**In-Situ Optical Reflection Measurement of a Si(100) Surface under Hydrogen Ion Irradiation**

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In-situ optical reflection measurements have been performed for a Si(100) surface under H⁺ irradiation to study dynamic change in the electronic structure of the silicon. The relative reflectance at 370 nm decreased almost linearly with displacement per atom (dpa) and was recovered by hydrogen release by 423 K annealing, suggesting that the change in the relative reflectance at 370 nm originates from the increase of hydrogen bonded to Si. With increasing H⁺ irradiation, the relative reflectance around 700 nm increased due to the formation of Si-H phase near the surface silicon. Furthermore, the broad minima of the relative reflectance shifted from 600 to 500 nm by H⁺ irradiation, probably correlating with amorphization or appearance of silicon micro/nano-crystal by displacement effect.

(Kceived January 20, 2004; Accepted March 30, 2004)

**Keywords:** silicon, optical reflection, hydrogen implantation

1. Introduction

Ion implantation (ion irradiation) is a powerful technique for modifying the near-surface properties of functional materials such as micro- and nano-crystals, alloys, semiconductors and electron devices. However, the kinetic energy of incident ions introduces lattice damage through electron excitation and atomic displacement, sometimes resulting in undesirable modification of the near-surface properties. In addition, the production of displaced atoms of which number is usually much larger than the number of the implanted ions makes the behavior of the implanted ions very complex.

The behavior and effect of hydrogen implanted in silicon are of considerable technological importance, because hydrogen interact with defect and/or impurities in silicon, thereby modifying the electrical properties of the semiconductors.¹ Although hydrogen in crystal silicon has been investigated extensively, and various configuration of hydrogen have been reported on the basis of infrared²-³ and Raman spectroscopy,⁴ the dynamic change in the electronic structure of silicon under H⁺ irradiation is still not understood well. Therefore, in order to understand the properties of hydrogen implanted silicon, in-situ analysis of electronic structure with fine depth resolution is very important. In the present study, we have applied the optical reflection technique to study the chemical effects of irradiated hydrogen on the electronic structure of the surface silicon.

2. Experimental

Sample used in this study were taken from a (100)-oriented silicon single crystal wafer, supplied by Shin-etsu Handotai Co., Ltd. Ion irradiation (H⁺ or He⁺) was carried out to the Si(100) clean surface in an ultrahigh vacuum (UHV) chamber equipped with an ion source. A differential pumping allowed the pressure of the irradiation chamber to be below 10⁻⁶ Pa, which was necessary to keep the sample surface clean during the H⁺ irradiation. Mass-analyzed ions accelerated up to 5, 7.5 and 10 keV were injected to the Si(100) sample through a slit of 5 mm in diameter with an incident angle of 90 degrees to the sample. The implanted ion flux was monitored by Faraday cup inserted in the beam line in front of the sample. Under the ion irradiation, UV-visible light from Xe lamp (Hamamatsu Photonics) was introduced with an incident angle of ca. 22.5 degrees to the sample. The reflected light was transmitted to a spectrometer (CP-200, JOBIN YVON) and detected by a multi-channel analyzer (OMA III, EG&G PRINCETON APPLIED RESEARCH). The photon intensity in the wavelength region of 280–720 nm was measured. The penetration depth of the light with the wavelength λ was calculated using the absorption coefficient μ(λ) of silicon.⁵ In addition to the in situ reflection measurements, diffusion reflectance spectra were also measured for the sample before and after the irradiation with the fluence of 1 x 10¹⁸ cm⁻² in the wavelength range of 400–1300 nm.

3. Results and Discussion

3.1 Depth profile of lattice damage in hydrogen irradiated silicon

Generally energetic hydrogen implantation into silicon is known to result in defects and Si-H layer formation.⁶,⁷ Under the irradiation of hydrogen ion with medium energy range (1–100 keV), the amount of produced defects is much larger than that of the implanted hydrogen atoms. Figure 1 shows the depth distribution of the displaced atoms per incident ion (dpa), for irradiations of 5, 7.5 and 10 keV H⁺ which were calculated by the TRIM92 code.⁸ Compared with the depth profile of the displaced atoms, the implanted hydrogen distributes a little deeper region. However, it has been reported that most of implanted hydrogen migrates to shallower region to be trapped at defects caused by the displacement.⁹ Therefore, in the present implantation condition, both the defects and hydrogen are distributed within 300 nm from the surface of Si.

3.2 Changes in optical reflection of silicon

Figure 2 shows the change of the relative reflectance spectra of Si(100) under 5 keV H⁺ irradiation with the implanted ion fluence. Here, the relative reflectance (dR/R) is defined as (Ia(λ) – Ib(λ))/Ib(λ), where Ib(λ) and Ia(λ) are

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photon intensities at a wavenumber, $\lambda$ nm, before and after H$^+$ irradiation, respectively. One can note three features, with increasing the fluence, a sharp negative peak at around 370 nm grew linearly, a broad minima shifted from 600 nm to 500 nm and a broad peak at around 700 nm grew.

Figure 3 compares diffusion reflectance spectra of silicon before and after the irradiation with the fluence of $1 \times 10^{18}$ cm$^{-2}$. A reflectance minima at around 520 nm and reflectance increase in the wavelength range of 600 nm to 1000 nm respectively correspond to the broad minima at 520 nm and broad peak at around 700 nm grew.

Figure 4 shows the changes of the relative reflectance at 370, 500 and 700 nm for silicon after the irradiation of H$^+$ with the fluence of $1 \times 10^{18}$ cm$^{-2}$. The heating temperature is 423 K.

Some of hydrogen implanted in Si at room temperature can be desorbed thermally below 500 K without significant annealing effect on the defects in silicon.\textsuperscript{7,10,11} We have made an additional experiment to see the change in the relative reflectance by hydrogen release as follows. After the H$^+$ irradiation with the fluence of $1 \times 10^{18}$ cm$^{-2}$, the irradiated silicon sample was gradually heated up to 423 K. After the temperature was reached at 423 K, the change of the relative reflectance was monitored at the fixed temperature at 423 K. Figure 4 shows the changes of the relative reflectance at 370, 500 and 700 nm with heating time. The relative reflectance around at 370 nm and 700 nm respectively increased and decreased with heating time and saturated, while that of 500 nm did not show any significant change. Above experimental results for hydrogen release clearly demonstrate that implanted hydrogen very likely contributes to the change in the relative reflectance at 370 nm and 700 nm under H$^+$ irradiation.
These results suggest that the implanted hydrogen also dominates the change in the relative reflectance around 700 nm. Considering that the penetration depth of the 700 nm light is ca. 2 μm which completely covers the damaged region, the relative reflectance includes information of both irradiated and unirradiated areas. The electronic structure of the damaged silicon layer would change by the chemical effect of implanted hydrogen.

As seen in Fig. 3, the sharp increase around 1100 nm for unirradiated Si, which corresponds to the edge of the band gap of silicon crystal, remains clearly after the irradiation. Therefore the broad increase around 600 to 1000 nm can be attributed to the electronic structure change or a new phase formation in the damaged region. Then reconsideration on the appearance of the reflectance minima at around 500–600 nm in Fig. 3 is required. That is, the minima is not a true minima, instead, the appearance of another edge due to the appearance of different electronic structure in the damaged region as discussed in the following section. Revisiting Fig. 2, one can note this band edge shifted from lower energy (around 600 nm) to higher energy (around 500 nm) side with increasing the fluence. In our separate observation of the reflectance of He irradiated Si, no new edge below 1000 nm appeared. Thus the relative reflectance increase around 700 nm in Fig. 2 corresponds the electronic structure change or appearance of a new phase in crystalline silicon caused by the H⁺ irradiation.

3.5 The origin of broad absorption around 500–1000 nm
As discussed above, H⁺ irradiation results the sharp (resonance like) absorption band at 370 nm which is assigned to Si-H formation, and the wide absorption band probably overlaps the upper conduction band of crystalline Si. In order to discuss on the origin of the latter wide absorption band, one should take the penetration depth of primary photon for the reflectance measurements into account. The penetration depth of the 500 nm photon is ca. 300 nm, which is nearly the same as the damaged region (see Fig. 1), while that of 1000 nm is much deeper than the damaged region as already mentioned. Therefore, the appearance of the broad absorption band in the relative reflectance around 500–700 nm could be attributed totally to the electronic structure change caused by H⁺ irradiation. Since the relative reflectance around 500 nm did not change after the release of hydrogen (Fig. 4) and the similar decrease around 500 nm was also observed for highly He⁺ irradiated silicon, the change in the relative reflectance could not be attributable to hydrogen effects but to the other origin.

Referring Fig. 2, the appearance of the broad minima shifting from 600 to 500 nm is very likely correspond to an appearance of a new phase in crystalline Si. Considering that the heavy hydrogen irradiation amorphizes Si, the damaged region of the H⁺ irradiated silicon, in the present work, could be somewhat porous or amorphous state. Porous silicon including silicon micro- and/or nano-crystals and/or amorphous silicon have been reported to absorb Ar or Nd:YAG laser with wavelength around 500 nm. To investigate whether such silicon microstructures are formed on the irradiated silicon surface, we obtained atomic force microscope (AFM) images of the irradiated silicon by H⁺ or He⁺ with the fluence of 1 × 10¹⁸ cm⁻², as shown in Fig. 6. In the
figure, the formation of particles with diameters of about several tens and/or hundreds nm is appreciable. Moreover, our separate Raman measurements showed the coexistence of silicon crystal and amorphous phases in silicon irradiated 5 keV D\textsuperscript{+} or He\textsuperscript{+} with the fluence more than 1 × 10\textsuperscript{17} cm\textsuperscript{-2}.\textsuperscript{15} Therefore, the appearance of the broad minima and its shift in Fig. 2 can be interpreted by amorphization or appearance of so to speak silicon micro/nano-crystals by atomic displacement effect. Above discussion is still speculative, and further works are required to confirm this. Nevertheless the in situ reflectance measurement was proved to be a useful diagnostic tool to monitor surface electronic structure change in Si (or may be other semiconductor materials) caused by ion irradiation.

4. Conclusion

In this work, we have applied the optical reflection technique to observe the modification surface layers of silicon crystal irradiated by hydrogen ions. With increasing H\textsuperscript{+} irradiation, the relative reflectance at 370 nm decreased while that around 700 nm increased. These demonstrate the chemical effect of implanted hydrogen on the electronic structure of irradiated silicon, i.e., the formation of hydrogen bonded to Si which causes the 370 nm absorption, and amorphization or appearance of micro/nano-crystal silicon in the irradiated regions and increasing the relative reflectance 600–1000 nm. Thus, this work demonstrates that in-situ measurements of the optical reflection were very effective for observing the dynamic change in electronic structure of the silicon and could be used as a diagnostic tool for observation of electronic structure change in other semiconductors under ion irradiation.

REFERENCES