JOURNAL OF MATERIALS SCIENCE **33** (1998) 253–258

# Effect of the surface treatment on the room-temperature bonding of Al to Si and $SiO_2$

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Bonding of polycrystalline Al to Si(1 0 0) and $SiO_2$ (fused silica) was carried out at room temperature by means of surface-activated bonding method. In the present work, different means of surface activation such as irradiation of an argon fast atom beam (FAB) and a hydrogen radical beam (RB) were used. Influence of the exposure to a vacuum atmosphere of the activated surfaces by fast atom irradiation on the bonding behaviour was investigated. The strength of the Al–Si joints sputter cleaned by FAB before bonding reaches as much as 32 MPa. When the activated surfaces were exposed to 30 L (where L is the abbreviation for langmuir ($1.33 \times 10^{-4}$ Pa s)) in the residual gases (mainly vapour), the strength of the Al–Si joint decreased to 20 MPa and approached that of the Al–$SiO_2$ joint. This indicates that the fracture strength of the joint of Al and Si with an intermediate layer of OH groups and oxide is close to that of Al and Si oxide. The adhesion between Al and Si deteriorated strongly because of hydrogen termination on the Si surface which had been irradiated by the hydrogen RB. On the contrary, bonding of Si with native oxides to Al was successful with the hydrogen RB irradiation.

## 1. Introduction

The surface-activated bonding (SAB) method [1, 2] is an advanced bonding technique based on adhesion phenomena in a vacuum. Solid surfaces are cleaned by ion or fast atom beam (FAB) bombardment in an ultrahigh vacuum (UHV) to remove native oxides and contaminations. Afterwards these surfaces are brought into contact. They often develop a very strong adhesive force. The conventional bonding methods, such as diffusion bonding between different materials, often produce brittle intermediate and high thermal stresses because of the bonding process carried out at high temperatures.

In the case of the Si–Al joint, the joint is usually annealed at a temperature below 773 K. The reliability of these bonds is affected by the properties of the Al–Si interface. The properties of the interface is changed by an annealing process at a temperature below 773 K after Al is deposited on Si. During the annealing, Si atoms dissolve into the Al [3]. By cooling the samples, Si crystalline precipitates in Al [3] and thermal stress remain at the interface. These phenomena are the reason why the reliability of joints decreases. Lower-temperature bonding is preferred to enhance the reliability of joints. In recent work, the bonding of Al to Si was carried out by means of a Si wafer direct bonding technique [4]. Before bonding, Al and Si treated each surface hydrophilically and removed interfacial wafer molecules for annealing above 623 K. In this way the bonding temperature could be lowered and the bond strength of 20 MPa was obtained. However, a bonding temperature of 623 K is still too high with regard to the problem of thermal residual stresses. In this work, room-temperature bonding of Al to Si and fused silica ($SiO_2$) was carried out by means of the SAB method.

For the realization of room-temperature bonding, FAB irradiation is used as the means of the surface activation. Native oxides and contamination on the surface are removed physically. In the present study, hydrogen radical beam (RB) irradiation was applied also as a method to activate Si(1 0 0) and $SiO_2$ (fused silica) surfaces to remove chemically the contamination from the surfaces. Anthony *et al.* [5] reported that oxide and contamination can be removed by a hydrogen RB without irradiation damage to a sample. We report the effect of conditions of the surface treatment on the bond strength of Al–Si, and Al–$SiO_2$ joints are examined.

## 2. Experimental procedure

Mirror-finished n-type Si(1 0 0) single-crystal wafers, $SiO_2$ (fused silica) wafers and polycrystalline Al (purity, 99.999%) were used for the experiments. Si and $SiO_2$ wafers had dimensions of 0.4 mm × 10 mm × 10 mm and 0.8 mm × 5 mm × 5 mm, respectively. Al rods of diameter 10 mm were manufactured on a hemispherical surface with a radius of curvature of 25 mm. After polishing, the samples were thermally annealed at about $2 \times 10^{-3}$ Pa and 773 K for 7.2 ks. To remove the changed surface layer, the samples were electrolytically polished with perchloric acid and ethanol with an input voltage of 15 V for 30 s. The Si

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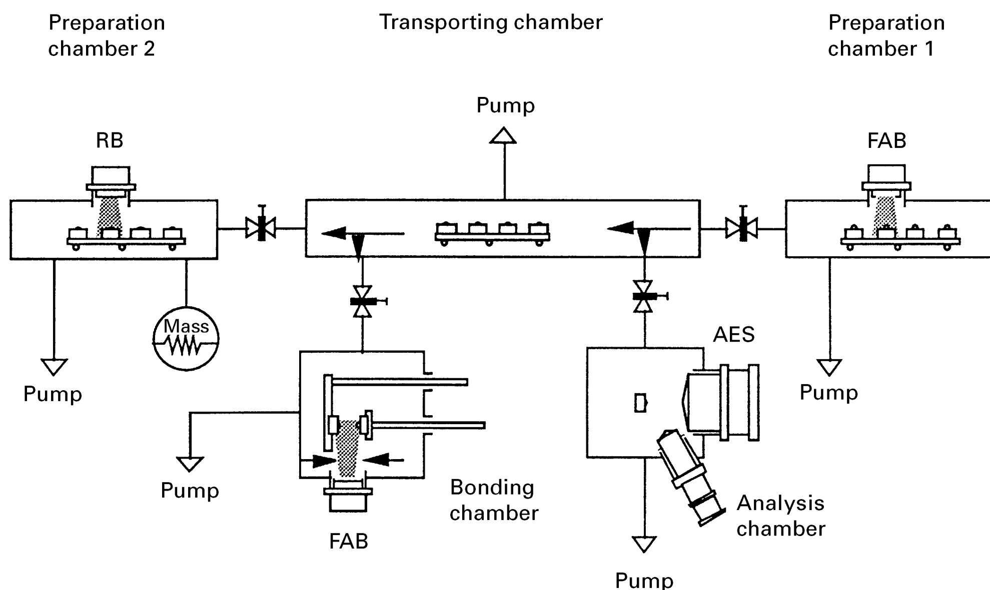


*Figure 1* Schematic view of the SAB machine.

TABLE I Ar FAB and H RB irradiation times and exposures (1 L = $1.33 \times 10^{-4}$ Pa s)

| Experiment | Irradiation time (s) | | | | | Exposure (L) |
|---|---|---|---|---|---|---|
| | Al | | Si, $SiO_2$ | | | |
| | FAB (chamber 1) | FAB (bonding chamber) | FAB (chamber 1) | FAB (bonding chamber) | RB (chamber 2) | |
| 1 | 420 | 300 | 300 (Si) | 300 | — | 0 |
| 2 | 420 | | 600 ($SiO_2$) | — | — | 30 |
| 3 | 420 | — | — | — | $3.6 \times 10^3$ | 15 |
| 4 | 420 | | 300 (Si) | — | $3.6 \times 10^3$ (after FAB) | 15 |
| 5 | 420 | | HF treatment (Si) | | | 15 |

and $SiO_2$ wafers were cleaned in acetone and ethanol with a supersonic wave machine.

A schematic view of the experimental apparatus that we used for the SAB experiments is shown in Fig. 1. The machine is made up of five UHV chambers consisting of bonding, analysis, transport and two preparation chambers. The samples can be transported, keeping the UHV. In the preparation chambers 1 and 2 of Fig. 1, samples can be irradiated by a FAB or a RB. Irradiation times and exposures for each experiment are indicated in Table I. The surfaces of all Al samples were sputter cleaned only by the FAB for a sputter time of 420–720 s. The surfaces of Si and $SiO_2$ were RB irradiated with and without a FAB before bonding in experiment 1, Si and $SiO_2$ were irradiated by a FAB for 300 s and 600 s, respectively, in preparation chamber 1. After transport of the samples into the bonding chamber, the samples of Si, $SiO_2$ and Al were irradiated by a FAB for 300 s immediately before bonding. In experiment 2, the samples were exposed to 30 L (where L is the abbreviation for langmuir ($1.33 \times 10^{-4}$ Pa s)) in the UHV chamber after irradiation by a FAB. The typical residual gases in the UHV chamber are indicated in Table II. The main residual gases in the UHV chamber were $H_2O$ molecules. In experiments 3 and 4, samples were irradiated by a RB. In experiment 4 the samples were sputter cleaned by a FAB for 300 s before irradiation by a RB. In experiment 5, the surfaces of Si samples were treated by HF and these were not irradiated. The cleaning process was controlled by Auger electron spectroscopy (AES) in the analysis chamber. The samples were bonded under a pressure of 24–74 N for 60 s. Estimations of the bonding strength of the joints were carried out by measuring the fracture stress by means of a tensile test.

TABLE II Typical residual gases in UHV at $7.4 \times 10^{-6}$ Pa in the preparation chamber 1

| Residual gas | Amount (mol%) |
|---|---|
| $H_2$ | 16.1 |
| $CH_4$ | 1.1 |
| $H_2O$ | 67.2 |
| $N_2$ and CO | 6.8 |
| Hydrocarbons | 8.7 |

## 3. Results and discussion

### 3.1. The effects of the fast atom beam and the radical beam irradiation on cleaning of the Al and Si surfaces

The Auger electron spectra of both Al and Si surfaces unsputtered and sputter cleaned by a FAB for 600 s are shown in Figs 2 and 3. Oxygen and carbon are found on the surfaces of Al and Si. These two impurities were removed by sputter cleaning with fast argon atoms. Subsequently, argon was found on the sputter-cleaned Al and Si surfaces. The amounts of Ar atoms on the Al and the Si surfaces were about 0.5% and 1%, respectively. Ar was driven into Si more than into Al. Ar was also detected by electron spectroscopy for chemical analysis on the $SiO_2$ surface after the tensile test. Ar is able to exist stably on the $SiO_2$ surface by FAB irradiation. It indicates that the joint produced by SAB contains Ar at the interface.

The Auger electron spectra of Si surfaces with and without RB irradiation are shown in Fig. 4. Oxygen and carbon were present on the surface of Si. After RB irradiation at 400 W for 4.2 ks, carbon was removed, but oxygen increased slightly, and sulphur and boron were found on the surface. It is possible that the increase in oxygen was due to the adsorption of $H_2O$ which occurred in the chamber during RB irradiation. The Auger electron spectrum of the Si surface which was sputter cleaned by FAB before RB irradiation, with and without RB irradiation, are both shown in Fig. 5. Ar was removed from the Si surface by RB irradiation. Sulphur and boron were not detected on either Si surface. Therefore, it might be concluded that these two impurities came from the oxide native layer of Si surfaces.

### 3.2. The bonding strength of Al–Si and Al–$SiO_2$ joints produced by surface-activated bonding with fast atom beam irradiation

The bonding strengths were estimated by means of tensile tests. The bonding strengths, which equal the

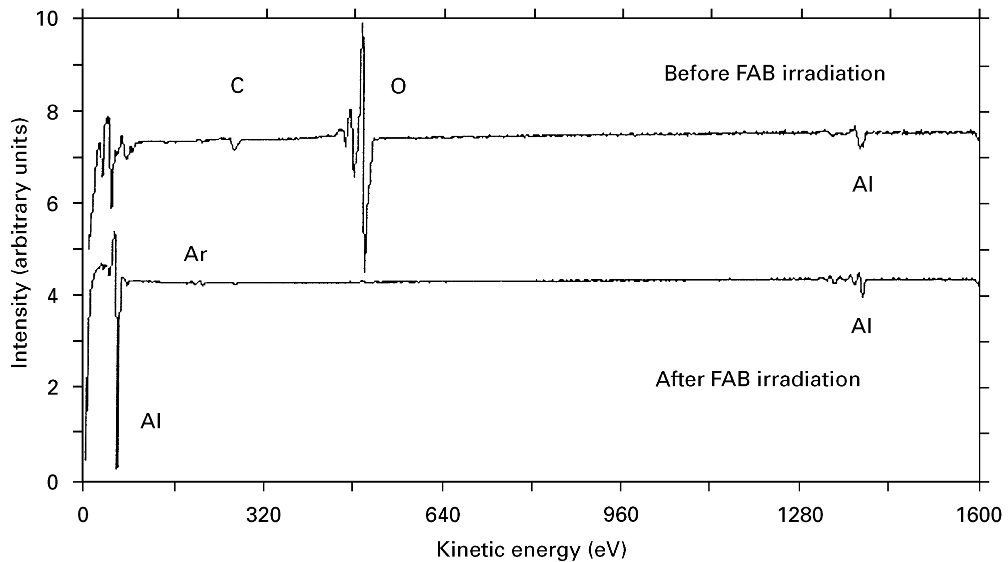


*Figure 2* Auger electron spectra of the Al surface before and after FAB irradiation.

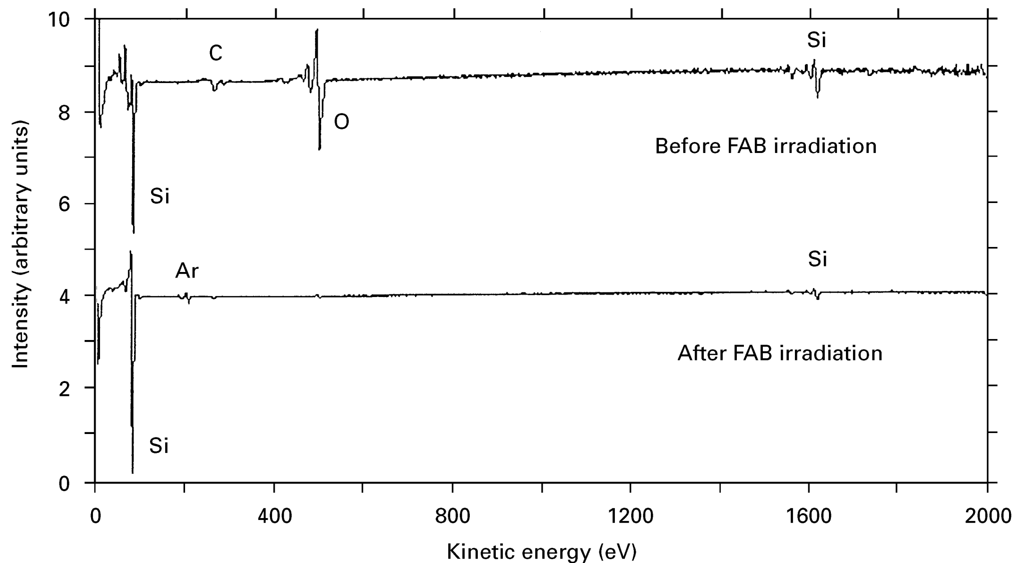


*Figure 3* Auger electron spectra of the Si surface before and after FAB irradiation.

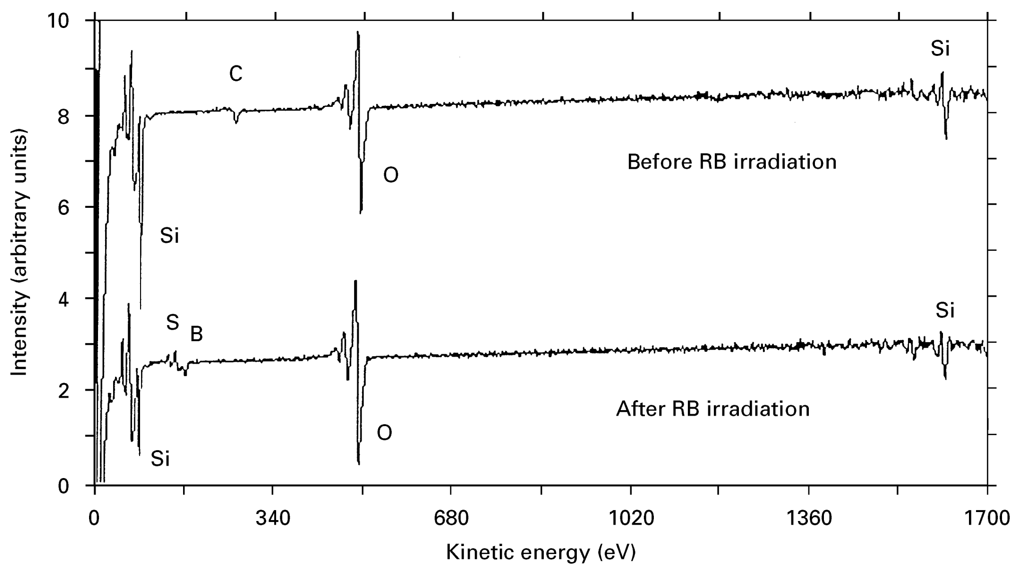


*Figure 4* Auger electron spectra of the Si surface before and after RB irradiation.

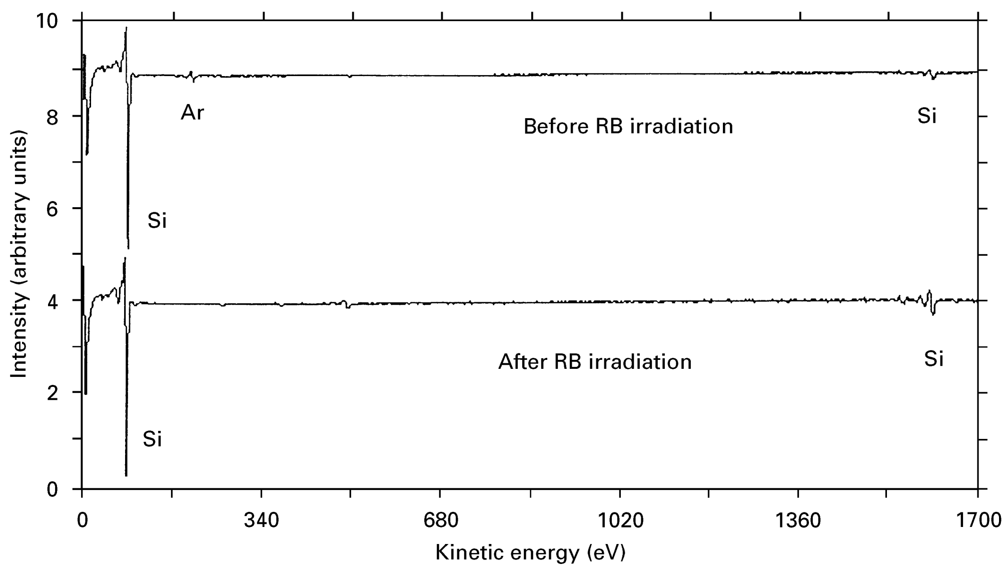


*Figure 5* Auger electron spectra of the sputter-cleaned Si surface by FAB before and after RB irradiation.

fracture stresses per contact area, were compared with each other using average values of the fracture strengths in Fig. 6. The horizontal axis shows various experiments as listed in Table I. The direct bonding of Al to Si produced by surface activation with FAB irradiation immediately before bonding has the highest value of the fracture strength at about 32 MPa (experiment 1). A fracture of the Al–Si joint occurred on the Si side. This means that the strength of the interface was higher than 32 MPa. The bonding strength of Al–$SiO_2$ (fused silica) joints was lower than that of the Al–Si joints. The observation by scanning electron microscopy showed that the fracture occurred at the interface of the Al–$SiO_2$ joint. The bonding strength of the Al–Si joints was weakened from 32 to 20 MPa by the activated surfaces exposed to residual gases, of which the main residual gases were $H_2O$ molecules as in Table II. The reactions of $H_2O$ on the Si and the Al surfaces are known to be as follows. $H_2O$ dissociates into H and OH on the Si(1 0 0) surface at 300 K [6]. Adsorption of water on clean Al(1 1 1) at 300 K is dissociative too. Adsorbed hydroxyl species can be produced at 300 K by prolonged water exposure [7]. In the case of our experiments, it is considered that adsorbed hydroxyl species exist on both sides of the Al and the Si surfaces. The bonding strength of the Al–Si joint that contained hydroxyl species at the interface would be closer to the bond strength of an Al–$SiO_2$ joint. The fracture mode of this joint was different from that of the direct bonding of Al–$SiO_2$. The dimple pattern of Al existed on the Si surface and the fracture started from near the interface into the Al side. The bonding strength of the Al–$SiO_2$ joint with exposure to residual gases was not changed much. It decreased slightly from 20 to 16 MPa.

## 3.3. The cross-sectional observation of the interface by transmission electron microscopy

The cross-sectional high-resolution transmission electron microscopy (TEM) image of Fig. 7 shows that the

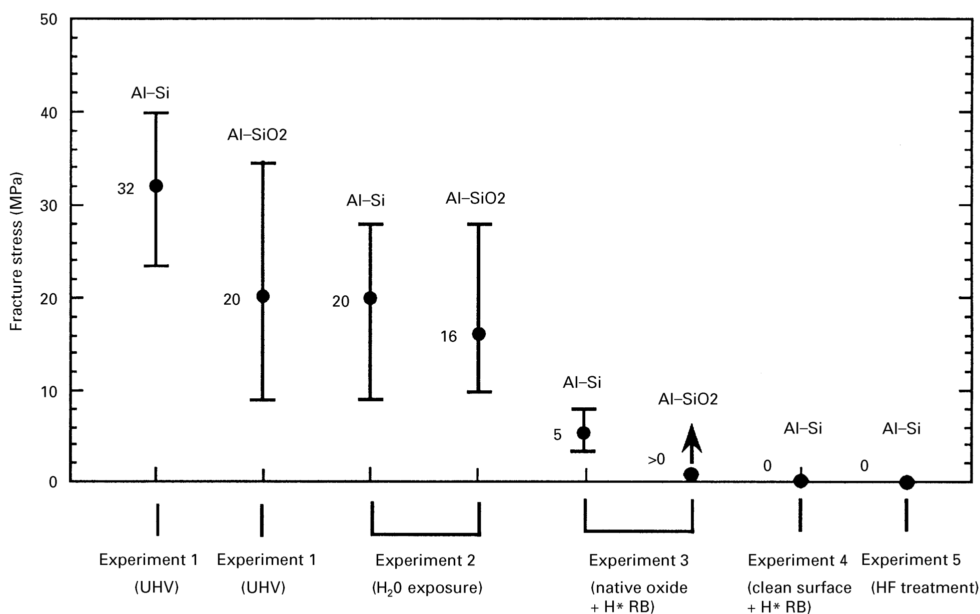


*Figure 6* Fracture stress of the Al–Si and the Al–$SiO_2$ joints for various bonding conditions. (●) average.

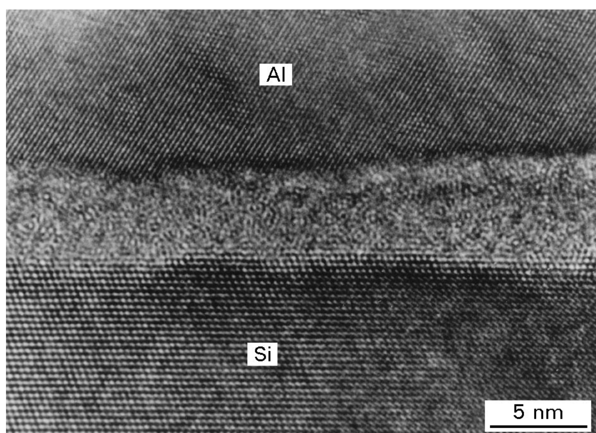


*Figure 7* Cross-sectional TEM image of an interface of Al–Si joint produced by SAB at room temperature.

Al–Si interface has an amorphous intermediate, which might be formed by the FAB irradiation in the presence of the residual gases. The surface activation of these samples was carried out by FAB irradiation for 1.8 ks and the background vacuum in the bonding chamber was $3.2 \times 10^{-5}$ Pa before bonding. After irradiation, the sample was exposed to the residual gases for about 30 s.

### 3.4. The effect of the radical beam irradiation on Al–Si and Al–$SiO_2$ bonding

The bonding of Al to Si with native oxide layer by hydrogen RB irradiation was successful. The average value of the bond strength of the joint was 5 MPa. The bond strength was much weaker than that of the joint obtained by FAB irradiation. When the Si surface was sputter cleaned by FAB irradiation before RB irradiation, Al could not be bonded to Si.

It is known that, at room temperature, no reaction occurred between a clean Si surface and hydrogen molecules. However, a reaction between reactive hydrogen atoms and Si can occur [8]. At room temperature, dangling bonds on the clean surface of Si(1 0 0) terminate with reactive hydrogen atoms, producing $SiH_2$ on the Si surface [9, 10]. SiH and $SiH_3$ occur at steps on the Si(1 0 0) surface. The bond energy of Si–H is 70.4 kcal mol$^{-1}$ whereas that of Si–Si is 42.2 kcal mol$^{-1}$ [11]. This indicates that the hydrogen bond, Si–H, is chemically stable. Therefore, in experiment 4, the Si surface is considered to be terminated by Si hydrides such as $SiH_2$, SiH and $SiH_3$. This hydrogen-terminated surface of Si could not be bonded to Al. The Si hydrogen terminated by HF treatment could not be bonded to Al either.

From the facts described above, we may conclude that a correlation of the bond strength of the Al–Si joints produced by SAB with different surface treatments can be indicated by typical symbols as follows (these symbols in the inequality are not chemical formulae):

$$\text{Al–Si} > \text{Al–O–Si} \geqslant \text{Al–(OH groups)–Si}$$

$$> \text{Al–(OH groups)–H–Si}$$

When considering the experimental results, the bonding strengths of the Al–Si and Al–$SiO_2$ joints produced by SAB under various conditions decreased in the following order: (i) direct bonding of Al to Si; (ii) direct bonding of Al to $SiO_2$ (fused silica); (iii) adsorption of residual gases such as $H_2O$ molecules; (iv) hydrogen termination of Si surface (not bondable).

## 4. Conclusions

AES measurements of sputter-cleaned and non-sputter-cleaned Al and Si surfaces by FAB and RB irradiation and the results of tensile tests demonstrated that the bond strengths of Al–Si and Al–$SiO_2$ (fused silica) joints produced by SAB depend strongly on the means of surface treatment. The sputter cleaning with a FAB resulted in high bond strength values. The bond

strength of the Al–Si joint decreased owing to adsorbed residual gases such as $H_2O$ on the activated surface and approached that of the Al–$SiO_2$ joint. The adhesion between Al and Si deteriorated strongly because of hydrogen termination on the Si surface.


## Acknowledgements
This work was supported in part by a grant-in-aid for scientific research from the Ministry of Education. The authors wish to thank Dr Y. Takahashi and Mr H. Takagi for support in the TEM investigations.


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*Received 19 April 1996*
*and accepted 30 July 1997*