Mechanism of Internal Gettering of Interstitial Impurities in Czochralski-Grown Silicon

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Results of the low-temperature precipitation of interstitial Fe ($\approx 250\,^\circ$C) in Czochralski-grown Si after different annealing treatments for the precipitation of oxygen are presented. It is concluded that the Fe solubility is not affected by the oxygen-precipitation process. The Fe-precipitation kinetics are found to be strongly accelerated by oxygen-precipitation–induced defects. Based on the results the mechanism of internal gettering is derived. For the first time the contribution of oxygen precipitates and dislocations to the internal-gettering process have been determined quantitatively.

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Internal gettering (IG) of metallic impurities in Czochralski-grown silicon (CZ-Si) by the precipitation of oxygen (also called intrinsic gettering) has proven indispensable in semiconductor technology to improve the yield of integrated-circuit devices. 3*d*-transition elements like Fe, Ni, and Cu are the prevalent contaminants in Si which, after rapid diffusion during a high-temperature treatment, degrade device performance either by forming metal silicides or by acting as recombination centers as isolated defects or small complexes. In addition to its technological importance IG has been the subject of extensive research[1] which is also reflected in the vast literature on O in Si.[2]

The terminology "gettering" has often been confused with heterogeneous precipitation. We will use a quite general definition of gettering, a modification of the one given by Ourmazd and Schröter:[3] Gettering means the reduction of impurities in part of a wafer by localizing them in predetermined regions (away from those to be occupied by devices). In the following we want to distinguish between internal and external gettering rather than calling it intrinsic or extrinsic. External gettering is brought about by intrinsic or extrinsic defects by an external treatment like ion implantation, phosphorus diffusion, surface damage, etc. Internal gettering is provided by intrinsic or extrinsic defects created in the interior of the crystal after annealing which up to now has been only achieved in CZ-Si by the precipitation of O.

IG becomes active after the following heat treatment:[4] annealing of the wafer above 1150 °C for the outdiffusion of O, followed by a nucleation of O precipitates at around 700 °C. Usually a third annealing at around 1000 °C is used to accelerate the O-precipitate growth. Because of the high supersaturation of O required for the formation of stable nuclei O precipitates do not form in the near-surface region where outdiffusion occurred. This results in a zone free of O precipitates (denuded zone) which will become the device area to be kept clean from metallic impurities.

Despite many publications on this topic the mechanism of IG has not been clarified yet. It is not even clear at which process step IG occurs: In most papers it is assumed without justification that it is a dynamic process occurring during a high-temperature treatment. The precipitation of O above 700 °C produces mainly three types of defects:[5] dislocations, stacking faults, and O precipitates. About 85% of the precipitated O is found as amorphous SiO_x ($x \approx 2$), the density of Si being lower than in the host matrix. Depending on the temperature the associated strain of the precipitates can be partly relaxed by the punching out of dislocations or by the emission of Si interstitials. The latter may result in the formation of extrinsic stacking faults. Most models of IG have incorporated the supersaturation of Si interstitials to be essential for efficient gettering.[3-8] Other papers have concentrated on the identification of gettering sites.[3,9,10] All of the three O-precipitation–induced defects were found to be decorated by metallic impurities.

In this paper we report a novel experimental approach to the understanding of the IG mechanism. We will show in the following that the low-temperature Fe-precipitation kinetics ($\approx 250\,^\circ$C) allow for the first time a direct quantitative evaluation of the IG process. The experimental results lead to the conclusion that *the mechanism of IG is based upon the difference between the precipitation kinetics of metallic impurities in the denuded zone and in the bulk near O precipitates.* The IG process requires the supersaturation of mobile metallic impurities which usually occurs in device processes during cooling. From our quantitative analysis we have identified O precipitates to be responsible for IG. Si interstitials were found not to be directly involved in the IG process.

In our study Fe was chosen as a model impurity because it is one of the most abundant contaminants in Si technology and its concentration can easily be detected by electrical measurements. We used Siltec *n*-type CZ-Si grown in ⟨100⟩ direction. The O and C contents measured by Fourier-transform infrared spectroscopy were $1.1\times10^{18}/\mathrm{cm}^3$ (IOC 88 standard) and $2\times10^{16}/\mathrm{cm}^3$, respectively. Preannealing at 700 °C was followed by annealing at 950 °C or 1050 °C to saturate the samples with Fe and simulate the final IG step. After quenching in ethylene glycol (rate $\approx$ 1000 K/s) the precipitation kinetics were determined from the decay of neutral interstitial Fe, Fe_i^0, upon isothermal annealing between 200 °C and 300 °C in an Ar:H_2 ambient. Electron paramagnetic resonance (EPR) was used to measure the concentration of Fe_i^0.

Figure 1 shows two typical examples of the decay of Fe_i^0 upon annealing at 280 °C. Curve I has been obtained after annealing at 700 °C for 4 h following 1050 °C for 2 h. It can clearly be seen that the kinetics are simple exponential from the very beginning. The dependence of the residual Fe concentration, C, on annealing time can be described by a time constant τ: $C=C_0\exp(-t/\tau)$. The dependence of τ on the annealing temperature shows an Arrhenius-type behavior with an activation enthalpy of 0.70 ± 0.03 eV which is in good agreement with the migration enthalpy for the diffusion of interstitial Fe (0.68 eV).[11] This strongly suggests that the precipitation kinetics are limited by the diffusion of interstitial Fe. Using Ham's[12] theory the time constant for precipitation can be related to the diffusion coefficient, D_i, of the precipitating species:

$$1/\tau=4\pi D_i n r_0\,, \tag{1}$$

where n is the density of the precipitates and r_0 is the mean radius. By contrast, in virtually O-free float-zone Si (FZ-Si) and shortly annealed CZ-Si a significant deviation from the exponential behavior was observed at the beginning of the precipitation, as illustrated by curve II in Fig. 1. This behavior is to be expected if the size of the precipitates vary considerably with annealing time.

Figure 2 shows the decay of the concentration of Fe_i^0 during annealing at 235 °C for samples preannealed at 700 °C for a time as indicated by the numbers at each curve. The as-quenched Fe concentrations obtained after annealing at 1050 °C for 2 h ($t=0$ min in Fig. 2) as well as the time constants vary by up to 1 order of magnitude. The reduction of the as-quenched Fe concentration turns out to be directly correlated with an accelerated Fe-precipitation kinetics: The Fe concentration found after quenching decreases exponentially with increasing $1/\tau$ of the Fe-precipitation kinetics.

The dependence of the time constant for the Fe precipitation on the precipitation of O clearly shows that heterogeneous precipitation of Fe dominates in Si with O-precipitation–induced defects. In that case a high impurity supersaturation is not necessary: The Fe precipitation during cooling can start immediately below the annealing temperature. Calculating the time constants at that temperature using Eq. (1), it takes about 0.1 s for all samples to reduce the Fe concentration from the value measured in FZ-Si to the one obtained after quenching. This is apparent from the intersection of the curves in Fig. 2 if negative times referring to the kinetics during quenching are rescaled by the Fe diffusion coefficient at around 1000 °C (factor 9×10^{-5}) where random motion during quenching is largest. Calculated from our quenching rate, 0.1 s is approximately the time Fe was able to diffuse during quenching. Based on these findings we conclude that the reduced Fe concentrations are the result of precipitation during quenching.

This conclusion has important consequences for the IG mechanism: (1) The precipitation of O does not affect the Fe solubility at 1050 °C. (2) The correlation between the as-quenched Fe concentration and the low-temperature Fe-precipitation kinetics shows that low-temperature precipitation annealing can be used to determine the precipitation kinetics of Fe at higher tem-

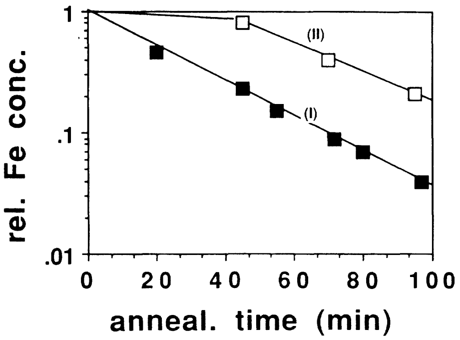

FIG. 1. Reduction of the concentration of interstitial Fe upon annealing at 280 °C. The concentrations are given with respect to the initial Fe concentrations of $7.2\times10^{14}/\mathrm{cm}^3$. Type-II curves were obtained in FZ-Si or shortly annealed CZ-Si; type-I curves, otherwise.

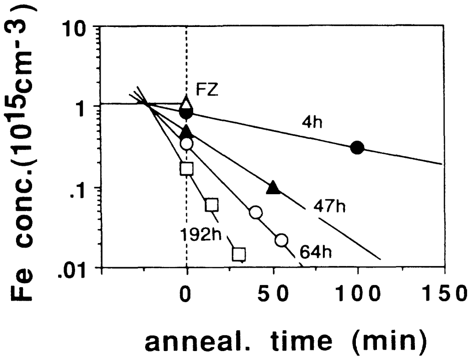

FIG. 2. Dependence of the Fe concentration on annealing at 235 °C. For $t=0$ min Fe concentrations as-quenched from 1050 °C are plotted. The numbers at each curve denote the preannealing time at 700 °C.

peratures as long as it is dominated by heterogeneous nucleation.

Our interpretation of the reduced Fe concentrations in CZ-Si does not require a new Fe-containing phase as proposed previously.[6] The solubility in CZ-Si is identical with that in FZ-Si independent of the annealing treatment. Neither does the emission of Si_i affect the solubility of interstitial Fe. Therefore a dynamic process of IG of interstitial impurities by Si_i can be excluded.

Assuming that the precipitation behavior of Fe in the denuded zone is comparable to as-grown CZ- or FZ-Si we propose the following model of IG of interstitial impurities. During a high-temperature treatment (T_0) contamination by an interstitial impurity will be distributed uniformly (concentration C_0) in the wafer irrespective of O precipitates and related defects. Upon reduction of the temperature (T_1) the impurities become supersaturated (equilibrium concentration $C_1 < C_0$), triggering the IG process.

(1) Any impurity supersaturation is precipitated heterogeneously in the bulk. In the denuded zone the heterogeneous nucleation rate is small, while homogeneous precipitation requires a high supersaturation, i.e., a high supercooling.

(2) After a short time the supersaturation in the bulk has disappeared, but not in the denuded zone.

(3) The concentration gradient of interstitial impurities between the denuded zone and the bulk is the driving force for diffusion into the bulk.

(4) Fe diffusing into the bulk will be precipitated immediately. The transport continues until the equilibrium concentration C_1 is reached in the denuded zone.

A microscopic model of IG is not complete without identification of the gettering site. Therefore we have measured the dependence of the Fe-precipitation kinetics on the high-temperature annealing time to compare it with the precipitation of O. One set of samples did not receive a 700 °C preannealing but only annealings for various times at 950 °C. Two other sets were preannealed at 700 °C for 4 h followed by a 950 °C or 1050 °C annealing. Figure 3(a) shows the change of the measured Fe-precipitation time constants with the high-temperature annealing time. Before and after each annealing the residual concentration of interstitial O was measured as shown in Fig. 3(b). Qualitatively both figures show a similar behavior.

(1) Without the low-temperature annealing the Fe and O precipitations are slow (low $1/\tau$ value).

(2) A 4-h preannealing at 700 °C is sufficient to drastically enhance the Fe as well as the O precipitation.

(3) For the two preannealed sets the Fe precipitation is faster after the 950 °C than after the 1050 °C annealing. The same holds for the O precipitation.

(4) The retardation of the Fe precipitation after long annealing times shows that a dissolution of the nucleation sites occurs. This is also indicated for the O precipitates from the interstitial O concentration which for long annealing times approaches the equilibrium concentration rather slowly.

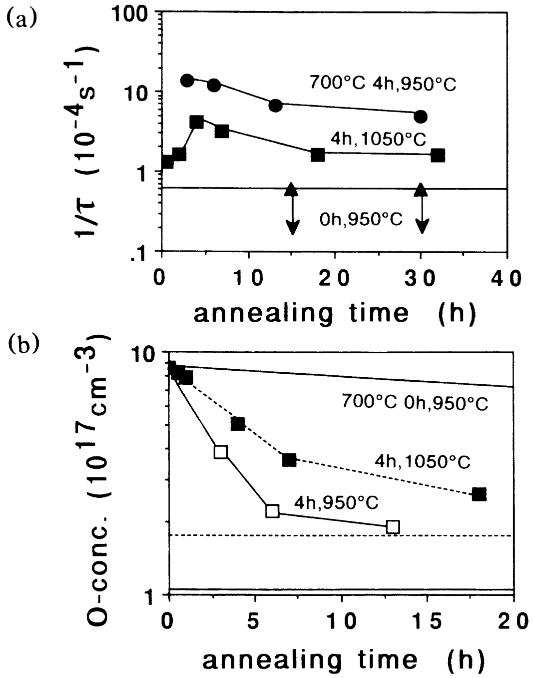

FIG. 3. Comparison between the Fe- and O-precipitation kinetics. (a) Dependence of the Fe-precipitation kinetics ($1/\tau$) on annealing time at 950 °C (triangles and circles) and 1050 °C (squares). The preannealing times at 700 °C are indicated. (b) Dependence of the interstitial O concentration on annealing at 950 °C (solid lines) or 1050 °C (dotted line). The horizontal lines indicate the solubility of oxygen at these temperatures. The preannealing times at 700 °C are indicated.

Binns *et al.*[13] have shown from a comparison with neutron-scattering and etch-pit-density measurements that Ham's theory of diffusion-limited homogeneous precipitation can be used to determine the density of O precipitates. In order to quantitatively compare the density of O precipitates and nucleation sites for Fe precipitation we have used Eq. (1) to calculate the products nr_0. Note that we can only compare the products because it is not possible to obtain n and r_0 separately from the Fe-precipitation kinetics. In the case of O we have determined the time constant of precipitation from the initial slope of the values in Fig. 3(b) corrected by the equilibrium concentration of interstitial O. Taking as reference the time at which about half of the O has precipitated the result is as follows: 3 h, 950 °C,

$$nr_0(\mathrm{O}) = 9.9\times10^5/\mathrm{cm}^2,\quad nr_0(\mathrm{Fe}) = 4.8\times10^5/\mathrm{cm}^2;$$

4 h, 1050 °C,

$$nr_0(\mathrm{O}) = 1.3\times10^5/\mathrm{cm}^2,\quad nr_0(\mathrm{Fe}) = 1.5\times10^5/\mathrm{cm}^2.$$

This overall agreement shows clear evidence that in our material it is the O precipitates that govern the Fe precipitation. Stacking faults and dislocations that have been proposed as gettering sites would have to be present in similar or even higher densities to provide a comparable nr_0. For stacking faults this is not the case. For dislocations we have used Ham's theory of diffusion-limited precipitation along cylindrical particles to calculate that at least 4×10^6 dislocations/cm^2 are necessary to account for the precipitation time constant in our fastest-precipitating material. We have experimentally deduced from the Fe-precipitation behavior in plastically deformed FZ-Si containing about 2×10^9/cm^2 dislocations[14] that, in fact, this is roughly the density necessary to obtain Fe-precipitation kinetics comparable to those shown in Fig. 2. As the dislocation density in CZ material is typically less than 10^5/cm^2, their gettering efficiency is about 4 orders of magnitude smaller than can be achieved by O precipitates. Therefore we expect that, in order to optimize IG processes, heat treatments that produce a high density of stable O precipitates have to be developed. The decoration of O precipitates by transition elements has been verified by high-resolution electron microscopy in the case of Ni.[3] Our identification of O precipitates as the dominant gettering sites provides a simple explanation of the different Fe-precipitation kinetics as was shown in Fig. 1. If the precipitation of Fe around the O precipitates does not change the radius substantially the precipitation kinetics will show a simple exponential decay of interstitial Fe from the very beginning (curve I in Fig. 1). In the other case a deviation of the simple exponential dependence occurs at the beginning of the precipitation process when the change in the precipitate radius is largest. It remains to be investigated whether the heterogeneous precipitation of interstitial impurities depends on the existence of strain fields around the O precipitates.

In summary, we have deduced from a quantitative analysis of the Fe-precipitation behavior in CZ-Si that the mechanism of IG is based upon an enhanced precipitation of interstitial impurities in the vicinity of O precipitates. For the first time IG efficiencies can be quantified by measuring the Fe-precipitation kinetics at low temperatures. We have identified O precipitates as the dominant gettering sites whereas dislocations and stacking faults do not seem to play a significant role. Our model has far-reaching consequences in the evaluation of gettering processes. It implies that a high-temperature step after IG will immediately release the impurities which is not the case for external gettering by phosphorus diffusion.[15] It predicts that the temperature at which gettering starts depends strongly on the impurity and its concentration. And finally we wish to point out that according to our results the Fe precipitation itself can be used to determine the density and average size of O precipitates and thus provides a convenient technique to study dissolution and coarsening phenomena of the O precipitation.

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