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Wetting of silicon single crystal by silver and tin, and their interfaces

S. SUGIHARA, K. OKAZAKI
Shonan Institute of Technology, 1-1-25, Tsujido Nishikaigan, Fujisawa Japan
K. SUGANUMA
National Defense Academy, 1-10-20, Yokosuka, Japan

A study of wetting of silicon single crystals and electrode metals was undertaken to investigate the wetting mechanisms and to clarify the interfaces between the silicon wafer and silver and tin. The experiments were performed using a high-temperature surface tension measuring equipment in vacuum and 5% H_2/Ar atmospheres (10^5 Pa). The contact angles were measured by taking photographs through a telescope during the wetting experiment. Silicon was wetted by silver with a contact angle of 42°, whereas it was not wetted by tin in vacuum and in the 5% H_2/Ar atmosphere. However, heat treatment of silicon in vacuum or 5% H_2/Ar atmosphere prior to the wetting experiment reduced the contact angles compared to the cases with no heat treatment. The bonding interfaces between silicon and silver are also discussed.

1. Introduction

Silicon single crystal is one of the most important and popular semiconductors used as electronic packaging for LSI. The semiconductors can perform electric functions due to the bonding of silicon to the electrode metals such as gold, silver, etc.

The surface solid state physics of the absorption of a metal (gold) on a silicon single crystal have been investigated [1], and the electronic structures as revealed by band calculations on the absorption of alkali metals and silver on the silicon surface have been discussed [2]. In addition, using electron spectroscopy for chemical analysis (ESCA), the SiO_2/Si interfaces were investigated to show contacting Si and SiO_2 (~ 1 nm thick) [3]. However, a study of the interfaces of silicon and metals was performed in terms of solid phase reactions at low temperature, to stimulate epitaxial growth of silicides [4], and various silicides on silicon, such as $CoSi_2$ [5] and $NiSi_2$ [6].

Silver is a popular electrode and tin oxide is also an important material for use as a transparent electrode in addition to indium-tinoxide (ITO). In the present work, wetting of silver and tin on silicon was carried out and the mechanisms are discussed by introducing a reactivity parameter which is a function of the oxidation potential and the metal ion radius. Furthermore, the Ag/Si interfaces were also investigated using high-resolution electron microscopy (HREM) and scanning electron microscopy (SEM).

2. Experimental procedure

The wetting experiments were performed on single crystals of silicon wafers (1 1 1) and (1 0 0) (Komatsu Metal and Electronic Co., Ltd), which were cut to a size of 14 mm × 14 mm. The electrode metals used for the wetting experiments were silver and tin with a block size of 3 mm × 3 mm × 3 mm (about 100 mg) having 99.99% purities. The experiments were carried out using a high-temperature surface-tension measuring apparatus (Fig. 1) with increasing temperature in vacuum (5×10^{-3} Pa). Each metal was placed on a silicon sheet, and the temperature was raised to 990 and 600 °C in the Ag/Si and Sn/Si systems, respectively. In the sessile-drop methods, there are two methods of heating the silicon sheet: one is in a vacuum (5×10^{-3} Pa), with heating to 200 °C at a rate of 7 °C min^{-1}, followed by further heating to 600 °C for dropping the tin, the other is in a 5% H_2/N_2 atmosphere under the same temperature conditions as described above. It was expected that the effects of SiO_2 on wetting could be evaluated using this method. Photographs of the system were taken through a telescope to measure the contact angles during the wetting experiment. After wetting, the systems were mounted in resin, cut with a diamond cutter, and then the specimens were used for analysis of the cross-sectional interfaces of systems such as Ag/Si and Sn/Si. The interfaces were investigated using SEM and electron probe microanalysis (EPMA).

In addition to the wetting experiments, silicon and silver were bonded at 950 °C for 5 min in a vacuum of 2–3×10^{-3} Pa to analyse the interfaces between Ag and Si (1 1 1) by high-resolution electron microscopy (HREM).

3. Results and discussion

3.1. Wetting behaviour

Fig. 2 shows the changes of contact angle with temperature for the Ag/Si (1 1 1) and Ag/Si (1 0 0) systems. As the silver was in contact with the silicon, it was first

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melted at around 840 °C, which is the eutectic temperature of silicon and silver. At a temperature lower than the melting point of silver (962 °C), the contact angles are 90° at 900 °C, but fall to 42° at 950 °C for both Si (1 1 1) and Si (1 0 0). Fig. 2 shows the wetting behaviour of Ag/Si (1 1 1) at 900 and 950 °C, for example. Generally, silver does not wet oxides such as $BaTiO_3$ and $Pb(Zr, Ti)O_3$, showing a contact angle of 90° at most (at 980 °C) as reported by Sugihara and Okazaki [7]. On the other hand, tin, which does not have a eutectic point, became partially melted on the silicon at 228 °C in a vacuum of 8×10^{-3} Pa. The shape of the tin after melting gradually became round with increasing temperature above the melting point of tin, as shown in Fig. 3. The contact angles were a 152° and 147° at 445 and 600 °C, respectively.

In the sessile-drop method (Fig. 3), tin, dropped on a silicon sheet at 415 °C whilst increasing the temperatures after the silicon sheet had been kept in a 5% H_2/N_2 atmosphere at 200 °C for 1 h, exhibited a contact angle of 134° at 450 °C. In the other sessile drop experiment, tin dropped on a silicon sheet at 420 °C after the sheet had been kept at 200 °C in a vacuum, had a contact angle of 138° at 465 °C. In the absence of heat treatment, the largest contact angle of 152° around 445 °C was obtained in any heat treatment described above.

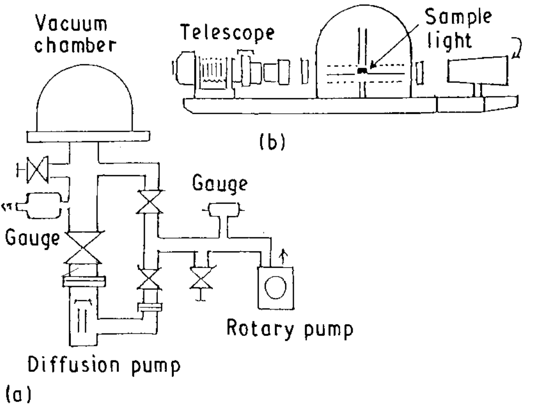

Figure 1 The high-temperature surface-tension measuring apparatus. (a) Outline of the vacuum system. (b) Inside the vaccum chamber and telescope.

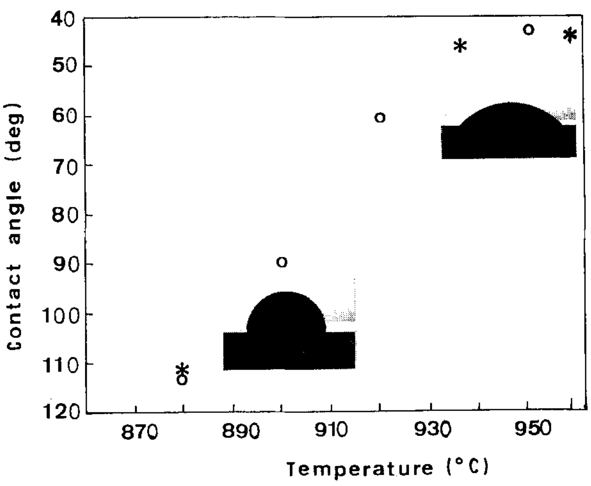

Figure 2 Wetting behaviour of single-crystal silicon by silver in a vacuum. (○) Si (1 1 1), (∗) Si (1 0 0).

Generally, silicon oxides are on presumed to be present on any silicon surface. The standard free energy of oxide formation is about 95 kcal g^{-1} mol^{-1} O_2 for tin, but 170 kcal g^{-1} mol^{-1} O_2 for silicon [8]. Therefore, silicon oxides on the surface are more stable than those of tin in this system. The thicknesses of the layers on the silicon were measured, using an ellipsometer, to be 280–300 nm, with little difference even after heat treatment in a more reducing atmosphere (5% H_2/N_2) than a vacuum. However, the oxide films originally existing on the tin will be further reduced, permitting it to wet silicon or SiO_2 surfaces

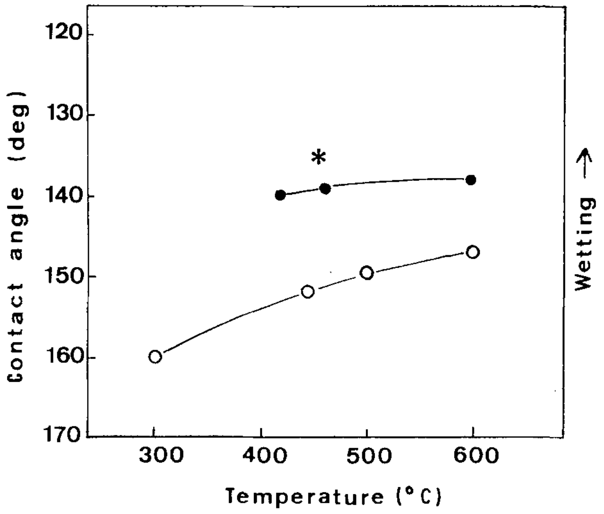

Figure 3 Changes of wetting properties of Si (1 1 1) with tin, using the sessile-drop method in (∗) 5% H_2/N_2, (●) vacuum; (○) tin dropped silicon, with no prior heat treatment, in vacuum.

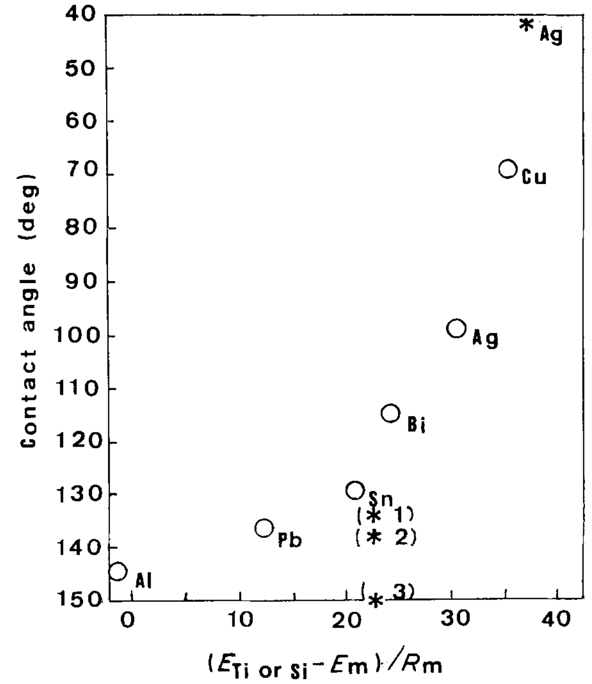

Figure 4 Dependence of contact angle on reactivity parameter, $(E_{Ti\ or\ Si} - E_m)/R_m$. $E_{Ti\ or\ Si}$ and E_m are the oxidation potential of titanium or silicon and the metal, respectively. R_m is the radius of metal ion. (○) Metal/PZT, (∗) Ag, Sn/Si. (∗1) and (∗2), in 5% H_2/N_2 and in vacuum by the sessile-drop method, respectively, (∗3) tin dropped on silicon with no prior heat treatment.

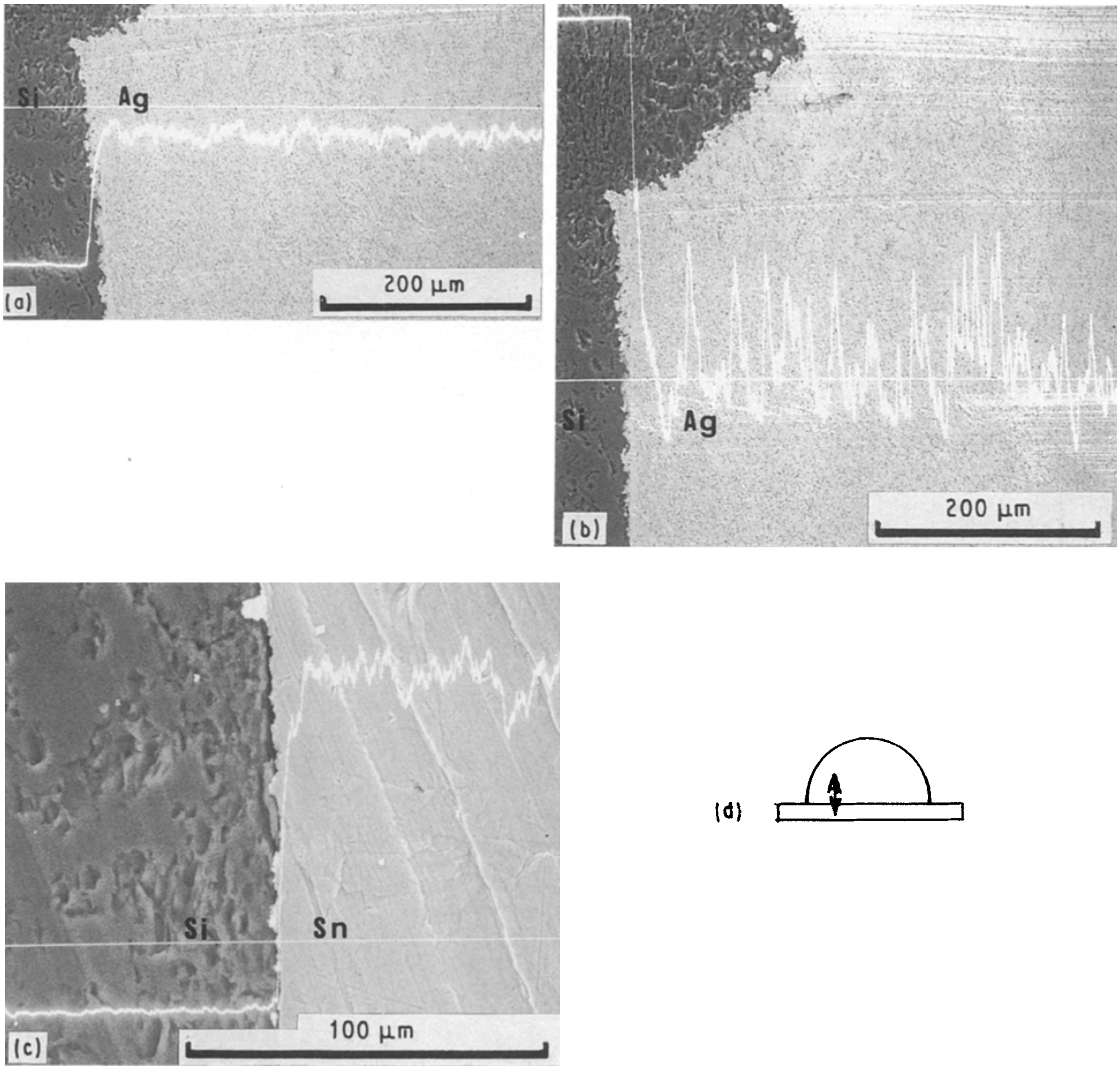

Figure 5 SEM line analyses of (a) scanning for silver and (b) scanning for silicon in the Ag/Si system, and (c) the Sn/Si system scanned for tin, and (d) the analysed interfaces.

as a result of the appearance of metallic tin in a 5% H_2/N_2 atmosphere. This seems to be the reason why the lowest contact angle was achieved in the 5% H_2/N_2 atmosphere in one of sessile-drop methods.

The contact angle directly represents the wetting properties, and it is assumed that the chemical reactions of a certain element in a base with molten metal will occur and the contact angle will be determined by the melting of a metal on a base. Therefore, the relation between oxidation potential of certain elements in a molten metal and base material, and the ionic radius of the molten metal, will be represented as the reactivity, P [9], that is, in the Sn/Si system, for example.

$$P = [E_{\mathrm{Si}} - E_{\mathrm{Sn}}]/R_{\mathrm{Sn}} \qquad (1)$$

where E_{Si} and E_{Sn} are the oxidation potentials of silicon and tin, respectively [10], and R_{Sn} is the ionic radius of tin. The radius of the element with the smallest ionization potential will be chosen for R_{metal} in the denominator of Equation 1, even if the base material contains various kinds of elements, as in ceramics. Fig. 4 shows the relationship between contact angle and reactivity for the Pb(Zr, Ti)O_3 ceramics as base material [9]. Copper and silver have larger reactivities and result in lower contact angles than those of aluminium and lead. The contact angles in the Ag/Si and Sn/Si systems are also plotted against reactivity in Fig. 4. Using the oxidation potentials of silver (− 0.8 V) and silicon (1.7 V), and the radius of silver (0.067 nm), the reactivity, P, is calculated to be 37.3 V in the Ag/Si system. In the Sn/Si system, P becomes 22.3 V from E_{Si} (1.7 V), E_{Sn} (0.14 V) and R_{Sn} (0.07 nm); the contact angles in each case are also indicated in the figure.

3.2. Interfaces between silver and silicon

SEM line analyses for the Ag/Si and Sn/Si systems are shown in Fig. 5. The analysed interfaces are illustrated in Fig. 5d. Both silver and silicon are found at the interfaces between them in the case of Ag/Si system, as

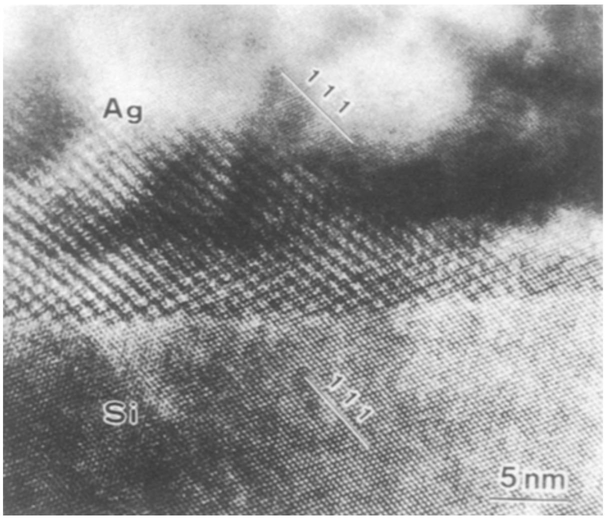

Figure 6 HREM images at interfaces after bonding silver and silicon (1 0 0) system.

shown in Fig. 5a and b whereas tin does not migrate into silicon as given in Fig. 5c. In addition to the wetting experiments, silver and silicon (1 0 0) were bonded at 950 °C in vacuum. Fig. 6 illustrates the interfaces between them as seen in HREM images to indicate the epitaxial bonding of silver with Si (1 0 0), and electron-beam diffraction patterns show a small lattice misfit (about 2°) at the interfaces, as shown in Fig. 7.

4. Conclusions

1. Around the eutectic point between silver and silicon, silicon was wetted by silver resulting in a contact angle of 42° at 950 °C. The wetting of silicon with silver does not depend upon the (1 1 1) and (1 0 0) faces of the single crystal, and silver was epitaxially bonded with silicon.

2. Tin did not wet silicon, having a contact angle of 150°, but wetting advanced slightly, giving a contact angle of 134° in a more reducing atmosphere of 5% H_2/N_2, although the film thicknesses (280–300 nm) of SiO_2 on silicon were little different with any heat treatment.

3. Wettability may be described by the relationship between the difference in oxidation potential for each element (in molten metal and base) and the ionic radius of the element in a molten material.

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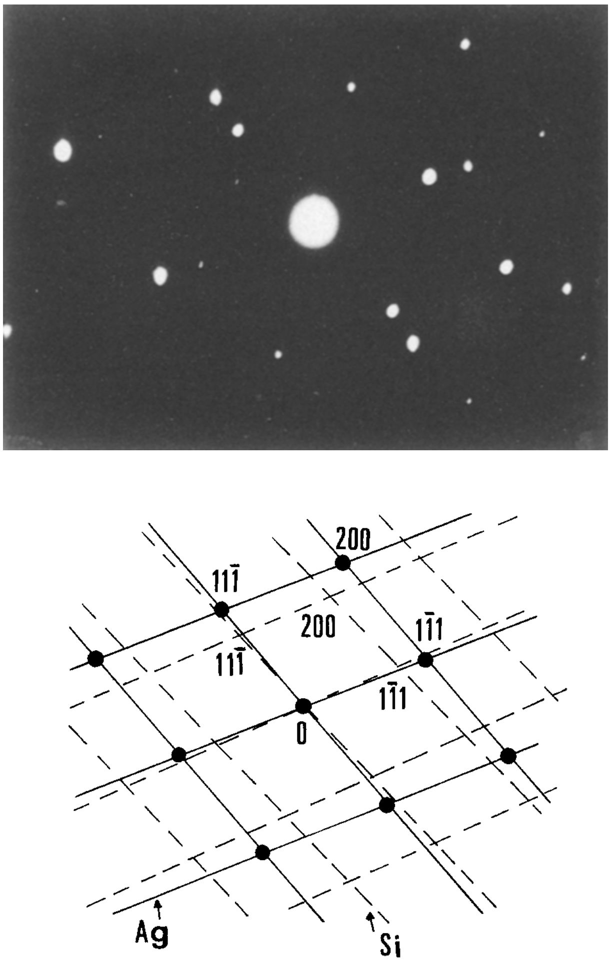

Figure 7 Electron-beam diffraction patterns at the interfaces of the bonded Ag/Si (1 0 0) system.

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