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Transient reflecting grating study of ion-implanted semiconductors

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Abstract: Surface modification of Si(100) wafers induced by argon–ion implantation (ion energy, 300keV; dose, $10^{11} - 10^{17}$ atoms/cm$^2$) was investigated using a transient reflecting grating technique. Effects of the implantation on velocity, intensity and onset time of surface acoustic waves (SAW) were discussed accompanying the acoustic anisotropy. SAW velocity dispersion was also examined for one of the lightly ion-implanted sample (dose, $10^{13}$ atoms/cm$^2$).

1. INTRODUCTION
Evaluation of surfaces and subsurfaces modified by ion implantation has great importance in material processing technology, particularly when it can be done using noncontact, non-destructive, in situ and highly sensitive techniques. Photothermal and related techniques are widely used for evaluation of ion-implanted semiconductors. However, they have their own weaknesses (i.e., lack of depth resolution and surface selectivity, difficulty in determining a one-to-one correspondence between the observable and the characteristic property of materials, etc.). To overcome them, we proposed laser–stimulated scattering microscope (LSSM),[1,2] whose operational principle is based on microscopic measurement of transient reflecting gratings (TRGs).[3–8] We have previously demonstrated that stimulated light scattering from TRGs can be used for distribution monitoring of both implanted ions [1] and thermal diffusivity [2] in semiconductors and for determining characteristic material constants, such as elastic moduli.[5] Here, we present our further experimental results on LSSM evaluation of surface modification induced by argon–ion implantation into n-type Si(100) wafers with various doses ($10^{11} - 10^{17}$ atoms/cm$^2$). We have determined velocity, intensity and onset time of surface acoustic waves (SAWs) for both [011] and [001] directions of SAW propagation. SAW velocity dispersion of one of the lightly ion-implanted Si(100) (dose, $10^{13}$ atoms/cm$^2$) was also examined.

2. EXPERIMENT
The ion-implanted Si(100) wafers were 0.6 mm thick and had an oxide layer, 2 nm thick, on the mechanically mirror-polished front surface. 300keV argon–ions were implanted into the surface at a room temperature. No further treatments were carried out after the implantation. The LSSM system used for the present experiment is the same as was described previously.[2] Two pump– and one probe– pulses stemmed from one mode–locked pulse of frequency–doubled Q–switched Nd: YAG laser (wavelength, 532 nm; pulse width, 84 ps) were used to excite and probe TRGs. The grating–spacing $\Lambda$ used was 2.90 $\mu$m. It was calculated from the crossing angle $\theta$ of the pump pulses as $\Lambda=\lambda/2\sin\theta$ where $\lambda$ is the wavelength of the laser light. The direction of grating vector was selected with respect to the crystallographic axis. The wavelength of the SAW is the same as the grating–spacing and the direction

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of acoustic propagation is parallel to the grating vector. A part of the probe light diffracted to one of the first-order spots was detected with a photomultiplier. A TRG response was equivalently obtained by recording the signal intensity as a function of probe–delay with respect to the pump pulses. Each of the TRG responses consisted of 512 points of data taken at even intervals in a time window of 5.33 or 12.8 ns width. To extract characteristic parameters from the responses, we used an empirical equation proposed previously,[5] where diffraction efficiency \( \eta \) is described by

\[
\eta(t) = R \{ I_e A \exp(-t/\tau_T) - \tau \cos[2\pi F(t+t_d) \exp(-t/\tau_A)] \}^2,
\]

where \( I_e \) is intensity of pump pulses, \( A \) is a constant, \( F \) is SAW frequency, \( t_d \) is SAW onset time, \( \tau_T \) and \( \tau_A \) are attenuation constants for temperature and SAW, respectively, and \( r \) is the ratio of the acoustic effect to the thermal effect of their contributions to grating amplitude. There are six parameters \((F, t_d, r, A, \tau_T, \tau_A)\), and each of them is related to a characteristic material parameter, namely, elastic modulus, recombination rate, expansion coefficient, optical absorbance, thermal diffusivity and acoustic viscosity, respectively. An experimental curve was fitted to Eq. (1) by a nonlinear least square method and without using data in \( t < 0.3 \) ns. Why these data were not used is they were seriously affected by photoexcited carriers,[8], thermal diffusion from the surface into the sample[2] and pulse width of the laser.

3. RESULTS AND DISCUSSION

Figure 1 shows the TRG responses of an intrinsic and six ion-implanted samples with the grating vector parallel to [001]. From the top to the bottom, the doses are 0 (intrinsic), \( 10^{11}, 10^{12}, 10^{13}, 10^{15}, 10^{16} \) and \( 10^{17} \) atoms/cm\(^2\), respectively. Each trace is normalized with its maximum amplitude and vertically shifted for good visibility. It is noted that the maximum amplitude was from 6 to 10 times larger than the intrinsic silicon for \( 10^{11} - 10^{13} \) atoms/cm\(^2\) doses and from 460 to 500 times larger for \( 10^{15} - 10^{17} \) atoms/cm\(^2\).[4] The peak indicated by an arrow is attributed to a concentration grating of photoexcited carriers.[8] It vanishes even by the ion dose as low as \( 10^{11} \) atoms/cm\(^2\) and, at the same time, the TRG response is beginning to change from that of the intrinsic Si(100). Surfaces of crystalline silicon are known to be transformed to the amorphous phase by an ion dose of \( 2 \times 10^{14} \) atoms/cm\(^2\) for the present condition.[9] The lower three traces in Fig. 1 (dose, \( 10^{15} - 10^{17} \) atoms/cm\(^2\)) are subjected to the effects of the phase transition. Thus, the changes in TRG responses reflect ion implantation effects on silicon surface. Next, we proceed to analyze these responses and to evaluate how ion implantation influences the surface to change the material parameters.

As an example, a TRG response is shown in Fig. 2 of the \( 10^{13} \) atoms/cm\(^2\) ion–implanted Si(100). The thick line is an experimental result and the thin line is the best–fitted curve of Eq. (1) (shifted downward). Since they agree well each other, the characteristic parameters can be estimated.

![Fig. 1](image1.png) **Dependence of TRG waveform on ion implantation dose.** The doses are \( 0, 10^{11}, 10^{12}, 10^{13}, 10^{15}, 10^{16}, 10^{17} \) atoms/cm\(^2\) from the top to the bottom, respectively. Each trace is normalized with its maximum.

![Fig. 2](image2.png) **Typical TRG response on an argon-ion-implanted silicon (100) with \( 10^{13} \) atoms/cm\(^2\) dose.** Grating vector // [001].
Ion dose dependence of SAW velocity $V_r (= F x \Lambda)$ is shown in Fig. 3. 'In.' indicates intrinsic. The estimated SAW frequency $F$ was ranging from 1.60 to 1.75 GHz. Its relative standard variation, estimated from repetitive measurement, was 0.3 – 0.7 % for the lower doses than $10^{13}$ atoms/cm$^2$ and 0.8 – 1.8 % for the higher doses. As shown in Fig. 3, at heavy doses over $10^{12}$ atoms/cm$^2$, the SAW velocity decreases, while at lighter doses than $10^{13}$ atoms/cm$^2$, the velocity increases both for [011] and [001] directions. If the surface layer is amorphous or amorphous-like, the SAW velocity is slower than the intrinsic Si(100) as in the heavy doses. However, below $10^{13}$ atoms/cm$^2$ dose, an increase in elastic moduli causes the velocity increase (cf., the implantation induces no serious density change under such light dose conditions). In other words, the ion implantation hardened the Si(100) surface. We will discuss the hardening later. Note that acoustic anisotropy was enhanced at the $10^{12}$ atoms/cm$^2$ dose.

As for the parameter $r$, the ion implantation made it decrease as shown in Fig. 4. The more ion dose resulted in the smaller $r$. Significant anisotropy in $r$ was not observed, except for the sample with the $10^{12}$ atoms/cm$^2$ dose. It is suggested again that there exist some special anisotropic structures formed under the Si(100) surface by the $10^{12}$ atoms/cm$^2$ implantation, but it is beyond our scope of the present study. Roughly speaking, the parameter $r$ is proportional to photothermally induced acoustic intensity when there is a temperature rise of a fixed amplitude. Hence, these results imply that the ion implantation suppressed volume expansion. The mechanism is not clear yet.

The SAW onset time $t_o$ also drastically changed due to the ion implantation. In Fig. 5, the difference $\Delta t$ is plotted, where the reference point, $\Delta t=0$, is the $t_o$ value of the intrinsic Si(100) measured with the grating vector parallel to [011]. Significant $t_o$ anisotropy was not observed throughout the experiments. The changes in $t_o$ are also observable in Fig. 1: The positions of the first acoustic peak for the $10^{11}$ – $10^{13}$ atoms/cm$^2$ doses are faster than that of (the highest peak of) the intrinsic sample; and, the acoustic phase reverses between $10^{13}$ and $10^{15}$ atoms/cm$^2$. The results contain information on the mechanisms of light-induced SAW generation and/or SAW detection by using reflecting diffraction of probe light. Decrease of $t_o$ observed at the doses below $10^{13}$ atoms/cm$^2$, is easily explained as the ion implantation accelerated nonradiative recombination rate. Even for the samples with higher doses than $10^{15}$ atoms/cm$^2$, the rising rate of the initial part was accelerated by the ion implantation as shown in Fig. 1. Two possible mechanisms are considered as causes of the phase–reverse: 1, change in the dominant mechanisms of acoustic generation from electronic dilation to photothermal expansion; and 2, change of detecting condition owing to multiple reflection of diffracted light in an amorphous layer made by the heavy implantation. We think the latter is more plausible although further experiments are necessary to identify the mechanism.

Concerning on the hardening observed for the samples with the lower doses than $10^{13}$ atoms/cm$^2$, SAW velocity dispersion was measured both for an intrinsic and an ion–implanted Si(100) (dose, $10^{11}$ atoms/cm$^2$) by changing grating–spacings $\Lambda$ from 1.65 to 3.66 µm. The corresponding SAW frequency was from 1.35 to 2.99 GHz. The results are shown in Fig. 6, where $K$ is a wavenumber ($= 2\pi/\Lambda$).
In such a system as a softer layer on a harder substrate, SAW velocity dispersion is approximately described as a linear function of $K$ when $KH << 1$, where $H$ is the layer thickness. Namely,

$$V_r(K) = V_{r(\text{substrate Rayleigh velocity})} + (\frac{dV_r}{dK})K.$$  \hspace{1cm} (2)\

The $(dV_r/dK)$ value is a negative constant that depends on elastic moduli of both layer and substrate and is proportional to $H$. If the layer is $\text{SiO}_2$, $H = 2$ nm and $KH << 1$. This equation was applied to analyze the data. Each result of a linear regression is also shown in Fig. 6 by four lines corresponding to two directions of acoustic propagation and two samples (intrinsic or ion-implanted). Two arrows pointing at certain values on the vertical axis indicate velocities of SAW propagating parallel to [001] (lower) and [011] (upper) directions on a (100) face of crystalline silicon, respectively, calculated using literature values of elastic modulus. For both the directions, the substrate Rayleigh velocities of the intrinsic and the ion-implanted Si(100) were the same within the experimental error, although all of them were larger than the corresponding calculated values. For both the directions, the slopes were gentler for the ion-implanted Si(100) than the intrinsic one. Using another sample of a 2 nm Si$_3$N$_4$ on p-type Si(100), it was experimentally confirmed that the slope was nearly horizontal when plotted on the same scale. This means little acoustic dispersion in SAWs on Si(100). The reason why acoustic dispersion was observed for the n-type sample is not clear, but it is considered that some stress existed near the SiO$_2$/Si interface and that it was released by the ion implantation. For reference, assuming the layer to be $\text{SiO}_2$ on Si(100), the layer thickness was estimated from the slope $(dV_r/dK)$. The thickness was ranging from 170 to 310 nm. These values were two orders of magnitude larger than the real thickness of $\text{SiO}_2$ on the samples.

So far, we have pointed out several findings and problems concerning on ion-implantation-induced changes in picosecond-time-resolved photothermal phenomena observed as TRG waveforms. Further investigations are waiting to be conducted by LSSM, a new microscopic technique using TRGs.