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Segregation and Thermal Dissociation of Hydrogen at the (110)/(001) Silicon Grain Boundary

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In this article, segregation and thermal dissociation kinetics of hydrogen at a large-angle general grain boundary in crystalline silicon have been investigated using deuterium, a readily identifiable isotope that duplicates hydrogen chemistry. Segregation or trapping of introduced deuterium (hydrogen) was found to take place at the (110)/(001) Si grain boundary. The segregation coefficient (k) of deuterium (hydrogen) at the grain boundary was determined as $k \approx 24 \pm 3$ at 100°C. Thermal dissociation of deuterium (hydrogen) from the grain boundary obeyed first-order kinetics with an activation energy of ~1.62 eV.

Keywords: silicon grain boundary, hydrogen segregation, thermal dissociation kinetics, multi-crystalline silicon, solar cells

1. INTRODUCTION

Hydrogen typically manifests in the deactivation of dopant atoms and the passivation of defects.[1,2] The latter quality has been utilized, for instance, to improve the minority-carrier lifetime of multi-crystalline Si (mc-Si) for solar cells and to enhance the on-state current and reduce the off-state current of poly-Si TFTs (Thin-Film Transistors).[3] It has been argued that nearly all H released by the post-deposition anneal of hydrogenated amorphous silicon nitride (SiN_x:H) films, which are deposited on mc-Si wafers to act as an anti-reflection coating, effuses out into the ambient rather than remaining in the bulk of Si.[4] The concentration and depth of H introduced into the floating-zone grown Si from an annealed SiN_x:H film have been determined using infrared spectroscopy for measurement of Pt-H complexes in Si. The H concentration introduced following the anneal at 600°C for 5 min. or 700°C for 10 min. was evaluated to be less than about 10^{14} cm^{-3}, which is too low to be detected by the SIMS (Secondary Ion Mass Spectrometry) technique due to its limited sensitivity.[5] H trapping at structural defects such as dislocations or grain boundaries (GBs) in hydrogenated mc-Si has been predicted based on indirect evidence obtained by electrically characterizing the positive effects of H passivation such as increased minority-carrier lifetime or a relative reduction of the electron-beam-induced-current contrast. Knowledge of segregation and thermal dissociation of H at structural defects in crystalline Si (c-Si), however, remains scarce. Study in this field has focused mainly on hydrogen-*impurity* pairs, while the area of segregated H at *GBs* is not fully understood. Thus, in this paper we report on a study of H segregation or trapping at a (110)/(001) Si grain boundary, which was prepared using direct-silicon-bonded (DSB) wafer bonding technology, as well as an investigation of thermal dissociation kinetics of H through measurement of the amount of trapped H at the GB. In performing quantification analyses of impurity segregation at interfaces by SIMS measurements, and measuring the depth profiles of impurities, thin-film structures can be conveniently utilized, particularly for detecting segregation of impurities at the interface between layers. In the case of GBs in mc-Si, the irregular configuration and non-uniformity of GBs make it difficult to obtain the reliable experimental data. For these reasons, a layered structure, composed of a hybrid orientation DSB wafer and used as a silicon grain boundary defect model,[6] was prepared for this study to investigate trapping and thermal behavior of H at the (110)/(001) silicon GB.

2. EXPERIMENTAL PROCEDURE

Hybrid orientation DSB wafers are composed of a (110) Si top layer bonded to a (001) Si substrate wafer. Both the (110) top layer and the (001) substrate are p-type Czochralski-grown silicon (Cz-Si) doped with boron with a concentration of 1.05×10^{15} cm^{-3} as determined by C-V characteristics. A

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(110) layer was transferred to the (001) substrate by hydrophilic wafer bonding and cleavage. Oxygen impurities inherent at the bonded interface can be readily removed by a high temperature annealing process (typically, about 1300°C for several hours) under vacuum for oxygen out-diffusion, thereby producing an interface that is essentially free of oxygen. Cross-sectional transmission electron microscopy revealed no interfacial oxide layer or oxide precipitates, and SIMS and ellipsometry measurements indicated no detectable oxygen at the bonded interface. Accordingly, the bonded interface can be treated as a GB between (110) and (001) grains. The bonded interface can be located at a predetermined depth from the surface. A bonded interface can accommodate various degrees of misfit, ranging from precisely controlled small angle boundaries to a variety of high-angle GBs.[7] With an increase of the twist/tilt angles, the density of the interfacial dislocations will increase, and eventually a large-angle general GB can be obtained. Figure 1 is a cross-sectional TEM image of a (110)/(001) DSB wafer, which is equivalent to a bonding with a 90° tilt angle around one <011> direction. The bonded interface studied here can be categorized as a large-angle general GB according to the concept of a coincident site lattice, the boundary type that is most effective in terms of reducing the carrier lifetime in polycrystalline Si. Hydrogen segregation of silicon GB has been investigated by using deuterium, a readily identifiable isotope that duplicates hydrogen chemistry. D detection with higher sensitivity than that of H detection was achieved with SIMS using a Cs^+ primary ion beam at 10 keV energy on a Cameca IMS 6f mass spectrometer. The depth resolution of the SIMS depth profiling was about 5 nm. Deuterium was introduced by boiling bonded Si wafers in heavy water (99.8 at. % D enriched) under dark conditions.[8] Cz-Si wafers doped with boron with a concentration of about 1.6×10^{15} cm^{-3} were also deuterated to serve as a control for comparison with as-deuterated bonded Si wafers. Rapid thermal annealing (RTA) was applied to the as-deuterated bonded Si sample using an AG Associates Heatpulse 210. C-V profiling was carried out using a capacitance bridge (1MHz) to investigate the bulk concentration of D. 1 mm diameter aluminum contacts were prepared on the (110) top layer by thermal evaporation. Ohmic contact was made on the back side of the sample by rubbing gallium-indium eutectic.

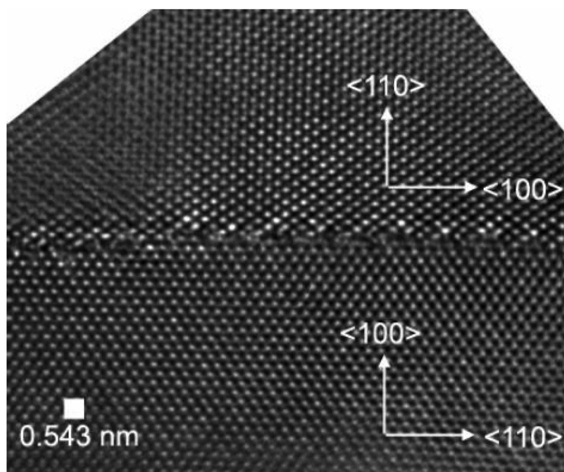

Fig. 1. TEM cross-section image of a (110)/(001) bonded (or 90° tilt) wafer showing the large-angle general grain boundary.

3. RESULTS AND DISCUSSION

First, deuterated Cz-Si wafers are reviewed. Very high deuterium concentration up to $3\sim4 \times 10^{18}$ cm^{-3} compared to the D concentration in the bulk (refer to Fig. 2(b)), was mea-

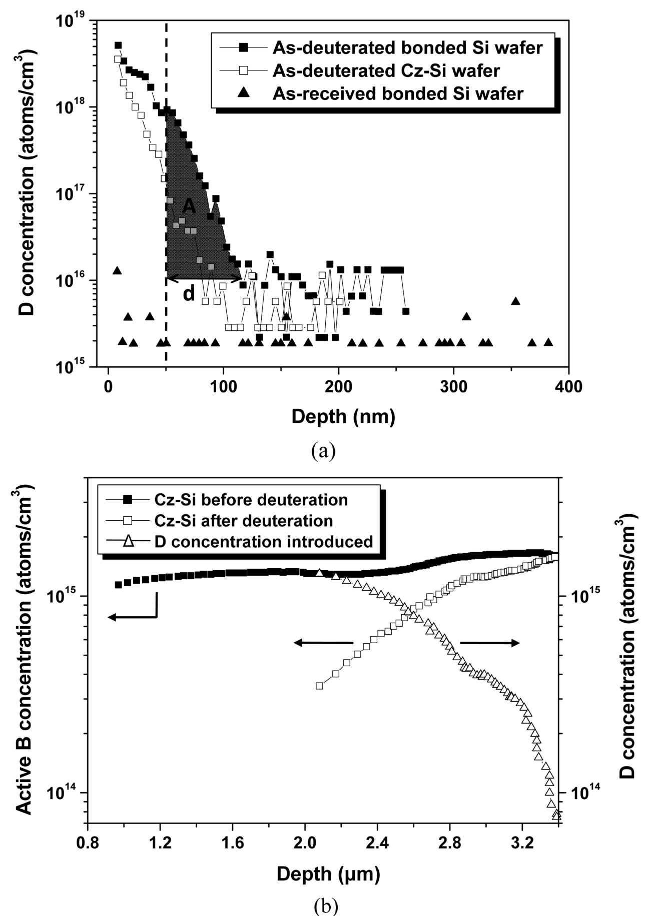

Fig. 2. (a) Secondary ion mass spectroscopy depth profile of D introduced in bonded Si wafers and Cz-Si wafers by boiling the sample in heavy water. No D was detected by SIMS for as-received (110)/(001) DSB Si wafers. The broken line indicates the (110)/(001) Si interface. A and d represent the integration of the D concentration profile on the right side of GB and the distance between the position of the interface and the tail of the profile intersecting the bulk D concentration of 10^{16} cm^{-3}, which was about 60 nm. (b) C-V depth profile of electrically active B in the bulk of Czochralski-grown Si wafers before and after D treatment. D introduced in the bulk was evaluated by quantifying the amount of the neutralized B content.

sured by SIMS within approximately 100 nm depth from the surface, as seen in Fig. 2(a). However, the concentration of D in the deeper regions was not detected by SIMS due to the detection limit of the SIMS technique, which is about 10^{16} cm^{-3}. The amount of D introduced in the bulk was evaluated by C-V profiling characterizing the electrically active boron concentration. D neutralizes the negatively charged B by pair formation. Hence, the concentration of D introduced was obtained by quantifying the amount of active B concentration deactivated by D, (see Fig. 2(b)).[8] The probing depth begins at the depth of the zero-bias carrier depletion region which was 2.1 μm for D-treated Cz-Si wafers. The D concentration comparable with a doping concentration of $\sim 1.6 \times 10^{15}$ cm^{-3} was observed at the initial probing depth and decreased with further increase in depth. The final probing depth of D, which was 3.4 μm, depends on the B doping level and is determined at the depth where the amount of D injected is not large enough to cause a measurable change in the active B concentration before and after D treatment. It is anticipated that the D concentration, which could not be measured by either SIMS or C-V at depths between 100 nm and 2.1 μm, ranges from 10^{15} cm^{-3} to 10^{16} cm^{-3}, considering the continuous D distribution inside the materials.

It has been suggested that the source of hydrogen (possibly OH complexes) is limited due to a reduction in the generation rate of injection centers at the silicon oxide/silicon interface as the oxidation rate of silicon in boiling water slows with time.[8,9] In addition, our experiments revealed that the injected hydrogen content decreased when the sample was boiled in a Piranha solution comprising a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2), which is a strong oxidizer used to clean organic residues off substrates. This indicates that the oxidized/hydroxylated surfaces might prevent the hydrogen source from being in-diffused, thus playing a role of a diffusion barrier. Hydrogen-boron pairs can be dissociated at the boiling point of water.[10] This indicates that the hydrogen injection efficiency is degraded once the hydrogen source is limited. The issue of source limiting is expected to be resolved by means of controlling the boiling time and removal of the silicon oxide. It was found that both the near-surface D (H) concentration and the permeation depth of D (H) increased repeatedly etching away the silicon dioxide and subsequent boiling. The resultant higher background concentration of D near the interface and the position of the interface in the proximity of the surface where the D concentration is much higher than that of D in the bulk led to enhancement of the ratio of SIMS signal-to-noise.

Deuterium (hydrogen) segregation at the free surface and GB was observed for D-treated bonded Si wafers, (see Fig. 2(a)). The D concentration at the GB was much higher than the background concentration profile of as-deuterated Cz-Si wafers. The GB acts as a D (H) trapping site and the trapping of D (H) was retained at 100°C for 1hr., which was the total boiling time for D injection. The amount of D segregated at the GB was calculated in units of D atoms per unit area (cm^2) of GB by integrating the D pile-up region in the vicinity of the GB where is larger than the bulk D concentration of 10^{16} cm^{-3}. The total amount of D segregated at the GB ($atoms/cm^2$) was obtained by doubling the integration of the profile on the right side of the GB (the shaded area labeled A in Fig. 2(a)) due to D pile-up at the free surface. It was assumed that the D concentration distribution with respect to the GB is symmetric. This assumption is reasonable in that the D profile that underwent a rapid thermal anneal at 800°C for 10 s., presented in Fig. 3, and which changed little compared to the D profile before annealing, showed a symmetric concentration distribution. The segregation coefficient (k) of D (H) at 100°C was determined as follows:

$$k = \frac{S_{GB}}{S_{bulk}} = \frac{(2 \times A)/(2 \times d)}{C_{bulk}} \approx 24 \pm 3 , \qquad (1)$$

where S_{GB} and S_{bulk} are the solubilities of the D concentration at the GB and in the bulk, respectively, A is the integration of the concentration profile on the right-hand side of GB, and d is the distance between the position of the interface and the tail of the profile intersecting with the bulk D concentration of 10^{16} cm^{-3}, which was about 60 nm.

Thermal stability or dissociation of D (H) segregated at the GB was examined by monitoring the variation in D concentration at the GB as a function of annealing temperature and time. The selected annealing temperatures were 200°C, 400°C, 600°C, 750°C, and 800°C. In the case of the anneal at 200°C and 400°C, the amount of introduced D (H) at GB was retained until 1hr., which was the maximum annealing duration employed in our experiments. Hence, these data

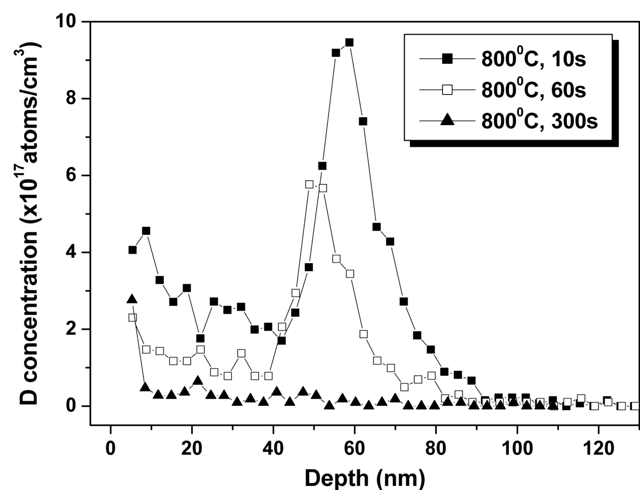

Fig. 3. SIMS depth profile showing the dissociation of D from grain boundary at 800°C as a function of annealing time.

could not be used to obtain the temperature-dependent dissociation frequency. On the other hand, from 600°C, the thermal instability of the trapped D (H) at the GB was observed within our annealing time frame and the concentration of D (H) at the GB decreased as a function of time. D (H) dissociation was faster at the surface than at the GB. The decay rate of D (H) content at the GB was accelerated at higher annealing temperatures. In the following, the time-dependent variation of D (H) at the GB at 800°C is briefly reviewed. Although the segregated D (H) at the GB is thermally dissociated rapidly at 800°C, the trapped D (H) at the GB can remain within the annealing time of 10 s, (see Fig. 3), suggesting that hydrogen passivation of the gap states of the GB can be sustained for short-time annealing at this high temperature. This experimental finding also illustrates why RTA–like process conditions, typically, about 10 s. at ~800°C, have been adopted in the fabrication of mc-Si solar cells to drive hydrogen into the bulk of Si, a process that is accompanied by a large increase in the minority-carrier lifetime due to passivation of impurities and defects in the Si substrate.

It was found that the D (H) concentration at the GB falls exponentially with time, indicating first-order exponential decay kinetics, seen in the inset in Fig. 4, which is a decrease in the measured amount of trapped D at GB (atoms/cm^2), ($D(t, T)$), according to the following law:

$$\partial D(t,T)/\partial t = -\nu D(t,T), \qquad (2)$$

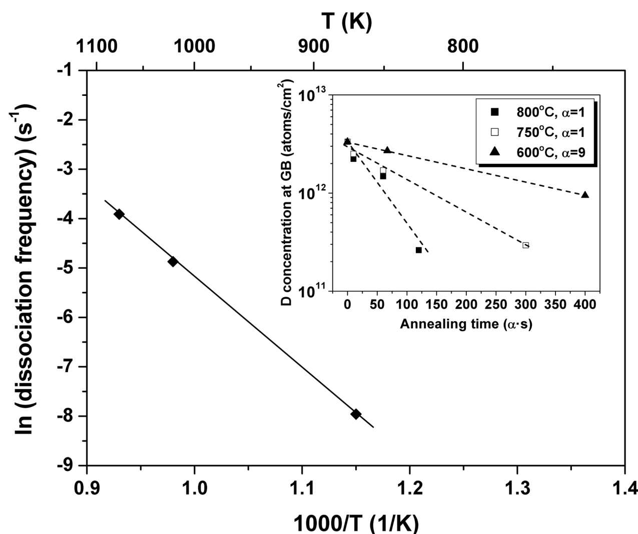

Fig. 4. Arrhenius plot of the measured dissociation frequencies of the trapped D at grain boundary. The solid line is a linear fit of $\ln\nu = \ln\nu_0 + (-E_A/KT)$ yielding E_A = ~1.62 eV. The inset shows the exponential decay of D at GB at several annealing temperatures. The annealing times at 600°C are adjusted by a factor $\alpha = 9$ to accommodate for the large time differences. The broken line represents the least-squares fit of $D(t, T) = D_0\exp(-\nu t)$ to the data for obtaining the decay time constant or dissociation frequency.

where ν is the dissociation frequency (s^{-1}) as a function of temperature governed by $\nu = \nu_0\exp(-E_A/KT)$, ν_0 is the dissociation attempt frequency (s^{-1}), E_A is the activation energy of the D (H) detrapping process, K is the Boltzmann constant, T is the annealing temperature in Kelvin, $D_0=D(0,T)$ is the initial value, and t is the annealing time. The data points of the measured D concentrations at the GB at different annealing temperatures and times have been fitted to $D(t, T) = D_0\exp(-\nu t)$ to extract the dissociation frequency at each selected annealing temperature. ν was then acquired by the relationship, $\nu = -\partial\ln(D(t,T)/D_0)/\partial t$.

Subsequently, the data of the natural logarithm of the dissociation frequencies were plotted against the inverse temperature (1/T, abscissa) for an Arrhenius plot to determine the activation energy (E_A). The Arrhenius plot provided an activation energy of ~1.62 eV for the dissociation of D (H) from the GB. The dissociation attempt frequency was ~7.8 × 10^5 s^{-1}.

4. CONCLUSIONS

Segregation and thermal dissociation kinetics of hydrogen at a large-angle general GB in c-Si have been investigated using D, a readily identifiable isotope that duplicates H chemistry. Introduced D (H) was segregated at the (110)/(001) Si grain boundary and its segregation coefficient (k) at the GB was determined as $k \approx 24 \pm 3$ at 100°C. Thermal dissociation of D (H) from the GB was accelerated at higher annealing temperatures and obeyed first-order kinetics with an activation energy of ~1.62 eV.

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REFERENCES

1. S. J. Pearton, J. W. Corbett, and T. S. Shi, *Appl. Phys. A* **43**, 153 (1987).
2. Y. Park, J. Lu, and G. Rozgonyi, *J. Appl. Phys.* **105**, 014912 (2009).
3. B. H. Kim, S. R. Lee, K. M. Ahn, and B. T. Ahn, *Electron. Mater. Lett.* **4**, 45 (2008).
4. C. Boehme and G. Lucovsky, *J. Appl. Phys.* **88**, 6055 (2000).
5. F. Jiang, M. Stavola, A. Rohatgi, D. Kim, J. Holt, H. Atwater, and J. Kalejs, *Appl. Phys. Lett.* **83**, 931 (2003).
6. M. Yang, V. W. C. Chan, K. K. Chan, L. Shi, D. M. Fried, J. H. Stathis, A. I. Chou, E. Gusev, J. A. Ott, L. E. Burns, M. V. Fischetti, and M. Ieong, *IEEE Trans. Electron Devices*

53, 965 (2006).
7. F. Fournel, H. Moriceau, B. Aspar, K. Rousseau, J. Eymery, J. Rouviere, and N. Magnea, *Appl. Phys. Lett.* **80**, 793 (2002).
8. A. J. Tavendale, A. A. Williams, and S. J. Pearton, *Appl. Phys. Lett.* **48**, 590 (1986).
9. W. Przyborski, J. Roed, J. Lippert, and L. Sarholt-kristensen, *Radiat. Eff. Defects Solids* **1**, 33 (1969).
10. C. Herring, N. M. Johnson, and C. G. Van de Walle, *Phys. Rev. B* **64**, 125209 (2001).