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On the dislocation–oxygen interactions in Czochralski-grown Si: oxygen diffusion and binding at low temperatures

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Abstract

The interaction between oxygen atoms and dislocations in Czochralski-grown silicon has been studied experimentally. Measurements concerning the locking of dislocations by oxygen atoms have been carried out in the temperature range 450–850 °C for different annealing times. Using samples with low oxygen content (2.6×10^{17} cm^{-3}) it has been possible to investigate the nature of binding of oxygen atoms to dislocations for temperatures lower than 700 °C for which diffusion of oxygen in silicon has well known 'anomalous' behaviour. It has been found that although the binding enthalpy for temperatures larger than 700 °C agrees well with the previously published value, its value is different for lower temperatures. We measured the oxygen–dislocation binding enthalpy to be about 0.2 eV in the temperature range of 450–650 °C.

1. Introduction

The presence of oxygen in Czochralski-grown (Cz-) silicon as an interstitial impurity in high concentrations ($(5\text{–}10) \times 10^{17}$ cm^{-3}) is one of the reasons that Cz-Si is used almost exclusively for the production of very-large-scale integrated circuits. In comparison to float-zone silicon, Cz-Si has a better mechanical stability and this is attributed to oxygen [1]. Since the mechanical strength of a crystal is determined by mobile dislocations, a suppression of dislocation motion results in higher mechanical strength [2]. At elevated temperatures typical for device processing, oxygen atoms diffuse to the dislocations effectively leading to immobilization, or locking, of dislocations [3, 4]. The stress needed to start a locked dislocation moving is called the unlocking stress and it depends on the number of oxygen atoms diffused to the dislocation.

We studied oxygen–dislocation interactions experimentally and theoretically for the temperature range of 450–850 °C for different annealing times and oxygen concentrations. Our results concerning medium and high oxygen concentrations have been published elsewhere [5, 6]. Here we present the results obtained using Cz-Si samples with very low oxygen concentrations. The use of samples with low oxygen content allows us to investigate the transport behaviour of oxygen atoms at lower temperatures ($<700\,^{\circ}$C) as well as the characteristics of their binding to dislocations. This low-temperature range is of interest because of the well known 'anomalous' oxygen transport behaviour at low temperatures [7, 8]. Since the number of oxygen atoms at the dislocation core is controlled by the diffusion of oxygen to the dislocation core, the study of the unlocking stress as a function of annealing time will produce some insights into oxygen transport.

Previously we reported that the oxygen transport and segregation to the dislocation core as a function of annealing time show five regimes [5]. Firstly, the number of oxygen atoms at the core increases almost linearly with the increasing annealing time. Following the initial rise, the unlocking stress then saturates, which indicates a steady-state regime. The value of the unlocking stress in the steady-state regime depends on annealing temperature and oxygen concentration. Assuming a Maxwell–Boltzmann distribution for oxygen atoms at the dislocation core, we were able to deduce the oxygen–dislocation interaction energy by using the temperature dependence of the unlocking stress. We also reported that following the saturation regime, the unlocking stress as a function of annealing time shows a sudden increase followed by a second saturation and a rapid decrease. This behaviour was attributed to precipitation of oxygen at the dislocation core.

In this paper we give the results of measurements carried out to determine the unlocking stress of dislocations in Cz-Si using samples with very low oxygen content. Following a short description of the experimental method employed, we present the experimental results. Moreover, we discuss the transport of oxygen atoms and their binding to dislocations.

2. Experimental method

Rectangular samples with dimensions 0.65 mm × 3 mm × 25 mm were cleaved from dislocation-free (001) Cz-Si wafers (p-type, 10 Ω cm). The oxygen concentration of samples was 2.6×10^{17} cm^{-3} (DIN 50438/I). Well defined dislocation arrays were then produced in a two-stage procedure. First the sample surface was damaged in a controlled manner to introduce dislocation sources. Then samples were stressed by employing a four-point bending technique at high temperatures to produce dislocation half-loops extending from damaged areas. After the generation of dislocations, surface damage was removed to prevent further dislocation generation during later stages of experiments.

Following the creation of dislocation arrays, samples were annealed at temperatures between 450 and 850 °C to allow oxygen to diffuse to dislocations to generate a locking effect. After this high-temperature treatment a surface layer of about 50 μm was removed to prevent any influence of oxygen out-diffusion. Afterwards, samples were stressed using a three-point bending technique to determine the unlocking stress. Since during the three-point bend test each dislocation array experiences a different stress, only those exposed to a stress larger than the unlocking stress grow while other dislocation loops remain the same size as after the four-point bending. A preferential etch was then used to determine the position of dislocation loops in the specimen, from which the unlocking stress was deduced. The temperature of the three-point bend test was the same for all specimens (550 °C) unless otherwise stated.

3. Experimental results and discussion

In figures 1(a)–(d) the unlocking stress is plotted at four different annealing temperatures. For comparison, previously published data for samples with higher oxygen content are also included in figures 1(a)–(c). In almost all experiments the initial rise and subsequent saturation

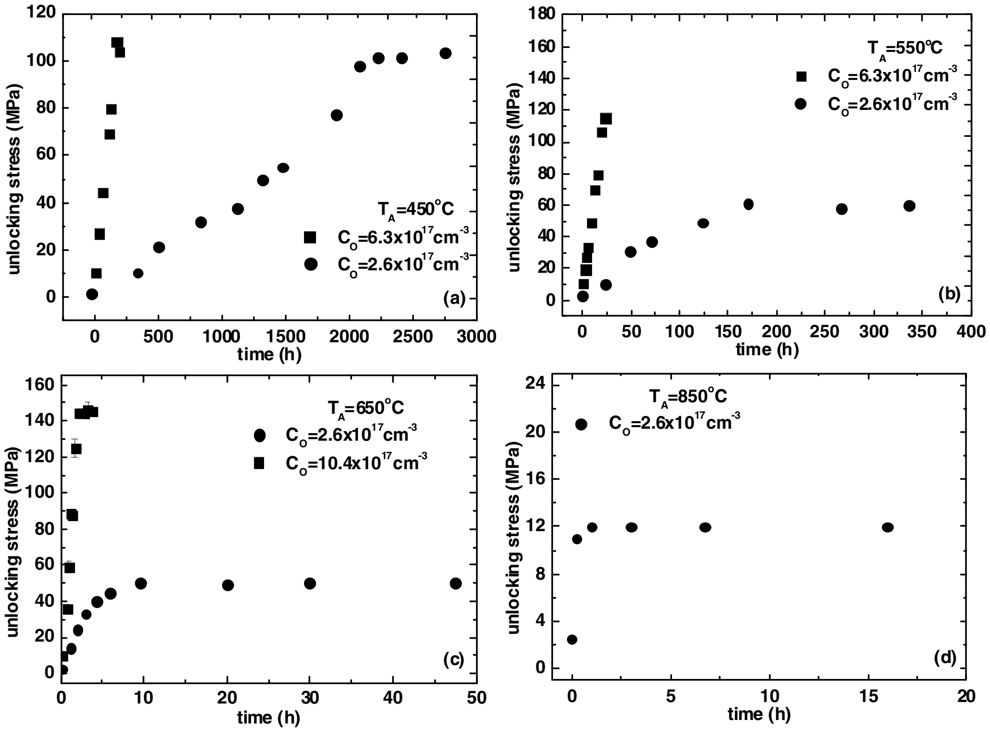

Figure 1. The unlocking stress as a function of annealing time for temperatures (a) 450 °C, (b) 550 °C, (c) 650 °C and (d) 850 °C.

were observed. For the 850 °C annealing, however, the initial rise regime was too short to capture experimentally; even the shortest possible annealing resulted in an unlocking stress value in the saturation regime. As one can see from the figures, at the early stages of annealing the oxygen concentration at the dislocation core increases rapidly; the rate of change of oxygen at the core for a given temperature is determined by the effective diffusivity of oxygen. Thus, an analysis of this regime yields information on the oxygen diffusivity [6].

With increasing annealing time, the concentration of oxygen at the core increases and when the local equilibrium with the background oxygen concentration is established the value of the unlocking stress saturates. The unlocking stress then becomes independent of time because the rate of capture and thermal excitation of oxygen away from the dislocation are nearly equal. In this regime the concentration of oxygen at the core decreases as the temperature increases. Since in the equilibrium state the oxygen atoms at the core will establish a Maxwell–Boltzmann concentration distribution, the saturation regime is characterized by the concentration of oxygen at the far field of diffusion C_O, and the interaction energy between an oxygen atom and a dislocation, ΔG. Assuming that the unlocking stress is proportional to the number of oxygen atoms at the dislocation core, the unlocking stress τ_u can be written as

$$\tau_u = K C_O \exp\left(-\frac{\Delta S}{k}\right) \exp\left(\frac{\Delta H}{kT}\right) \tag{1}$$

where for the oxygen–dislocation binding energy the thermodynamic relationship $\Delta G = \Delta H - T\,\Delta S$ is used. In equation (1), K is the proportionality factor, ΔS is the entropy change, ΔH is the enthalpy change, k is Boltzmann's constant and T is the absolute temperature.

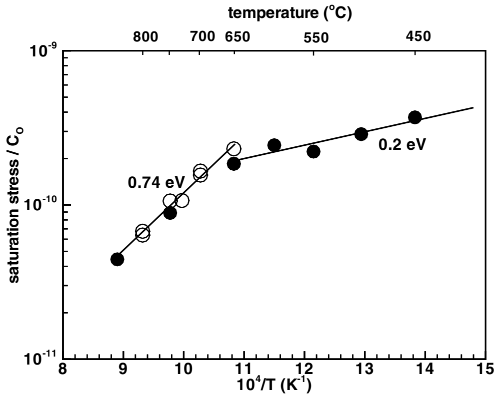

Figure 2. The saturation stress normalized by the oxygen concentration as a function of the reciprocal temperature. Closed circles indicate the results obtained in this work using low-oxygen-content samples. Previous data obtained using samples with higher oxygen concentration (open circles) [5] are also shown.

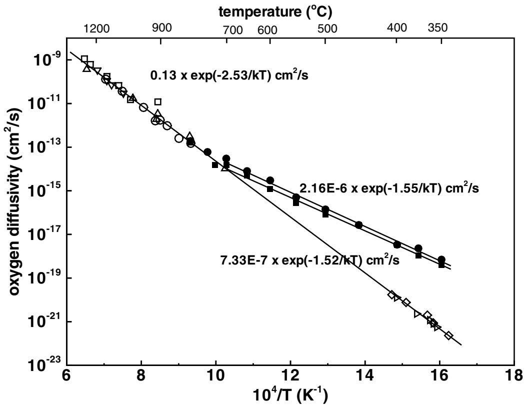

Figure 3. Oxygen diffusivity as a function of the reciprocal temperature [6]. Open symbols show data obtained by other workers [9]. Closed symbols show data obtained using samples with two different high oxygen contents [5, 6]. The best fit to the data is also shown for each case (lines).

An Arrhenius plot of the saturation values of the unlocking stress obtained from figure 1 can be used to determine the value of ΔH. In figure 2, values of the unlocking stress normalized by the oxygen concentration are shown for temperatures between 450 and 850 °C together with the best fit to equation (1). The striking observation from figure 2 is that not just one but two different oxygen–dislocation interaction enthalpies can be deduced. For temperatures larger than 650 °C, ΔH is 0.74 eV. The new binding enthalpy measurements presented here for the low-oxygen-content specimens are in very good agreement with our previous data obtained for specimens with higher oxygen content in the temperature range 650–850 °C. However, the low-oxygen-content specimens have allowed us to measure the saturation behaviour at much lower temperatures than was previously possible. Our new data have shown a markedly different behaviour in the low-temperature range of 450–650 °C. In this regime a binding enthalpy of 0.2 eV has been found.

Figure 3 shows a plot of effective diffusivity versus temperature obtained for high-oxygen-content samples by analysing the initial rise in the dislocation unlocking stress as a function of time. From these data we have inferred that the species responsible for oxygen transport in silicon are different in different temperature ranges. Above 650–700 °C our results are consistent with transport being controlled by single oxygen atoms as determined by other workers. But below this temperature a different species dependent on the oxygen concentration is responsible for the transport of oxygen.

Comparison of the binding enthalpy data with the diffusivity data suggests that below 650–700 °C the movement of oxygen in silicon is effected by a species other than the single oxygen atoms and that this also results in dislocation locking by a species different from that at high temperatures. In this case the binding enthalpy is 0.2 eV compared to the high-temperature value of 0.74 eV. Work is under way to determine the nature of the species responsible for the low-temperature behaviour.

4. Conclusions

The experimental study of dislocation locking by oxygen atoms in the temperature range of 450–850 °C using Cz-Si samples with very low oxygen content has produced some unexpected results. Although the locking of dislocations by oxygen as a function of annealing time follows similar trends to what was observed previously at temperatures larger than 650 °C, lower-temperature treatments result in a significantly different oxygen–dislocation binding behaviour. We found an oxygen–dislocation binding enthalpy of about 0.2 eV at lower temperatures which is markedly different to the binding enthalpy of 0.74 eV found at higher temperatures. From comparing the binding enthalpy data with the diffusivity data for oxygen, it has been suggested that below 650 °C the transport and binding of oxygen in silicon are by a species other than single oxygen atoms.

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