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STUDY OF THE MECHANISMS OF OXYGEN PRECIPITATION IN RTA ANNEALED Cz-Si WAFERS

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Abstract. In this paper, the influence of the rapid thermal annealing of single crystalline Cz-Si wafers on the evolution of the concentration of interstitial oxygen as well as oxygen in precipitated oxide phase was investigated by infrared spectroscopy. The wafers were preliminary furnace annealed to create the precipitate seeds. The concentration of interstitial oxygen was shows to decrease considerably as a result of annealing during up to 40 min together with the growth of the concentration of precipitated oxygen. This effect depended on the purity and defect structure of initial wafers. The kinetic model was developed to account for the observed effects based on the modification of the solubility level for interstitial oxygen induced by defects as well as its diffusivity. Obtained results of simulation agree well with the experimental data.

Introduction

Crystalline Si is undergone thermal processing on all the stages of its production and application as a basic material for semiconductor devices. During thermal treatment, the formation and modification of different defect types (from ordinary point defects and their clusters to different kinds of dislocation loops), doping with impurities, and, finally, the interaction of the latter with defects take place. All these processes determine electrical, optical, and a number of other properties of resulting Si material. A great number of processes is related to the precipitation of oxygen, which is a universal impurity in silicon. Oxygen can be in different states in silicon, namely distributed interstitial oxygen that usually prevails, molecular Si-O_x complexes, and precipitated in form of SiO_2 inclusions. In its turn, SiO_2 phase in crystalline silicon can have different structural modifications, from the strained coesite-like, whose molecular volume is higher than that of Si, to the quartz-like form that consists of 6-member rings and has a molecular volume almost coinciding with that of cubic Si.

Rapid thermal annealing (RTA) is ordinarily used in Si technology to stimulate the SiO_2 precipitate dissolution. For such processes, the temperatures above 1200°C are applied [1, 2]. In this work, we use RTA treatment of Si samples but apply lower annealing temperature (850°C) to study the effect of this kind of annealing on the silicon oxide precipitate formation. This method is attractive since it is fast and potentially offers a simplification and cost saving in the technological procedures of Si wafer treatment.

1. Experimental

We carried out the experiments with 3 mm thick p-type (100) Cz-Si wafers cut from the ingots 150 to 300 mm in diameter. Two series of samples were used, namely cut from the bottom and the top part of Si ingot, respectively. The concentration of interstitial oxygen was about (8÷9)×10^{17} cm^{-3}. Infrared (IR) spectroscopy with the analysis of the shape of adsorption band at the valence Si–O bond oscillations was used to determine the concentration of oxygen in interstitial and precipitated in SiO_2 phase states as well as the structure of SiO_2 inclusions [3]. The Fourier IR spectrometer PerkinElmer BXII was used for the measurements. The type and the size of defects as well as related mechanical tension were determined from the curves of diffraction reflection as well as from the diffuse scattering, which was measured using the X'Pert PRO MRD X-ray diffractometer [4]. To modify the structural state of oxygen in Si samples, we underwent them to the two-stage furnace annealing, namely at 800°C during 20 h to form Si nuclei for precipitation and then RTA annealing at 850°C in air for different times.

2. Results

The growth defects of both interstitial and vacancy types were observed in initial samples. Thermal treatments led to the decrease of the contribution of interstitial defects, especially in the samples with greater Si purity (see Fig. 1).

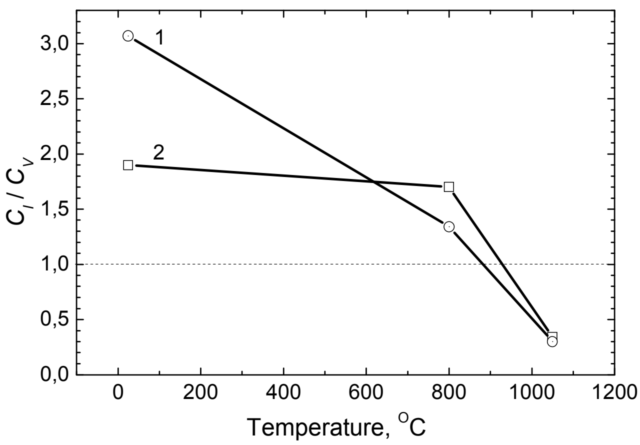

Fig. 1. Dependence of the ratio of the concentrations of grown-in defects of interstitial- and vacancy-types on the temperature of the furnace annealing of Cz-Si wafers with reduced (1) and increased (2) structure imperfection.

The concentration of precipitated oxygen in the initial samples was small (~2 – 5 ×10^{16} cm^{-3}). It formed rather relaxed phase that consisted mainly of 6-member rings of SiO_4 tetrahedra. The stage of furnace anneals led to the considerable decrease of the concentration of interstitial oxygen as well as to the increase of the concentration of precipitated oxygen. These changes were more considerable in the wafers with more enhanced defect structure (see Table 1). Moreover, the structural state of oxygen precipitated in oxide phase in such samples changed also and the molecular complexes $SiOSi_3$ и SiO_2Si_2 appeared.

RTA led to the decrease of the concentration of interstitial oxygen even more, especially in the less pure samples – up to 30 %. The concentration of precipitated oxygen in phase increased considerably. At this, the precipitates contained complex sets of Si complexes with different oxidation degrees. At the same time, the precipitation processes of oxygen in separate phase were far less extensive in the "pure" samples. The phase itself remained in form of weakly strained SiO_2 regions consisting of 6-member rings of SiO_4 tetrahedra (see Table 1).

Table 1.

Bottom part of ingot					
Treatment	O_i (relative area at 1108 cm^{-1})	6-member rings SiO_4 (relative area at 1080 cm^{-1})	4-member rings SiO_4 (relative area at 1060 cm^{-1})	SiO_2Si_2 (relative area 1036 cm^{-1})	$SiOSi_3$ (relative area at 1000 cm^{-1})
initial	97 %	3 %	–	–	–
furnace	79 %	10%	4%	6,8%	0,2 %
RTA (26 min)	66%	13%	7%	12%	2 %

Top part of ingot		
Treatment	O_i (relative are at 1108 cm^{-1})	6-member rings SiO_4 (relative area at 1080 cm^{-1})
initial	97 %	3 %
furnace	96 %	4%
RTA (26 min)	93%	7%

3. Method of calculation

A mathematical model was developed to describe the kinetics of oxygen precipitation in crystalline Si wafers subjected to RTA thermal treatment at 850°C. It used a possible change of oxygen diffusivity in Si wafers being RTA annealed comparing to the respective published values related to the furnace anneals. In addition, a possible change of the solubility limit of interstitial oxygen in Si due to the interaction with point defects introduced by RTA was taken into account.

The mass-balance equations for mobile (C_i) and bound (C_p) oxygen and (average) precipitate radius are obtained as follows [5]:

$$\frac{dC_i}{dt} = -\frac{dC_p}{dt} = kN_p(C_i - C_{if}) \qquad (1)$$

$$\frac{d(R^2)}{dt} = 2D\frac{C_i - C_{if}}{C_{pr} - C_{if}} \qquad (2)$$

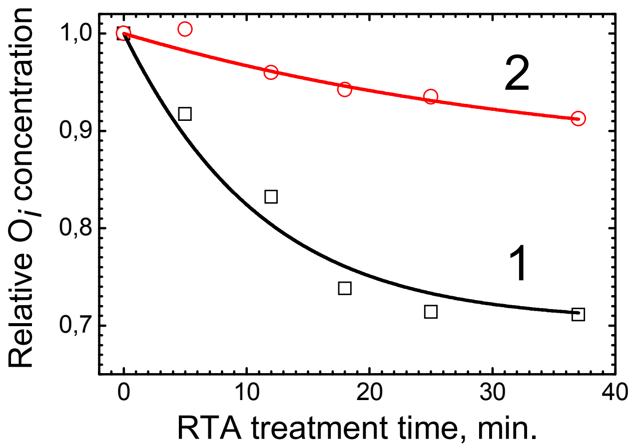

Fig. 2. Dependence of the relative concentration of interstitial oxygen on the RTA treatment time at 850°C in Si wafers cut from the bottom (1) and the top (2) part of ingot. Dots are the experimental results, solid lines are the results of simulation.

where $k = 4\pi DR$ is a rate constant for diffusion-limited growth/decay of a precipitate with radius R, C_{pr} is the oxygen concentration in SiO_2 phase, C_i is the current concentration of interstitial oxygen atoms in Si, and N_p is the number of precipitates per unit volume of silicon. C_{if} is the equilibrium concentration of mobile oxygen near a curved SiO_2/Si interface. It is expressed as follows taking the Gibbs-Tompson effect into account:

$$C_{if} = C_{eq}\exp\left(\frac{2\gamma\Omega}{Rk_BT}\right) \qquad (3)$$

where C_{eq} is an equilibrium solubility of oxygen in silicon matrix, γ is the specific interface free energy of the interface of SiO_2 precipitate / Si matrix, Ω is the atomic volume of oxygen in the new phase, and T is the temperature of annealing.

In the framework of the model developed, the experimentally observed kinetics of oxygen precipitation was reproduced (Fig. 2). The ratio of the solubility limits of interstitial oxygen for the Si wafers cut from the top and the bottom part of Si ingot was found to be ~ 1.5.

4. Conclusion

In conclusion, we have suggested a new economical method for the formation of SiO_2 precipitates in Si wafers based on the RTA annealing of Si samples at comparatively low (close to

850°C) temperatures. Obtained precipitates do not introduce mechanical stress in Si wafers but can be used as collecting gettering centres for metal impurities without harmful influence on the Si crystal bulk.

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