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# SEMICONDUCTOR WAFER BONDING: SCIENCE, TECHNOLOGY, AND APPLICATIONS

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## THE EFFECT OF A PLASMA PRETREATMENT ON THE Si/Si BONDING BEHAVIOUR

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The effect of plasma treatments (reactive ion etching in oxygen- and/or fluorine-containing plasmas) on Si/Si wafer bonding was investigated. Etching in SF<sub>6</sub> caused a bonding behaviour generally known from hydrophobic (HF etched) samples, whereas adding O<sub>2</sub> to the feed gas caused the Si(100) surfaces to become hydrophilic and spontaneous bonding was achieved. Plasma treatments in mixtures of oxygen with SF<sub>6</sub> or CHF<sub>3</sub> result in higher interface bond energies than for hydrophilic bonded wafer pairs already after annealing at T ≥ 400°C. Very strong bonds, however, are even obtained by lower temperature annealing (T ≤ 400°C) after plasma treatments in O<sub>2</sub>

### INTRODUCTION

Silicon wafer direct bonding is a technology promising for VLSI, semiconductor power and sensor device applications [1]. For most applications, an additional annealing step at higher temperatures is required after the initial room-temperature bonding in order to increase the bonding strength. There are, however, numerous applications such as the bonding of processed wafers for sensor fabrication, which allow only short postannealing at relatively low temperatures such as 400°C. Therefore, an activation process of the bonding surfaces is desirable, which causes high interface energies already at relatively low temperatures. One possibility of such an activation process is the preparation of interface layers of glass or TMOS (hydrolyzed tetramethoxysilane) which increase the interfacial energy by a factor of 2, or more, with respect to bonded hydrophilic wafer pairs (e.g. [2]). In some cases, however, interface layers are not compatible with device requirements, or their preparation cannot be integrated into the device fabrication process. Another possibility is the modification of surface bonds by plasma processes. Analyses of the bonding behaviour of silicon surfaces exposed to oxygen [3], Ar [4], or Ar/H<sub>2</sub> [5] plasmas showed an appreciable increase in the bonding strength. Treatments in oxygen plasma cause the formation of a thin oxide layer at the bonding interface, whereas surfaces cleaned (etched) in an Ar/H<sub>2</sub> plasma are bondable only after a thermal desorption of hydrogen at temperatures between 400°C and 600°C. Interfaces prepared by the latter procedure are atomically flat, showing no intermediate interface layers. But the bonding strength after room temperature bonding is about the same as for normal hydrophilic wafer bonding. Therefore, other plasma pretreatments compatible with modern device processes are required. Fluorine compounds such as SF<sub>6</sub>, CHF<sub>3</sub>, or CF<sub>4</sub> and

their mixtures with O<sub>2</sub>, N<sub>2</sub>, or H<sub>2</sub> are widely applied. All these gases are characterized by a different selectivity of etching silicon or SiO<sub>2</sub>. Therefore, the present paper is concerned with the application of pretreatments in fluorine-containing plasma to wafer bonding. Results of these experiments are compared to pretreatments in an oxygen plasma.

## EXPERIMENTAL

Czochralski-grown silicon wafers (diameter 4 in., p-type,  $\rho = 30 - 50 \Omega \cdot \text{cm}$ ) were used for the experiments. After cleaning in standard RCA1,2 solutions, the wafers were plasma treated and subsequently bonded under dry conditions, or by an additional water flushing using the microcleanroom set-up [6]. For the plasma treatment (reactive ion etching, RIE) at 13.56 MHz the following processes were used:

- etching in SF<sub>6</sub> (100%) at a pressure of 25 Pa for 20 sec, a flow rate of 64 sccm SF<sub>6</sub>, and a rf power of 220 W,
  - etching in SF<sub>6</sub>/18.9%O<sub>2</sub> mixtures (SF<sub>6</sub> : O<sub>2</sub> = 60 : 14) at a pressure of 1.4 Pa for up to 160 sec, and a rf power of 80 W,
  - etching in CHF<sub>3</sub>/O<sub>2</sub> (25sccm/10sccm) at a pressure of 20 Pa for up to 20 sec, and a rf power of 200 W,
  - etching in O<sub>2</sub> at a pressure of 150 Pa for up to 15 min, and a rf power of 600 W.
- All processes were carried out under cleanroom conditions.

The bond energy was measured by the crack opening method in air. Some treatments (especially with oxygen plasma), however, cause the bond energy to increase and the crack opening method to fail. Therefore, the fracture stress was measured by tensile tests. The morphological variations of the plasma-treated surfaces and the structure of the bonding interface were characterized by different microscopic and spectroscopic methods.

## RESULTS

### Analysis of plasma treated surfaces

Treatments in fluorine-containing plasmas cause the surface roughness to increase (table 1). For instance, due to a plasma process in SF<sub>6</sub>/O<sub>2</sub> for 40 sec the surface roughness increased by a factor of more than 2 with respect to an otherwise identical RCA-cleaned wafer. An analogous roughness results from chemical etching in 1% HF solutions for 10 min [7]. The roughness is associated with first indications of a granular structure, which however, is substantially less pronounced than for etching in a CF<sub>4</sub>/O<sub>2</sub> plasma for the same time.

Results of spectroscopic ellipsometry (VASE) are shown in fig. 1 for a sample etched in SF<sub>6</sub>/O<sub>2</sub>. For modelling the plasma-etched surface, a 2-layer model is assumed on top of bulk silicon consisting of a disturbed silicon layer, about 5.2 nm thick, and an oxide layer. Other common models such as the Bruggeman effective-medium approximation (EMA layer) used for interpreting HF-etched surfaces [8] fail. For the disturbed silicon layer (Si-V), the silicon data for refractive index  $n$  and extinction coefficient  $k$  are fitted. But as fig. 1 also

shows, the differences of both are very small. The physical meaning of the disturbed layer is that it represents a layer damaged by plasma etching. This interpretation is supported by other investigations demonstrating that plasma etching causes Si lattice defects [9,10]. Furthermore, VASE measurements on surfaces analogously etched in other gases ( $\text{CF}_4/\text{O}_2$ ,  $\text{CHF}_3/\text{O}_2$ ) are interpreted on the basis of the same model. The thickness of the disturbed (damaged) layer and the data for  $n$  and  $k$  are slightly different, indicating the different degree of damage due to the etching by different gases. As other authors showed (e.g. [11]), the damage is annihilated by an appropriate postannealing.

Furthermore, etching in pure  $\text{O}_2$  causes the formation of a thin oxide layer on the surface. Its thickness mainly depends on the process time. A logarithmic dependence is observed. After long exposure times, however, a damaged layer is also detected by VASE measurements. Measurements of the contact angle of samples treated in an oxygen plasma show that they are strongly hydrophilic. Contact angles of  $2^\circ$  or less (detection limit of the method) are observed. In contrast, measurements on samples treated in a fluorine-containing plasma show that the hydrophilicity is strongly affected by the concentration of oxygen added to the gas phase. Processes with a pure fluorine plasma cause hydrophobic surfaces (especially  $\text{SF}_6$ ).

#### Wafer bonding

Wafers pretreated with the various plasmas mentioned, except those pretreated in  $\text{CF}_4$ , show a more or less spontaneous bonding. The bond energy, measured after room-temperature bonding and additional annealing, is increasing with annealing temperature, and with the oxygen concentration increasing in the fluorine-containing gases (figure 2). Wafers treated with pure  $\text{SF}_6$  show a bonding behaviour generally known from hydrophobic (HF-etched) samples (fig. 3). The dependence of the bond energy on the annealing temperature and the structure of the interface are also analogous. In contrast to that, wafers treated in a  $\text{SF}_6/\text{O}_2$  plasma bond spontaneously. All data measured after bonding at room temperature show that the interface energy  $\gamma$  is significantly higher than for bonded hydrophilic wafer pairs. Moreover,  $\gamma$  clearly increases if the wafers are etched in the  $\text{SF}_6/\text{O}_2$  plasma for up to 40 sec. Further prolonging the plasma treatment causes  $\gamma$  to decrease again. The data showed appreciable differences of  $\gamma$  between the bonding under dry conditions, and with a preceding water flushing. After bonding under dry conditions at room temperature  $\gamma$  varies by a factor of about 2 for plasma treatments up to 40 sec, whereas after more extended treatments there is no difference. The increased value of  $\gamma$  at room temperature (as compared to that of normal hydrophilic bonding) indicates a change of the surface structure, i.e. the treatment in the  $\text{SF}_6/\text{O}_2$  plasma increases the number of active sites. Assuming OH-groups as the active sites for bonded hydrophilic wafers, the differences in  $\gamma$  measured between bonding under dry conditions and with a preceding water flushing suggest that especially under room-temperature conditions the active sites produced by the plasma treatment are characterized by a higher affinity for bonding  $\text{H}_2\text{O}$  molecules via OH-groups on the surface, resulting in an increased surface energy  $\gamma$  during bonding. The complexity of the mechanism is demonstrated by the dependence of  $\gamma$  on the annealing temperature (figure 4). For  $T < 400^\circ\text{C}$ , plasma-treated wafer pairs bonded with a preceding water flushing yield values of  $\gamma$  similar to those of bonded hydrophilic wafers. After annealings above  $400^\circ\text{C}$ ,  $\gamma$  is higher than for bonded hydrophilic wafers. Moreover,  $\gamma$  values measured after annealing plasma-treated wafers bon-

ded under dry conditions, are substantially lower than for a bonded hydrophilic wafer pairs (fig. 3).

There is an analogous behaviour also with respect to the interface defect generation (bubble generation) between  $\text{SF}_6$ (100%) etched wafers and hydrophobic ones on the one hand, and  $\text{SF}_6/\text{O}_2$  etched wafers and hydrophilic ones, on the other. Figure 4 shows infrared microscope images of the same wafer pair after room-temperature bonding and after annealings at 200, 400, and 600 °C, respectively, for 1 hour. Here, plasma etching in  $\text{SF}_6/\text{O}_2$  and a preceding water flushing before bonding were applied. The generation of bubbles seems to be similar to that observed in bonded hydrophilic wafer pairs. Further annealing at higher temperatures reduces the bubble density. Interfaces without bubbles may be realized after single-step annealing at high temperatures. The same holds true also for  $\text{SF}_6/\text{O}_2$  etched and dry-bonded wafer pairs as well as for samples etched in pure  $\text{SF}_6$ , only.

Wafers bonded after being treated with an oxygen plasma result in bond energies of 0.1 to 0.2 J/m<sup>2</sup> after bonding at room temperature. The bond energy increases, however, substantially with increasing temperature (fig. 2). Strong bonds arise already after annealing at 300°C for short times. The generation of interface defects (bubbles) during annealing is mainly affected by the duration of the plasma treatment and the water flushing before bonding. Infrared microscopy did not reveal any bubbles on the samples plasma-treated before being water flushed. In contrast to that, bubbles appear in dry-bonded wafer pairs after the same annealing. This suggests that treatments in an oxygen plasma also crack residual carbon hydrogen compounds on the wafer surface, which are removed by water flushing.

#### Interfacial structure

Cross-sectional samples were prepared for high-resolution electron microscopy after annealing wafer pairs at 1100°C for 5 hours. Typical images of the interface structure are shown in figure 5. For instance, etching in pure  $\text{SF}_6$  and  $\text{SF}_6/\text{O}_2$  causes an interface structure analogous to that after chemical etching in HF solutions. Moreover, there are no differences in the interface structure of  $\text{SF}_6/\text{O}_2$ -etched samples between wafer pairs bonded with a preceding water flushing, and without. The oxide layer on the surface is always removed and both Si surfaces are directly bonded to each other. The bonded interfaces are not atomically flat as for etching in  $\text{Ar}/\text{H}_2$  plasma [5]. Instead, the interface represents a 1 to 2 nm thick defective layer. Most of the defects within the layer are of a rod-like morphology and oriented parallel to {111} lattice planes. They cannot be observed in plan-view samples due to their 1-dimensional extension. Rod-like defects were shown to consist of silicon self-interstitials rather than of foreign phases composed of impurities detected by SIMS [11]. The reason for such a defective interface layer is assumed to be the same for  $\text{SF}_6$  or  $\text{SF}_6/\text{O}_2$  etched wafer pairs as described for HF-etched ones. For the latter, an accommodation process of two rough surfaces during annealing was suggested [7].

Furthermore, etching in  $\text{CHF}_3$  causes a completely different interface structure. Here, an amorphous layer is detected in the interface. The intermediate layer is assumed to consist of fluorocarbons and/or hydrocarbon compounds, forming residual layers on the silicon surface during the plasma treatment [12]. Note that the interface is not atomically flat. In some cases cavities, which are more than 10 nm deep, are observed. In contrast, bonded interfaces

of wafer pairs treated with oxygen plasma are atomically flat and characterized by a thin ( $d \approx 2n$ ) oxide layer.

## CONCLUSIONS

Wafers pretreated with various plasmas show a more or less spontaneous bonding. The bond energy, measured after room-temperature bonding and additional annealing, is increasing with the temperature of annealing and with the oxygen concentration increasing in the fluorine-containing gases. Treatments in  $SF_6/O_2$  mixtures caused a hydrophilic bonding behaviour, but a higher interface bond energy than for hydrophilic bonded wafer pairs. There is, however, no intermediate (oxide) layer at their Si/Si interface. The highest bond energies are measured for wafer pairs pretreated in an oxygen plasma already after annealing at  $T < 400^\circ C$ .

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Table 1: Results of roughness analysis on plasma-etched Si(100) surfaces.

Data were collected from AFM measurements (analyzed area  $1 \times 1 \mu m^2$ ).

	Rms (Rq) [nm]	Ra [nm]	Rmax [nm]
RCA cleaned sample	0.128	0.102	1.176
$CHF_3/O_2$ , 40 sec	0.317	0.255	2.778
$SF_6/O_2$ , 40 sec	0.268	0.215	2.116
$O_2$ , 5min	0.157	0.125	1.523
$CF_4$ , 40 sec	1.114	0.898	9.423

2	si <sub>o2</sub>	22.461 Å
1	si_v4	52.57 Å
0	si_jell	0.5 mm

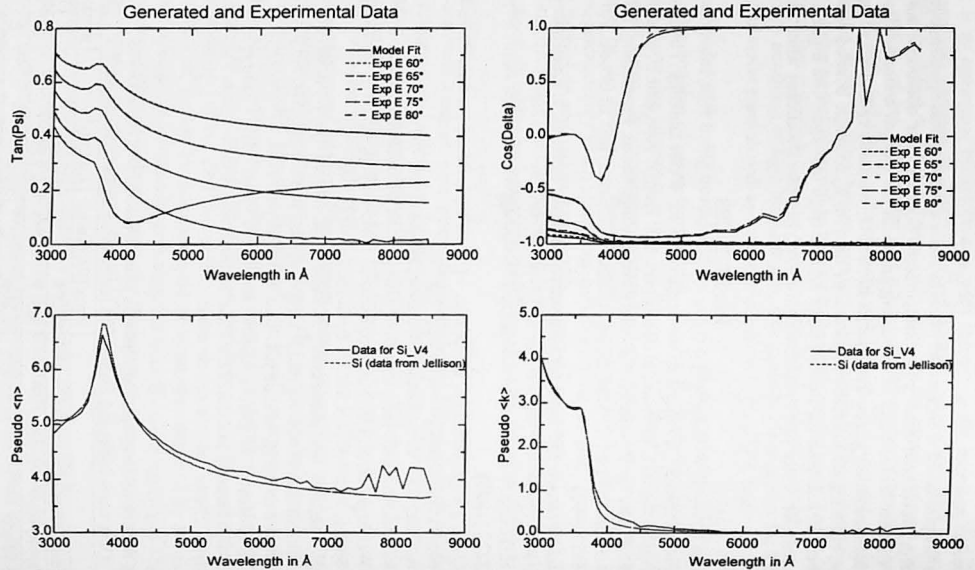
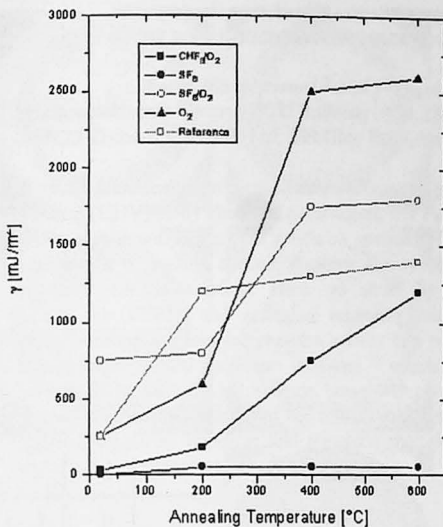


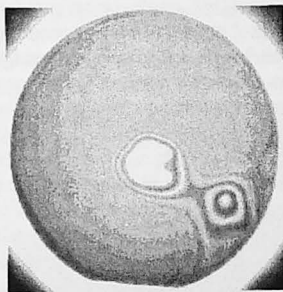
Figure 1: Ellipsometric analysis of a Si(100) surface etched in a  $\text{SF}_6/18.9\%\text{O}_2$  plasma for 40 sec. The model used for data fit (a), the experimentally generated data for the amplitude ratio  $\Psi$  (b) and the phase shift difference  $\Delta$  (c) as well as the data used for refractive index  $n$  (d) and extinction coefficient  $k$  (e) for modeling the disturbed layer (Si-V).

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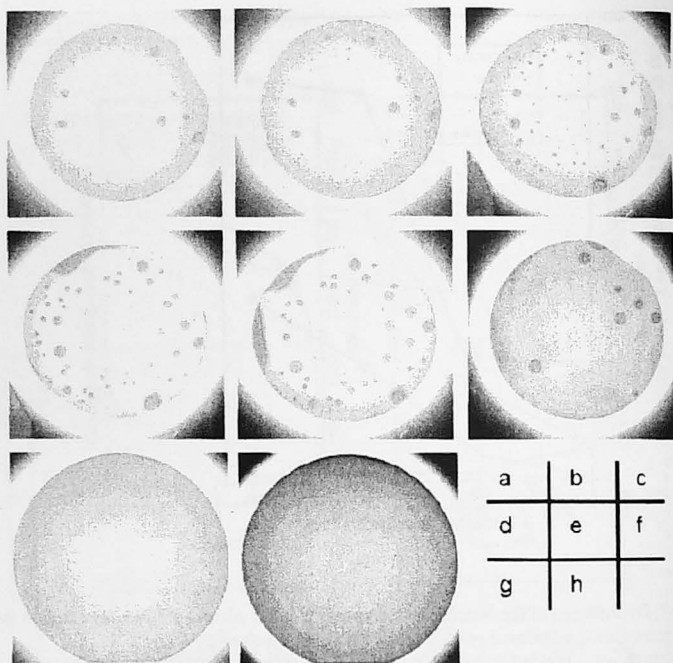




**Figure 2:** Dependence of the interface bond energy  $\gamma$  on the plasma pretreatment and on the temperature during additional annealing for 1 hour after bonding. The figure shows a bonded hydrophilic wafer pair as reference (data for equilibrium conditions). Measurements by the crack propagation method.



**Figure 3:** Plasma-treated (SF<sub>6</sub>, 1 min) and subsequently bonded wafer pair. Infrared microscope image after room-temperature bonding.



**Figure 4:** Infrared transmission images of bonded wafer pairs pretreated by etching in an  $\text{SF}_6/\text{O}_2$  plasma (a – f) and an  $\text{O}_2$  plasma (g,h).  
a – f - Images of a wafer pair after room-temperature bonding (a) and after annealing for 1 hour at 200°C (b), 400°C (c), 600°C (d), 800°C (e), and 1100°C (f).  
g,h - Image of a wafer pair after room-temperature bonding (a) and after annealing at 300°C for 5 hours.



**Figure 5:** Electron microscope image of the interface of a bonded wafer pair pretreated in a  $\text{SF}_6/\text{O}_2$  plasma for 40 sec. After bonding the wafer pair was annealed at 1100°C for 5 hours.