

Vacancy formation during oxidation of silicon crystal surface

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To study the formation of interstitials and vacancies during oxidation of silicon crystals, we applied a quenching method, namely, oxidation at high temperatures in mixed gases of water vapor and H₂ followed by the quenching into water. Contrary to our expectation, the vacancy concentration was higher than that of the thermal equilibrium during the short duration of oxidation. © 2008 American Institute of Physics. [DOI: 10.1063/1.2979708]

From our point of view, one of the greatest problems in the study of lattice defects in silicon crystals is to experimental determination of the formation energy of a vacancy (*V*) and an interstitial (*I*). They have been studied since the 1950s with unsuccessful results, and the agglomerations of these point defects, which deteriorate device performance, have been found as voids and dislocations, respectively, in as-grown crystals. As for the vacancy formation energy, we applied a quenching method, namely, heating specimens in H₂ gas followed by quenching into water and subsequent annealing of specimens at 450 °C.¹ As a result of the last procedure, quenched-in vacancies form VH₄, a cluster of one vacancy and four hydrogen atoms. We determined the optical absorption intensity of VH₄, instead of the *V* concentration, after quenching from various temperatures. With the use of this method, we determined the vacancy formation energy in a high-purity silicon crystal to be 4.0 eV,¹ which is in good agreement with the result of the first principle calculation.² Moreover, we found that it strongly depends on the species of dopants,³ which has not yet been theoretically explained.

The next problem is to determine the interstitial formation energy, for which we applied the above quenching method in this experiment. We first studied specimens under oxidation since it is usually said that interstitials are formed during oxidation.⁴ Hence, we expected a high concentration of interstitials and a low concentration of vacancies in those specimens. Contrary to our expectation, we found the vacancy concentration to be high in those specimens as shown below.

Specimens were prepared from a floating-zone grown *p*-type Si crystal (the electrical resistivity was about 1500 Ωcm at room temperature). After mechanical shaping and chemical etching, specimens were sealed in quartz capsules together with a drop of water and hydrogen gas. The specimen size was about 6 × 6 × 11 mm³. Stress-induced interstitial formation is favored due to oxidation of this specimen since the dilatational strain field is induced by SiO₂ in the surface regions of the specimen. They were then heated at high temperatures for various periods and were quenched into water. The color of the specimen surface was blue, clearly indicating the oxidation of the surface. Mixed hydrogen gas does not have any effect to generate point defects since the reaction between Si and H₂O, i.e., Si + 2H₂O → SiO₂ + 2H₂, is faster than that between Si and H₂. The role

of hydrogen is to form complexes with vacancies and interstitials during quenching and to prevent the decrease in thermal equilibrium vacancies and interstitials at the quenching temperature during quenching. Without hydrogen, concentrations of thermal equilibrium vacancies and interstitials are thought to decrease by mutual annihilation (*V* + *I* → Si atoms at regular lattice sites) and/or the formations of clusters of vacancies and interstitials, which are difficult to detect. To form IH₂,⁵ a complex of one interstitial and two hydrogen atoms, we annealed specimens at 300 °C for various periods after quenching. We did not detect the 1987 cm⁻¹ peak which is due to IH₂. So instead, we attempted to detect vacancies. After annealing at 450 °C for 1 h, we measured optical absorption due to VH₄ at about 7 K with a resolution of 0.25 cm⁻¹. The VH₄ peak position is at the wavenumber of 2223 cm⁻¹,⁵ and the vacancy concentration is proportional to the 2223 cm⁻¹ peak intensity.

Figure 1 shows the relation between the 2223 cm⁻¹ peak intensity and the oxidation time at various temperatures. The diffusion rate of vacancies is so fast at temperatures used in this experiment that the distribution of vacancies is thought to be homogeneous except 10 min annealing.⁶ Generally, the peak intensity, and hence the vacancy concentration, increases with the oxidation time for short periods and then slightly decreases. The vacancy concentration is higher as the oxidation temperature becomes higher. Comparing the three curves, it is noticed that the peak intensity is almost constant from the oxidation time of 10–100 min in the case of oxidation at 1325 °C. This suggests that the vacancy formation is very fast at this temperature. At the other two ox-

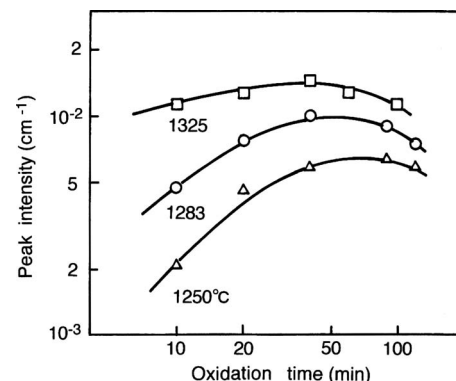


FIG. 1. Dependence of VH₄ peak intensity on oxidation time. The numbers are the oxidation temperature.

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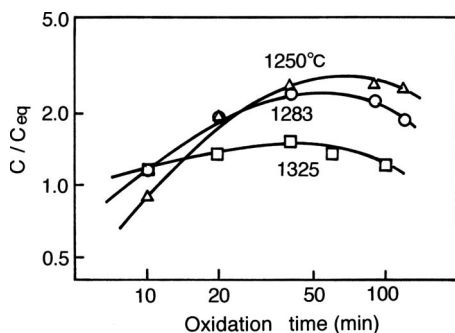


FIG. 2. Dependence of the degree of supersaturation of vacancies on the oxidation time. The numbers are the oxidation temperature.

dation temperatures, however, the vacancy formation seems to occur gradually with the oxidation time for short periods. For the long oxidation time, the vacancy concentration reaches at the maximum and then slightly decreases. To understand this behavior, it should be remembered that, as described above, a drop of water was encapsulated together with a specimen. Therefore, there are two possible reasons for the decrease for long oxidation time, namely, nature itself or a shortage of water. To examine these possibilities, we plan to study the formation of vacancies during continuous supply of water vapor.

Figure 2 shows the relation between the degree of supersaturation of the vacancy and the oxidation time. The degree of supersaturation is defined as the ratio of peak intensity under oxidation to that of thermal equilibrium without oxidation. The latter was determined in a high-purity Si crystal.¹ Figure 2 clearly shows that the degree of supersaturation is greater at lower oxidation temperature for long oxidation time. This indicates that the apparent formation energy of vacancies during oxidation is smaller than that without oxidation. Even after 100 min oxidation, the vacancy concentration does not reach a constant value at each temperature.

Because our results were contrary to the generally accepted idea that only interstitials are formed by oxidation of Si crystals, we studied the literature to better understand the oxidation-induced point defects. We found several papers⁷⁻⁹ which showed vacancy formation to be due to oxidation of Si crystals: Hu,⁷ and Francis and Dobson⁸ found shrinkage of a stacking fault due to oxidation at above critical temperature and interpreted it to be due to vacancy formation associated with oxidation. Francis and Dobson,⁸ and Tan and Gösele⁹ proposed that the formation mechanism of vacancies as well as that of interstitials depends on the oxidation temperature and/or the thickness of the oxide layer. According to them, the oxidation process at high temperatures and/or at thick oxide layers is different from that at moderate temperatures and/or at thin oxide layers. The difference is due to the relative diffusion rates of O₂ and Si (SiO in case of Tan and Gösele) in the SiO₂ film. At temperatures higher than the critical temperature of about 1200 °C, which depends on the oxidation conditions and the surface orientation, Si atoms near the Si/SiO₂ interface diffuse into the SiO₂ film and form SiO₂ particles in the SiO₂ film with O₂ which counter-diffuse into the SiO₂ film from the surface. Simultaneously, vacancies diffuse into Si crystals from the interface and the vacancy concentration in Si crystals becomes higher than that of thermal equilibrium. If their proposal is correct, our temperatures correspond to their high temperature region and

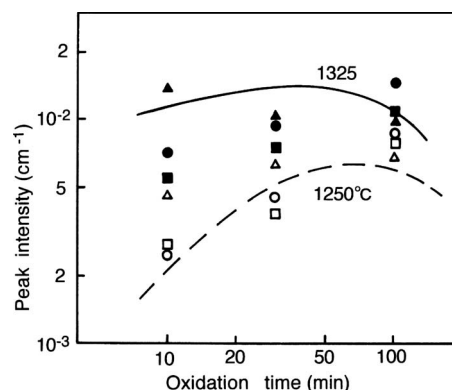


FIG. 3. Dependence of VH₄ peak intensity on the oxidation time. Solid and dashed lines cited from Fig. 1 correspond to the oxidation temperatures of 1325 and 1250 °C, respectively. The triangles, squares, and circles correspond to the preoxidized film thicknesses of 0.6, 1.1, and 1.6 μm, respectively. Solid and open symbols show the results of 1325 and 1250 °C oxidation, respectively.

hence the degree of supersaturation is higher than 1.

To check the dependence of vacancy concentration on the thickness of the oxide film in the above proposal, we studied the vacancy formation due to oxidation of preoxidized Si crystals. The preoxidation was performed with the use of wet oxygen. Hence, vacancies formed during preoxidation were annihilated during cooling after preoxidation since we did not supply H₂ gas. Figure 3 shows the results. In this experiment, preoxidation films were grown with the thicknesses of 0.6, 1.1, and 1.6 μm, respectively, indicated by triangles, squares, and circles in Fig. 3. (Specimens with the thicknesses of 0.6, 1.1, and 1.6 μm are abbreviated as th(0.6), th(1.1), and th(1.6), respectively, hereafter.) Solid and dashed lines are the results shown in Fig. 1. Open and solid symbols are the results of specimens oxidized at 1250 and 1325 °C, respectively. The data of Fig. 3 seem to show large scatter. This tendency, however, is rather systematic. First, we describe the behavior of the vacancy concentration at the oxidation temperature of 1250 °C. At an oxidation time of 10 min, the vacancy concentration decreases as the oxide film becomes thicker. This dependence is opposite that expected from the above proposal. At 30 min, the vacancy concentration in th(1.6) becomes higher than that of th(1.1). At 100 min, the vacancy concentration is larger for the specimen of thicker oxide film and the difference of the vacancy concentration between the pre-existent oxide films becomes small. At 1325 °C, the transition of the relation between the vacancy concentration and the film thickness at 1250 °C occurs at shorter oxidation time, namely, the vacancy concentration in the th(1.1) is smaller than that of th(1.6) after 10 min oxidation. Regarding Fig. 3, in summary, the magnitude of vacancy concentration does not always coincide with the thickness of oxide film at both temperatures. Moreover, the dependence of vacancy concentration on the thickness of the pre-existent film is greater for shorter oxidation time. Hence, we should introduce other factors besides relative diffusion rates of O₂ and Si (or SiO) to explain our results. This is a future task.

In conclusion, with the use of a method, namely, oxidation and quenching in a mixed atmosphere of water vapor and hydrogen gas, we detected a supersaturated vacancy in oxidized Si crystals.

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