PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT III, 1963

Oxygen Impurity Atmospheres around Dislocation in Silicon*

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Photoscanning data on small-angle grain boundaries suggest the influence of oxygen impurities upon the electrical behavior of edge dislocations in silicon. Magnitude and polarity of the grain boundary photoresponse may be changed by heat treatments. These changes can be correlated with the known phase transitions of oxygen in silicon.

Evidence is presented for the important influence of oxygen atmospheres upon the electrical behavior of edge dislocations in silicon.

Silicon crystals with small-angle grain boundaries ("bicrystals") are grown. The angle of misfit between the two grains is not larger than about 10 degrees. The grain boundaries can therefore be regarded as a regular array of evenly spaced edge dislocations. These bicrystals can be produced with or without[1] employing quartz crucibles; therefore bicrystal material with varying concentration of oxygen contamination is obtained.

Photoresponse measurements[2] are performed on such bicrystal specimens.[3] A small light spot is scanned across the grain boundary, resulting in a photovoltage, measurable across the two grains. This photovoltage has varying polarities, depending upon the thermal history of the sample. In "as-grown" silicon bicrystals with low p-type bulk conductivity, the grain boundary acts as an electron collector, thus appears to have n-type behavior. This had been reported already by other authors.[4),5)] Our large number of additional measurements indicate that other bicrystals of n-type bulk conductivity or of high p-type conductivity do not exhibit any photovoltage. An oxygen-free bicrystal with low p-type bulk conductivity was also found to give no photoresponse.

Upon heat treating samples with n-type grain boundary behavior at 1100°C for 15 minutes in a hydrogen atmosphere, the polarity is reversed. The boundary now collects holes. The magnitude of the response furthermore depends upon the cooling rate after the heat treatment. Impurity diffusion treatments also result in p-type boundaries. Prolonged heating at 450°C does not change the polarity. However, a heat treatment, done at 1300°C in hydrogen with subsequent quenching almost completely annihilates a previous p-type behavior.

Electrochemical staining methods applied to beveled bicrystal slices, utilizing intense illumination, result in p-n junction delineations at the grain boundary. The observed polarities are in accordance with the photoresponse data.

These observations are in striking contrast to previous results, obtained by several authors[6),7)] with germanium bicrystals. Germanium grain boundaries showed p-type behavior under all circumstances, even after impurity diffusions. This was attributed directly to the "dangling bond" core structure of the dislocations, which should have acceptor character.

The different behavior of silicon can obviously not be explained in a similar way. It seems to be best accounted for by the assumption of oxygen impurity atmospheres around the dislocations. Oxygen in silicon has been extensively studied.[8)] It is known to exist in several forms; dissolved, in SiO_n^+-complexes, or precipitated as SiO_2.

The measurements obtained thus far are in full agreement with the known kinetics of oxygen point defects in silicon. For ex-

* Work supported by the U. S. Air Force, Rome Air Development Center.

ample, the change of photoresponse polarity at 1100°C can be correlated to a formation of SiO_2-precipitates. Upon heat treatments at 1300°C, the oxygen is again dissolved in the lattice, which could account for the disappearance of the photoresponse.

It is therefore clear that not simply the isolated core structure is important for the electrical properties of edge dislocations in Si. The decisive physical factor is rather given by the interaction of the dislocations with point defects; in particular with oxygen impurities. From infrared transmission data[9] and studies on fracture and deformation,[10] it had also been postulated that dislocations in Si are affected by impurity atmospheres and constitute preferential sites for SiO_2 precipitation. The present photoresponse data give further support to these ideas.

References

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DISCUSSION

Iizuka, T.: By what mechanism does oxygen contribute to the *n*-type behavior of grain-boundary?

Queisser, H. J.: At the present time the experimental evidence is insufficient to decide upon a particular model. SiO_4-complexes, preferentially formed at the boundary dislocations, could cause the *n*-type behavior of the "as-grown" crystals. The *p*-type photoresponse is more difficult to explain; if the oxygen hypothesis proposed here is correct, a SiO_2/Si-interface should result in this polarity of the photovoltage.