Optical Third-Harmonic Generation in Reflection from Crystalline and Amorphous Samples of Silicon

Charles C. Wang, J. Bomback, W. T. Donlon, C. R. Huo,[a] and J. V. James
Research Staff, Ford Motor Company, Dearborn, Michigan 48121
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This Letter reports optical third-harmonic generation in reflection from ion-implanted samples of silicon. The third-harmonic signal is found to exhibit certain novel polarization and rotational dependences, which can be understood with the aid of measurements using electron and ion beam techniques. Our observations provide quantitative information on the transformation from the crystalline to the amorphous state of silicon.

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With the advent of high-repetition-rate Nd-doped yttrium-aluminum-garnet (YAlG) lasers, it is now practical to study the weak signal associated with optical third-harmonic generation (THG) from the surface of semiconductors.[1,2] The process of THG[3] differs from that of second-harmonic generation in that its existence does not require the lack of inversion symmetry, and thus may be operative even in the bulk of such centrosymmetric crystals as silicon and germanium. In practice, THG in reflection originates from a layer near the surface whose depth is determined by the depth of penetration of the incident beam, or the escape depth of the generated third-harmonic radiation, whichever is shorter. By variation of the wavelength of the incident radiation, different effective depths for the radiating region may be obtained. For example, with the infrared radiation near 1.06 μm from the Nd-doped YAlG laser, the escape depth for the third-harmonic radiation is very short, giving an effective depth for the generating layer of about 100 Å. The purpose of this Letter is to report THG from ion-implanted samples of silicon, for which the intensity of THG tends to decrease with increasing ion dose until a critical dose is reached. By correlating these observations with measurements of transmission electron microscopy (TEM) and ion channeling, we demonstrate that THG can be used as a unique *in situ* nondestructive technique for monitoring the transition from the crystalline to the amorphous state of silicon.

In centrosymmetric crystals such as silicon with $m3m$ symmetry, the lowest-order nonlinear optical effects are those associated with an induced polarization which is third order in the electric field strength. This induced polarization contains a Fourier component at the third-harmonic frequency of the incident field $\mathbf{E}(\omega)$, whose ith Cartesian component may be given phenomenologically as[3]

$$P_i(3\omega) = BE^2E_i + (A-B)E_i^3, \qquad (1)$$

where A and B are the two independent nonvanishing coefficients of the nonlinear polarizability tensor and are, in general, frequency dependent. The first term results in THG which is polarized the same as the incident beam, independently of the crystalline orientation. The second term in Eq. (1) is anisotropic, i.e., it exhibits the rotational symmetry of the crystalline medium, and may give rise to a polarization component of the THG perpendicular to that of the incident laser beam. According to Eq. (1), THG from (100), (110), and (111) surfaces of silicon should exhibit fourfold, twofold, and threefold rotational symmetry, respectively. Changes in this anisotropic behavior can be used as a measure of departure from the crystalline state since no such rotational dependence should be observed in either amorphous or polycrystalline samples.

The experiments were performed with the collimated output from a Q-switched Nd-doped YAlG laser operated at a repetition rate of 10 Hz.[1,2] The diameter of the beam was adjusted so that the energy density was kept below the threshold for annealing of implanted samples. The output from the laser was incident normally (or sometimes obliquely) upon the sample through a dichroic mirror; the third-harmonic wave and the incident infrared radiation reflected from the sample surface were separated before detection. Silicon samples were mounted on a platform which could be rotated about its surface normal by a stepper motor. For certain measurements, both the dichroic mirror and the silicon sample were housed in a chamber evacuated to less than 10^{-3} Torr with the aid of a sorption pump. (No difference in the measurements was observed when the chamber was evacuated to a much lower pressure of 10^{-6} Torr.)

As was found in earlier experiments,[1] a substantial amount of third-harmonic power was generated in the air and in various optical components along the path of the incident laser beam. In our present experiments, the detected third-harmonic signal results primarily from the addition in amplitude of the third-harmonic waves generated at the dichroic mirror, at the sample,

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and in the air between the sample and the dichroic mirror. Furthermore, THG from the dichoic mirror was found experimentally to be comparatively negligible. Figure 1 depicts typical variations of the third-harmonic signal as a function of the distance between the sample and the dichroic mirror. This phenomenon is well understood,[1] being a result of interference between the third-harmonic waves generated by the sample. It can be shown that despite this interference, it is still possible to deduce the nonlinear coefficient for the sample from the observed third-harmonic signals. (Alternatively, measurements could also be, and indeed were, performed in vacuum in order to avoid the interference from air.)

In Fig. 2, THG is observed as a function of the rotation angle about the surface normal of the sample for (100), (110), and (111) surfaces of silicon. Samples of polycrystalline silicon were also studied in a similar manner, but no detectable rotational dependence was observed. These results were obtained with the incident beam polarized in the plane of incidence (p wave), and the THG polarized perpendicular to the plane of reflection (s wave). Similar results were also obtained with other polarization configurations for the incident and the THG radiation. In these results, the induced third-harmonic polarization is seen to exhibit fourfold, twofold, or threefold rotational symmetry, and can all be fitted in accordance with Eq. (1) to yield an approximate value of $A/B = 0.75$.

THG has also been studied as a function of the ion dose for various silicon samples implanted with B, Si, P, and As ions. Figure 3 shows the results of these studies obtained with 50-keV phosphorus ions. In Fig. 3(a), the positions of the extrema similar to those depicted in Fig. 1 assume essentially two discrete values, with an abrupt change occurring at a critical dose density. In Fig. 3(b), the ratio of the angular-dependent part to the average part of THG is also seen to remain constant, and to vanish abruptly once the same critical ion dose is exceeded. The average THG [Fig. 3(c)] decreases with increasing dose, exhibiting a sharp minimum at the critical dose. However, it begins to increase again beyond the critical dose and approaches a constant value at still higher dose densities. Similar results were also obtained with samples implanted with other ions, although the critical dose density at which abrupt changes occur was found to decrease with increasing ion mass. The fact that Si-implanted samples also exhibit similar dependences is particularly interesting, as it rules out the possibility of any important role played by impurity absorption.

The dependence of critical density on the type of ions implanted suggests that the dependences observed in Fig. 3 are associated with the process of amorphization accompanying ion implantation. It is known through TEM observations[4] that there exists a threshold dose density, below which only point-defect

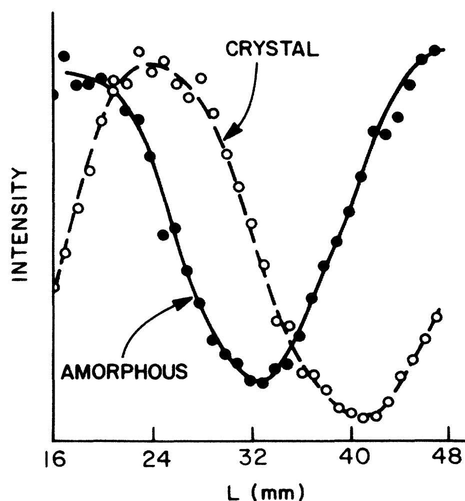

FIG. 1. Oscillatory behavior of the reflected third-harmonic power as a function of the distance L between the sample and the dichroic mirror.

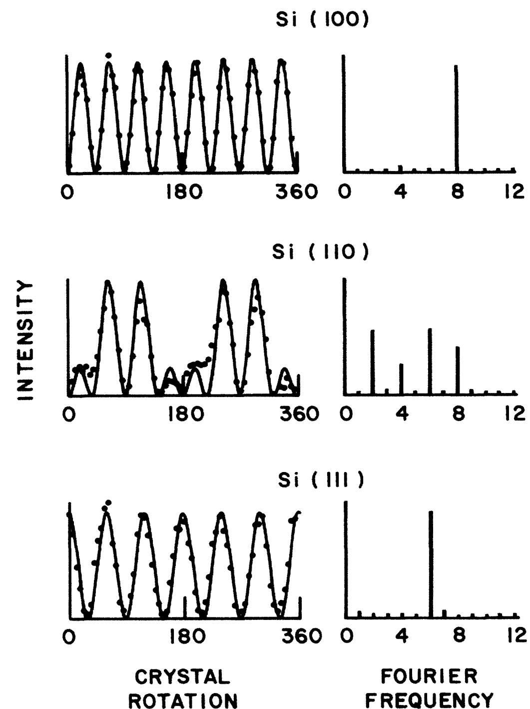

FIG. 2. Rotational dependence of THG signal from (100), (110), and (111) samples when the samples are rotated about the surface normal of the sample. These results were obtained with an angle of incidence of 45°. The incident beam was polarized in the plane of incidence and the THG signal with a polarization perpendicular to the plane of incidence was detected. The angular Fourier spectra of the observed THG signal are also shown.

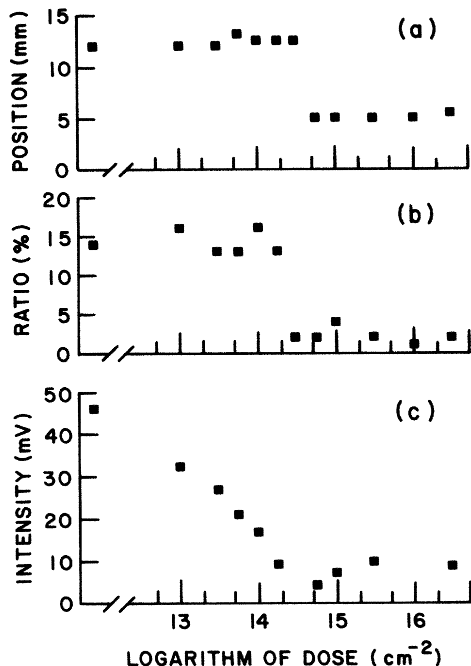

FIG. 3. Dose dependence of (a) the position of extrema in Fig. 1; (b) the ratio of the rotation-dependence part to the average of the THG signal; and (c) the average THG intensity. The left-most points on the plots represent results from pure (unimplanted) silicon. The results in (b) and (c) were taken in vacuum to avoid the interference due to air.

clusters are observed near the surface. Above this threshold density, an amorphous layer is known to form below the surface, and grow with increasing dose both toward the surface and deeper into the bulk. TEM measurements performed on the samples used for Figs. 3 confirm that the samples implanted with a critical dose as determined by THG do exhibit a surface layer containing residual crystalline regions[4] or crystallites imbedded in already amorphized regions. For samples with doses exceeding the critical value, the density of these crystallites within 10 nm of the surface decreases with increasing dose, and disappears altogether at still higher dose densities where the THG approaches a constant level.

The importance of this correlation between THG and TEM measurements can be strengthened further with ion-channeling measurements on the same samples. For example, the intensity of the dechanneling signal is a measure of the extent of lattice damage in the surface region. The decrease in the average THG presented was seen to correlate well with an increase in the dechanneling signal.[5]

On the basis of the correlations noted above, we believe that the dose dependences observed in Fig. 3 can be understood readily. As was pointed out before,[1] the position of the extrema depicted in Fig. 1 is determined by the linear optical properties of air and the sample under investigation and by the relative phase of its nonlinear susceptibilities; the observed shift in the position of the extrema will thus have to be due to a difference in the linear and nonlinear optical properties of the samples. The results in Fig. 3(a) would follow if the samples with less than critical dose are crystalline but with small damaged regions, and the samples with greater than critical dose are essentially amorphous. The critical ion dose occurs when the surface region responsible for the detected THG is a mixture of amorphous and crystalline Si. The extent of the change in the position of the extrema observed in Fig. 3(a) is also comparable with the calculated changes in the linear optical factors for the overall THG using the appropriate formula[1] and the optical constants for the crystalline and amorphous samples of silicon.[6] Second, the vanishing of any rotational dependence in Fig. 3(b) for samples with greater than the critical dose is consistent with the amorphization of these samples with very few crystallites remaining; the constant ratio of the angular-dependent part to the average THG for samples with less than critical density would also follow if the residual crystallites are oriented the same way as in the undoped crystalline sample, and the amorphized regions have a lower nonlinear susceptibility than the crystalline state. The former condition was indeed observed to be the case with the aid of dark-field images and convergent-beam electron-diffraction patterns obtained in the electron microscope,[4] and the latter condition was borne out in Fig. 3(c) which shows that the third-order susceptibility for crystalline silicon may be about a factor of 2 larger than that for the amorphous silicon. One might also add in this connection that the sharp minimum in Fig. 3(c) is most likely due to a reversal in sign of the overall third-harmonic amplitude. This would happen if the harmonic amplitude generated by the amorphous region is equal in magnitude but opposite in sign to that generated by the residual crystallites.

It is interesting to speculate on the cause of the reduction in the nonlinear susceptibility when the samples make a transition from crystalline to amorphous state. The difference in the density[7] is too small and is also of the wrong sign to account for the observed reduction in the susceptibility. One likely reason for the reduction is that silicon atoms are somewhat more tightly bound in the amorphous state, resulting in reduced nonlinear polarizability.

Unlike other techniques such as TEM, THG can provide nondestructive *in situ* monitoring of properties within surface regions. With use of high-peak-power, picosecond pulses for excitation, the third-harmonic signal can be enhanced significantly without the danger of annealing of the sample under investigation. As such, THG should prove very useful in research in-

volving ion-implanted samples.

One of us (C.C.W.) enjoyed several useful discussion with Professor John D. Dow. Preliminary results of this research were presented at the March Meeting of the American Physical Society held in Baltimore, 1985.

[(a)]Present address: Wayne State University, Detroit, MI 48202. Permanent address: Institute of Physics, Beijing, China.

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