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Hydrogen-plasma-enhanced oxygen precipitation in silicon

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Abstract. Czochralski-grown silicon crystals with different carbon concentrations have been heat-treated in μ -wave hydrogen plasma in the temperature range 500–700 °C. For comparison, control samples have been treated in a furnace in a nitrogen ambient. Infrared (IR) absorption measurements show that the loss of oxygen atoms from solution due to the formation of SiO₂ precipitates is strongly enhanced by the H-plasma treatment in both carbon-lean and carbon-rich Si crystals. The loss of oxygen is accompanied by the loss of substitutional carbon atoms from solution in the C-rich samples. The frequencies and shapes of the IR absorption bands associated with the precipitates are different in C-rich and C-lean crystals, indicating the formation of different types of precipitate particle. The former bands (C rich) are similar following heat treatments in a H-plasma or in N₂ gas. It is inferred that a fast diffusing species penetrates into Si crystals during the H-plasma treatment, leading to a catalytic enhancement of oxygen diffusion that in turn leads to enhanced precipitation. Possible mechanisms for the enhanced oxygen diffusion and precipitation are discussed briefly.

1. Introduction

Silicon crystals grown by the Czochralski (CZ) method contain interstitial oxygen atoms (O_i) at a concentration close to 10¹⁸ cm⁻³. Diffusion of the O_i atoms during processing treatments at elevated temperatures leads to their agglomeration with the formation of SiO_x (1 ≤ x ≤ 2) precipitates [1–4], with the advantages that they capture fast-diffusing Fe and other metallic atoms introduced inadvertently during the manufacture of integrated circuits. In the temperature range 700–1300 °C, the rate of oxygen diffusion is generally found to be ‘normal’, with $D_{O_i} = 0.13 \exp(-2.53 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$. However, for $T < 700 \text{ °C}$ it may be necessary to invoke enhancements of D_{O_i} by orders of magnitude to explain the rate of oxygen agglomeration and measured in- or out-diffused profiles [4, 5]. Such ‘enhancements’ have been ascribed to decreases in the energy barrier for O_i diffusion jumps due to interactions with intrinsic defects (vacancies or self-interstitials), a second O_i atom (fast-diffusing dimer) or impurity atoms (H, C, N, Fe etc) [4, 5]. The enhancement mechanisms are not fully understood, but are important for precise control of oxygen aggregation at temperatures lower than 700 °C [3].

It has been verified that enhanced O_i diffusion occurs in Si samples when hydrogen is introduced, either by pre-exposure to a radio-frequency (RF) plasma (at 150–500 °C) or to

H₂ (D₂) gas at 600–1300 °C [6–13]. Enhancement factors are well documented for samples annealed in the range 225–450 °C. Extrapolations of these data for $T \geq 600$ °C imply no enhancements [7, 8], but the situation is not clear for hydrogenated samples annealed at $T > 500$ °C. Studies of the growth of SiO₂ formed by two-step annealing at 700 and 1000 °C in CZ-Si pre-hydrogenated at 1270 °C revealed enhanced O_i precipitation [11]. It was proposed [11] that: (a) there was an increase in the concentration of the nucleation sites for oxygen precipitation and/or (b) O_i diffusion was enhanced. Enhanced O_i out-diffusion during anneals of Si in H₂ gas in the range 1000–1200 °C has been observed [12, 13], but no enhancements at 1200 °C due to hydrogen were found in other work [14].

There is a need to clarify the effect of hydrogen on O_i diffusion and precipitation for $T > 500$ °C. In this paper we present measurements of the loss of oxygen from solution due to the formation of oxide precipitates resulting from heat treatments of CZ-Si crystals in a μ -wave hydrogen plasma in the temperature range 500–700 °C.

2. Experiment

Samples for this study were prepared from boron-doped p-type and phosphorus-doped n-type Czochralski-grown silicon crystals with initial resistivities of ~ 12 and $20 \Omega \text{ cm}$, respectively. The concentration of oxygen in the samples, determined by means of optical absorption measurements [15], was in the range $1.1\text{--}1.35 \times 10^{18} \text{ cm}^{-3}$. Carbon-lean ($[\text{C}_S] \leq 10^{16} \text{ cm}^{-3}$) and carbon-rich ($[\text{C}_S] = 4.7\text{--}5.6 \times 10^{17} \text{ cm}^{-3}$) samples were investigated. The H-plasma treatments of mechanically polished samples were carried out in a μ -wave plasma-assisted CVD (MPCVD) reactor at 2.45 GHz with a hydrogen flux of 200 sccm, a pressure of 8 mbar, power 800 W and a fixed sample temperature in the range from 450 to 700 °C. For comparison, control samples were treated at the same temperatures in a furnace in a nitrogen ambient. After the treatments the samples were cleaned and rinsed in HF.

Optical absorption measurements were made at 10 K or 295 K in the wavenumber range $400\text{--}4000 \text{ cm}^{-1}$ at a resolution of 1.0 cm^{-1} using a Bruker IFS 113v Fourier-transform infrared (FT-IR) spectrometer. Reference spectra taken from an oxygen-free float-zone-grown sample were subtracted from spectra of CZ-Si samples to eliminate the intrinsic phonon absorption. The absorption spectra of some samples in their as-grown state were subtracted from their spectra following the heat treatment to reveal the difference spectra.

3. Experimental results

Figure 1 shows IR absorption spectra at 295 K of carbon-lean CZ-Si samples in their as-grown state (spectra 1) and after treatments at 650 °C for 40 hours in a μ -wave H-plasma or in a nitrogen gas ambient (spectra 2), together with their difference spectra (3). The as-grown samples show absorption lines 514, 560, 1013, 1107 and 1226 cm^{-1} due to local vibrational modes (LVMs) of isolated O_i atoms [16, 17], except the line at 1013 cm^{-1} , recently identified as an LVM of the oxygen dimer [18, 19]. The treatment in the nitrogen ambient resulted in only a small decrease ($\sim 3\%$) in the intensities of the O_i modes, but after the hydrogen plasma treatment, the strengths of these LVM modes showed a decrease by more than 45% from their initial values. A broad absorption band over the range $1000\text{--}1300 \text{ cm}^{-1}$ appeared in the spectra of the plasma-treated carbon-lean sample.

Figure 2 shows the spectra at 295 K of carbon-rich CZ-Si samples in their as-grown state (spectra 1) and after treatments at 650 °C for 40 hours in a H-plasma or in N₂ ambient (spectra 2). The difference spectra are presented in figure 2 as well (spectra 3). Additional absorption

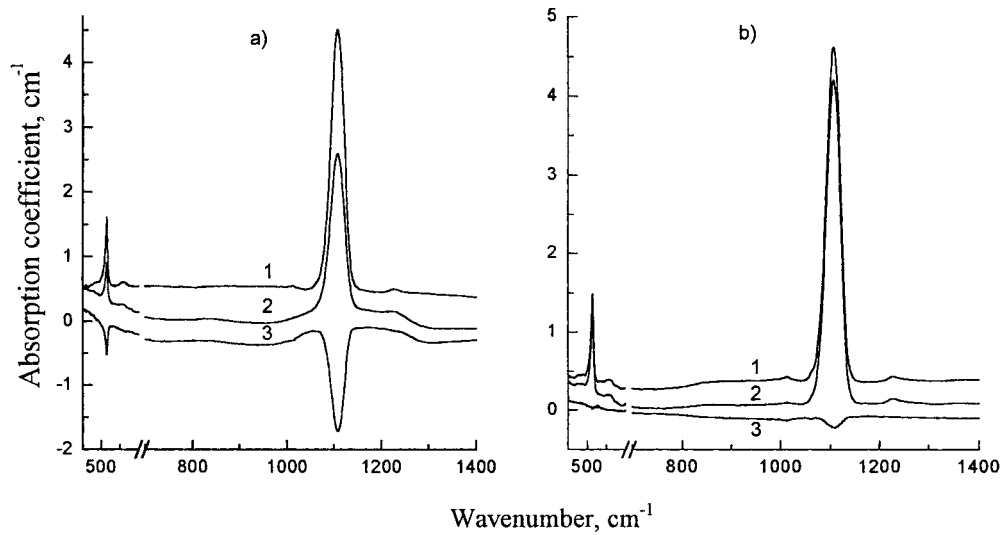


Figure 1. Infrared absorption spectra at 295 K of carbon-lean CZ-Si samples in as-grown state and after treatments in (a) hydrogen plasma and (b) nitrogen gas ambient: (1) as grown, (2) after treatment at 650°C for 40 hours, (3) difference between spectra (2) and (1).

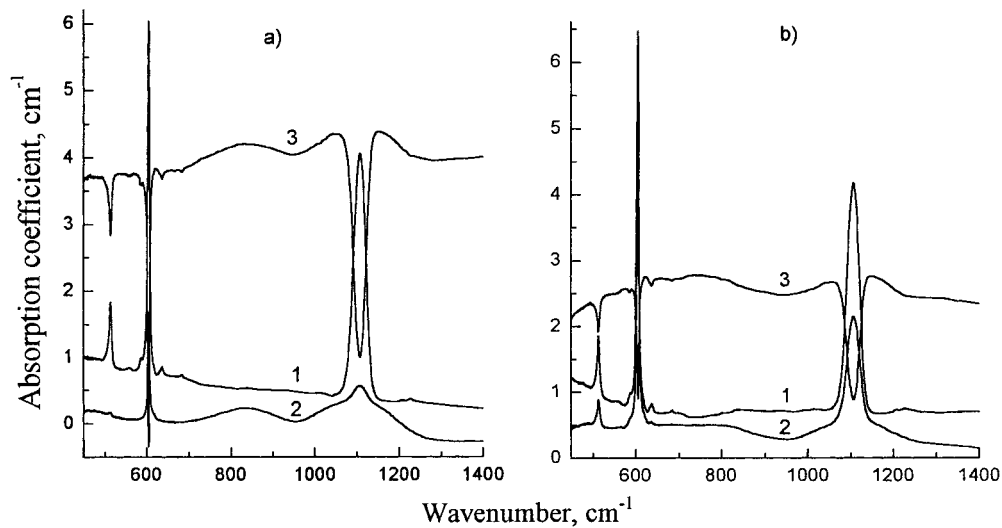


Figure 2. Infrared absorption spectra at 295 K of carbon-rich CZ-Si samples in as-grown state and after treatments in (a) hydrogen plasma and (b) nitrogen gas ambient: (1) as grown, (2) after treatment at 650°C for 40 hours, (3) difference between spectra (2) and (1).

lines at 587, 605, 637, 684.5 and 1207 cm^{-1} are present in the spectra of as-grown carbon-rich samples. The lines at 605 and 1207 cm^{-1} are due to substitutional carbon atoms and the other three modes are related to a $\text{C}_5\text{-O}_i$ complex [20]. Substantial losses of oxygen and carbon atoms from solid solution (about 50 and 30% of initial values, respectively) were observed after the treatment of the carbon-rich samples in nitrogen gas. The treatment in hydrogen plasma resulted in more than 90% reduction of $[\text{O}_i]$ and $\sim 80\%$ of $[\text{C}_5]$. Two broad bands centred at about 840 and 1100 cm^{-1} appeared in the spectra of C-rich samples after these treatments.

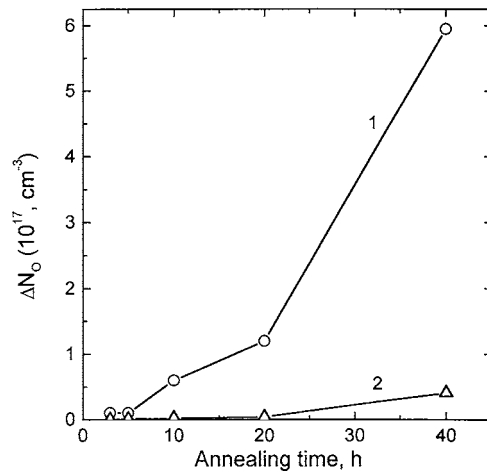


Figure 3. Kinetics of the loss of interstitial oxygen atoms from solid solution upon treatment of carbon-lean CZ-Si samples at 650 °C in: (1) H-plasma and (2) nitrogen gas ambient.

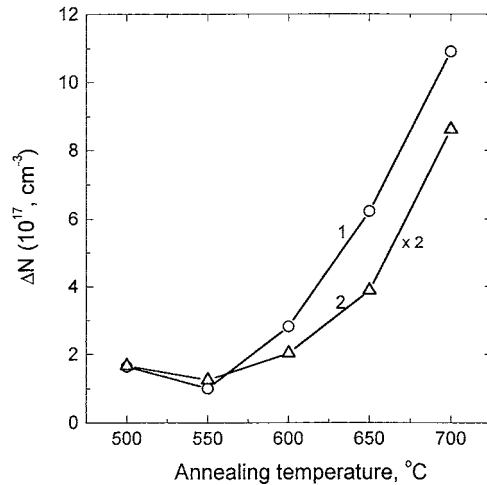


Figure 4. Concentrations of (1) interstitial oxygen atoms and (2) substitutional carbon atoms which were removed from solid solution upon treatments of carbon-rich CZ-Si samples in H-plasma at different temperatures. Duration of the treatments was 10 hours. The values of $[\Delta C_S]$ are doubled.

The strengths of the IR absorption line at 1107 cm^{-1} (α_{1107}) at room temperature is usually used to determine values of $[O_i]$ [1, 2, 15]. However, this procedure can lead to significant errors in the $[O_i]$ determination in Si crystals containing a high density of oxygen precipitates, because of a strong overlap of the band at 1107 cm^{-1} with oxide precipitate bands (see figures 1 and 2). For the present samples measured at 295 K, we determined $[O_i]$ from the strength of an oxygen-related band at 514 cm^{-1} , for which there is no overlap with absorption related to carbon impurities [21]. A calibration coefficient for the calculation of interstitial oxygen concentration on the basis of α_{514} was determined as $1.2 \times 10^{18} \text{ atoms cm}^{-2}$ from the measurements of α_{514} and α_{1107} for a large number of as-grown samples. The difference spectra (after–before treatments) have been also used for the calculation of the loss of single oxygen and carbon atoms from solid solution in the present study.

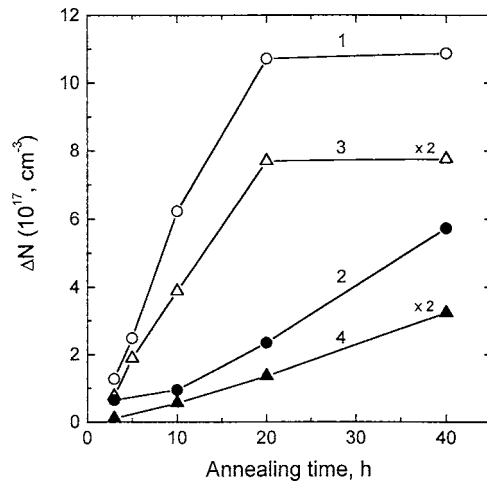


Figure 5. Kinetics of the loss of (1) and (2) interstitial oxygen atoms and (3) and (4) substitutional carbon atoms from solid solution upon treatment of carbon-rich CZ-Si samples at 650 °C in: (1) and (3) H-plasma and (2) and (4) nitrogen gas ambient. The values of $[\Delta C_S]$ are doubled.

Figure 3 compares the kinetics of oxygen loss for treatments at 650 °C in a hydrogen plasma with that in nitrogen gas ambient for carbon-lean CZ-Si samples, showing that the O_i loss is greatly enhanced by the H-plasma treatment. The loss of O_i in C-lean CZ-Si due to H-plasma treatments at 650 °C can be significantly increased by pre-heat treatments of the samples in H-plasma at 450 °C. For example, more than 85% reduction of the initial oxygen concentration was observed in a sample which was subjected to two step annealing (450 °C for 3 h+650 °C for 38 h) in hydrogen plasma. Carbon-lean samples have been also treated at different temperatures in the range 500–700 °C with a duration of 10 hours. No significant changes in the strengths of the lines at 514 and 1107 cm^{-1} have been observed after such treatments.

Figure 4 shows the loss of isolated O_i and carbon atoms after H-plasma treatments at different temperatures for 10 h for carbon-rich samples. Figure 5 shows the kinetics of $[O_i]$ and $[C_S]$ loss for treatments at 650 °C in hydrogen plasma and in nitrogen gas ambient. There is a correlation of the losses for both treatments, both of which are significantly enhanced during H-plasma treatments.

4. Discussion

4.1. Oxygen precipitation in carbon-lean Si due to H-plasma treatments at 500–700 °C

It was shown earlier that heat treatments of CZ-Si in an RF hydrogen plasma in the range 225–450 °C resulted in: (a) enhanced thermal double donor (TDD) formation in bulk material, (b) correlated enhanced rates of loss of oxygen from solid solution and (c) enhanced removal of stress-induced dichroism of the 9 μm oxygen LVM [6–10]. It was inferred that a rapidly diffusing hydrogen-related species permeated throughout the silicon and led to enhanced oxygen diffusion and consequently to the above-mentioned effects. However, theoretical investigations of microscopic mechanisms of H- O_i interaction [22–25], leading to enhanced O_i diffusion, remain controversial. In addition, the extrapolation of the experimental results to higher temperatures implied a negligible enhancement effect due of hydrogen [7, 8], although enhancements at these more elevated temperatures have not been studied prior to the present work.

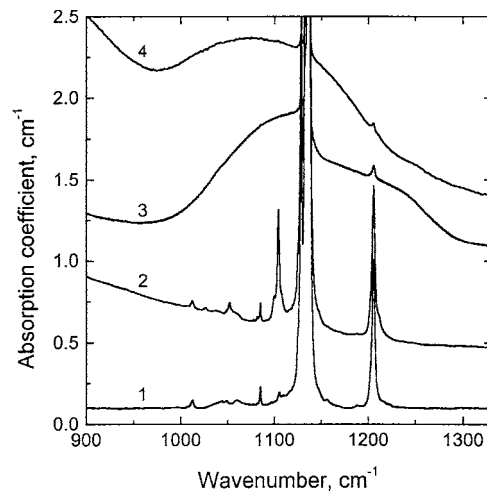


Figure 6. Infrared absorption spectra at 10 K of (1) and (3) carbon-lean and (2) and (4) carbon-rich CZ-Si samples: (1) and (2) before and (3) and (4) after treatments in hydrogen plasma (3) at 450 °C for 3 hours + at 650 °C for 38 hours and (4) at 650 °C for 40 hours.

It is demonstrated in this work (figures 1 and 3) that the heat treatments of carbon-lean CZ-Si in a H-plasma at 650 °C lead to significantly enhanced loss of $[O_i]$ with the formation of SiO_2 precipitates that give rise to broad IR absorption bands in the range 1000–1300 cm^{-1} . Figure 6 shows the optical absorption spectra at 10 K in the range 900–1300 cm^{-1} for C-lean and C-rich CZ-Si samples before and after H-plasma treatments at 650 °C. Low temperature measurements allow the separation of the absorption of the oxide (precipitates) from that due to O_i atoms that becomes very sharp at 10 K, whereas the oxide precipitate-related bands remain broad. Computer simulations showed that the broad absorption in the range 970–1300 cm^{-1} for the carbon-lean Si sample consists of at least two absorption bands with maxima at about 1100 and 1218 cm^{-1} . The kind of precipitate giving rise to the 1100 cm^{-1} band is unclear, while the line at 1218 cm^{-1} can be associated with disc-shape amorphous sub-stoichiometric SiO_x ($x < 2$) [2, 26].

The enhanced O_i precipitation upon H-plasma treatments may result from: (a) enhanced O_i diffusion or (b) enhanced formation of nucleation sites for the growth of oxide precipitates (with or without enhanced O_i diffusion). The latter process seems not to play the major role during heat treatment of low-carbon as-grown Si in the range 600–700 °C. Our data (figures 3 and 5) show that for carbon-lean CZ-Si samples a rather long incubation period (up to 10 h at 600–700 °C) occurs in the precipitation process upon H-plasma treatment, in contrast to the behaviour of carbon-rich samples where oxygen precipitation starts without any delay. Such a period is usually associated with the time required for the formation of precipitate nuclei. It should be mentioned that the incubation period was reduced significantly after preliminary heat-treatment of carbon-lean CZ-Si samples in H-plasma at 450 °C for 3 h. H-plasma treatments at 450 °C are known to result in effective formation of the TDs [6–10], which might serve as nucleation sites for oxygen precipitates during following heat treatments at higher temperatures.

An alternative possibility, mentioned above, is that the enhanced oxygen precipitation is related to enhanced oxygen diffusion. The interaction of fast-diffusing hydrogen-related species with interstitial oxygen atoms may result in the enhanced oxygen diffusion at 600–700 °C, probably, in a similar manner as known to occur at lower temperatures [7, 9]. For

some reasons, e.g. higher solubility of hydrogen and/or change in its main state from molecular to atomic form, hydrogen-enhanced oxygen diffusivity at 600–700 °C may be essentially higher than that expected from the extrapolation of low-temperature values. Further investigations are needed, however, to verify this suggestion.

4.2. Effect of carbon on oxygen precipitation at 500–700 °C

The presence of carbon atoms in concentrations higher than $3 \times 10^{16} \text{ cm}^{-3}$ is known to enhance oxygen precipitation significantly in CZ-Si [2]. There are two different mechanisms and two types of precipitate in C-rich CZ-Si crystals treated at temperatures below or above 800–850 °C [2, 27–29]. O_i precipitation below 800 °C is accompanied by significant loss of carbon from solution, while above 850 °C the loss of substitutional carbon is quite weak. Heat-treatments of C-rich crystals below 800 °C resulted in the appearance of broad IR spectral bands with maxima at about 850 and 1100 cm^{-1} [28, 29]. The line at 850 cm^{-1} was not observed from crystals annealed at temperatures higher than 850 °C, but instead a broad line with maximum at about 1220 cm^{-1} appeared. It was suggested that below 800 °C carbon provides direct heterogeneous seeding sites for oxygen precipitation, while at temperatures higher than 850 °C carbon plays a catalytic role in the oxygen precipitation [28].

The results of the present study of oxygen precipitation in C-rich CZ-Si crystals are consistent with the previously published results [27–29]. Our data (figures 1–3, 5) show that the loss of interstitial oxygen atoms from solid solution is significantly enhanced in C-rich samples compared with that in C-lean ones. The loss of oxygen is accompanied by the loss of substitutional carbon atoms from solid solution. The ratio of lost oxygen atoms per lost carbon atom varies from 2 to 3 depending on annealing temperature and time. A new result of the present study is that the rates of the loss of both oxygen and carbon atoms from solution are enhanced significantly upon treatment of C-rich CZ-Si samples in hydrogen plasma.

Broad absorption bands with maxima at about 840 and 1100 cm^{-1} appeared in the spectra of C-rich samples after treatments in H-plasma as well as in nitrogen gas ambient (figures 2 and 6). The similarities in positions and shapes of the bands after different treatments indicate that H-plasma treatment does not influence the type of precipitate in C-rich samples but only their formation rates. It can be inferred from these observations that a fast-diffusing species which penetrates into Si crystals is responsible for the enhanced O_i precipitation but acts in a catalytic role so that it is not incorporated directly into the growing precipitates. Carbon atoms seem to be directly involved in the process of oxygen precipitation upon different treatments at 500–700 °C providing heterogeneous seeding sites for oxygen precipitates as suggested in [28].

5. Conclusions

Silicon containing oxygen-related precipitates are widely used in Si-based microelectronic technology for gettering various undesirable metallic impurities. Effective formation of oxide precipitates requires heat-treatments of CZ-Si wafers at rather high temperatures (>1000 °C). However, for the fabrication of future integrated circuits, treatments at lower temperatures are needed, requiring further investigation.

The present FTIR absorption measurements have shown that the loss of O_i atoms from solution and the formation of oxygen precipitates is strongly enhanced in bulk CZ-Si samples that are heat-treated in a hydrogen plasma in the temperature range 500–700 °C. This may be due to the enhancement of O_i diffusion by their interactions with a fast-diffusing hydrogen species that penetrates into the bulk of Si samples during H-plasma treatment at elevated temperatures. Further studies are required, however, to understand details of the H-plasma-enhanced oxygen precipitation at temperatures in the range 500–700 °C.

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