Grain Boundary Structure and Segregation in Direct-Bonded Silicon Bicrystal

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In order to examine the effect of bonding methods on the properties of bonded interface in silicon, bicrystals with $(\bar{1}12)\Sigma 3$ coincidence boundaries were prepared by direct-bonding and hot-press bonding. Boundary structures and segregation in the bicrystals were studied by HRTEM and EDS. Main results are as follows.

(1) A small amount of oxygen segregation and oxide particles were observed along the boundaries in the hot-press bonded bicrystals, whereas neither segregation nor oxide formation were observed in the directly bonded ones.

(2) For the direct-bonded bicrystals, the HRTEM observation revealed two kinds of periodic structures, possibly of periodic dislocation arrays, along the boundary. They were successfully described by the geometric models based on the coincidence and O-lattice theories.

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I. Introduction

A number of direct-bonding techniques to make use of activated joining surfaces have been developed so far. In order to make the surface active, ultrasonic vibration⁽¹⁾, ion-bombardment under a ultra-high vacuum⁽²⁾ and so on have been proposed. Recently, it was found that self-adhering takes place when a pair of clean, mirror-polished silicon surfaces are contacted at room temperature, provided that the surfaces have been activated in an inorganic acid solution⁽³⁾. This direct-bonding technique is very convenient, because no particular apparatus is needed and the surface flatness of commercially available mirror-polished wafers is sufficient to be joined. Hence, the technique has been applied to the semiconductor device⁽⁴⁾. To date, however, no detailed studies on the grain boundary structure and the grain boundary segregation have been done in the direct-bonded silicon bicrystals.

In this study, in order to clarify the boundary properties, bicrystals with the $(\bar{1}12)\Sigma 3$ coincidence boundary were prepared by the direct-bonding and conventional hot-press techniques. The resulting boundaries in both bicrystals were examined by the high-resolution electron microscopy (HRTEM) and the energy dispersive X-ray spectroscopy (EDS).

II. Experimental Procedures

1. Preparation of bicrystals

Single crystal blocks, *ca.* 2 mm × 2 mm × 2 mm, with top and bottom surfaces parallel to (110) were cut out with a low speed diamond wheel from a high purity single crystal (n-type, 6N, P ≤ 0.2 ppm, O ≤ 20 ppm, C ≤ 60 ppm) grown by r.f. floating zone melt technique (supplied by Sumitomo Sitix Co., Kyushu Division). Then, pairs of crystals, whose surfaces were perpendicular to the (110) plane were cut out from the blocks such that the angle made by (001) planes in each pair of crystals was a misorientation angle of ϕ (see Fig. 1). The surfaces to be

Fig. 1 Schematic illustration of Si bicrystal with $\langle 110 \rangle$ tilt boundary of misorientation angle, ϕ .

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joined were polished with #240~#1500 water-proof emery papers and finally buff-finished to the mirror plane with diamond paste of 1 μm in particle size. For polishing, a specially designed jig⁽⁵⁾ was used to ensure the excellent flat planes.

Oriented single crystals to be joined were pickled with 20% hydrofluoric acid to remove the oxide film, and then activated for 300 s in an inorganic acid solution of hydrofluoric acid, nitric acid and water in the volume ratio of 1:4:5. Finally a pair of oriented single crystals were stacked and self-adhered in the inorganic acid solution. They were dried in blowing hot air and then heated at 1570 K for 10.8 ks under a vacuum of 2.7 mPa to achieve the complete bonding. The details of the bonding mechanism can be found in the references⁽³⁾⁽⁴⁾.

Hot-pressed bicrystals were prepared in the following manner. The oriented single crystals prepared in the same manner as described above were cleaned in the 20% hydrofluoric acid, rinsed in acetone, dried and then joined at 1600 K under 20 MPa for 1.8 ks in a vacuum of 2.7 mPa using an electrically controlled hydraulic machine and finally annealed *in-situ* at 1600 K for 7.2 ks without load in order to obtain the grain boundary being in equilibrium.

The resulting bicrystals have $(\bar{1}12)\Sigma 3$ coincidence boundaries with $\phi = 70.5^\circ$ (Fig. 1).

2. TEM observation and EDS measurement

For TEM observation, thin sheets, approximately 500 μm thick and 2 mm in square, were cut out parallel to (110) plane, perpendicular to grain boundary plane, from the bicrystal using a low speed diamond wheel, and mechanically polished to *ca.* 50 μm in thickness, and then buff-polished with diamond paste of 1 μm in particle size. Finally the sheets were Ar^+ -milled into foils; the Ar^+ -milling conditions employed were 4 kV, 0.4 mA and a beam angle of 15° .

The HRTEM observations were carried out with a JEOL JEM-2000EX/T at 200 kV. The many-beam lattice image was formed using a [110] axial illumination. The direct magnification was $\times 600000$ and observations were conducted viewing a television monitor which further magnified 16-fold.

The chemical analyses of grain boundaries and adjacent grain interiors were conducted using a JEOL JEM-2010F equipped with a field emission gun. The EDS measurements were carried out with converged beam of 0.7 nm in diameter in places thin enough for the high resolution observation. The measurements were performed 4 times in each place to confirm the reproducibility.

III. Results and Discussion

1. TEM observation

Figure 2(a) and (b) show TEM images of a boundary prepared by the direct-bonding. Figure 2(a) is an edge-on view of the boundary showing a fairly good interface joined without any pores. Figure 2(b) is a highly oblique

view of the boundary, taken using the weak-beam technique. The image reveals that the boundary appears fairly clean and there exist no impurity inclusions. Furthermore, strain contrasts with a spacing of *ca.* 8.6 nm, indicated by arrows in the figure, are seen on the boundary. The periodic contrasts are believed to arise from a dislocation array.

Figure 2(c) is a weak-beam image of a boundary in the bicrystal prepared by the hot-pressing. It is seen that many inclusions, possibly oxide particles, exist along the boundary and disturb the boundary structure. These inclusions are often observed in the hot-pressed interface⁽⁶⁾.

Figure 3 shows a high-resolution image of the same boundary as shown in Fig. 2 (a) and (b). The high-resolution image reveals that steps are present along the boundary at an almost equi-separation: the mean value is 8.8 ± 0.5 nm, which is very close to that of dislocation spacing shown in Fig. 2(b), and the step height is 0.23 ± 0.5 nm. Since the misorientation angle of this boundary deviates by about $1.5 \pm 0.5^\circ$ from the exact $(\bar{1}12)\Sigma 3$ misorientation, if the DSC (displacement shift complete) dislocations with $b = (a/6)[1\bar{1}2]$, which is perpendicular to the grain boundary plane, are assumed to be introduced to accommodate the small deviation, the predicted dislocation spacing and the step height are 8.5 and 0.22 nm, respectively; these values agree well with the measured ones mentioned above. In addition to the DSC dislocation array, a shorter periodic grain boundary structure of 0.9 ± 0.1 nm are also observed. In view of the O-lattice theory, for $(\bar{1}12)\Sigma 3$ coincidence boundary with the misorientation angle of 70.5° , the transformation matrix relating to the adjacent crystals acquires rank 1 by multiplying a unimodular transformation so that the O-lattice should consist of O-planes. Furthermore, the orientation of the boundary plane is perpendicular to the O-planes. Hence, it is expected that lattice dislocations with $b = (a/2)[1\bar{1}0]$ must be present along the boundary with a spacing of 0.9 nm corresponding with the O-plane spacing: this value agrees well with that of observed periodicity. Therefore, the shorter periodic structure is likely to be due to a lattice dislocation array. The fact that the grain boundary structure can be described by the dislocation models indicates that the grain boundary in equilibrium can be formed by the direct-bonding.

2. Analysis of grain boundary segregation

In order to examine the boundary segregation, the EDS measurements have been carried out using a JEOL JEM-2010F. The apparatus allows to analyze the chemical composition of a small area with a convergent beam of as small as 0.7 nm in diameter. Since the measurements were conducted at such an area that the high-resolution observation was possible, information from an area of as small as about 2 nm in diameter should be obtained even after full accounts were made of the beam scattering.

Figures 4(a) and (b) show the EDS spectra obtained from the boundaries in the direct-bonded bicrystal and in the hot-pressed one, respectively. As shown in Fig. 4, no

Fig. 2 TEM micrographs of the $(\bar{1}12)\Sigma 3$ coincidence boundary obtained by the direct-bonding technique (a) and (b), and by the hot-pressing one (c): (a) bright-field image of edge-on view of the boundary, (b) and (c) weak-beam images of highly oblique view of the boundaries.

definite sign of EDS peaks was recognized except of those of oxygen and silicon. The peak height of oxygen obtained from the hot-pressed bicrystal was about twice

as high as that from the direct-bonded one.

Figure 5 shows O/Si intensity ratios, $I_{\text{O}}/I_{\text{Si}}$, as a function of distance from the boundary. The data scattering

Fig. 3 High-resolution image of the $(\bar{1}12)\Sigma 3$ coincidence boundary obtained by the direct-bonding technique.

was so small that error-bars were well within the data point marks shown in the figure. In the hot-pressed bicrystal, the characteristic intensity ratio of oxygen is clearly dependent on the distance; i.e., the ratio $I_{\text{O}}/I_{\text{Si}}$ shows a peak at the boundary and decreases with increasing distance, whereas the ratio is independent of the dis-

Fig. 4 The EDS spectra (a) and (b) obtained from the boundaries in the direct-bonded bicrystals and in hot-pressed one, respectively.

Fig. 5 The EDS characteristic intensity ratio of oxygen and silicon, $I_{\text{O}}/I_{\text{Si}}$, as a function of distance from the boundary.

tance in the direct-bonded bicrystal. Absolute values of the ratio $I_{\text{O}}/I_{\text{Si}}$ are higher in the hot-pressed bicrystal than in the direct-bonded bicrystal even at a distance as far as 4 nm away from the boundary. This observation implies that in the process of hot-press the specimen surfaces adsorbed oxygen before bonding and that the oxygen diffused into the crystal interior during bonding and annealing processes. It is known that the measured ratio $I_{\text{O}}/I_{\text{Si}}$ decreases with increasing specimen thickness owing to the X-ray absorption of the K-line of oxygen. In this study, however, the effect is negligible because the measurements were performed in the region of almost

the same thickness.

In the direct-bonded bicrystal, the ratio $I_{\text{O}}/I_{\text{Si}}$ was very small and did not vary with the distance, indicating that there is no oxygen segregation at the boundary. The small oxygen peak possibly arises from adsorbed oxygen on the specimen surface, because oxygen content in the bulk is less than 20 ppm which should be beyond the detectable limits.

It is concluded that the silicon direct-bonding is a useful technique to obtain a clean and stable interface without any segregation.

IV. Conclusion

In order to examine the effect of bonding methods on the properties of bonded interface in silicon, bicrystals with $(\bar{1}12)\Sigma 3$ coincidence boundaries were prepared both by direct-bonding and hot-press bonding. The boundary structure studied by TEM and the boundary segregation measured by EDS with the micro beam method were compared in both bicrystals. The main results are as follows.

(1) A fairly good interfaces joined were obtained by direct-bonding.

(2) There was no definite sign of grain boundary segregation in the direct-bonded bicrystal, whereas in the hot-pressed bicrystal some oxygen segregation and oxide formation were observed along the boundary and the segregation was distributed across the boundary though the amount of segregation was small.

(3) Two kinds of periodic dislocation arrays were observed along the boundary in the direct-bonded bicrystal. The structures were found to be described by dislocation models based on the coincidence and O-lattice theories, indicating that fairly stable boundary can be obtained by the direct-bond technique.

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