Correlation of Thermal History and Thermal Donor Formation

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Abstract

Effects of high temperature annealing at 1050 °C on the formation of oxygen-related thermal donors in Czochralski-grown silicon single crystals have been investigated. Resistivity measurements have shown that the highest maximum concentration of donor states after a subsequent isochronal annealing step at 450 °C is introduced in the as-grown material while the yields obtained in pretreated samples decrease rapidly with increasing pre-anneal time. While the initial formation rate depends on the initial content of dissolved oxygen corresponding to the well-known fourth-power law, the total yield is additionally a function of the starting conditions. It appears that several types of precipitation kinetics exist owing to parallel diffusion mechanisms and that only a small fraction of the formed oxygen clusters are realized as donor complexes. However, IR studies have shown that the ratio of the concentrations of the different donor specimens and therefore their kinetical behaviour are independent of the thermal history.

1. Introduction

When using Czochralski-grown silicon (CZ-Si) single crystals in device processing, defects associated with oxygen are still one of the most important material problems. Owing to supersaturation, oxygen shows a wide variety of aggregation phenomena [1] dependent on the thermal process conditions. This well-known behaviour, described by several homogeneous [2, 3] and heterogeneous [4, 5] nucleation mechanisms, is the result of various interactions between oxygen and other crystal defects.

One special way of complexing, which represents a topic of actual discussion, is the generation of nine different well-characterized microdefects during low temperature treatment of Czochralski-grown silicon in the range 300–500 °C which act as shallow donor centres, the so-called "thermal donors" (TD1–TD9) [6]. The formation of these defects has been shown to have an influence on the electrical performance of integrated circuits. Since the early work of Kaiser *et al.* [7] a large number of alternative structural models and formation mechanisms have been proposed [8–11]; however, they cannot explain all experimental observations consistently.

A very important aspect emerging in kinetical investigations seems to be the influence of the starting material on subsequent thermal processes. The initial conditions are characterized by a unique set of grown-in and process-induced defects, implying a specific system of competitive interaction mechanisms. The result is a large variation of the effective diffusivity of oxygen demonstrated recently in dispersing treatments at 1200–1300 °C [11] and by pre-annealing at 900 °C [12].

The present paper reports a study of the formation of oxygen-related donor complexes in relation to the thermal history. Therefore the investigations are extended to a two-stage heat treatment (1050 and 450 °C) more adjusted to real process conditions. A comparison with the results achieved with specimens exposed to a single temperature step only should show whether the third and fourth-power laws [7] are also applicable for donor formation in pretreated crystals.

2. Experimental details

The samples used in this study were prepared from boron-doped ($\rho \simeq 10\ \Omega$ cm), commercially available CZ-Si single-crystal wafers. The concentration of interstitial oxygen was 10^{18} atoms cm^{-3} according to the IR absorption at 9 μm [13]. Substitutional carbon was below 10^{16} atoms cm^{-3}. The residual oxygen, normally incor-

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porated in various aggregated forms in the silicon lattice, such as precipitates, thermal donors or C–O complexes, cannot be determined quantitatively using standard IR techniques. In order to study the dependence of TD formation on the thermal history, all samples were subjected to a two-step heat treatment. Pre-annealing at 1050 °C in a high purity nitrogen ambient for times between 0.5 and 240 h produces different stages of precipitation and is followed by an isochronal annealing step at 450 °C for up to 150 h. The IR measurements were made with a Nicolet model MX10 Fourier transform IR (FTIR) spectrometer. IR studies at liquid helium temperature allow the two series of bands associated with the helium-like electronic transitions of the nine different double donors (TD1–TD9) to be obtained [6]. Electrical measurements at room temperature were performed using a conventional four-point probe technique to determine the concentration of generated donors [14], assuming that these defects act as double donors [15].

3. Results

Heat treatment of as-grown CZ-Si at 1050 °C for 0.5–240 h leads to different stages of oxygen precipitation. The corresponding changes of the dissolved oxygen concentration have been plotted against the 1050 °C pre-annealing time. Figures 1 and 2 show the results obtained with short and long annealing periods. The first phase of annealing is characterized by an anomalous oxygen behaviour. Within the first 2 h we observe a slight decrease and then a slight increase of the concentration followed by a nearly constant value until 10 h (see Fig. 1, upper curve), whereas a continuous decrease of the interstitial oxygen concentration due to agglomeration and out-diffusion processes with increasing annealing time might have been expected. In fact, such behaviour was first observed after heating periods of more the 10 h (see Fig. 2, upper curve).

Subsequent isochronal heat treatment at 450 °C effects additional loss of dissolved oxygen. In the same figure, results after 10, 20 and 150 h subsequent annealing (450 °C) are shown. The difference in the concentration after the preliminary precipitation growth treatments is similar for the as-grown material and for samples submitted to a short pre-annealing time (below 10 h), but disappears completely for samples with prolonged preheating times at 1050 °C (above 160 h).

Parallel to the IR studies, the corresponding changes of the resistivity before and after each heat treatment have been measured. Figure 3 shows the development of the resistivity of samples with different preheat times at 1050 °C as a function of the duration of the second isochronal annealing step at 450 °C. The electrical behaviour of the as-grown sample differs strongly from the pretreated specimens. Annealing for 7 h at 450 °C is sufficient to generate such a high

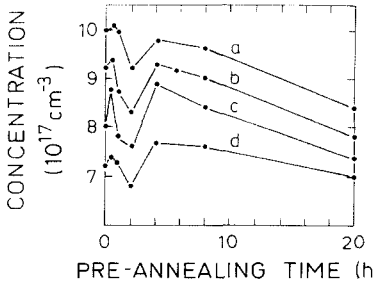

Fig. 1. Interstitial oxygen concentration after different isochronal heat treatments at 450 °C as a function of the pre-annealing time at 1050 °C: (a) no subsequent annealing step; (b) 10 h; (c) 20 h; (d) 150 h.

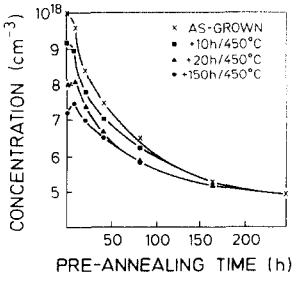

Fig. 2. Interstitial oxygen concentration after different isochronal heat treatments at 450 °C as a function of the pre-annealing time at 1050 °C.

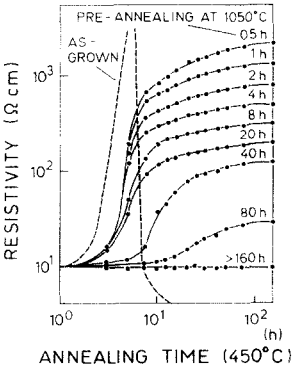

Fig. 3. Dependence of the resistivity on the two-step annealing process (1050 and 450 °C).

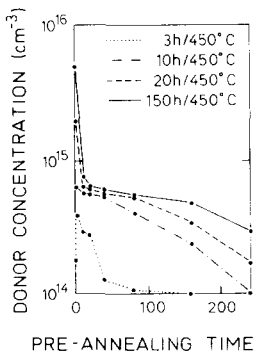

Fig. 4. Generated thermal donor concentrations after the two-step annealing process (1050 and 450 °C) as a function of the pre-annealing time at 1050 °C, using the standard calibration for phosphorus and boron. The four curves correspond to four different isochronal heat treatments at 450 °C.

density of thermal donors that compensation of the major carriers takes place, which leads to a type conversion. However, the resistivity of the samples subjected to preheat treatments tends towards a limiting value, which decreases with increasing duration of the preliminary high temperature step. Prolonged pretreated specimens (above 160 h at 1050 °C) even show no changes during the two-step process (see Fig. 3).

Accepting the assumption that oxygen-related donor complexes act as double donors [15], the measured resistivity data allow the calculation of their total concentration. Figure 4 illustrates the dependence of the donor concentration on the pre-anneal time after four different second annealing steps at 450 °C. The first annealing phase (0–10 h at 1050 °C) points to a cooperation of several oxygen-related diffusion processes. The formation of thermal donors for samples with a 3 h second anneal reaches a maximum if a short pre-anneal (0.5 h) was made, but disappears again for longer low temperature treatment at this temperature. The curves in Fig. 4 show once again the substantial difference in donor formation between the as-grown and the pre-annealed material. The most interesting aspect seems to be the very significant increase of the donor concentration in the sample without pre-annealing in comparison to the specimen with only 0.5 h pre-anneal time. Moreover, there seems to be no influence of short-time treatments in the range 0.5–20 h (1050 °C) on donor formation during subsequent annealing. We found nearly the same values for all processes. Prolonged annealing up to 240 h effects the expected

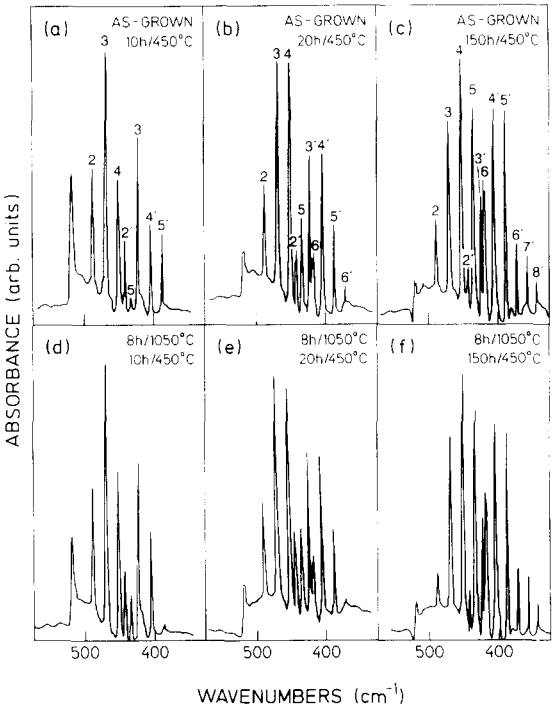

Fig. 5. Comparison of the absorption spectra of the thermal donor complexes in (a)–(c) as-grown and (d)–(f) pre-annealed (8 h at 1050 °C) samples. The spectral features are labelled by their donor complex number: 1–$2p_{\pm}$ transitions (1–6); 1–$2p_0$ transitions (1′–8′).

lowering of TD formation owing to the low concentration of dissolved oxygen.

The total number of TD defects depends strongly on the thermal history; consequently the question of which kind of thermal donors is formed is of great importance. Figure 5 shows the electrical transitions of the different neutral TDs (D_i^0, $i = 1$–8) of an as-grown ((a)–(c)) and a preheated (8 h at 1050 °C) ((d)–(f)) specimen with the same isochronal annealing steps at 450 °C. The figures (a) and (d), (b) and (e), etc. are nearly congruent. They only differ insignificantly in the absolute values of the absorption coefficients. This means that the same types of electrically active Si–O complexes [6] are formed, even in the case of quite different resulting electrical resistivities. Therefore the formation kinetics of these electrically active specimens depends only on the annealing time at 450 °C. No influence of thermal history on the formation of a special donor complex is observed. The ratio of the observed absorptions and their changes with increasing annealing time correspond well with the results obtained by other authors [10, 11].

4. Discussion

4.1. Interstitial oxygen behaviour and precipitation stages during heat treatment at 1050 °C

Heat treatments of as-grown CZ-Si at 1050 °C initiate several diffusion-controlled processes. At this temperature oxygen as the main impurity becomes extremely mobile and therefore is responsible for a variety of process-induced defects. The corresponding changes of dissolved oxygen determined by the IR technique, which is equal to the total amount of precipitated oxygen, point out that different stages of precipitation are produced during the high temperature annealing between 0.5 and 240 h. It is assumed that in the as-grown crystal a certain density of stable nuclei exists which will grow during the annealing process.

At the beginning of the annealing step (below 2 h) an anomalous behaviour of the interstitial oxygen concentration, illustrated in Fig. 1, occurs which is dependent on the starting conditions defined by the as-grown material. (1) The presence of a certain number of oxide microprecipitates in the as-grown material [16] with their variety of size distribution and density due to growth conditions and cooling rate represents a specific set of starting parameters. As a consequence of high temperature annealing, selective growth of microprecipitates takes place depending on their initial radius [17]. Only the aggregates whose radii are larger than the critical radius are stable and grow. Smaller grown-in Si–O units dissolve—which means that homogeneous nucleation is negligible under this thermal condition – leading to an increase of the oxygen concentration. (2) Furthermore, essential conditions for heterogeneous nucleation, which requires other impurities or structural irregularities, are to some extent present in the as-grown crystal. Mainly substitutional carbon, normally incorporated in the silicon lattice at a concentration of 10^{15}–10^{16} atoms cm^{-3}, seems to be able to act as a nucleation site [5].

Thus the behaviour of oxygen in CZ-Si can be described by a system of competitive reactions where the starting situation is not entirely well defined. The favoured kinetical and thermodynamical processes are decisive for the slight decrease or increase of the interstitial oxygen content. The result is a fluctuating behaviour of the interstitial oxygen concentration if the as-grown material is annealed at a high temperature for short times.

During further heat treatment for up to 10 h at 1050 °C the concentration of interstitial oxygen is nearly constant. This annealing phase can be regarded as a homogenization process, where atomic impurities and dopants are dispersed and there is a supersaturation of single point defects, while intrinsic point defects (silicon self-interstitials, vacancies) are substantially annealed out. Generation and growth of nuclei of oxide precipitates are greatly reduced.

The expected loss of interstitially dissolved oxygen due to agglomeration takes place after longer heat treatments. Efficient precipitation seems to begin first after a high temperature annealing for more than 20 h. Such behaviour can be explained by the nucleation incubation model recently proposed by Tan and Kung [18]. During a certain incubation period, where homogeneous nucleation is retarded, small but numerous dislocation loops are formed which act as sites for heterogeneous nucleation.

4.2. Thermal history and thermal donor formation

Isochronal annealing at 450 °C generates microdefects which have double donor character effecting a shift of the electrical properties of a sample owing to the added electron density. The results illustrated in Figs. 3 and 4 show that TD formation is a very sensitive function of thermal history. Three different phases related to a certain precipitation stage, already described above, have been found.

(1) The first is the as-grown state, which is the result of a complex thermal history during crystal growth and cooling. The sample additionally annealed at 450 °C shows, in contrast to preheated specimens, the expected value for the total concentration of electrically active oxygen clusters.

(2) Pre-annealing for between 0.5 and 10 h effects homogenization of the crystal defects. In spite of nearly the same initial O_i content of all samples after the preheat treatment a distinct relation between the limit value of the donor concentration and the thermal history is observed. The corresponding resistivity variation from the starting value decreases continuously with increasing pre-annealing time. However, the changes are not as large and significant as between the as-grown and 0.5 h pretreated sample.

(3) Further preheat treatment up to 240 h

effects a drastic lowering of the thermal donor formation. Owing to enhanced heterogeneous nucleation, oxygen precipitation occurs, which appears to prevent as a competition reaction the generation of donor complexes. Prolonged pre-annealed samples (above 160 h) do not change their resistivity during a subsequent heat treatment at 450 °C.

4.3. Influence of thermal history upon thermal donor formation kinetics

It has been well established that the phenomenon of "thermal donors" observed after heat treatment of CZ-Si at 450 °C is composed of several different electrically active oxygen clusters [6]. Results obtained from IR measurements at liquid helium temperature show numerous IR absorption bands due to the two series of electrical transitions of the helium-like double donors [6]. Up to now nine different specimens have been detected, allowing in particular the identification of the different donor clusters.

Absolutely unexpected is the result that the IR spectra of the as-grown and the different pre-heated samples are nearly congruent after isochronal heat treatment steps. With the exception of prolonged pre-annealed (above 80 h) samples, even the same values for the absorption coefficients are obtained (Fig. 5). This phenomenon points to a kinetic mechanism of donor formation which is quite similar in all cases. Both the thermal history and the initial concentration of dissolved oxygen do not show any influence on the formation of specific kinds of donor complexes and their corresponding concentrations, although the total concentrations of TDs, determined by resistivity measurements, are significantly lower for samples with long preheat treatment than for those with short pre-anneal times or, especially, for the as-grown material.

The observed dependence of the initial production rate of these active species on the initial oxygen concentration, displayed in Fig. 6, is in good agreement with the result achieved by Kaiser *et al.* [7]. Irrespective of the thermal history, the fourth-power dependence is valid for all samples. In contrast to this result, no linear correlation between initial oxygen concentration and maximum donor formation was found (Fig. 7). It appears that the expected third-power dependence is only valid for untreated material. This result points to different kinetic mechanisms, already discussed by other authors [11].

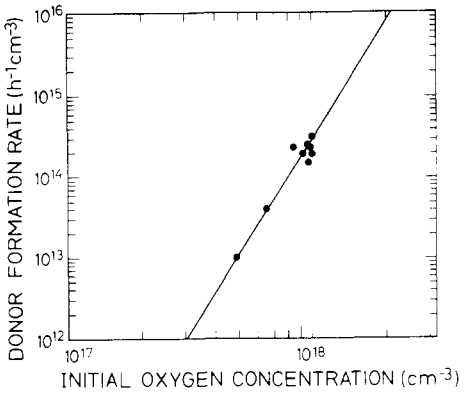

Fig. 6. Initial donor formation rate as a function of the initial oxygen concentration. The slope of the straight line is 4.2.

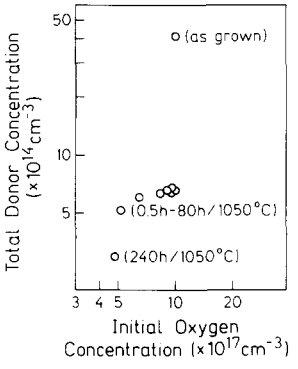

Fig. 7. Maximum donor concentration as a function of the initial oxygen concentration.

4.4. Ratio of precipitates and donors

Assuming that only the formation of thermal donors takes place during this process, we can correlate the changes in O_i with the corresponding changes in resistivity to calculate the average number of oxygen atoms of a donor complex. The value is between 20 and 400 per donor. However, the results of several investigations over the last few years have shown that this kind of defect consists of smaller SiO units or $Si_{(i)}O$ units [9, 11], which indicates that oxygen also takes part in other processes besides donor formation. The main reaction appears to be the growth of electrically inactive oxide precipitates, while the formation of electrically active species is only a side effect. Different competitive reactions could be responsible for this phenomenon.

It is well known that local lattice strain produced by the aggregation process during the 1050 °C treatment gives rise to a dependence of the effective diffusivity of oxygen on the time of annealing. The extent of donor formation as well as the ratio of electrically active and inactive

oxygen-related complexes are influenced by a certain stage of precipitation. Annealing of as-grown material at 450 °C introduces a concentration of donor states corresponding to the well-known third-power dependence [7]. In contrast to this result, in samples pre-annealed for between 0.5 and 20 h, where homogenization of all impurities takes place, fewer donors are produced although the initial oxygen concentration is nearly the same. Further preheat treatment (above 20 h) enhances the nucleation and growth of oxide precipitation accompanied by a lowering of the dissolved oxygen concentration and thus leads to a significant decrease of donor formation. The results indicate that the presence of a certain content of oxygen may not be the only factor in thermal donor formation.

Oxygen complexes are electrically active as shallow thermal donors if a defined configuration of the oxygen atoms is realized in the silicon lattice. Bourret *et al.* have found that these clusters form linear chains in the 110 direction [19]. The arrangement of such structures is probably a kinetically controlled process, which gives rise to a large number of side reactions where simultaneous formation of SiO clusters with the same number of oxygen atoms but different alignment occurs. This points to several types of precipitation kinetics during processing.

5. Conclusions

Effects of high temperature annealing at 1050 °C on the formation of oxygen-related thermal donors in CZ-Si have been investigated. The experimental data were compared with results achieved from samples without preheat treatment.

It has been shown that donor formation is a highly sensitive function of thermal history. Depending on the duration and type of the preheat processes, the yields of donor states generated after an isochronal low temperature step at 450 °C can vary strongly. Three phases of starting conditions corresponding to different stages of precipitation are observed.

The highest concentration is obtained after treatment of as-grown material, which represents a system of undefined thermal history due to the crystal growth process. There is evidence of the existence of hidden amounts of oxygen in the as-grown wafers and it is reasonable to assume that they partly exist as smaller units, which might act as nucleation sites for precipitates or donor clusters respectively.

Pre-annealing at 1050 °C for 0.5–10 h effects homogenization of pre-existing defects and removal of a large number of nuclei. In spite of a similar initial oxygen concentration, the donor concentration is essentially lower and decreases only slightly with increasing annealing time.

If the crystal is subjected to prolonged pre-anneal treatment for up to 240 h, the donor formation tends towards zero. Enhanced nucleation due to process-induced crystal defects and lowering of the dissolved oxygen content are responsible for this behaviour.

The content of a certain amount of interstitial oxygen is not the only factor in the generation of oxygen donors. Numerous defect-associated interactions appear to play an essential role in this process. The well-known third-power proportionality between the initial oxygen and the maximum concentration is only valid for untreated material. However, the initial production rate does not show any influence of the thermal history.

It appears that several types of precipitation kinetics exist, depending on the thermal process conditions, as a result of parallel diffusion mechanisms, which may be described by combinations of different diffusion coefficients. Only a small fraction of the formed oxygen clusters are realized as donor complexes. It is possible that internal oxygen gettering is favoured owing to local strain fields associated with oxygen aggregates formed during 1050 °C heat treatment.

Although the donor formation reacts sensitively upon thermal processes, IR studies at liquid helium temperature have shown that the formation kinetics and the proportion of the single-donor species are independent of any thermal history.

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