UV Activation Treatment for Hydrophobic Wafer Bonding

S. L. Holl†, C.A. Colinge*,
K.D. Hobart, F.J. Kub,

California State University
*Department of Electrical and Electronic Engineering
† Department of Mechanical Engineering
6000 J Street, Sacramento, California 95819-6019

Naval Research Laboratory
4555 Overlook, S.W.
Washington, D.C., 20375

ABSTRACT

Enhanced hydrophobic bond-strength can be achieved by exposing prime grade silicon wafers to ultraviolet (UV) light and heat prior to bonding. The following independent variables were explored: platen temperature, UV exposure time, oxygen containing versus non-oxygen containing (nitrogen only) bonding atmosphere, and annealing temperature. The results suggest exposure to UV can be used as an activation process which removes the passivation of the silicon surface rendering the silicon highly reactive. Exposure of silicon wafers to UV appears to be a promising low-temperature surface activation method.
INTRODUCTION

Silicon wafers show a significantly increased affinity for bonding dependent on the chemical processing method used on the surfaces. Chemical processing methods which have been investigated include: chemical cleaning [1], oxygen plasma exposure [2, 3], and argon sputtering/in-situ oxidation [4]. It is desirable for commercial applications to develop a cleaning/surface activation method that does not require elevated temperatures or exotic bonding conditions. The authors hypothesize that the surface energy of silicon wafers can be enhanced when exposed to UV and thermal energy. Further, the subsequent bond strength between activated layers will be increased if the bonding occurs in an oxygen free environment.

To investigate the effect of the various processes intended to create highly reactive silicon surfaces that are free of hydrogen, hydrogen terminated silicon wafers were placed in a chamber capable of providing an inert (nitrogen only) environment on a platen heated between 23°C and 200°C. Within the chamber some samples were exposed to UV while others were not. After surface activation the wafers were immediately bonded either in nitrogen or air. Prior to bonding the activated surfaces will react immediately when exposed to air thus altering the surface, which then results in reduced bond strength [5]. Bonding in a controlled atmosphere (nitrogen) prevents extensive contamination of the highly reactive surfaces which should produce increased bond strength. There are three advantages of using UV exposure coupled with bonding in N₂:
(1) other materials besides silicon can be bonded, (2) wet chemistry is eliminated, and (3) the energetic ions of plasma are not required [2,3].

EXPERIMENTAL

The activation/bonding chamber utilized a Samco International Model UV-1 which was placed inside a larger closed chamber (glove box) that could be evacuated and charged with nitrogen. The experimental set-up is shown in Figure 1. The Model UV-1 has a 200 mm chuck capable of heating the wafer from room temperature to 300°C. The UV lamp within the Model UV-1 produces energy with approximately 85 percent 254 nm wavelength (4.8 eV) and 15 percent 185 nm wavelength (6.7 eV) at 15 mW/cm². The UV-1 can be used with or without UV exposure, and can be evacuated and charged with other gases. An ultra pure N₂ atmosphere was used for these experiments.

Three-inch prime grade <100> silicon wafers were used in all of these experiments. To generate data that were most useful for comparison to previous work [5,6], wafers were treated systematically using heat, UV exposure, and bonding atmospheres. Bond strengths were measured using the crack propagation technique for wafers annealed at temperatures up to 300°C. In preparation for the activation treatment, wafers were chemically cleaned using SC1 (NH₄OH:H₂O₂:H₂O). The wafers were next rinsed in de-ionized water (DI), followed by a mega sonic DI rinse, then dipped in HF, and spin-dried rendering the wafers hydrophobic. Once the cleaning and drying process was completed,
the wafers were directly loaded into the load lock of the glove box and finally transferred to the Samco tool. The Samco chamber was purged with ultra pure N\textsubscript{2} at atmospheric pressure.

Wafers were heated for several different durations and at several different temperatures with and without UV in an N\textsubscript{2} atmosphere. After removal from the chamber the activated wafers remained in an N\textsubscript{2} environment in the glove box where the bonding process was performed. In most cases bonding was initiated by gently pressing the center of the wafer, however after UV exposure some wafers began to bond spontaneously [5]. Immediately after bonding, wafers were annealed for 24 hours. All annealing was conducted under normal, ambient atmospheric conditions. Wafers were imaged before and after annealing using an infrared (IR) source. In some cases, additional imaging was done using an acoustic Sonoscan.

**RESULTS**

**IR and Sonoscan Images of Wafers Bonded after UV vs. No-UV**

Figures 2 and 3 show IR images of bonded wafers following a five minute 200°C activation in the Samco tool. Wafers in Figure 2 were exposed to UV while wafers in Figure 3 were not. Both wafer pairs have a small number of voids most likely due to surface particles. After both bonded pairs were annealed for 24 hours at 300°C differences that appear significant began to emerge. The wafers exposed to UV appear to have no additional void
generation after annealing (Figure 4) compared to immediately after bonding (Figure 2). The wafers that were not exposed to UV prior to bonding show significant increase in thermally generated intrinsic voids after low-temperature annealing (Figure 5) compared to immediately after bonding (Figure 3).

To investigate if there were voids that the IR camera was unable to detect, a Sonoscan was used to image both bonded pairs. The Sonoscan images clearly show both wafers had more defects in the bond than were apparent using only the IR evaluation technique (Figures 6 and 7). It is clear, however, that the wafers exposed to UV have significantly smaller voids (Figure 6) than the bonded pairs without UV treatment (Figure 7). This may be due to removal of surface passivation (hydrogen) by the UV exposure which in turn reduces intrinsic void generation.

When a much higher annealing temperature of T>700°C was used for 24 hours the small voids generated during the low-temperature anneal disappeared. In addition, annealing the UV exposed wafers (platen T=200°C) at or above 300°C resulted in full bond strength. When wafers were not exposed to UV, with all other parameters being equal, full bond strength was only achieved at T>600°C.

**Bonding in N₂ vs. Bonding in Atmosphere**

Five different experiments were performed. The first experiment focused on the bonding atmosphere, comparing wafers bonded in normal, ambient atmosphere to those bonded in
N₂. All wafers were exposed to UV radiation for varying times while the platen temperature was held at room temperature. After exposure to UV the wafers were bonded either in ambient atmosphere or in N₂ only. The bond strength of the wafers was measured after a 24 hour period. Without annealing there was no significant difference in bond strength when comparing the wafers bonded in N₂ to wafers bonded in ambient atmosphere (Figure 8).

In the second experiment, the platen temperature was increased from 23°C to 200°C while the wafers were exposed to UV. The wafers were then bonded in either air or N₂ (Figure 9). The wafers were annealed at room temperature for 24 hours. The data indicate a significant increase in surface bond strength when wafers were bonded in either air or nitrogen when the platen temperature during exposure was 200°C.

The result shows an enhanced surface activation due to heating the wafers prior to bonding. This indicates that UV along with moderate thermal energy (T ≤ 200°C) can greatly increase bond strength of un-annealed samples. The bond strength increased by approximately five times compared to the strength achieved with a platen temperature of 23°C (Figure 8). The combination of UV and thermal energy likely caused a reduction of the hydrogen on the wafer surface leaving the surface highly reactive.

The effect of the bonding atmosphere was apparent. The results (Figure 9) indicate that if the wafers are not exposed to oxygen, water, or other components of the normal, ambient atmosphere the surface bond strength increases by approximately ten times
A temperature of 23°C may not have been high enough during the surface activation step to remove the surface passivation layer (most likely hydrogen termination) consequently the surface is not composed of active silicon atoms but has retained the hydrogen which must be removed to complete the direct Si-Si bond.

Bonding in the system purged with ultra pure nitrogen does not completely eliminate the presence of water in the bonding atmosphere. Although the partial pressure of water is quite small (0.0279 atm), it is assumed that the activated surfaces will have at least a monolayer of water on each surface prior to bonding. This layer prevents a direct Si-Si bond, however the bond strengths of those wafers bonded in N₂ are significantly stronger than those bonded in ambient atmosphere. It is likely that this increase is because of the reduced variety of adsorbed species and contaminants present on the activated surfaces. Infrared (IR) multiple internal transmission (MIT) has been used to characterize the molecular species present at the bond interface of hydrogen terminated silicon [7]. Investigation into the exact nature of the species present at the bonded surface of UV activated wafers using MIT is suggested. Additional studies of activated wafers bonded in a completely non-reactive environment are warranted.

Comparison of bond strengths resulting from wafers exposed to UV radiation at three different platen temperatures were made (Figure 10). Although there is not an apparent linear relationship of bond strength with increasing platen temperature, it is clear that at platen temperatures of 100°C and higher a significant increase in bond strength occurs.
The dramatic increase in bond strength associated with wafers heated at 200°C while exposed to UV and bonded in nitrogen is further evidence that the combination of heat, UV, and an inert environment results in the removal of the surface passivation thus activating the silicon bonds.

Annealing Temperature Effects

As shown in Figure 10, bond strength increases as the platen temperature increases for wafers exposed to UV. To investigate if heat is sufficient to activate the silicon surface, experiments were conducted heating the wafers with and without exposure to UV, then bonding in N\textsubscript{2} atmosphere and annealing at various temperatures. There is no increased bond strength with increased annealing temperature for wafers bonded at 23°C; in fact there is no difference between wafers exposed to UV and those not exposed to UV if the activation process is conducted at room temperature. When a platen temperature of 100°C or more is used for the activation, the bond strength increases significantly regardless of exposure to UV (Figure 11). This indicates that heat alone in an inert environment can be used as an effective activation treatment. However, the highest bond strength was achieved with platen temperature at 200°C with UV exposure. The silicon surfaces were sufficiently reactive when exposed to UV at a platen temperature of 200°C such that an anneal of 300°C resulted in full bond strength.

\textbf{CONCLUSION}
The effect of exposing silicon wafers to UV radiation while heating demonstrated that bond strength was dependent on UV exposure time and platen temperature. The highest bond strength was found for UV exposure in conjunction with 200°C wafer heating.

During UV exposure, in particular the 185 nm wavelength (6.7 eV), the radiation energy is sufficient to alter the hydrogen terminated silicon surface. Exposure to UV radiation activates the silicon surface by the removal of surface passivation thus forming a highly reactive silicon surface. Furthermore, the nitrogen environment prevents the reactive silicon from adsorbing significant amounts of water or other unwanted species at the surface prior to bonding. Measurements of bond strength for wafers bonded in nitrogen show a significant increase when compared to those bonded in air. We hypothesize that UV treated wafers will physisorb species such as water when exposed to air, which interferes with the direct Si-Si bonding. The additional water must by removed by diffusion from the surface or consumed by reaction at the surface. Sonoscan images show a reduction of thermally generated voids and void size after low-temperature annealing for wafers that were exposed to UV and bonded in nitrogen. The small voids are a result of desorbed hydrogen from the silicon surface during the low-temperature anneal. UV exposure reduces the initial hydrogen concentration prior to bonding and thus reduces voids found after low-temperature anneal when compared to wafers with no UV exposure. Annealing the bonded wafers (both UV and heat-treated, and heat-treated only) at higher temperatures (T≥750°C) eliminated all the small hydrogen-generated voids.

REFERENCES


**Figure 1:** Flow diagram of UV system.

**Figure 2:** IR image of wafers immediately bonded following 5 minute UV exposure at 200°C.

**Figure 3:** IR image of wafers immediately bonded following 5 minutes at 200°C without UV exposure.

**Figure 4:** With five minute UV exposure, platen T=200°C, and annealed at 300°C for 24 hours.

**Figure 5:** Without UV exposure for five minutes, platen T=200°C, five minutes, and annealed at 300°C for 24 hours.

**Figure 6:** Sonoscan image of bonded wafers with five minute UV exposure, platen T=200°C, and annealed at 300°C for 24 hours.

**Figure 7:** Sonoscan image of bonded wafers without UV exposure for five minutes, platen T=200°C, five minutes, and annealed at 300°C for 24 hours.

**Figure 8:** Wafers exposed to UV at varying times for room temperature. Wafers were either bonded in air or nitrogen and bond strength was measured after 24 hours at room temperature.
**Figure 9:** Wafers exposed to UV at varying times for 200°C. Wafers were either bonded in air or nitrogen and bond strength was measured after 24 hours at room temperature.

**Figure 10:** Wafers exposed to UV with varying platen temperatures. Wafers were annealed for 24 hours and bond strength was measured.

**Figure 11:** Bond strength for wafers exposed/not exposed to UV at varying platen temperatures. Wafers were annealed at 23°C, 50°C, and 100°C for 24 hours.