[3]Brad Mattson, Solid State Technol. 60 (January 1980).
[4](a) T. W. Hickmott, Appl. Phys. Lett. 15, 232 (1969). (b) J. L. Vossen, J. J. O'Niell, Jr., G. W. Hughes, F. A. Taft, and R. Snedeker, J. Vac. Sci. Technol. 17, 400 (1980).
[5]P. S. Burggraaf, Semiconductor International, March 1980, p. 26.
[6]Hughes Aircraft Co., Interim Report No. FR81-76-538, Nov. 1980.
[7]H. M. Kim, S. S. Tai, S. L. Groves, and K. L. Schuegraf, in Proceedings of the Eighth Conference on Chemical Vapor Deposition, Electrochemical Society Proceedings, Vol. 81-7 (1981), p. 258.
[8]J. W. Peters, in Technical Digest of the International Electron Devices Meeting 1981, p. 240.
[9]J. H. Clark and R. G. Anderson, Appl. Phys. Lett. 32, 47 (1978).
[10]R. W. Andreatta, C. C. Abele, J. F. Osmundsen, and J. G. Eden, Appl. Phys. Lett. 40, 183 (1982).
[11]N. R. Greiner, J. Chem. Phys. 47, 4373 (1967).
[12]M. Zelikoff and L. M. Aschenbrand, J. Chem. Phys. 22, 1680 (1954).
[13]H. S. Johnston and R. Graham, Can. J. Chem. 52, 1680 (1974).
[14]J. Zavelovich, M. Rothschild, W. Gornik, and C. K. Rhodes, J. Chem. Phys. 74, 6787 (1981).
[15]J. Wong, J. Electron. Mater. 5, 113 (1975).

Effect of oxide precipitates on minority-carrier lifetime in Czochralski-grown silicon

Masami Miyagi

Ibaraki Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai, Ibaraki 319-11, Japan

Kazumi Wada and Jiro Osaka

Musashino Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Musashino-shi, Tokyo 180, Japan

Naohisa Inoue

Research and Development Bureau, Nippon Telegraph and Telephone Public Corporation, Musashino-shi, Tokyo 180, Japan

The effect of oxide precipitate in Czochralski-grown silicon crystals on minority-carrier lifetime was investigated. The oxide precipitates generated by heterogeneous nucleation in as-grown crystals were found to decrease the lifetime. On the other hand. the oxide precipitates generated by homogeneous nucleation decreased the lifetime when their length was greater than 100 Å. The minority-carrier lifetime was nearly proportional to the reciprocal of the oxide precipitate length.

PACS numbers: 72.20.Jv,81.40.Rs,61.70.Rj

About 10^{18} at./cm^3 of oxygen atoms are contained in Czochralski-grown (CZ) silicon crystals. These oxygen atoms precipitate when cooled during crystal growth or annealed after crystal growth. These oxide precipitates act as nuclei of secondary defects, such as stacking faults or dislocation loops, which are generated during the device fabrication.[1] It is well known that stacking faults and dislocation loops degrade the device characteristics, but there are few reports on the effect of oxide precipitates on electrical properties.[2] Because most of electrical methods for defect characterization [such as capacitance-voltage (C-V) method, capacitance-time (C-t) method, etc.] need device fabrication, it is impossible to avoid the generation of secondary defects. Therefore, it is difficult to characterize only oxide precipitates by these methods.

Using noncontact photoconductive decay method, minority-carrier lifetime can be measured without device fabrication.[3] Therefore, the electrical property of oxide precipitates can be investigated by this method without any effects of secondary defects. In the present work, effects of oxide precipitates, which are in as-grown crystal or generated by relatively low-temperature annealing, on minority-carrier lifetime are clarified by noncontact photoconductive decay method.

Two kinds of oxide precipitates are contained in as-grown CZ silicon crystal. One of them is about 10 Å in size and is generated by homogeneous nucleation in the process of cooling during crystal growth. This is referred to as "as-grown microprecipitate." Their density is estimated to be 10^8–10^{11}/cm^3, which increases with increasing oxygen concentration in the crystal. Another one is about 1000 Å in size and is generated by heterogeneous nucleation resulting from some fluctuations during crystal growth. This is referred to as "as-grown large precipitate." Their density is estimated to be 10^3–10^6/cm^3.

Homogeneous nucleation of oxide precipitates is generated not only by cooling during crystal growth but also by annealing. Oxide precipitates, whose sizes are greater than the critical radius at an annealing temperature, grow by annealing. Annealing temperature dependence of nucleation rate and annealing time dependence of oxide precipitate size were previously reported.[4,5] Their results which are related

to the discussion in this work are as follows. Nucleation rate of oxide precipitates has a maximum value at about 700 °C. Oxide precipitate size is proportional to 3/4 power of annealing time and increases with increasing annealing temperature.

An as-grown, dislocation-free, boron-doped CZ silicon crystal 8 cm in diameter and 22 cm long grown in the ⟨100⟩ direction was used in this experiment. Interstitial oxygen concentration and carbon concentration of the crystal were $8-12 \times 10^{17}$ at./cm^3 and less than 2×10^{16} at./cm^3, respectively. In the crystals with such oxygen and carbon concentrations, the oxide precipitate density had been reported to depend only on the oxygen one.[6] Resistivity of the crystal was 8 Ω cm. Specimens were sliced and polished on both sides to 1 mm thick. Some of them, whose interstitial oxygen concentration was 8.2×10^{17} at./cm^3, were annealed at 750 °C or 850 °C in Ar atmosphere. Annealing time was 0.5–25 h at 750 °C and 0.5–50 h at 850 °C. The minority-carrier lifetime of as-grown specimens and annealed specimens was measured by a noncontact photoconductive decay method. Specimens for lifetime measurement were coated with sodium dicromate to reduce the surface recombination. Then, the specimens were etched in Wright solution several tens of microns to obtain the oxide precipitate volume density after removing the surface layer about 100μ in order to get rid of the denuded zone for annealed specimens. With this treatment, oxide precipitates could be observed as hillocks by optical microscope.

Figure 1 shows the lifetime and the hillock density distribution along the crystal axis in the as-grown crystal. Near the crystal shoulder, the lifetime decreased with increasing hillock density. Hillocks in as-grown crystal represent the as-grown large precipitates. Figure 1 indicates that the lifetime in as-grown crystal is dependent on the density of as-grown large precipitates. Although the density of as-grown microprecipitates was considered to be larger than that of as-grown large precipitates,[7] as-grown microprecipitates did not affect the lifetime. It is because the size of as-grown microprecipitates is too small, as is discussed later.

In Fig. 2, the lifetime and the hillock density are plotted against the 850 °C annealing time. For the purpose of discussion, the hillock density curve was divided into three regions.
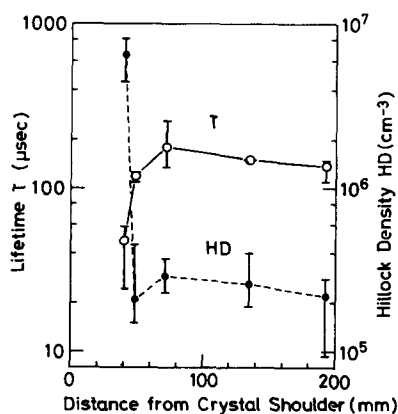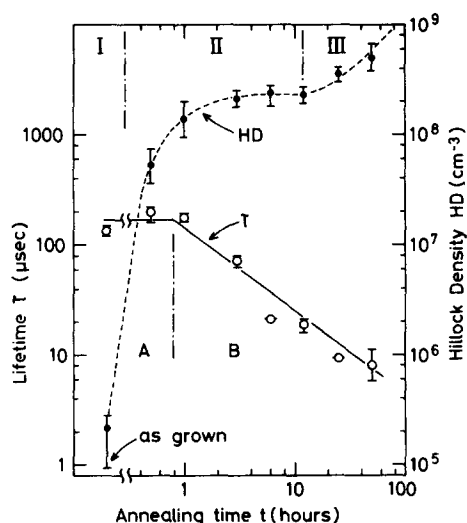

FIG. 2. Lifetime and hillock density as a function of annealing time at 850 °C.

In region I, that is, in as-grown crystal, only as-grown large precipitates were observed. In region II, as-grown microprecipitates whose sizes were greater than the critical radius at 850 °C grew up gradually to be observed as hillocks, and then, in the 3–12-h annealing region hillock density saturated. It indicates that only the size of the oxide precipitates changed while their density did not in this region. In region III, oxide precipitates nucleated by the annealing grew up and were observed as hillocks. On the other hand, the lifetime curve was divided into two regions. The lifetime was constant in the region from as-grown to 1-h annealing (region A), and decreased with increasing annealing time in the region greater than 1-h annealing (region B).

In Fig. 3, the lifetime is plotted against the 750 °C annealing time. The oxide precipitate density of the samples annealed at 750 °C could not be measured by etching technique because the oxide precipitate density was too high. The dotted line shows the oxide precipitate density estimated by using the nucleation rate of 8×10^5/cm^3 s, which was previously reported.[4] The lifetime was constant in the region from as-grown to 8-h annealing (region A ') and decreased with increaing annealing time in the region greater than 8-h annealing (region B '). The decreasing rate of lifetime in re-

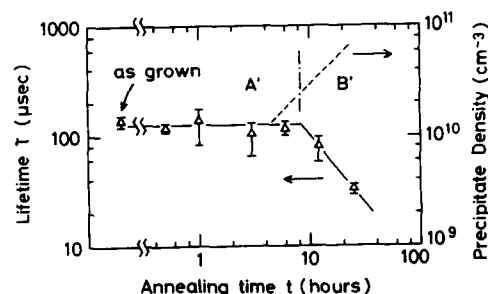FIG. 1. Lifetime and hillock density distribution along the crystal axis in the as-grown crystal.

FIG. 3. Lifetime and oxide precipitate density as a function of annealing time at 750 °C. Dotted line shows the oxide precipitate density estimated by using the nucleation rate of 8×10^5/cm^3 s (see text).
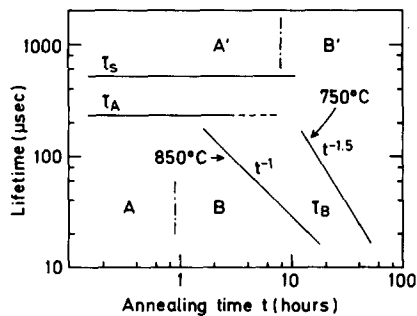
FIG. 4. Annealing time dependence of the individual components of the lifetime in the 850 and 750 °C annealing. $\tau_s = 500\,\mu$s, $\tau_A = 220\,\mu$s, oxide precipitate size is proportional to $t^{3/4}$.

gion B' was larger than in region B in Fig. 2. This is discussed later.

The effect of oxide precipitates on the lifetime is quantitatively discussed below. Measured lifetime τ can be written as

$$1/\tau = 1/\tau_s + 1/\tau_0 = 1/\tau_s + 1/\tau_A + 1/\tau_B,$$

where τ_s is the effective lifetime resulting from the surface recombination, τ_0 is that determined by oxygen precipitation, τ_A is that dependent on as-grown large precipitates, and τ_B is that dependent on as-grown microprecipitates and nucleated precipitates during the annealing. Figures 2 and 3 were interpreted and the above components were discriminated by the following consideration as shown in Fig. 4. τ_s was estimated to be about $500\,\mu$s, which was independent of annealing temperature and time. In regions A and A', τ was constant and had the same value in both the 850 and 750 °C annealing. It indicates that τ_0 was dominated by τ_A in these regions, because as-grown microprecipitates grew larger without visible effect on τ. τ_A was constant, about $220\,\mu$s, because further growth of as-grown large precipitates was not so large as their initial size (about 1000 Å). In regions B and B', lifetime degradation took place, reflecting the effects of as-grown microprecipitates and the nucleation during the annealing. τ_B was separated from τ_s and τ_A in these regions. Visible effect of as-grown microprecipitates took place when

their sizes exceeded 100 Å (1 h in the 850 °C annealing and 8 h in the 750 °C annealing). In region II of the 850 °C annealing, the as-grown microprecipitate growth only affected τ_B, which was proportional to the reciprocal of annealing time t. It is to be noted that the oxide precipitate size L is given as $L \propto t^{3/4}$. Therefore, it is concluded that the lifetime is nearly proportional to the reciprocal of the platelet precipitate length. In region III of the 850 °C annealing and region B' of the 750 °C annealing, precipitate growth and nucleation simultaneously took place and affected the lifetime. On the 750 °C annealing, $\tau_B \propt t^{-1.5}$, which shows that precipitate density gave additional effect to precipitate size effect. It is to be noted that the lifetime is inversely proportional to the cubic root of the stacking fault density.[8] On the 850 °C annealing, the annealing time dependence of the lifetime was equal between regions II and III. It is considered that the precipitate density effect was hindered by the size effect in the 850 °C annealing.

In the above discussions, the following three assumptions were made: (1) $L = 0$ at $t = 0$. (2) Oxide precipitates nucleate by annealing at $t = 0$. (3) Growth of as-grown large precipitates is negligible compared to that of as-grown microprecipitates and nucleated precipitates due to annealing.

[1] H. Takaoka, J. Osaka, and N. Inoue, Jpn. J. Appl. Phys. Suppl. **18–1**, 179 (1979).

[2] L. C. Kimmerling, H. J. Leamy, and J. R. Patel, Appl. Phys. Lett. **30**, 217 (1977).

[3] Y. Mada, Jpn. J. Appl. Phys. **18**, 2171 (1979).

[4] J. Osaka, N. Inoue, and K. Wada, in *Proceedings of the 11th International Conference on Defects and Radiation Effects in Semiconductors (Institute of Physics Conference Series No. 59*, edited by R. R. Hasiguchi (The Institute of Physics, Bristol and London, 1980), pp. 527–532.

[5] K. Wada, N. Inoue, and K. Kohra, J. Cryst. Growth **49**, 749 (1980).

[6] K. Hoshikawa, H. Kohda, and K. Ikuta, Jpn. J. Appl. Phys. Suppl. **20-1**, 241 (1981).

[7] N. Inoue, J. Osaka, and K. Wada, The Electrochemical Society 1979 Fall Meeting, Abstract No. 542.

[8] K. Ikuta, Y. Matsuoka, and H. Takaoka, Jpn. J. Appl. Phys. Suppl. **19-1**, 621 (1980).