Effect of high-magnetic-field on dislocation-oxygen impurity interaction in Si

I Yonenaga and K Takahashi
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai, 980-8577, Japan
E-mail: yonenaga@imr.tohoku.ac.jp

Abstract. This paper reports effects of magnetic-treatments on an interaction between dislocations and oxygen impurity in Si. Though oxygen impurity in Si has a strong effect of immobilizing dislocations due to preferential segregation and formation of precipitates along dislocations at elevated temperatures, the capability of immobilization of the oxide precipitates against dislocations decreases under an application of magnetic field higher than 5 T and loses almost completely at 10T. These results suggest a spin-dependent solid-state reaction in oxygen impurity-dislocation interaction in Si.

1. Introduction
Utilization of a high magnetic field has received keen attention in recent years for clarifying basic properties of materials and also for the development of various devices incorporating magnetic, superconductive, and spintronic materials. The properties and structures of crystalline defects like as dislocations, which affect the functionalities of various types of materials, including semiconductors, are being investigated by various methods, with rather weak magnetic fields, for example, Hall effect, EPR- and NMR-spectroscopic measurements. By detecting the accompanying paramagnetic centers such as electrons, holes, radicals, excitons, and so forth with such methods, the properties and structures of defects can be identified. It is interesting to investigate a possibility to modify defect properties and structures, accompanying atomic displacements, through interactions with magnetic impurities under a magnetic field. Though such research is even now quite limited, Russian groups recently reported enhancement of plasticity with dislocation motion in ionic crystals, metals and alloys and semiconductors with paramagnetic impurities under a low magnetic field up to 2 T [1–3]. Thus, we may expect pronounced effects on defect modifications by application of high magnetic field.

Silicon, non-magnetic, contains paramagnetic oxygen impurity in a concentration of $\sim 10^{18}$ cm$^{-3}$. It is well known that oxygen impurity interacts with dislocations [4, 5], and thus the interaction may be modified under a high magnetic field. Herein, this paper reports preliminary results of dislocation-oxygen impurity interactions in a typical semiconductor Si influenced by magnetic treatments at high temperatures under a high field up to 10 T.

2. Experiments
Specimens were prepared from a dislocation-free CZ-Si crystal (p-type: $13 \Omega \cdot$cm) which contained oxygen impurities in a concentration of $1.1 \times 10^{18}$ cm$^{-3}$ determined by FT-IR spectroscopy. The specimens were of a rectangular shape, approximately $2 \times 3 \times 15$mm$^3$ in size, and with the long axis in...
the direction \([\overline{1}0]\) and the side surfaces parallel to (111) and (11\overline{2}). The surfaces were finished chemically with HF:HNO₃ reagent at a ratio 1:5 at 30–40°C following mechanical polishing. Scratches were drawn on the (111) and (1\overline{1}₁) surfaces along the [1\overline{1}0] long axis at room temperature (RT) with a diamond stylus. Such scratches serve as preferential generation centers for dislocations when stressing the specimen at elevated temperatures.

First, specimens were pre-annealed at 900°C for 15 min to form oxygen precipitates along dislocations nucleated around the scratch induced in advance. Then, specimens were magnetic-treated at 700°C under an application of magnetic field up to 10 T for duration from 1 hour in a furnace installed into a cyclo-cooled superconducting magnet (11T-CSM) in the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University. The treatments were conducted in a flowing argon gas atmosphere.

The magnetic-treated specimens were, then, stressed at 700°C in a vacuum by means of three-point bending along the [11\overline{2}] axis. Dislocations generated and moved into the matrix from the scratch were detected by observing the etch pits, developed by the Sirtl etchant [6] at 20°C. The geometry of the specimens as well as the details of the experimental procedure have been described in a previous article [4, 5].

3. Results
The generation and motion of dislocations from a scratch into the matrix under various stresses was investigated in various magnetic-treated specimens together with as-grown and pre-annealed specimens.

Figure 1 shows the distribution of dislocation etch pits on the (111) surface of an as-grown specimen that was subjected to a maximum resolved shear stress of 30 MPa by three-point bending at 700 °C for 60 min. Linear arrays of etch pits emerging from the scratch in both the upward and downward directions are those of dislocations emitted from the scratch. It is seen that dislocations are generated preferentially from the scratch under applied stress.

The distance travelled by the leading dislocation in an array of dislocations that generated and merged from a scratch into the matrix during a 60 min stress pulse at 700°C was determined by observation of their etch pits. Figure 2 shows the relation between the travelling distance of leading dislocations against the resolved shear stress for as-grown, pre-annealed at 900°C for 15 min and then magnetic-treated CZ-Si specimens under a magnetic field of 10 T for 1 hour at 700°C. In the figure it is known that there is no dislocation generation from a scratch in a stress region lower that 15 MPa, that is, a critical stress for dislocation generation from a scratch exists in all the CZ-Si specimens. Once the stress exceeds the critical stress, the travel distance in the specimens increases with stress. At stress higher than 20 MPa, the travelling distances of the various specimens are almost comparable. The magnitude of the critical stress depends strongly on the adopted treatments. For example, the critical stress for dislocation generation is ~5 and 15 MPa in as-grown and pre-annealed CZ-Si, respectively, while the critical stress is as low as ~8 MPa in the specimen under 10T, same as that of the as-grown specimen.

Figure 3 shows the variation in the critical stress for dislocation generation against the intensity of the magnetic field for the duration of 1 hour at 700°C. A line
superimposed in the figure is the critical stress for dislocation generation in the as-grown (CZ-Si) specimen. By application of magnetic field for 1 hour at 700°C, the critical stress shows a dramatic reduction against the applied magnetic field: the critical stress first keeps ~ 15MPa until the magnetic field of ~5T and then decreases steeply to approach to a stress level of the as-grown specimen at 900°C Si crystals.

Figure 2. Travel distance of leading dislocations generated from a scratch during a 60-min stress pulse at 700 °C in Si crystal magnetic-treated at 700°C with 10 T plotted against the stress together with those in as-grown and pre-annealed at 900°C Si crystals.

Figure 3. Variation in the critical stress for dislocation generation against the magnetic field intensity of the magnetic treatment at 700°C in Si crystals.
4. Discussion
The observed results suggest that dislocation generation from a surface scratch in CZ-Si is significantly affected by the magnetic treatment.

First the following should be noted: The existence of a critical stress for dislocation generation has been often observed for dislocations in Si and other semiconductors [e. g., Refs. 4, 5, 7] doped with certain kinds of impurities, including oxygen. Indeed, no appreciable critical stress is measured for dislocation generation in oxygen-free Si crystals. The phenomenon is well recognized that dislocations are nucleated from a scratch and then immobilized through the segregation and complex formation of impurity atoms along the dislocation lines due to a dislocation-impurity interaction, even while the crystal is being heated to elevated temperatures. Concretely, oxygen impurity in CZ-Si has a strong immobilization effect of dislocations due to preferential segregation and formation of SiO$_2$ complexes along dislocations at elevated temperatures [4, 5]. Therefore, the critical stress for dislocation generation from a scratch observed in the present study in CZ-Si can be understood as the stress required to initiate dislocation motion from the immobilized state and to penetrate into the matrix crystal, which can be detected macroscopically as dislocation generation from the scratch.

In the above-mentioned concept, it is understood in the present results that the magnetic treatments can affect immobilization phenomenon of oxygen impurity or their complexes against dislocations in Si through modification oxygen-dislocation interaction. The underlying microscopic process induced by application of high magnetic field is not clear at present, however it may note that as a plausible model Russian group proposed singlet- to triplet-state transition by exposure to a magnetic field up to 2 T [3]. That is, oxygen complexes may lose the ability to immobilize dislocations due to the singlet-to-triplet-state transition by exposure to a magnetic field, resulting in easy motion of dislocations.

The details of dislocation-impurity interaction in Si doped including various impurities, especially paramagnetic impurities and the basic mechanism of the spin-dependent solid-state reaction will be clarified in a future, together with theoretical approach. The clarification is important for understanding the kinetics and the process of the solid-state chemical reactions on defects in materials.

5. Summary
The present article has revealed that magnetic field has an apparent modification effect on dislocation-oxygen impurity interaction in Si. The critical stress for dislocation generation, the process of which is governed by release dislocations from SiO$_2$ complexes, decreases under a magnetic field higher than 5 T and loses almost completely at 10T. These results suggest a spin-dependent solid-state reaction in O impurity-dislocation interaction in Si.

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