Oxide precipitation at silicon grain boundaries

E. Schroer, S. Hopfe, P. Werner, and U. Gösele
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle/Saale, Germany
G. Duscher and M. Rühle
Max-Planck-Institut für Metallforschung, 70174 Stuttgart, Germany
T. Y. Tan
Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708-0300

(Received 7 October 1996; accepted for publication 14 November 1996)

Oxygen precipitates at various grain boundaries in crystalline silicon, formed after prolonged high temperature annealing, grow within a narrow size distribution. This narrow size distribution appears to depend on the specific grain boundary. On the basis of this observation a model is derived which is based on the energy balance between grain boundary energy, Si/SiO2 interface energy, and an additional term describing the energy of the ledges of the faceted precipitates. This model predicts an energy minimum for a defined size of the precipitates. © 1997 American Institute of Physics.

During Czochralski (CZ) crystal growth oxygen is incorporated in silicon with a concentration close to its solubility at the melting point. At elevated temperatures the oxygen becomes mobile and forms SiO2 precipitates if present in supersaturation by either homogenous or heterogeneous nucleation. A recent review of Borghesi et al. summarizes the present knowledge on oxygen precipitation in silicon. The growth of precipitates is controlled by the diffusion of oxygen in silicon. Initially all precipitates nucleated will grow until most of the oxygen beyond the solubility value has been incorporated in the precipitates. In a final stage of Ostwald ripening the large precipitates grow at the expense of the smaller ones. The driving force during Ostwald ripening is the reduction of the interface energy. For normal oxygen precipitation a wide range of precipitate sizes is present which changes with time and depends on the oxygen concentration. In this letter we will report that oxygen precipitates at grain boundaries grow under certain conditions to a defined maximal size within a narrow size distribution.

Considering only interfacial energy changes, the energy change during precipitate growth at a grain boundary is given by the reduction of the grain boundary energy and the SiO2/Si interface energy. In the case of small grain boundary energy—compared to the SiO2/Si interface energy—a large precipitate size is energetically favorable. For a higher grain boundary energy—compared to the SiO2/Si interface energy—the energy minimization results in a high density of small precipitates. In this case the formation of a continuous layer is expected. Therefore, an energy minimization considering only areal type interface energy contributions will not allow to describe the formation of a narrow size distribution of the precipitates.

We investigated the growth of SiO2 precipitates at two different grain boundaries. One was a Σ 33 grain boundary of a CZ–grown bicrystal and the other one was fabricated by hydrophobic bonding2,3 of two (001) oriented CZ–grown silicon wafers with an intentional misorientation of 12°. These structures were annealed under several conditions.

Subsequently, the SiO2 precipitates formed at the grain boundaries were investigated with conventional and high resolution transmission electron microscopy (CTEM, HRTEM).

A narrow size distribution of the SiO2 precipitates at the grain boundary for both grain boundaries was found. Even after a prolonged annealing of 5 days at 1100°C, only the precipitate density has increased but not the precipitate size. CTEM and HRTEM micrographs of typical SiO2 precipitates with the typical size at the two types of investigated grain boundaries are shown in Fig. 1. Analogous to the case of bulk precipitates, the precipitates at the grain boundaries are faceted. The interfaces of the SiO2 precipitates and the silicon matrix are found to be parallel to the {111} planes of silicon. This is consistent with the proposal of Jaccodine who argued that the lowest surface energy of silicon is in (111) orientation because the lowest bond density is in this orientation.

An octahedron shaped precipitate structure was observed at the bonded grain boundary. The precipitates at the Σ 33 grain boundary consist of two tilted pyramids. In Fig. 2 a histogram of the precipitate width w is shown for the two investigated grain boundaries. From this figure we estimate a mean precipitate base width of w b = 15.3 nm with a standard deviation of ± 3 nm at the 12° tilt grain boundary and w b = 11.3 nm (± 1.3 nm) is the width perpendicular to the (011) orientation along the Σ 33 grain boundary.

We will show that taking into account a contribution from a ledge energy beside the usual SiO2/Si interface and grain boundary energies leads to a minimum energy associated with precipitates of a certain size. Recently a similar concept has been applied by Shchukin et al.5 to explain the narrow size distribution of InAs islands on GaAs surfaces during molecular beam epitaxial growth of quantum dots. For simplicity we will evaluate the energy specifically for the geometrically simple case of the rotationally twisted grain boundary which involves octahedrally shaped precipitates.

The interfaces between the octahedron like structure of the precipitate at the bonded grain boundary consists of (111) planes on the silicon side. The base of the octahedron is

*Electronic mail: erwin@mpi-msp-halle.mpg.de

Downloaded 03-Nov-2004 to 195.37.184.165 Redistribution subject to AIP license or copyright. See http://apl.aip.org/apl/copyright.jsp
located in the plane of the silicon grain boundary. The octahedron has a base width $w$. The interface energy of an octahedron shaped precipitate is given by

$$E_{int} = 2\sqrt{3}\sigma_{(111)}w^2 = \sigma_I w^2,$$

(1)

where $\sigma_{(111)}$ is the interface energy per unit area in the (111) orientation, and $\sigma_I = 3\sqrt{2}\sigma_{(111)}$ is a combination of interface energy and geometrical factors. Furthermore a ledge energy of the SiO$_2$ precipitates is given by

$$E_{ledge} = 4(\gamma_{base} + 2\gamma_{bt})w = \gamma_I w,$$

(2)

where $\gamma_{base}$ is the energy per unit length of the ledges at the base, $\gamma_{bt}$ that of the ledges from the base to the top of the octahedron, and $\gamma_I = 4(\gamma_{base} + 2\gamma_{bt})$ is an abbreviation for an averaged ledge energy per unit length including additional geometrical factors.

The total energy per unit area of the grain boundary is then given by

$$\sigma_{total} = n(\sigma_I w^2 + \gamma_I w) + (1 - n w^2)\sigma_{Si/Si},$$

(3)

where $n$ is the number of the precipitates per unit area and $\sigma_{Si/Si}$ is the grain boundary energy per unit area. For a given volume of precipitated oxygen per unit area $\sigma_{total}$ shows a minimum with respect to $w$ for

$$w_B = \frac{2\gamma_I}{(\sigma_{Si/Si} - \sigma_I)}.$$

(4)

With a precipitated volume $v = \sqrt{2/3n}w_B^3$ per unit area this corresponds to an areal density of precipitates of

$$n = \left(\frac{2(\sigma_{Si/Si} - \sigma_I)}{\gamma_I}\right)^3 \left(\frac{3v}{\sqrt{2}}\right).$$

(5)

From these two expressions one can conclude that there is a certain maximal size $w_B$ of the octahedron shaped precipitates which is only dependent on material parameters and the geometry of the grain boundary. The density $n$ of the precipitates at the grain boundary changes linearly with the volume $v$ of precipitated oxygen at the grain boundary.

Rewriting the total energy expression of Eq. (3) in a reduced form one obtains

$$\frac{\sqrt{2}}{3v} \frac{\sigma_{total} - \sigma_{Si/Si}}{\gamma_I} = w^{-2} - \frac{\sigma_{Si/Si} - \sigma_I}{\gamma_I} w^{-1}.$$

(6)
The dependence of the reduced energy on the precipitate base length $w$ is shown in Fig. 3 for various parameters

$$a = (\sigma_{\text{Si/Si}} - \sigma_{\text{f}}) / \gamma_f.$$  (7)

In experiments with bonded wafers it is possible to change the parameter $a$ by varying the interface energy $\sigma_{\text{Si/Si}}$ of the grain boundary by changing the twist angle $\theta$. The grain boundary energy $\sigma_{\text{Si/Si}}$ per unit area of a twist boundary with a rotational angle $\theta$ containing only screw dislocations is given by

$$\sigma_{\text{Si/Si}}(\theta) = \frac{\mu b}{4\pi} \ln \left( \frac{2}{\theta} \right).$$  (8)

where $\mu$ is the shear modulus and $b$ is the length of the Burgers vector. For silicon the shear modulus is given by $\mu_{\text{Si}} = 0.7 \times 10^{11}$ N/m$^2$ and $b = 0.384$ nm. For $\theta = 12^\circ$ the surface energy is $\sigma_{\text{Si/Si}}(12^\circ) = 6.3$ eV/nm$^2$. For the $\Sigma 33$ grain boundary the interface energy has been calculated by Möller and Kohyama et al. to be about $6.3$ eV/nm$^2$.

Let us now consider the range of values which the parameter $a$ can adopt.

(i) The lowest value is $a = -\sigma_{\text{f}} / \gamma_f$. This is the case of $\sigma_{\text{Si/Si}} = 0$ and corresponds to precipitate growth in silicon bulk material. In this case there is a critical size $w_c$ separating the stable from the unstable precipitates. The final stage of precipitation follows Ostwald ripening.

(ii) In the case of $-\sigma_{\text{f}} / \gamma_f < a < 0$ the effective interface energy of the precipitates at the grain boundary is given by $\sigma_{\text{f}} - \sigma_{\text{Si/Si}}$. In this case the critical nucleus size $w_c$ at the grain boundary is reduced compared to the critical size of a precipitate nucleated in the silicon. Therefore, an enhanced precipitation rate at the grain boundary compared to the rate in bulk silicon is expected. In this regime of $a$ the final stage of precipitation is still dominated by Ostwald ripening since an energy reduction is obtained by increasing the precipitate size.

(iii) In the case of $a = 0$ there is no change in interface energy during the precipitate growth, because $\sigma_{\text{f}} = \sigma_{\text{Si/Si}}$.

This value of $a$ marks the transition between Ostwald ripening and the existence of a maximum precipitate size with a narrow size distribution.

(iv) $a > 0$ marks the regime in which the precipitate size $w$ attains a certain size $w_h$ which is given by Eq. (4). An increased precipitate density $n$ which is given by Eq. (5) accounts for an increased overall volume $V$ of precipitated oxygen during the course of precipitation.

From our experimental results in the case of a bonded twist grain boundary the parameter $a$ can be determined from Eq. (4) as $a = 0.13$ nm$^{-1}$. For an estimated grain boundary energy $\sigma_{\text{Si/Si}}(2^\circ) = 6.3$ eV/nm$^2$ of the bonded wafers one can estimate the maximum interface energy $\sigma_{\text{111}}$ to be less than $1.8$ eV/nm$^2$ from the experimental verified fact that $a > 0$ holds for this grain boundary. This value of $\sigma_{\text{111}}$ is consistent with previously reported values of the SiO$_2$/Si interface energy between $0.56$ eV/nm$^2$ and $3.12$ eV/nm$^2$.

Let us finally compare the generation of precipitates at a silicon grain boundary with the transformation of an initially continuous thin buried oxide layer separating two silicon crystals. Ahn et al. demonstrated that a continuous oxide layer is transformed to oxide precipitates if the adjacent silicon crystals are rotated by an angle of less than approximately $\theta = 3^\circ$. Otherwise the oxide layer did not change its topology. From this result Ahn et al. concluded that in the case of a rotational angle larger than $\theta = 3^\circ$ the interface energy between the oxide and the silicon crystals is less than the interface energy between the two silicon crystals. However, as we have shown in the present letter, during the diffusion of oxygen to a silicon grain boundary precipitates are formed rather than a continuous oxide layer even if the rotational angle is considerably larger than $\theta = 3^\circ$. This difference between the behavior of a pre-existing layer and the topology formed by precipitation can be explained by the existence of an energy barrier which prevents the transition from the higher to the lower energy configuration.

One of us (T.Y.T.) acknowledges support by the Alexander von Humboldt Foundation via a U.S. Senior Scientist Award.