Si layer improves the surface root mean square roughness to 2.9 Å. The polished $a$-Si wafers were dipped in 0.3% HF solution for 2 min to remove any oxide followed by immediate bonding with an HF-dipped normal hydrophobic silicon wafer in air at room temperature. The bonding energy of $a$-Si/Si pair reaches 1000 mJ/m$^2$ at 200 °C and silicon fracture energy of 2500 mJ/m$^2$ at 300 °C. No interface bubbles were observed at these temperatures.

Since $a$-Si layer has a very open structure as evidenced by TEM images, it is most likely that as soon as H atoms were released from surfaces of the $a$-Si layer (starting at ~200 °C)[8] and the Si wafer (starting at ~300 °C)[5] at the bonding interface they were trapped immediately by many dangling bonds inside the $a$-Si layer.

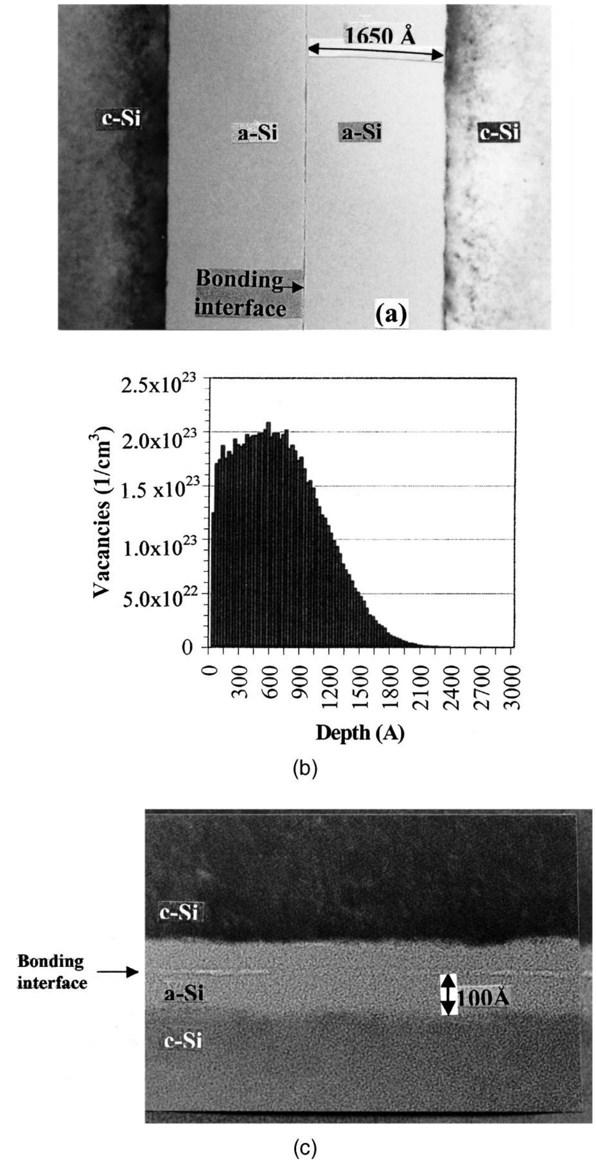


FIG. 2. (a) Cross-sectional TEM image of bonded $As^+$-implanted and HF-dipped silicon wafer pair after 400 °C annealing. $a$-Si: Amorphous silicon; $c$-Si: Crystalline silicon. (b) SRIM2000 simulation results of vacancy distribution on $As^+$-implanted surface. (c) TEM image of the interface of bonded $As^+$-implanted and HF-dipped silicon wafer pair ($As^+/As^+$) after annealing at 450 °C for 24h just before completion of recrystallization of the interface amorphous layer. $As^+$-implantation conditions: Dose: $9\times10^{14}$ $cm^{-3}$ and energy: 180 keV. $a$-Si: Amorphous silicon; $c$-Si: Crystalline silicon.

The interface amorphous layer can be formed by simple argon (Ar) plasma treatment of HF-dipped silicon wafers at reactive ion etch (RIE) mode. The pressure was 30–100 mTorr during Ar plasma treatment with a rf power of 80–200 W at 13.56 MHz applied for 15 s to 20 min. The Ar plasma treated silicon wafers were dipped in 2% HF again to remove any surface oxide followed by room-temperature bonding in air. The ~200–400 V self-bias voltage during Ar plasma treatment created an amorphous layer ~15–30 Å in thickness. The bonding energy reaches silicon fracture energy at 400 °C and no interface bubbles were observed at these temperatures by an infrared imaging system.

Recently, it was reported that subsurface boron (B) in silicon can weaken surface Si—$H_x$ bonds so that H may be

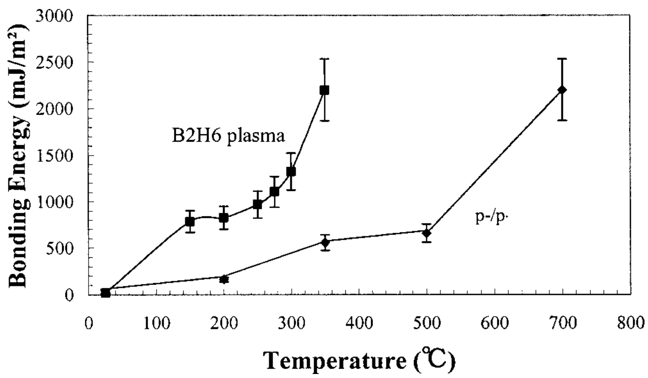


FIG. 3. Bonding energy as a function of annealing temperature of bonded $B_2H_6$ plasma treated and HF-dipped silicon wafer pairs. For comparison, that of bonded pair of conventional HF-dipped silicon wafers ($p^-/p^-$) is also presented.

released at lower temperatures.[9] However, bonding energy enhancement at low temperatures was not observed when two heavily B-doped ($2\times10^{19}$ $cm^{-3}$) silicon wafers were HF dipped and bonded. It is speculated that in order to enhance the bonding energy, a defective layer must also be present at the bonding interface to trap the released H. For this reason, HF-dipped silicon wafers were treated in $B_2H_6$ plasma for 1 min. A mixed gas of 20 sccm of 0.5% $B_2H_6$/99.5% He and 20 sccm Ar was used in $B_2H_6$ plasma treatment in inductor coupled plasma RIE mode with rf power of 29 W at 5 mTorr vacuum level. A 100 V self-bias voltage was generated under these conditions. A total amorphous layer, ~20 Å thick, with a B peak concentration of $\sim2\times10^{20}$ $cm^{-3}$ was observed at the bonding interface by using TEM and secondary ion mass spectroscopy. After $B_2H_6$ plasma treatment, the wafers were dipped in diluted HF again to remove any oxide on the wafer surfaces followed by bonding in air at room temperature. The bonding energy as a function of annealing temperature of the $B_2H_6$ treated wafer pairs is shown in Fig. 3. Indeed, the bonding energy was enhanced even at <200 °C and was ~800 $mJ/m^2$ at 150 °C and ~1100 $mJ/m^2$ at 250 °C, and reaches the fracture energy of bulk silicon at 350 °C. For comparison, the bonding energy as a function of annealing temperature of conventional HF-dipped silicon wafer pairs is also shown in Fig. 3. The bonding energy as a function of annealing time was also measured and shows that after 5 h annealing, the bonding energy already reaches 90% of the final saturated value at 275 °C.

In summary, it has been found that by introducing a nanometer-scale H trapping defective silicon layer on bonding surfaces, the bonding energy of hydrophobic silicon wafers can reach silicon fracture energy of 2500 $mJ/m^2$ at 300 to 400 °C. Adding boron atoms on bonding surfaces can reduce surface hydrogen release temperature but, in order to achieve high bonding energy, the released hydrogen must be removed from the bonding interface. Many prebonding treatments are available for low-temperature hydrophobic wafer bonding including formation of an amorphous silicon layer by $As^+$ implantation, by $B_2H_6$ or Ar plasma treatment, or by Si sputter deposition, followed by HF dip and room temperature bonding in air. The interface amorphous layer may be recrystallized by annealing at elevated temperatures, e.g., at 450 °C for $As^+$-implanted samples.

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