

INFLUENCE OF ANNEALING PROCESS ON ULTRAFAST CARRIER DYNAMICS FOR AN ION-IMPLANTED SILICON SURFACE

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ABSTRACT

We investigated the change of carrier properties in the ultrafast time range during annealing for a Si surface that has an amorphous layer by ion-implantation using a spectroscopic transient reflecting grating method. We observed a drastic change in the carrier properties when a transition from amorphous to crystal occurred. In case that the surface includes an amorphous layer for a short annealing time, carriers were trapped to different energy states according to the annealing time because annealing change the distribution of defect states complicatedly. Furthermore, we found that some defects remained even after crystallization, and that they induced another relaxation channel other than a usual relaxation to a band edge.

KEYWORDS

amorphous, Si, ultrafast carrier dynamics, ion-implantation, anneal, transient reflecting grating, defect states, trap

INTRODUCTION

Ion-implantation techniques play an important role in semiconductor device technology and are widely used in fabrications for many types of devices [1]. In the process of ion-implantation, an as-implanted material has a large amount of defects in its surface region and they induce amorphization in

the surface layer. Postimplantation annealing must be performed for the material to remove implantation-induced defects and to recover the electrical activation of the doped atoms. The recovery process during thermal annealing is technologically important, and so as-implanted and post-annealed surfaces are analyzed mainly by spectroscopic ellipsometry, Raman spectroscopy and Rutherford back scattering for investigating structural, physical and chemical properties of the materials. The methods give information on optical properties, lattice vibration and a spatial distribution of implanted species [2].

For future semiconductor technology, ultrafast carrier dynamics of devices must be clarified for technological innovations, as their fast response and size reduction are needed. Recently, optical pump-probe techniques have clarified carrier properties in the ultrafast time range from femtoseconds to nanoseconds [3-7]. Some such studies paid attention to carrier dynamics for crystalline Si (c-Si) and amorphous Si (a-Si) as representations of device materials. Summarizing the results, for c-Si, carriers photoexcited to extended states initially decay to a band edge in a few picoseconds, and they decrease due to Auger recombination processes in nanoseconds time range [4,5]. Different from the relaxation processes for c-Si, photoexcited carriers in a-Si decay mainly due to bimolecular recombination about a picosecond, while a part of the photoexcited carriers are trapped [6]. It is well known that a-Si shows a phase transition to c-Si by thermal annealing, but it has not been examined how the annealing changes carrier properties in the ultrafast time range during the process.

For the last five years, we have studied ultrafast carrier dynamics at crystalline and as-implanted Si surfaces using ultrafast photothermal methods [7]. Conventional photothermal methods give only one transient response for a single probe wavelength, and thus it is difficult to distinguish some processes occurring at the same time. To get more detailed information, we have improved a transient reflecting grating (TRG) method, one of the photothermal methods, to offer a spectroscopic measurement. The method has a possibility to measure carrier density change directly at each excited state, defect state, and so on. We applied the TRG spectroscopic method to an ion-implanted Si surface after being annealed for different times, and aim at clarifying the influence of annealing process on ultrafast carrier dynamics, focusing on a transition from amorphous to crystal, defect density, and distribution of defect states. Also, we will show the validity of the TRG spectroscopy as a measurement method for ultrafast carrier properties for semiconductor devices.

EXPERIMENTAL

The TRG equipment and principle were described in detail in another paper [8]. A brief explanation is given here. In the TRG technique, two crossed pump pulses are incident at a solid surface and, as a result, the focused spot is irradiated with a pulse of an interference pattern. The complex refractive index (\tilde{n}) at the spot changes due to a physical property change. After the pump pulses irradiation, a probe pulse is also incident there, and the complex refractive index change is detected through a diffracted light of the probe light. The signal intensity is theoretically proportional to $(\Delta n)^2 + (\Delta k)^2$, where the refractive index of a sample is $\tilde{n} = n + ik$. Using a white light as a probe pulse, carrier density change at various energy states optically coupled to the probe wavelength can be measured. With regard to c-Si, $\Delta \tilde{n}$ is dominated by excited free carriers for longer wavelength, while $\Delta \tilde{n}$ due to a temperature rise is a dominant factor for shorter wavelength.

A regeneratively amplified titanium sapphire laser (CPA-1000: Clark-MXR Inc.) was used as a light source. The pulse train wavelength was 800 nm, with a repetition rate of 1 kHz and a pulse width of 200 fs, in full width at half maximum. The pulse was separated into pump and probe pulses using a partial reflective mirror. The pump pulses were frequency doubled to a wavelength of 400 nm (3.1 eV), and then further divided into two pulses by a half mirror. The two pump pulses were crossed and irradiated onto the same spot of the sample surface, to coincide in time to form an interference pattern. The pump intensity was 1.76 mJ/cm². The interval of the interference fringes was 2.13 μm. The probe pulse was focused to heavy water to generate a femtosecond white-light continuum after passing through a computer-controlled optical delay line. Used wavelengths ranged from 450 nm (2.75 eV) to 750 nm (1.91 eV). The probe pulse was irradiated at the center of the spot. The reflected diffracted light with a rainbow of colors spread like a fan due to the diffraction conditions. It was detected with a spectrometer after being collected and focused by a lens. The polarizations of the pump and probe light were cross-polarized to prevent any coherent effects.

The original sample is an Arsenide ion-implanted Si (10¹⁵/cm²) wafer. The sample was annealed at 450 °C in N₂ atmosphere. It was annealed for various time from 0 to 180 minutes. Hereinafter, the original sample and the annealed samples are referred to as “as-implanted Si” and “annealed Si (annealed time)” respectively. To roughly estimate the crystallinity of the samples, the reflectance spectra are used. c-Si has two main optical transitions at 370 nm and 270 nm for E₁ and E₂. Generally speaking, the crystallinity is increased, as the peak width is narrower.

RESULTS AND DISCUSSION

Reflectance spectra are shown in Fig.1 for a c-Si and the ion-implanted Si annealed for different times. The spectrum for the c-Si showed clear two peaks at 370 nm and 270 nm corresponding to the

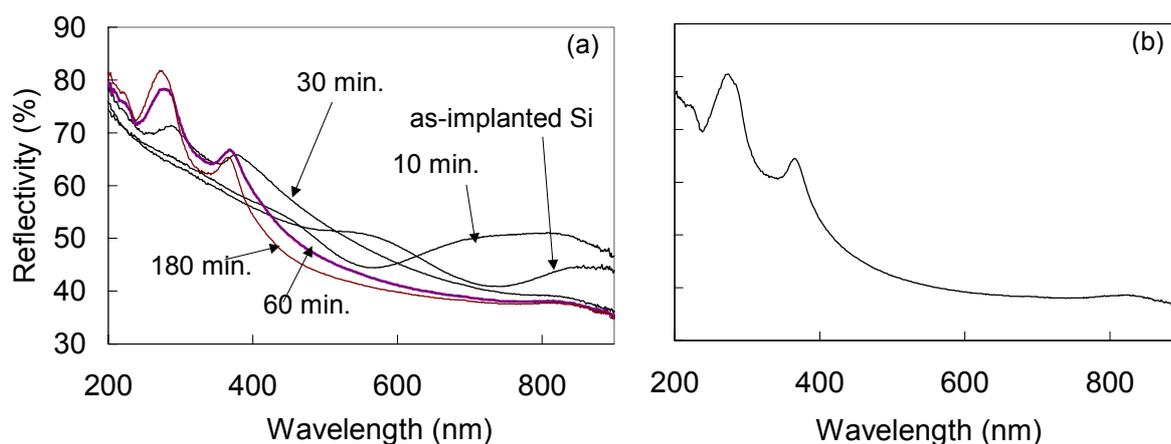


Fig. 1. Reflectance spectra for (a) as-implanted Si and ion-implanted Si annealed for various times and for (b) c-Si

optical transitions for silicon respectively. The spectra for as-implanted and annealed Si (less than 20 min.) didn't show any peaks for E₁ and E₂. These spectra showed a broad peak extending the measured wavelength range. The peaks for the E₁ and E₂ appeared after the annealing time has passed over 30

minutes, and the two peaks got sharper with increasing the annealing time. Considering the spectral change for each annealing time, it was understood that annealing induced the following three-step structural change. 1. Until 20 minutes, some structural changes occurred in the amorphous layer. 2. From 30 to 60 minutes, a phase transition from amorphous to crystal occurred. 3. More than 60 minutes, the crystallized layer gradually got close to a defect-free crystal.

Next, TRG spectra were measured for each sample. Although the transient waveforms depended on the probe wavelength, the mutual relation of the relaxation time among the samples showed similar tendency for every probe wavelength. In this study, we pay attention to the dynamics of photoexcited carriers, not to the temperature rise and fall, and so the transient signals measured at longer wavelength (687nm) are compared (Fig. 2(a)). The relaxation processes of the as-implanted Si and

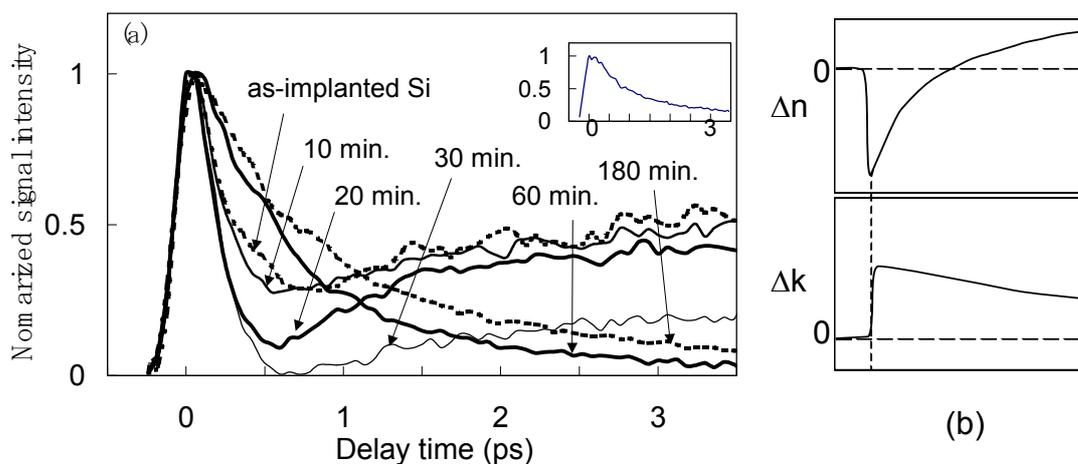


Fig. 2. (a) TRG responses for as implanted Si and ion-implanted Si annealed for various times at the probe wavelength of 687 nm, and the annealed samples are indicated with arrows and annealing times. For reflectance, a transient response for c-Si is shown in the inset. (b) Schematic illustrations for likely behaviors Δn and Δk in this time range in case of a-Si.

annealed Si (less than 30 min.) consisted of mainly two components; the faster one decayed in several hundred femtoseconds and the slower one raised about 1 ps and kept almost constant, while the annealed Si (more than 60 min.) have only a decay component in several picoseconds. From other reports, for c-Si, it is understood that carriers photoexcited to extended states initially decay to a band edge in several picoseconds [4,5]. While for a-Si, the decay initially occurs due to bimolecular recombination, and a part of the carriers are trapped into defect states and remains there for more than 500 ps [3,9]. Thus, it can be said that the transient responses for the annealing time less than 30 minutes and longer than 60 minutes mainly correspond to those for a-Si and c-Si respectively. Also the results of the reflectance spectra support the consideration. Namely, for the as-implanted Si and the annealed Si (less than 30 min.), the faster and slower components correspond to bimolecular recombination and trapped carriers at defect states. Also the slower component includes a temperature rise effect corresponding to the signal increase after 1 ps. For the annealed Si (more than 60 min.) responses mean a relaxation of carriers from extended to band edge states. Main features of the signals can be explained based on the carrier dynamics for pure c-Si and a-Si, but the change of the transient responses depending on the annealing time is not understood.

Before the consideration, it is necessary to clarify the causes of a refractive index change for silicon in order to understand the TRG signal origin.

In general, a density change of photoexcited carriers and temperature rise are the causes for Δn , while Δk results from an absorption change of the probe light due to free carriers at extended and band edge states, and trapped carriers at defect states [10]. As to a-Si, it is known that Δn is negative for a generation of photoexcited carriers, while it is positive for temperature rise. Then Δn changes from negative to positive as the photoexcited carriers decrease due to bimolecular recombination and consequently the following temperature is raised [11]. Δk is known to be positive due to an absorption change of trapped carriers at defect states, and it monotonously decreases as the trapped carriers

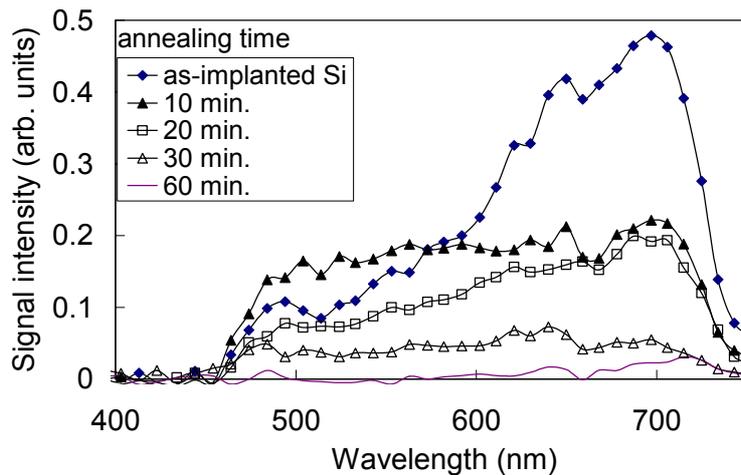


Fig.3 TRG spectra at 3 ps after the pump pulses were incident, for as-implanted and ion-implanted Si annealed for 10-60 min

recombines [6]. Considering the TRG signal is proportional to $(\Delta n)^2 + (\Delta k)^2$, the TRG signals of the as-implanted Si and the annealed Si (less than 30 min.) cannot be explained only by Δn or Δk , and they include both components. (The schematic illustration of typical Δn and Δk responses is shown in Fig. 2(b) for explaining a TRG signal for a-Si.) Fig. 2(a) indicates Δk contribution became weaker with an increase of annealing time. The result means a reduction of the number of trapped carriers due to a decrease in defect states. For c-Si, only Δn is a major component and is induced by a generation of photoexcited carriers. The TRG signals for the annealed Si (more than 60 min.) consist of one component that corresponds to a relaxation of carriers to a band edge. But only the process cannot explain the decay processes because the relaxation time gets longer with an increase of the annealing time. The reflectance spectra showed annealing after 60 minutes still made the sample crystallinity change, and the result indicates some structural defects remain even after a phase transition. Thus, we suggest that some carrier trapping processes accelerate the carrier relaxation.

As mentioned above, Δk component for a-Si corresponds to an absorption change due to carriers trapped at defect states for a probe wavelength. It is expected that the wavelength dependent on Δk gives information on the distribution of trapped carriers in energy states. So we show the TRG spectra at 3ps in Fig. 3, when the rate of Δk component is large in the TRG signal.

With an increase of annealing time, the most striking feature is a reduction of the peak around 700 nm until 10 min., and subsequently the spectral waveforms changed complicatedly. We believe that the change

reflect the distribution of trapped carriers in energy states. Although thermally induced Δn component must be subtracted, the main interpretation may be the same because Δn due to a temperature rise does not depend too much on the samples. By initial annealing of 10 minutes, the intensity of the peak around 700 nm decreases remarkably and the peak gets broader. Further annealing made the signal intensity smaller, changing the spectral waveform. These results suggest that the distribution of trap states changed complicatedly, decreasing the whole number of the states, although further exact analysis must be performed on a defect density, a distribution of energy states, a refractive index change due to a temperature rise, and so on, and now we are doing them.

CONCLUSION

We investigated carrier properties in ultrafast time range during annealing for an ion-implanted Si, which causes a phase transition from amorphous to crystal. We observed that carrier properties drastically changed in the transition from amorphous to crystalline and that the defect properties also affect the ultrafast carrier dynamics. When the TRG spectra will be correctly related to a defect density and a distribution of its energy state, the obtained information can provide a useful policy for manufacturing devices where carriers are controlled in the ultrafast time range.

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