Electronic properties of dislocations introduced mechanically at room temperature on a single crystal silicon surface

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ABSTRACT

This paper focuses on the effects of temperature and environment on the electronic properties of dislocations in n-type single crystal silicon near the surface. Deep level transient spectroscopy (DLTS) analyses were carried out with Schottky electrodes and p^+–n junctions. The trap level, originally found at $E_C - 0.50$ eV (as commonly reported), shifted to a shallower level at $E_C - 0.23$ eV after a heat treatment at 350 K in an inert environment. The same heat treatment in lab air, however, did not cause any shift. The trap level shifted by the heat treatment in an inert environment was found to revert back to the original level when the specimens were exposed to lab air again. Therefore, the intrinsic trap level is expected to occur at $E_C - 0.23$ eV and shift sensitively with gas adsorption in air.

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1. Introduction

Dislocations in silicon have been intensively studied since the beginning of integrated circuit (IC) technology because as defects they degrade the performance of electronic devices. Deep level transient spectroscopy (DLTS) [1] has been applied to study the trap levels of dislocations in n-type single crystal silicon [2,3]. The trap level at approximately $E_c - 0.52$ eV was attributed to dislocation in those studies. The dislocations surveyed since then have been emitted to the bulk by plastic deformation at a temperature above the brittle ductile transition (BDT) temperature because dislocations are rarely introduced in bulk silicon due to its brittleness at room temperature.

During the recent development of micro electro-mechanical systems (MEMS), the mechanical properties of silicon have attracted an increasing amount of attention. In spite of its brittleness, it was recently found that silicon is susceptible to fatigue fracture under repeated application of mechanical stress [4]. The mechanism of fatigue damage accumulation in silicon is still controversial [5]. Quite recently, however, some evidence was found to indicate that dislocations in silicon could be emitted and mobile, even at room temperature [6,7]. These findings strongly suggest that fatigue damage accumulation could be attributable to dislocations on the surface. There are few commonly known fatigue characteristics, but it is known that the fatigue lifetime decreases significantly with humidity [8,9].

Because the mobility of dislocations is also known to be influenced by dopants [10] that produce different Fermi levels relative to the level of dislocation [11], changes in the mechanical properties due to humidity may also be accompanied by changes in the electronic properties.

The present paper reports the electronic behavior of dislocations mechanically introduced at room temperature near the surface of silicon. DLTS [1] was used to examine the specimens, whose surface was damaged by indentation or scratching, but not subjected to further plastic deformation under a temperature higher than BDT. Instead, a milder heat treatment was performed in a number of different environments. The focus of the analysis was then to see if the electronic state of the dislocations changed with the surrounding gas species.

2. Specimen preparation

Two types of Schottky specimens and a p^+–n specimen were prepared for this study. Both the types of Schottky specimens were made of a CZ n-type single crystal silicon wafer (resistivity: 1–5 Ω cm, thickness: 525 μm, surface orientation: (1 0 0)) with evaporated Au Schottky electrodes on the surface. Before depositing Au, one type of the Schottky specimens were indented by a Vickers hardness tester to introduce dislocations at an applied load of 50 gf and a loading time of 10 s. There were 36 indents made on each electrode. After exposure periods to lab air, which varied among individual specimens from one day to a week, the indents were covered with Au electrodes. An optical microscope image of the electrode is shown in Fig. 1. Because of the rough
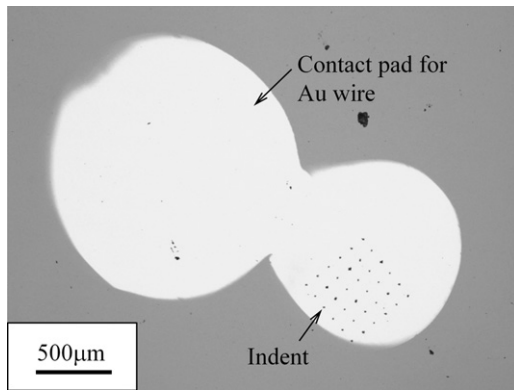
Fig. 1. Optical micrograph of Schottky specimen.
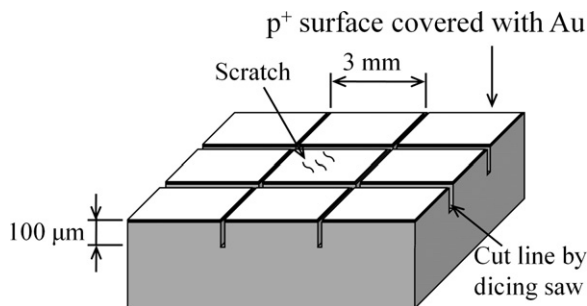

Fig. 2. Schematic illustration of p$^+$–n specimen.

surface topography of the indents, the Au film deposited on them was partially broken so that gas molecules in the atmosphere could access the dislocations on the surface. The other type of Schottky specimens was prepared also with Au electrodes but they had not been indented before Au deposition. After deposition they were scratched over the Au with a diamond pen in the vacuum cryostat chamber. Ohmic electrodes were prepared on the back side of both the types of specimens by rubbing with Ga–In alloy.

The p$^+$–n specimen was also made of a CZ n-type single crystal silicon wafer (resistivity: 1–10 Ω cm, thickness: 380 μm, surface orientation: (1 0 0)). Boron was doped by ion implantation to a dose of 10^{15}/cm^2 at an acceleration voltage of 10 kV, creating a p$^+$ layer on the surface. The doped layer was estimated to be approximately 33 nm thick. The surface was then coated with evaporated Au for the ohmic contact to the p$^+$ layer. Fig. 2 shows a schematic diagram of the p$^+$–n specimens. The surface covered with Au was cut by a dicing saw into 3 mm $\times$ 3 mm square blocks with a groove depth of 100 μm. Each block was used as an individual specimen. Dislocations were introduced after the cutting process by scratching the surface over the Au with a diamond pen in lab air. The back surface of the specimen was heavily doped with phosphorus and covered with evaporated Au to create an ohmic contact.

3. Experiment

A heat treatment at 350 K was performed on several specimens to observe the effects of three different gas environments, to which the specimen surface was exposed, on the trap level. It was performed in either N$_2$ or lab air at atmospheric pressure, or in vacuum. The heater installed in the cryostat table was used for this purpose. The specimens were heated at a rate of 3 K/min until they reached 350 K. The temperature was held for 15 min and then cooled at a rate of 1.5 K/min. In the cases of the N$_2$ and lab air

conditions, the chamber was evacuated again with a rotary pump halfway through the process of cooling the specimen below 325 K. This was done to avoid possible recovery of the state of specimens back to the original conditions before the heat treatment.

DLTS measurements were carried out on a cryostat table as the temperature decreased from 300 K in a chamber evacuated by a rotary oil pump, under a bias voltage between -0.5 V and -5 V and a pulse width $T_P = 100$ ms. The depletion layer widths in the Schottky specimens were determined to be 0.8 μm and 1.8 μm at the -0.5 V and -5 V bias conditions, respectively. In the p$^+$–n specimens, the widths were 1.0 μm and 2.4 μm at the -0.5 V and -5 V bias conditions, respectively. These conditions were commonly applied to all experimental specimens. Time-dependent changes in the junction capacitance were measured with a Boonton 7200 capacitance meter and processed into a DLTS signal with a bipolar rectangular weighting function [12] using a personal computer.

For the indented Schottky specimens, DLTS measurements were performed before and immediately after the heat treatment while keeping the specimens in the vacuum chamber, to observe the changes in the signals. Some of the specimens that exhibited trap level change due to the heat treatment were exposed once again to lab air. After these specimens were kept for a given period of waiting time in lab air, DLTS measurement was performed again and the trap levels were compared with those from the specimens kept in vacuum for a similar waiting time after the heat treatment. DLTS signals of the scratched Schottky specimens were obtained immediately after scratching without any exposure to lab air. After these specimens were kept for a given period of waiting time in lab air, DLTS measurement was carried out again. For the p$^+$–n specimen, DLTS measurements were performed three times in a similar manner as in the case of the indented Schottky specimens, i.e., two days after it had been scratched in lab air allowing the specimens to adsorb sufficient gas molecules, immediately after the heat treatment in vacuum, and after exposing the specimen again to lab air for 1 h.

4. Results and discussion

Fig. 3 shows a typical DLTS signal obtained in this study. The time constant of these lines is $\tau = 19.1$ ms. The flat signal without any distinctive peaks was obtained from a Schottky electrode
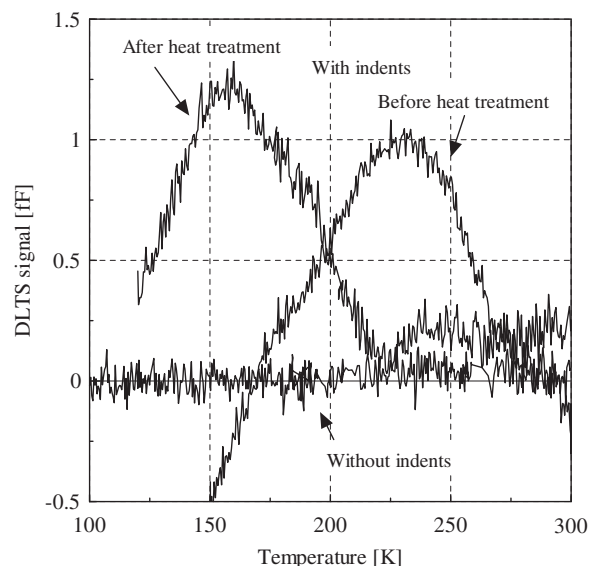

Fig. 3. DLTS signals obtained from Schottky specimens.

without any damage. In contrast, the signal from the indented specimen, observed 18 days after the electrode deposition, has a distinctive peak at 230 K. The trap level from this peak was determined to be $E_c - 0.54$ eV, which is known to be related to dislocation [2]. After the heat treatment at 350 K, the peak that was originally observed at 230 K was shifted to a lower temperature. The trap level analyzed from this peak also shifted to $E_c - 0.24$ eV, which was 0.3 eV shallower than that observed before the heat treatment.

To further investigate this trap level shift, the effects of three different gas environments during the heat treatment were compared. The data obtained are shown in Fig. 4, in which the positions of the trap levels are plotted along the ordinate, while the abscissa indicates the state of the specimens, i.e., before and after the heat treatment in different environments. The large data scatter observed in Fig. 4 is expected, mainly due to the weak DLTS signal. The horizontal dashed lines indicate the average trap levels for individual conditions. Before the heat treatment, the average trap level appeared at $E_c - 0.50$ eV. The values obtained from the group of specimens heated in vacuum or N_2 gas shifted to $E_c - 0.22$ eV or $E_c - 0.26$ eV, respectively. In contrast, the heat treatment in lab air did not cause any significant change in the trap level. The trap level shift was clearly correlated to the environment and appeared only when the specimen was heated in inert environments, such as vacuum or nitrogen. These phenomena suggest that the shift in the trap level was probably caused by the desorption of gas molecules present in lab air that had been adsorbed before the heat treatment, not including nitrogen. From this point of view, the large data scatter in Fig. 4 may also be attributable to the scatter in the amount of molecules transported through the surface. In addition to the varying period of exposure time to lab air without any humidity control before electrode deposition, the area of crack openings on the indented surface and the gaps in electrode covering the surface may also vary significantly among individual specimens because of the rough surface topography of indents as mentioned before. When the specimens were heated in an inert environment, the adsorbed molecules were expected to quickly detach from the dislocations. The same desorption process should take place when the specimen is heated in lab air; however, when the molecules of interest were included in the environment, adsorption also took place at the same time. Therefore, the dislocations were still in contact with gas molecules, leading to no significant change after the heat treatment in lab air.

The results of the DLTS measurement, performed after the specimens were exposed to lab air again as explained in the previous section, are plotted in Fig. 5, as a function of the waiting time in either vacuum or lab air from the measurement
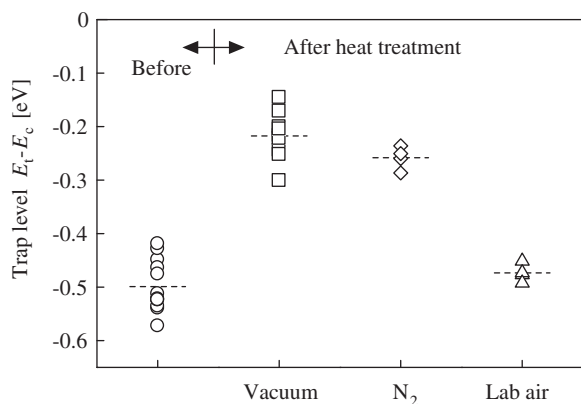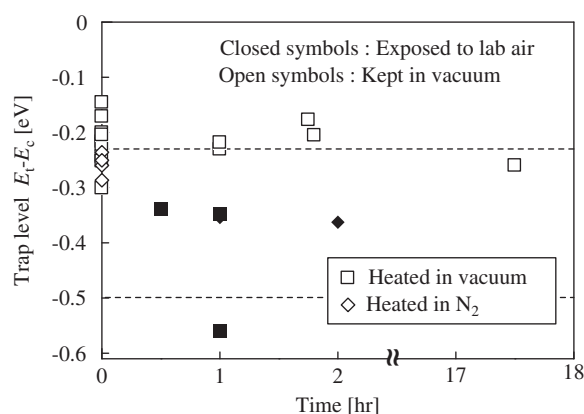

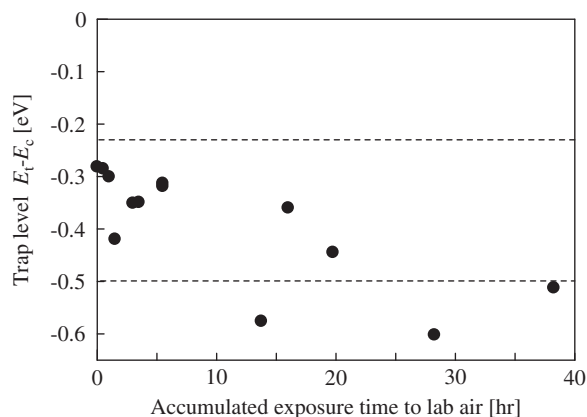Fig. 5. Time-dependent change of dislocation trap level after heat treatment.

Fig. 6. Time-dependent change of dislocation trap levels after the specimens were scratched in vacuum.

immediately after the heat treatment. Two horizontal dashed lines in the figure indicate the average trap levels before and after the heat treatment in an inert environment. These values are $E_c - 0.50$ eV and $E_c - 0.23$ eV, respectively. The trap levels from the group of specimens kept in vacuum did not change until an exposure time of 17 h. In contrast, the trap levels obtained from those exposed to lab air seem to shift back to deeper positions, although there is substantial variation in the values. To further investigate this trend, the results obtained from the Schottky specimens scratched in vacuum are shown in Fig. 6 in the same way as those shown in Fig. 5. The measurements made immediately after the scratch in vacuum exhibit shallower trap levels, similar to those obtained after the heat treatment in an inert environment. The dislocations introduced in vacuum do not have any chance to capture gas molecules. After exposure to lab air, the trap level gradually deepens as the exposure time increases, and after approximately 20 h, the trap level saturates at the level obtained from the specimens indented in lab air.

These facts support the hypothesis that the intrinsic trap level of the dislocation is $E_c - 0.23$ eV, and it shifts to a deeper level ($E_c - 0.50$ eV) when gas molecules from lab air are captured. The transition time observed in Fig. 6 should correspond to the diffusion process of the gas molecules along the dislocation, from the surface to the depth detectable by DLTS. Finally the results obtained from the p^+–n specimen are shown in Fig. 7. The time constant of these lines is also $\tau = 19.1$ ms. The trap level before heat treatment was determined to be $E_c - 0.49$ eV, and the measurement after the heat treatment in vacuum exhibited a trap level that was shifted to $E_c - 0.25$ eV. At the measurement after exposing the specimen to lab air again for 1 h, the trap level
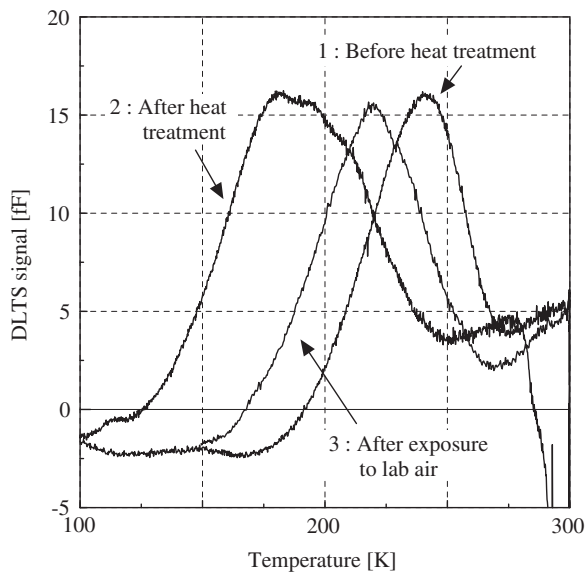

Fig. 4. Effect of environment during the heat treatment on the behavior of the trap level.

Fig. 7. DLTS signals obtained from a p^+–n specimen.

changed by heat treatment at 350 K in vacuum or nitrogen. DLTS measurement revealed that the trap level observed in specimens that were indented in lab air was $E_c - 0.50$ eV, which is similar to the value reported in the literature. However, the level shifted to $E_c - 0.23$ eV when the specimen was heated in an inert environment. These changes were reversible and repeatable and were probably caused by the adsorption and desorption of gas molecules from the surrounding atmosphere to and from the dislocations. Because the trap level obtained in specimens that were scratched in vacuum was found to be $E_c - 0.23$ eV, this level is expected to be the intrinsic state of dislocations without any adsorbed gas molecules.

Acknowledgment

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shifted back to $E_c - 0.46$ eV. The same reversible and repeatable change was observed, regardless of the specimen type. The molecules of interest might be water, as indicated by the significant reduction of the fatigue lifetime with humidity [8,9] and the correlation between the changes in the electronic and mechanical properties [10,11], but when the size and mobility are considered, they are more likely to be hydrogen.

5. Conclusion

The electronic properties of dislocations mechanically introduced near the surface of n-type single crystal silicon were easily