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Formation mechanism of grown-in defects in silicon

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Abstract

Problems resulting from the trend toward small-scale and highly integrated circuits used in semiconductor devices are caused by grown-in defects in the silicon crystal. Although a great many researchers have investigated the nature of these defects, their systematical formation mechanism is not clarified. Findings reveal that the intrinsic point defects and oxygen are closely related to the formation mechanism. Assuming the complex is composed of vacancies and oxygen atoms between relatively high temperatures in silicon, the formation mechanism of grown-in defects is examined, and also a system of three equations for diffusions of vacancies, self-interstitials and oxygen atoms is presented in detail, using the complex as a sink and source of vacancies and oxygen atoms in silicon.
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1. Introduction

The presence of oxygen in silicon wafers can be both beneficial and detrimental in device production [1]. Oxide precipitates and other defects associated with them are useful for gettering metallic impurities away from device regions and for increasing the mechanical strength of the wafers. On the other hand, they take part in the formation of needless donors or electrically inactive precipitates.

Although single oxygen atoms in silicon are electrically inactive, they can form electrically active clusters. Findings reveal that oxygen forms silicon-oxide precipitates at temperatures typical of device processing and interacts easily with vacancies or self-interstitials in silicon. It is, furthermore, found that oxygen decorates dislocations and stacking faults, takes part in the formation of voids, and forms defects together with nitrogen. As mentioned above, oxygen is both an industrially and academically interesting impurity in silicon.

In the present study, we assume a complex (VaO) composed of a vacancy (Va) and an oxygen atom (O) between high temperatures in the silicon crystal. In the silicon crystal near the melting point, VaO may be accepted as a lattice site oxygen atom rather than the complex. The present model indicates that most oxygen atoms and vacancies are incorporated into the crystal as a complex VaO from the solid/liquid interface. The reversible reaction between VaO and Si is considered so as to agree with anomalous oxygen precipitation (AOP) phenomena in silicon.

It is also widely known that the vacancy type microdefects zone, the interstitialcy type microdefects zone, the defect-free zone and the R-OSF (oxidation stacking fault) zone may appear in the crystal. Findings reveal that the formation of grown-in defects in silicon depends on v/G values (v: crystal growth rate; G: temperature gradient near the solid/liquid interface) [2].

The present model shows that the complex VaO resolves into a vacancy and an oxygen atom; in other words, it becomes their sink and source between high temperatures in silicon. We could systematically explain their formation mechanisms in accordance with experimental results, although it is qualitative. In accordance with the present model, furthermore, a system of three equations for the diffusion of vacancies, self-interstitials and oxygen atoms

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in silicon is derived. In the early stage just after being removed from the furnace during crystal growth, approximate solutions of the system are analytically obtained.

2. Anomalous oxygen precipitation (AOP)

When a silicon crystal is thermally treated in the rapid cooling, AOP occurs in the vacancy-rich region [3]. On the other hand, when a silicon crystal with AOP was heated up to temperatures higher than about 1600 K and then the crystal was thermally treated in the slow cooling, AOP disappears [3]. The generation and annihilation of AOP is thus reversible. It is also considered that SiO_2 becomes a nucleus of AOP. It is, therefore, reasonable that a reversible chemical reaction relevant to SiO_2 occurs in the crystal.

It is reasonable that the defect-free zone is formed by the recombination between vacancies and self-interstitials and also that self-interstitials are in the supersaturated state near the solid/liquid interface as a characteristic of the silicon crystal in which the density of solid state is smaller than that of liquid state. In connection with the complex VaO between high temperatures in the silicon crystal, we assume the following:

(i) Most oxygen atoms and vacancies are incorporated into the crystal as a complex VaO from the solid/liquid interface. The concentration of VaO is approximately equal to that of self-interstitials near the interface.

(ii) When the temperature rapidly goes down, the complex VaO resolves into Va and SiO_2 according to the reversible reaction of

$$2\mathrm{VaO} + \mathrm{Si} \rightleftharpoons \mathrm{SiO_2} + \mathrm{Va}. \tag{1}$$

SiO_2 is resolved into Va and Si by reacting with Va between temperatures higher than 1600 K.

(iii) For the usual slow cooling process, the reversible reaction of

$$\mathrm{VaO} \rightleftharpoons \mathrm{Va} + {}^{\mathrm{I}}\mathrm{O} \tag{2}$$

occurs between relatively high temperatures, where ${}^{\mathrm{I}}\mathrm{O}$ is the interstice site oxygen atom.

The reaction of $2\mathrm{VaO}+\mathrm{Si}\rightarrow\mathrm{SiO}+\mathrm{Va}$ occurs violently according to the rapid temperature decrease and AOP is formed by the nucleus of SiO_2. Eq. (1) shows that the AOP appearance region becomes vacancy-rich and the reverse reaction indicates that AOP disappears between high temperatures. In accordance with Eq. (2), VaO becomes a sink or source of vacancies and oxygen atoms.

3. Microdefects in CZ silicon

The vacancy type microdefects appear between v/G values larger than the typical value $(v/G)_{\mathrm{V}}$, while the interstitialcy type ones appear between values smaller than the typical value $(v/G)_{\mathrm{I}}$, where $(v/G)_{\mathrm{I}}<(v/G)_{\mathrm{V}}$. Thus, experimental results indicate that self-interstitials are more incorporated into the crystal from the solid/liquid interface as v is relatively smaller or G is larger. It is also well known that the vacancy type microdefects zone, the R-OSF zone, the defect-free zone and the interstitialcy type microdefects zone simultaneously appear under the condition of $(v/G)_{\mathrm{I}}<v/G<(v/G)_{\mathrm{V}}$. The cross section of the silicon crystal is schematically shown in Fig. 1 in this case.

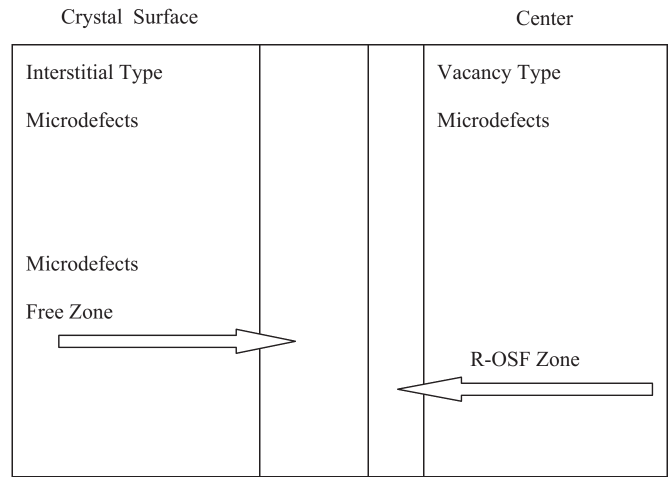

Fig. 1. Schematic diagram of grown-in defects in CZ silicon.

As shown in Fig. 1, the defect free zone appears between R-OSF and self-interstitial-rich zones. As mentioned above, since the concentration of VaO (vacancy source) in the crystal is approximately equal to that of self-interstitials near the melting point, this zone is formed by the recombination of vacancies and self-interstitials.

It is thought that self-interstitials are relatively more incorporated into the large G value region than the small one, as a characteristic of a material in which the solid density is smaller than the liquid one. The temperature gradient G gradually becomes large from the crystal center toward the outside. Therefore, the interstitialcy and vacancy type microdefects are formed by the excess self-interstitials in the outside region and by the excess vacancies in the center region, respectively.

4. Void defects and R-OSF in CZ silicon

As the temperature goes down, a great deal of vacancy is generated by the chemical reaction $\mathrm{VaO}\rightarrow\mathrm{Va}+{}^{\mathrm{I}}\mathrm{O}$ in silicon. As mentioned above, self-interstitials in the crystal near the center region are fewer than those near the outside, so the center region becomes vacancy-rich. As a result, the void defects are locally formed by excess vacancies when the reaction occurs violently between the temperatures near about 1400 K. It is believed that the inside of void defects is oxidized by a part of the oxygen atoms generated in the reaction.

The ingot rotation during the crystal growth exerts centrifugal force not on vacancies but on self-interstitials.