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Interface microstructure between silicon and silver formed after eutectic brazing reaction

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The interface structure between silicon and silver after the eutectic reaction at 950 °C has been examined primarily by using high-resolution transmission electron microscopy. Silver almost became a single crystal and a unique interface structure was found, where a special orientation relationship across the interface was recognized. The dominant relationship was obtained as $\{1\,1\,1\}_{Ag} \| \{1\,1\,1\}_{Si}$ and $[1\,1\,0]_{Ag} \| [1\,1\,0]_{Si}$. The lattice arrangement model of the interface showed that the interface expressed by this relation has a good lattice match across the interface.

1. Introduction

Silicon has been widely used as one of the major semiconductors, which can be found in every package of integrated circuits. Because all silicon devices are electrically connected with other parts, silicon must be bonded with metallic electrode materials such as gold, silver, aluminium, and so on. Mechanical integrity and electrical reliability are required for these interfaces. The interface structures must be controlled not only on a macroscopic but also a nanometre scale. A number of research works on silicon/metal interfacial phenomena, therefore, have been intensively carried out over several decades as demands increase to establish reliable bonding at the interfaces [1–4]. However, most of the works have focused on the interface formed by a low-temperature process, i.e. the physical deposition of a metal layer on the silicon substrate by various methods. The structure of such a silicon/metal interface is believed to be critical in determining the Schottky barrier height. Some comprehensive reviews on the structure of such interfaces can be found in the literature (e.g. [5]).

On the contrary, for physically deposited interfaces, there are only a few works on the brazed interface between silicon and metals, though brazing silicon with electrodes is frequently used in the practical production of the devices. We have reported the wetting phenomenon between silicon single crystals and silver below and above the melting temperature of silver [6]. Because this system has a eutectic reaction around 840 °C (the melting temperature of silver is 990 °C), silver became liquid below 900 °C on the silicon substrate and its contact angle was about 90°. With increasing temperature, the contact angle finally decreased to 40° at 990 °C. Thus, it can be said that the combination of silicon and silver is a wettable system. On the other hand, silicon and silver neither have mutual solubilities nor form any compound in all temperature ranges. Thus the atomic binding between silicon and silver is weak compared with Si–Si and Ag–Ag bindings. Thus, from the scientific stand point, it is very interesting that silver wets silicon well but that the atomic binding between silver and silicon is weak.

Therefore, it is worthwhile to seek an understanding of the interface structure between silicon and silver not only from the technological stand point, but also from scientific interest. In the present work, the interface structure was investigated primarily by high-resolution transmission electron microscopy (HRTEM). Most of the previous works on the physically deposited interfaces have used surface analytical techniques such as electron spectroscopy for chemical analysis (ESCA) or low-energy electron diffraction (LEED). Using HTREM one can obtain visible ideas of atomic arrangements on the interfaces.

2. Experimental procedure

2.1. Materials and eutectic brazing

The silicon used in the present study was two single-crystal wafers oriented in the directions of the $\langle 1\,1\,1 \rangle$ and $\langle 1\,0\,0 \rangle$ axes ($\langle 1\,1\,1 \rangle$ wafer 2 Ω cm p-type; $\langle 1\,0\,0 \rangle$ wafer 2–6 Ω cm p-type). The thickness of the wafers was about 500 μm and their surfaces were optically flat. They were cut into small pieces of about 5 mm square. The silver used was 99.99 wt % pure and was granular, being about 5 mm diameter. The silver granules were pressed into a sheet 200 μm thick.

Silicon discs and silver sheets were piled up layer-by-layer and were placed in the vacuum furnace. Brazing treatment was carried out at 950 °C, which is below the melting temperature of silver for 5 min in a vacuum of about 5×10^{-5} torr (1 torr = 133.322 Pa). After brazing, the joints were furnace-cooled.

2.3. Microstructural observation

Microstructure of the brazed interface was observed by optical microscopy (OM), scanning electron microscopy (SEM) and conventional and high-resolution transmission electron microscopy (CTEM and HRTEM).

The layered joint was cut perpendicular to the interface for OM and TEM. TEM foils were prepared by mechanical thinning followed by argon-ion thinning. The transmission electron microscope used was a Jeol JEM200CX operated at 160 kV.

Some joints were dipped into a dilute solution of nitric acid in order to observe the morphology of the reacted surface of the silicon after the melting of silver. The reacted surface was observed by SEM.

3. Results and discussion

3.1. Interface morphology

Fig. 1 shows the optical micrographs of the interfaces between silicon and silver. The interfaces have peculiar steps on both silicon surfaces. In the silver layer, many silicon islands were observed, which are formed by the eutectic reaction between silver and silicon. The eutectic temperature of this system is 865 °C [7]. During heating, liquid appears at this temperature and a certain amount of silicon and most of the silver melted at 950 °C. During cooling, the eutectic structure shown in the micrograph was formed. Along the bottom line of the steps on the surface of the silicon, small silver islands were aligned, as indicated by the arrows in the photographs. From this fact it is likely that dissolved silicon in the eutectic melt crystallized on the silicon surface and the crystallization was so rapid that the silver islands were left along the bottom line of the crystallized silicon steps. In the photograph of the Si (1 1 1) crystal, a depleted zone of a silicon island about 10 μm thick is clearly observed in the silver layer along the interface. This also supports the above reaction mechanism.

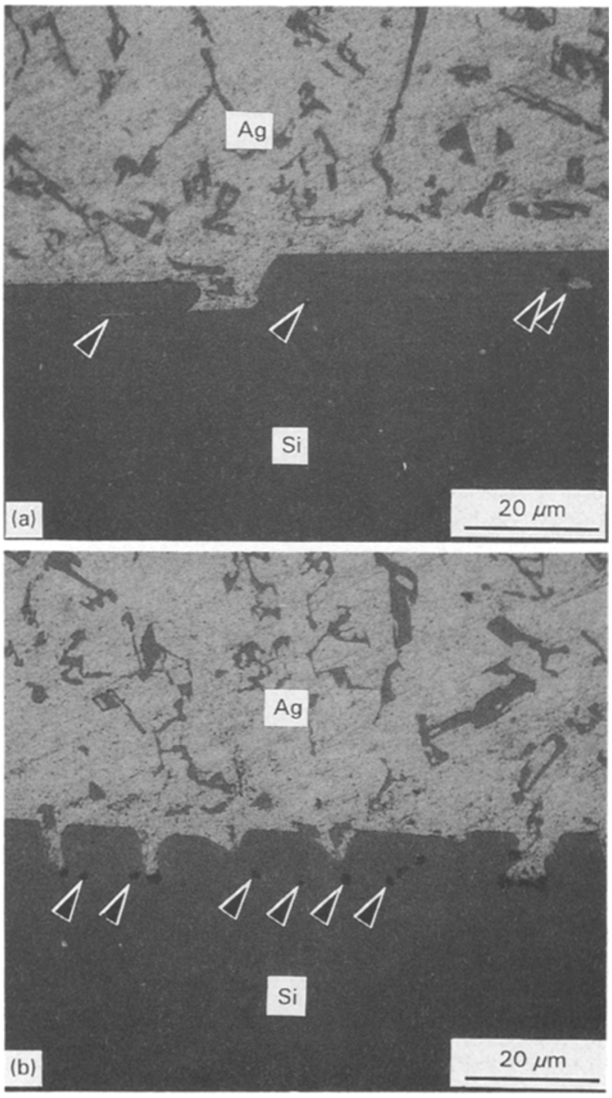


Figure 1 Optical micrographs of Ag/Si interfaces. (a) Ag/Si (1 1 1) interface, (b) Ag/Si (1 0 0) interface.

Fig. 2 shows the morphology of the silicon crystallization on the silicon substrate observed after removing the silver layer. Different morphologies of the crystallization of silicon depending on the crystallographic orientation of the substrate were clearly observed. From the crystallographic orientation relationship, all surfaces of the crystallized silicon steps were surrounded by its {1 1 1} planes. Therefore, the steps look like triangular hills with a flat top on the (1 1 1) surface face and pyramids on the (1 0 0) surface. At the contact point between two steps, narrow gaps are observed, which are formed by the depletion of

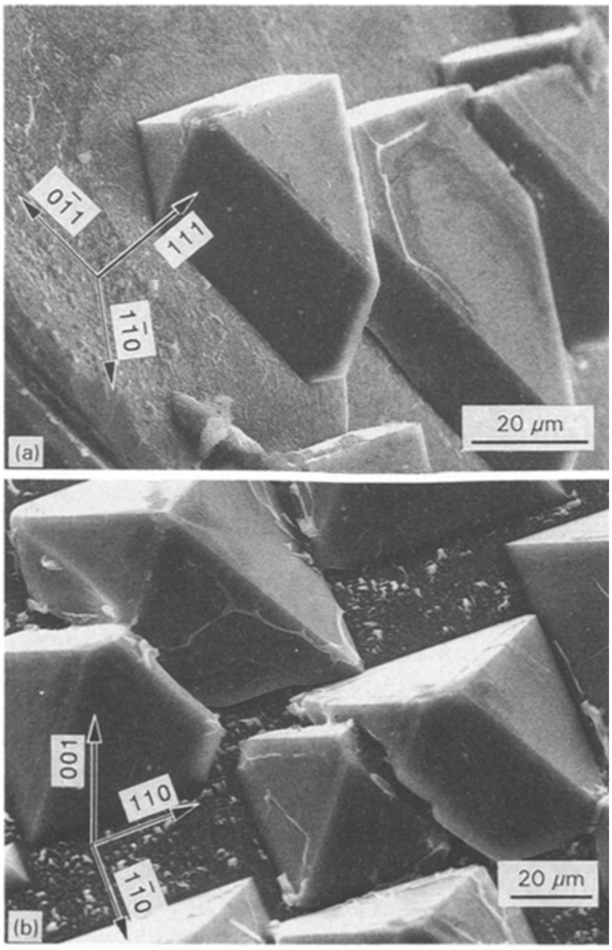


Figure 2 Scanning electron micrographs of silicon steps formed on silicon substrates. The silver layer was removed by acid etching. (a) (1 1 1) surface, (b) (1 0 0) surface.

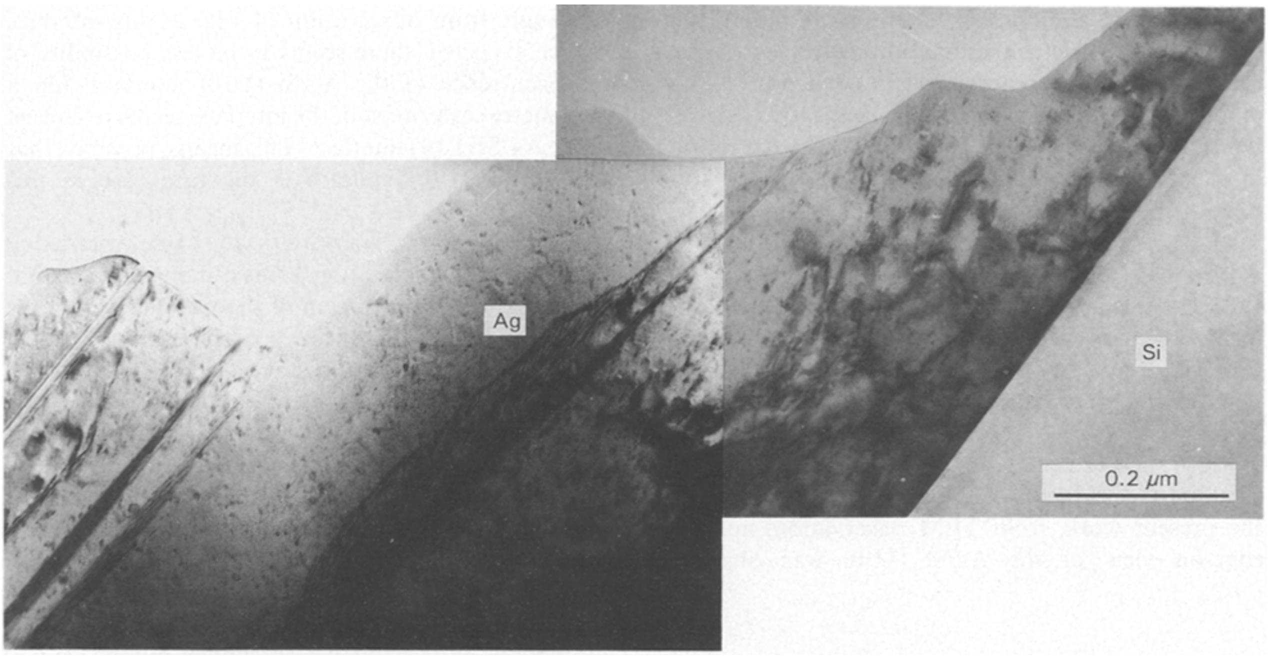
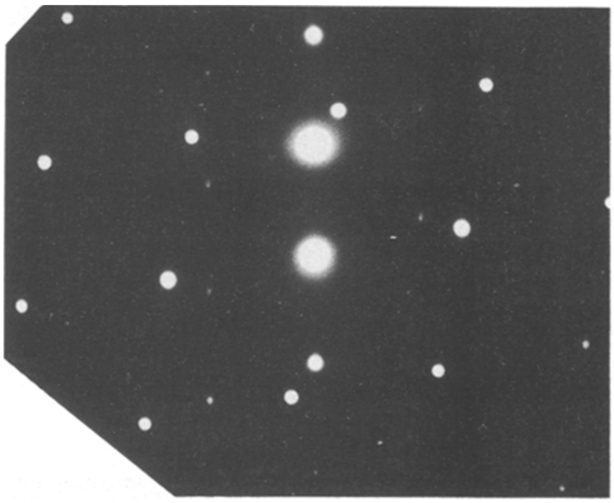


Figure 3 Transmission electron micrograph of the interfacial region of Ag/Si (1 1 1). The electron beam was parallel to the [1 1 0] axis of silicon.

silicon in liquid silver near the step that crystallized previously.

3.2. TEM observation

Fig. 3 shows a transmission electron micrograph of the interface, in which the silicon surface directed towards the ⟨1 1 1⟩ direction. The interface is microscopically flat. Inside the silver, dislocation structure and planar defects parallel to the interface were observed. Such defects in silver were introduced during cooling from the brazing temperature by thermal expansion mismatch between silicon and silver. It is noteworthy that silver was almost single crystal without any grain boundary. This fact indicates the presence of a certain preferential orientation relationship between silicon and silver.



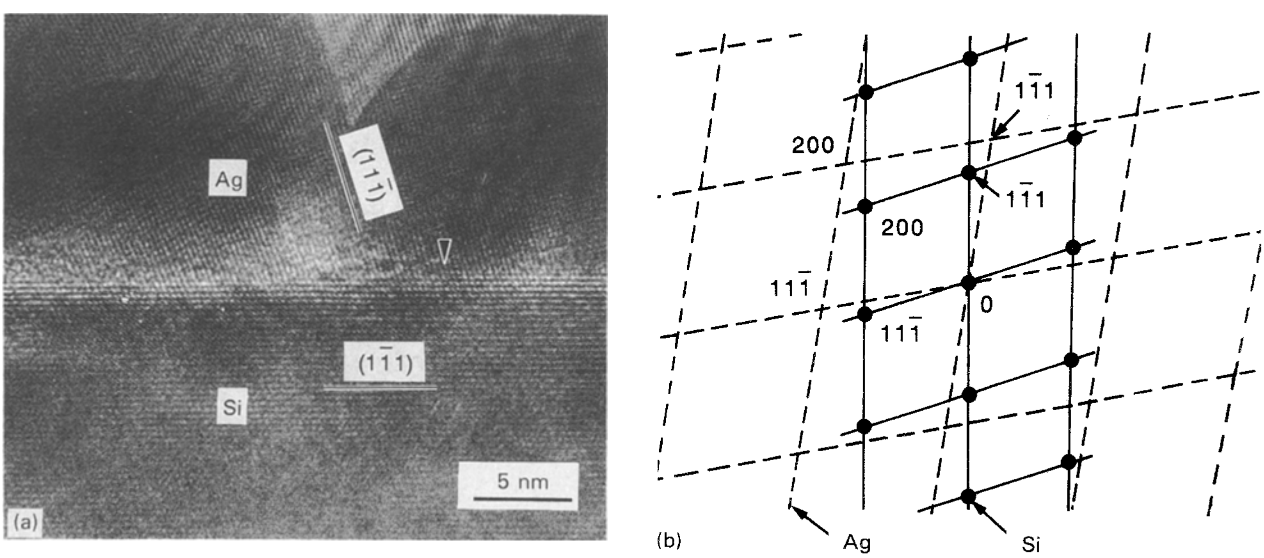


Figure 4 (a) HTREM micrograph of the Ag/Si (1 1 1) interface with (b) its diffraction pattern. The interface is viewed edge-on and the electron beam is parallel to the [1 1 0] axis of silicon. The arrow shows the atomic ledge of the (1 1 1) plane of silicon.

Fig. 4 shows the HRTEM micrograph of the interface with the electron diffraction pattern, in which silicon had a (1 1 1) surface before reaction. Silicon maintained the (1 1 1) surface but the atomic ledge on the Si (1 1 1) surface was observed. From the diffraction pattern, the following approximate orientation relationship is derived.

$$\{1\,1\,1\}_{Ag} \| \{1\,1\,1\}_{Si} \quad [1\,1\,0]_{Ag} \| [1\,1\,0]_{Si} \qquad (1)$$

Both crystals are slightly inclined towards each other from the above orientation. This relationship, was however, frequently observed. Fig. 5 shows the other part of the interface. A similar relationship was recognized.

Fig. 6 shows the interface of the Ag/Si (1 0 0) surface. The interface is inclined against the electron beam. In the present work, from TEM observation, no exact edge-on view of the Ag/Si (1 0 0) was observed. Although, from observation of Fig. 2, this interface will be expected, there seems to be less possibility of the occurrence of the Ag/Si (1 0 0) interface. On a nanometre scale, most of the interface seems to consist of the Ag/Si (1 1 1) interface. This means, possibly, that the Ag/Si (1 0 0) interface is the rare case in this reaction system.

From the diffraction pattern, the same orientation relationship as in Relation 1 was obtained here. Combined with the observation of the morphology of the silicon steps on the silicon substrate after reaction, shown in Fig. 2, this interface is the (1 1 1) face of silicon.

Other types of interface were observed in this system. Fig. 7 shows a transmission electron micrograph of the interface of a crystallized silicon island/matrix in the silver layer. The interface was also flat. In silicon, stacking faults were observed. This defect was on the (1 1 1) plane of silicon (see the diffraction pattern in Fig. 7b). Fig. 8 shows HRTEM of the interface with a diffraction pattern, which is shown by the square region in Fig. 7. Here, the same orientation relationship was obtained, but both crystals are in the

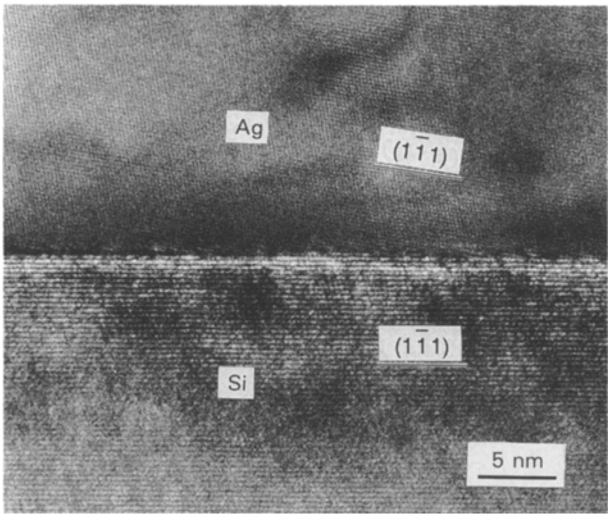
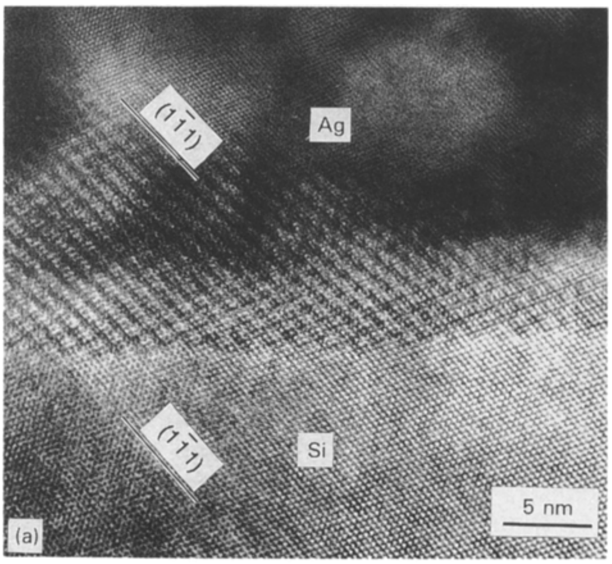


Figure 5 HTREM micrograph of the Ag/Si (1 1 1) interface. Compared with Fig. 4, silver is slightly rotated around the [1 1 0] axis.



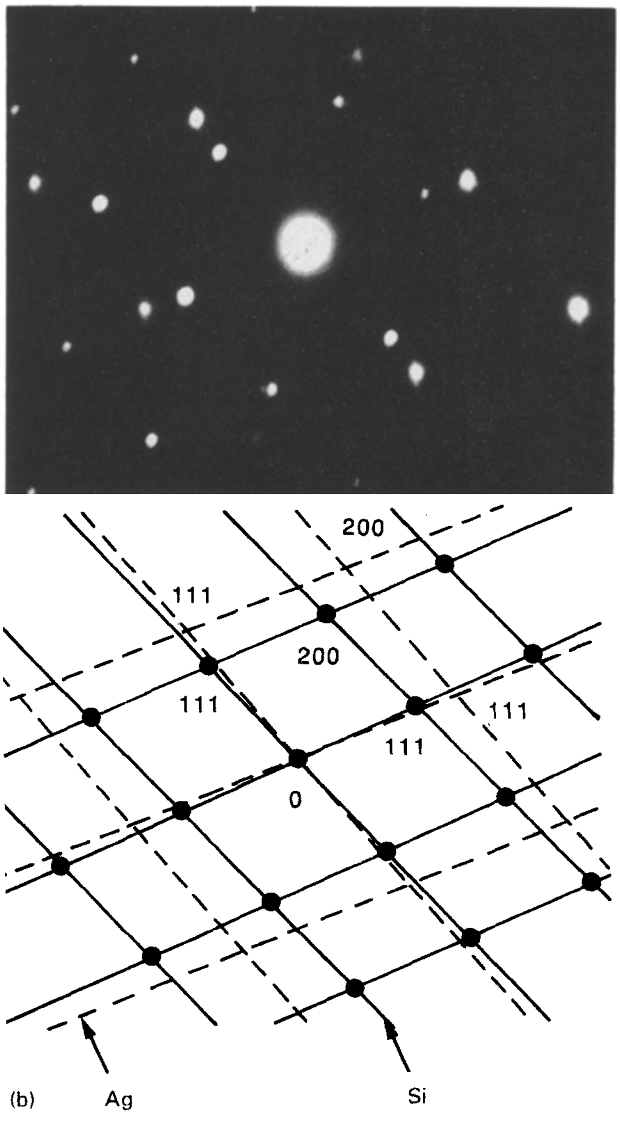


Figure 6 (a) HTREM micrograph of the Ag/Si (1 0 0) interface with (b) its electron diffraction pattern. The electron beam is parallel to the [1 1 0] axis of silicon. The interface is inclined to the beam.

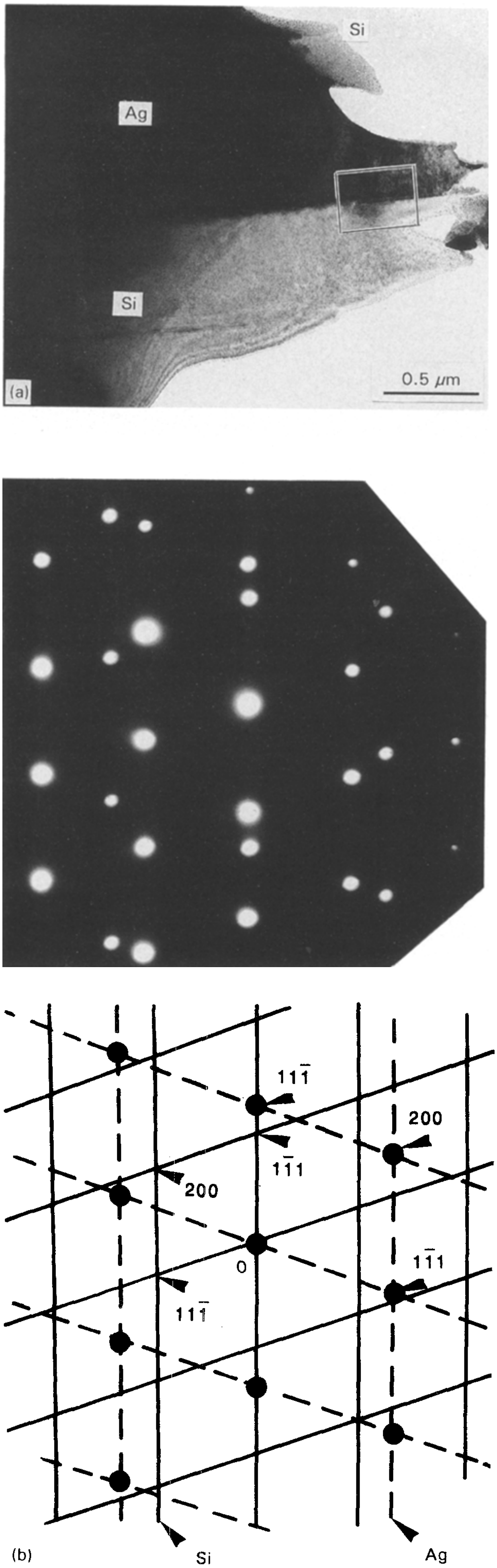


Figure 7 (a) Transmission electron micrograph of a silicon island in the silver layer, with (b) its diffraction pattern.

symmetric arrangement and resemble a twin structure in a monolithic crystal.

Another orientation relationship was obtained in the silicon island/silver matrix interface. Fig. 9 shows a transmission electron micrograph of such an area with its electron diffraction pattern. The interfaces in the photograph are also flat and the (1 1 1) planes of both phases are parallel to each other. From the electron diffraction pattern, however, the following relationship was obtained

$$\{1\,1\,1\}_{Ag}\|\{1\,1\,1\}_{Si}\ [1\,1\,0]_{Ag}\|[2\,1\,1]_{Si} \qquad (2)$$

As seen in the diffraction pattern, this relation is not an exact one. Both crystals are inclined towards each other by a few degrees. Such a relationship was a rare case. Fig. 10 shows the HTREM micrograph of the same area. The interface is formed by the (1 1 1) planes of both crystals and, therefore, this interface is one of the twist boundaries of the $\{1\,1\,1\}_{Ag}|\{1\,1\,1\}_{Si}$ interface.

3.3. Interface atomic matching between silicon and silver

After the eutectic reaction, silicon steps grew on the silicon substrate, maintaining the epitaxial relationship with the substrate. The steps were surrounded by the $\{1\,1\,1\}$ planes of silicon. The original surface and these side planes of silicon formed the unique interfaces with silver expressed by Relation 1. Because silicon has a diamond cubic lattice system, the $\{1\,1\,1\}$ plane becomes the close-packed plane. The atomic layer of the crystallizing silicon grows on the $\{1\,1\,1\}$ close-packed plane layer-by-layer. After the formation of the silicon surface, the silver layer crystallizes on silicon maintaining the epitaxial relationship.

The interface atomic arrangements expressed by Equation 1 can be illustrated by Fig. 11. Because of the very similar symmetry of both crystals on the $\{1\,1\,1\}$ planes, there is close matching, repeated every few atomic layers. The lattice constant of silicon is 0.54307 nm and that of silver is 0.40862 nm. The ratio of the Ag/Si lattice constant is approximately 3/4. This

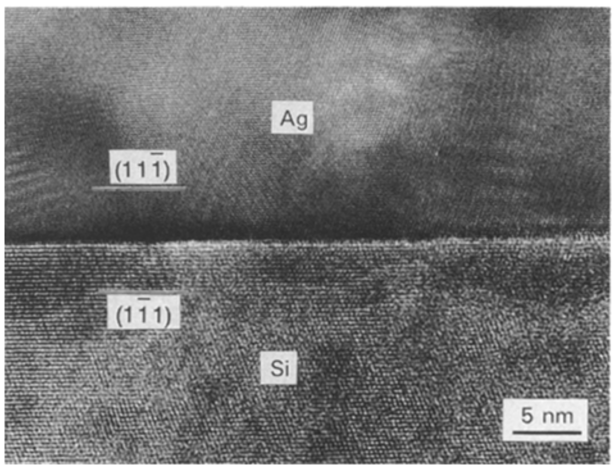


Figure 8 HTREM micrograph of the square region shown in Fig. 7. The electron beam is parallel to the [1 1 0] axis of silicon.

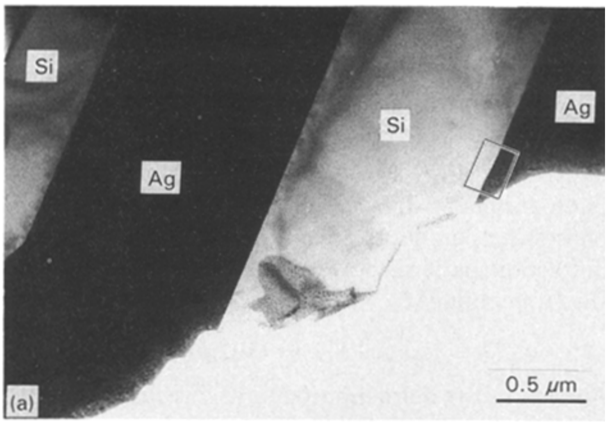
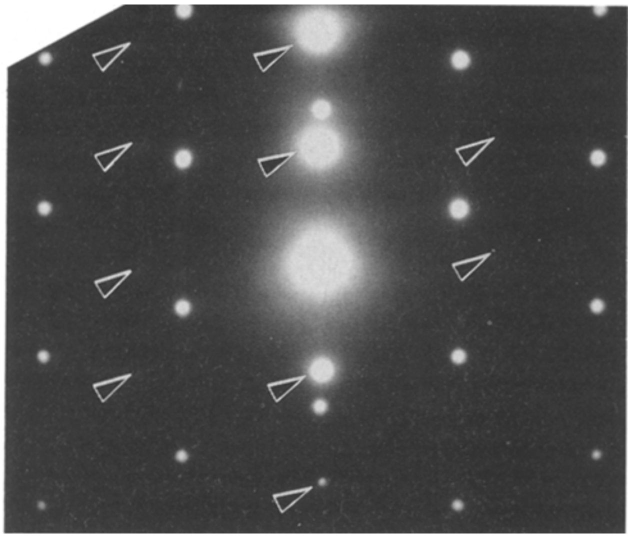


Figure 9 (a) Transmission electron micrograph of silicon islands in the silver layer with (b) its diffraction pattern.



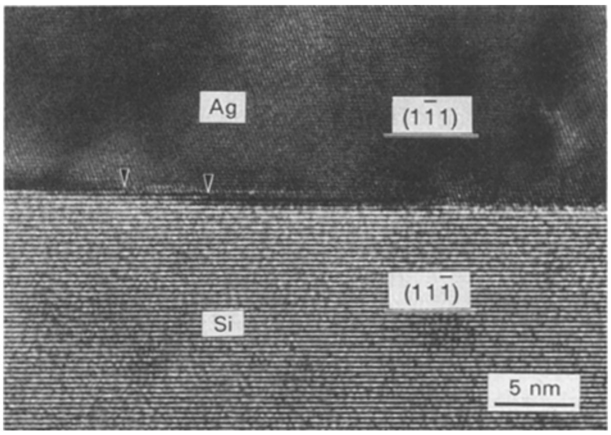
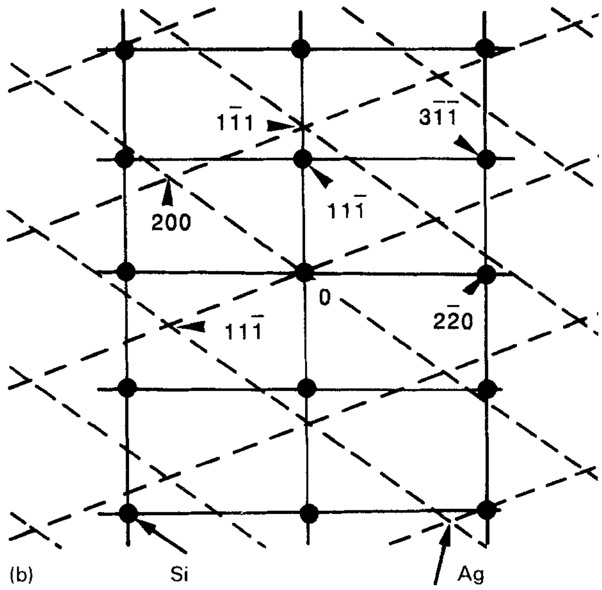


Figure 10 HTREM micrograph of the square region in Fig. 9. Atomic ledges are observed at the points arrowed.



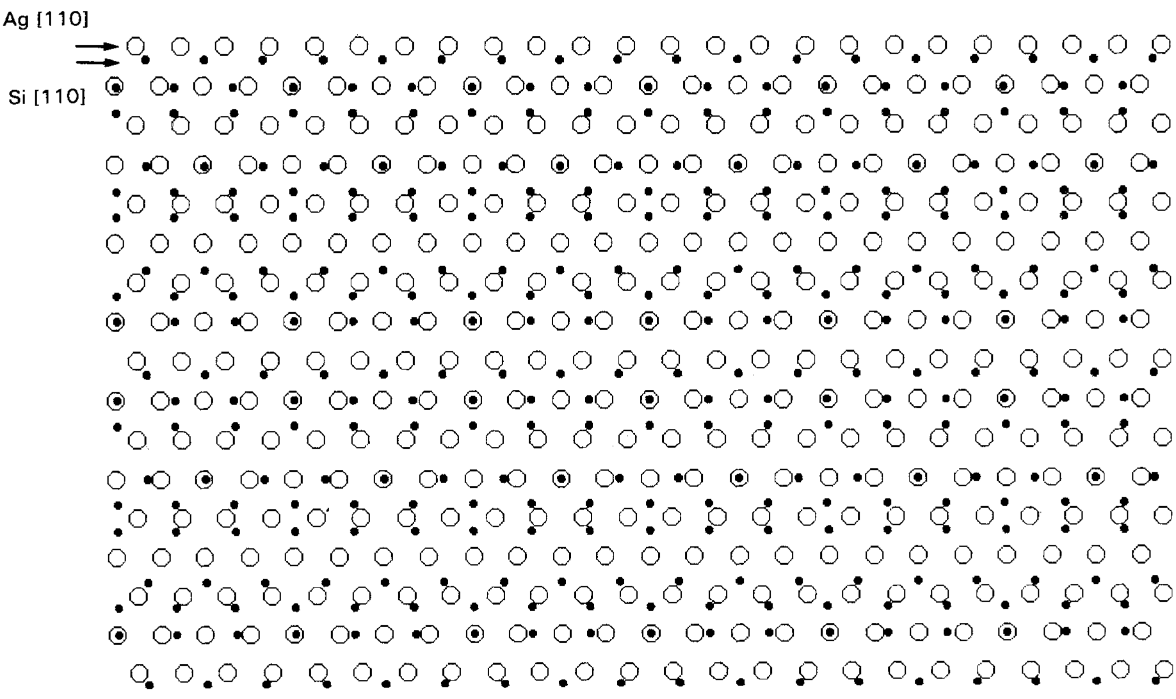


Figure 11 Superposition of the atomic arrangements of the (1 1 1) planes of (○) silver and (●) silicon crystals in the case of the $[1\,1\,0]_{Ag} \| [1\,1\,0]_{Si}$ relationship.

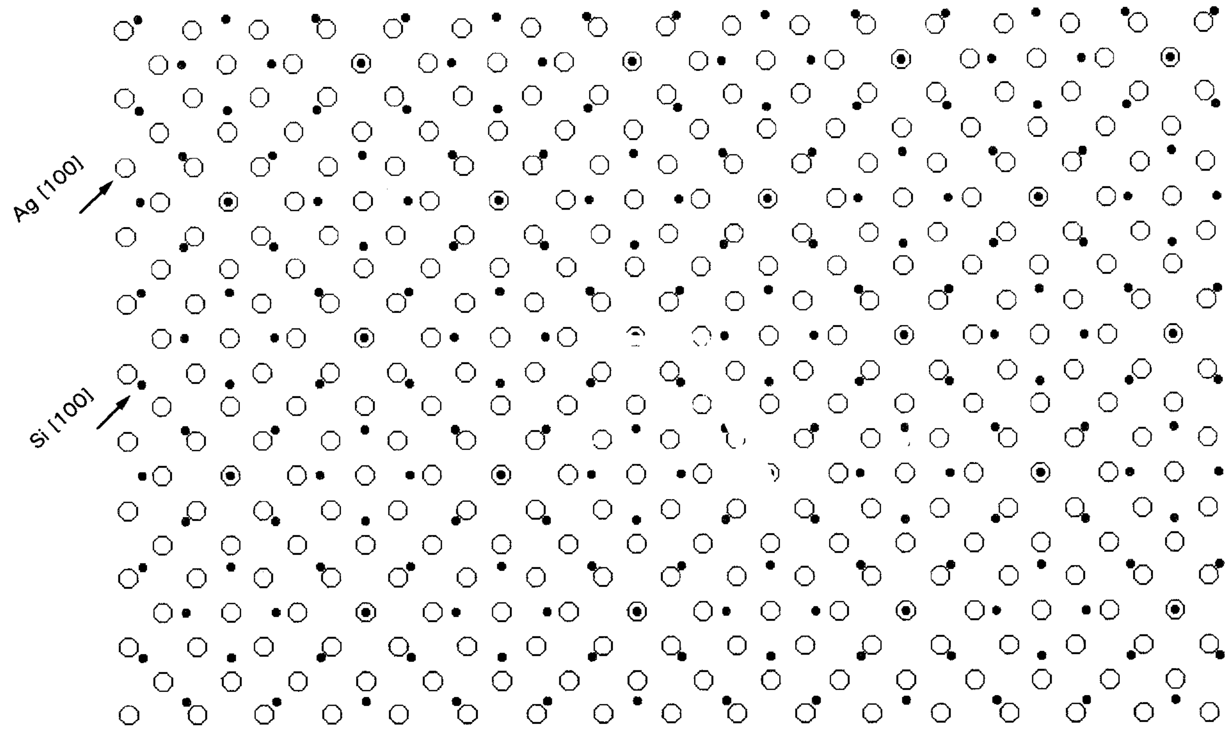


Figure 12 Superposition of the atomic arrangements of the (1 1 1) planes of (○) silver and (●) silicon crystals in the case of the $[1\,1\,0]_{Ag} \| [2\,1\,1]_{Si}$ relationship.

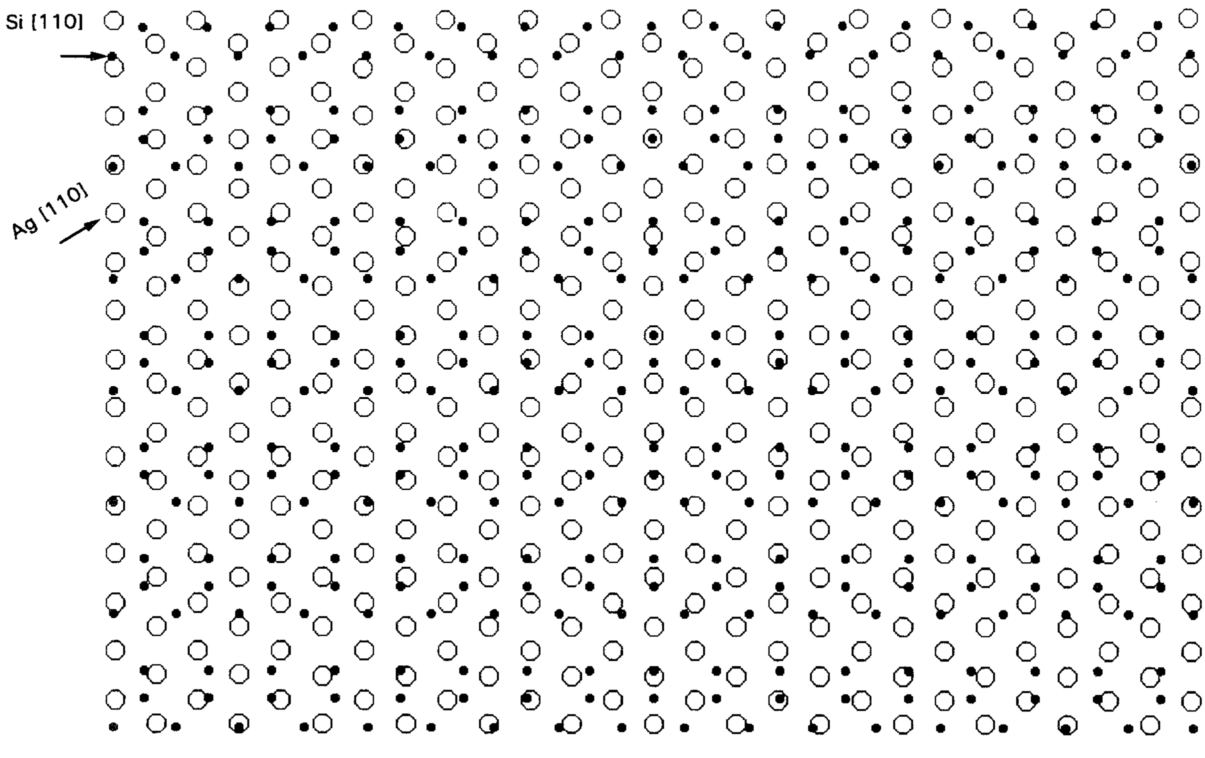


Figure 13 Superposition of the atomic arrangements of the (1 0 0) planes of (○) silver and (●) silicon crystals in the case of the $[1\,0\,0]_{Ag} \| [1\,0\,0]_{Si}$ relationship.

means that every third atom in silicon meets the fourth atom in silver in the ⟨1 1 0⟩ direction in both crystals. The mismatch in this relation is about 0.3%. Such good matching is seen in Fig. 11. In addition, part of the silicon atoms in the octahedral site in a silicon unit cell meet silver atoms.

Relation 2 is illustrated by Fig. 12. The coincidence across the interface is much less than in Fig. 1, which implies the reason why such a crystallographic orientation relationship was less observed. On the contrary, Fig. 13 shows another possibility of good lattice matching which will occur on the low index plane interface, e.g. the $\{1\,0\,0\}_{Ag} \| \{1\,0\,0\}_{Si}$ interface. This relation was not found in the present experiment. Here, again, every third atom of silicon meets every fourth silver atom in the $\langle 1\,0\,0 \rangle$ arrays. Only the density of the matching atoms is less than that of Relation 1.

The lattice matching between silicon and silver across the interface is the best in Relation 1. HTREM observation showed that this relationship is dominant in the Si/Ag interface formed by brazing. Thus, this interface structure is the most stable in the Ag/Si system after the eutectic brazing reaction. This conclusion coincides well with previous observations on the same Ag/Si (1 1 1) interfaces formed by the physical deposition of silver on a silicon substrate at much lower temperatures [5]. Therefore, this crystallographic relationship has one of the lowest energy states for the Ag/Si system in the wide range of temperatures.

4. Conclusion

The present work examined the interface structure between silicon and silver, which is one of the important combinations in various electronics devices, by using high-resolution transmission electron microscopy. After the eutectic reaction at the interface, a unique interface structure was found. The dominant crystallographic orientation relationship obtained was $\{1\,1\,1\}_{Ag} \| \{1\,1\,1\}_{Si}$ and $\{1\,1\,0\}_{Ag} \| \{1\,1\,0\}_{Si}$. The lattice arrangement model of the interface showed that the interface expressed this relation has a good lattice match across the interface.

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