Raman-scattering study of ion-implantation-produced damage in Cu_2O

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We present a Raman-scattering study of damage in Cu_2O which we have implanted with 90- and 180-keV Cd ions with doses ranging from 1.5×10^{11} to 1.5×10^{15} cm^{-2}. The Raman scattering was performed prior to annealing in order to study primarily the implantation-produced lattice damage. Using two argon-laser lines close to resonance with the 1*S* blue exciton, we observe changes from the pure-crystal Raman spectrum at all implantation doses. The unusual sensitivity of the technique can be interpreted in terms of damage-induced broadening of the intrinsic exciton states.

I. INTRODUCTION

A number of recent experiments have probed the effects of damage on the Raman spectra of crystals. In some cases, it is found that small amounts of damage or small numbers of impurities modify the pure-crystal (space-group) selection rules so that zone-center phonons appear in normally forbidden polarizations[1] or normally Raman-inactive phonons become Raman active.[2-4] In heavily damaged or amorphous materials[5,6] and in heavily doped crystals,[7] however, the crystal-momentum selection rules break down, and the observed spectra can be described in terms of the density of phonon states over the entire first Brillouin zone. We report here on our study of these effects in the semiconductor Cu_2O using ion implantation to introduce controlled amounts of damage. In several respects cuprous oxide is an especially interesting crystal for such a study. First, it has a rich phonon spectrum with one Raman-active phonon, two infrared-active phonons, and three phonons normally neither ir nor Raman active. Second, Cu_2O has electric-dipole-allowed exciton states conveniently accessible with an argon-ion laser which allows one to probe the effects of damage on the electronic structure and on the exciton-phonon couplings, as well as the effects of damage on the phonon spectrum itself. Third, near these exciton states Cu_2O has very high optical absorption, so that the laser beam penetrates only the implanted region and does not reach the undamaged crystal substrate. Resonance Raman scattering has been used in silicon[8] to study impurity electronic states at impurity densities as low as 5×10^{15} cm^{-3}. In this work, however, we study primarily the effects of ion-implantation-produced damage on the resonance Raman spectra, since we find that all effects are independent of implanted-ion type[9] and depend only on implantation dose.

II. EXPERIMENTAL

The 0.5-mm-thick samples were cut from nearly-single-crystal Cu_2O boules which were grown by a floating-zone method[10] followed by anneal treatments. These crystals were mechanically polished and then etched in concentrated nitric acid to remove the damaged surface layer which otherwise strongly perturbs the Raman spectra.[3] X-ray and neutron diffraction studies show the presence of many low-angle (1–2°) grain boundaries in these crystals, and thus no attempt was made to attain specific alignments in the implantation process. Seven samples were implanted at room temperature with 180-keV Cd^{++} ions in doses ranging from 1.5×10^{11} to 1.5×10^{15} ions/cm^2 and one sample with 1.5×10^{15} Cd^+ ions/cm^2 at 90 keV. The dose rate ranged from less than 10^{11} ions/cm^2 sec to 10^{12} ions/cm^2 sec. The projected range R_p and projected range straggling ΔR_p of 180-keV Cd ions in Cu_2O are 0.038 μm and 0.010 μm, respectively, calculated on the basis of the formulation by Lindhard *et al.*[11] using the computer code as given by Johnson and Gibbons.[12] At 90 keV the projected range and range straggling are 0.021 μm and 0.006 μm, respectively. Assuming that half of the Cd ions lie within ΔR_p of the projected range, we estimate that the mean ion densities range from 3.8×10^{16} cm^{-3} to 3.8×10^{20} cm^{-3} for the 180-keV implants and to 6.0×10^{20} cm^{-3} for the 90-keV implant. The calculation of the ion stopping shows that the nuclear-energy loss is independent of energy and is at least a factor of 5 greater than the electronic-energy loss over the entire range of a 180-keV Cd projectile in Cu_2O. Thus, we shall assume that the damage in these unannealed samples is evenly distributed along the length of the Cd projectile track. In a later paragraph, we shall discuss further a model of the amount and distribution of lattice damage consistent with our experimental results.

For the Raman scattering we used the 4880- and 4765-Å lines of an argon-ion laser and a spectrometer system consisting of a $\frac{3}{4}$ m double spectrometer scanned synchronously with a third monochromator. The use of this triple monochromator system was essential in observing Raman features within 100 cm^{-1} of the exciting line in this strongly absorbing region of Cu_2O. The laser beam was incident at approximately 10° to the unoriented sample face, and the scattered light was observed normal to the crystal face. All data were obtained with the laser light polarized in the plane of incidence, with no analysis of the scattered-light polarization, and with the samples conduction cooled to liquid-nitrogen temperature.

III. RESULTS AND DISCUSSION

Some of the spectra obtained with 4880-Å radiation are shown in Fig. 1 where features arising from zone-center phonons are identified as follows: a Raman-allowed mode Γ_{25^+} (515 cm^{-1}), two infrared-allowed modes $\Gamma_{15}^{(1)-}$ (LO, 154 cm^{-1}) and $\Gamma_{15}^{(2)-}$ (TO, 635 cm^{-1}, LO, 665 cm^{-1}); one mode neither Raman nor ir-allowed Γ_{12}^- (109 cm^{-1}); two second-order overtones, $2\Gamma_{12}^-$ (218 cm^{-1}) and $2\Gamma_{15}^{(1)-}$ (308 cm^{-1}); a second-order combination $[\Gamma_{15}^{(1)-}(\mathrm{LO}) + \Gamma_{15}^{(2)-}(\mathrm{LO})]$ (820 cm^{-1}); and a fourth-order overtone $4\Gamma_{12}^-$ (436 cm^{-1}). The pure-crystal spectrum (trace a) shows strong scattering only from the second-order $2\Gamma_{12}^-$ overtone with some very weak scattering from most of the other features. Weak scattering from Raman-forbidden first-order modes such as those at 109, 154, 635, and 665 cm^{-1} probably results from intrinsic selection-rule violation mechanisms in the pure crystal which have been seen very near resonance with several excitons in Cu_2O.[2,3,13] With a dose of 1.5×10^{11} ions/cm^2, the spectrum (trace b) changes considerably. Some symmetry selection-rule violation due to implantation-produced lattice damage may be involved in the slight enhancement of some Raman-forbidden modes; however, the increase in intensity of the Raman-allowed features at 218 and 515 cm^{-1} cannot be understood simply on this basis. Furthermore, any model of implantation-related effects should explain the very strong increase of the forbidden 154-cm^{-1} line that is observed in Fig. 1 (trace b). At higher implantation doses (traces c and d), the first-order peaks gradually weaken and finally merge into broad continua which suggest density-of-states spectra characteristic of very heavily damaged or amorphous materials. With heavy damage, crystal-momentum selection rules no longer apply to the Raman scattering and phonons of all momenta within the Brillouin zone can participate in the Raman scattering. Much of the low-damage behavior is closely related, we believe, to the fact that the Raman scattering is done near resonance with narrow exciton

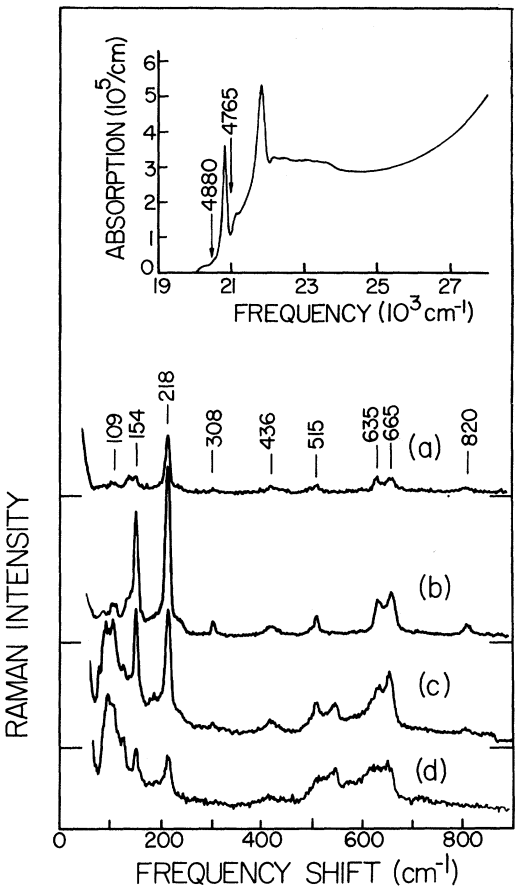

FIG. 1. Raman spectra obtained with 100-mW power at 4880 Å showing the effects of increasing Cd-implantation dose: a, unimplanted; b, 1.5×10^{11}; c, 1.5×10^{13}; d, 5.3×10^{14} ions/cm^2. The labeled features are described in the text. The same vertical scale was used for all traces with the 218-cm^{-1} peak in trace a corresponding to 125 counts/sec. The insert is taken from Ref. 2.

features. The insert in Fig. 1 shows the absorption spectrum of Williams and Porto,[2] obtained from reflectivity measurements on pure Cu_2O, and the positions of the 4880- and 4765-Å laser lines on either side of the 1S "blue" exciton are shown by arrows. The 4880-Å line lies 350 cm^{-1} (approximately five half-widths) below this exciton where the skin depth in the pure crystal is approximately 0.5 μm. However, the skin depth in the heavily damaged samples appears not to exceed the implantation depth of approximately 0.04 μm, since almost no sharp crystalline-like Raman features remain in the spectrum of Fig. 1, trace (d).

The 4765-Å laser line produces some of the strongest Raman signals of any of the argon-laser lines in pure Cu_2O because it lies only 140 cm^{-1} (approximately two half-widths) above the peak of the 1S blue exciton, and spectra obtained with this radiation are shown in Fig. 2. The Raman-shifted

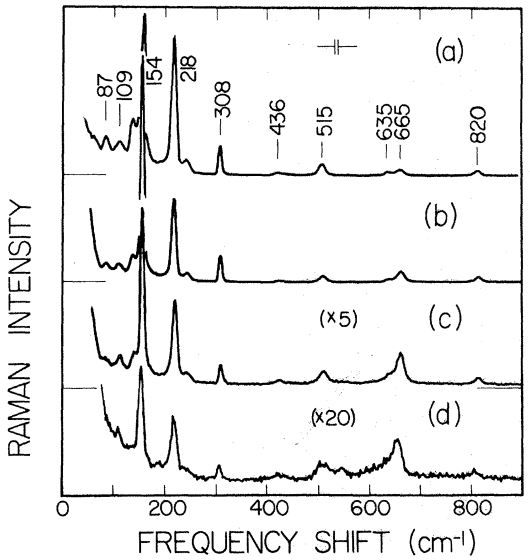

FIG. 2. Raman spectra obtained with 100 mW of 4765 Å excitation with the same Cd-ion implantation doses as in Fig. 1. Note the change in vertical scale for traces c and d. The 218 cm^{-1} peak height in trace a corresponds to 13 000 counts/sec. Instrumental resolution was 6 cm^{-1}.

photons corresponding to the 218- and 154-cm^{-1} lines are within one half-width of the center of the resonance, and the enhancement of these lines in the pure crystal is easily seen in trace (a) of Fig. 2 in comparison with trace (a) of Fig. 1. As damage is introduced in Cu_2O, all of the zone-center features excited by 4765-Å radiation decrease rapidly in intensity in contrast with the behavior observed for 4880-Å excitation. In the spectra from samples which received high doses, Fig. 2 (traces c and d), one again observes broad continua; however, the zone-center features remain stronger than those observed with 4880-Å excitation. In pure Cu_2O the skin depth at 4765-Å is approximately 0.1 μm; however, broadening of the exciton states should increase the absorption by a factor of 2–3, so that the skin depth in damaged samples is expected to nearly match the implantation depth.

Two aspects of the damage-related behavior are of particular interest. First, we shall examine the structure of the broad bands observed at high-implantation dose. Second, we shall examine the dependence of the Raman-line intensities on implantation dose and propose a model for understanding the detailed behavior.

Experiments on some amorphous materials[5,6] have shown that the Raman spectra can be closely related to the phonon density of states in the pure-crystalline material by plotting a reduced intensity[5] I_R such that $I_R(\omega) = \omega[n(\omega)+1]^{-1} I(\omega)$, where $I(\omega)$ is the measured intensity at the frequency shift ω, and $n(\omega)$ is the Bose-statistical-population factor. In Fig. 3, trace (a), we show the reduced Raman spectrum from the Cu_2O sample with the highest implantation dose (viz. 1.5×10^{15} ions/cm^2 at 180 keV). [Before reduction, the spectrum is nearly identical to that of Fig. 1, trace (d).] Unfortunately, it is not possible to compare this spectra directly with the density of phonon states in pure crystalline Cu_2O, since no inelastic neutron scattering has been reported, and since the only existing theoretical dispersion curves were calculated before some of the zone-center frequencies were properly assigned. However, the band from approximately 500 to 700 cm^{-1} appears well separated from other modes in trace (a) of Fig. 3 and has upper and lower frequencies which correspond to the infrared-active (LO) mode at 665 cm^{-1} and the Raman-active mode at 515 cm^{-1}. We have obtained an unambiguous second-order spectrum from undamaged Cu_2O in the region from 1000 to 1400 cm^{-1}, which is plotted in trace (b) of Fig. 3. Note that we have compressed the horizontal scale by a factor of 2 to facilitate a direct comparison with the first-order scattering of trace (a). For the second-order spectrum, we have removed in the usual way the Bose statistical factor by multiplying the observed intensity $I(\omega)$ by the factor $[n(\frac{1}{2}\omega)+1]^{-2}$. The strong correspondence between the reduced spectra shown in Fig. 3 indicates that two conclusions can be drawn. First, the second-order spectrum is composed primarily of overtone scattering of two identical phonons with momenta $+\vec{q}$ and $\Delta\vec{k}-\vec{q}$, where

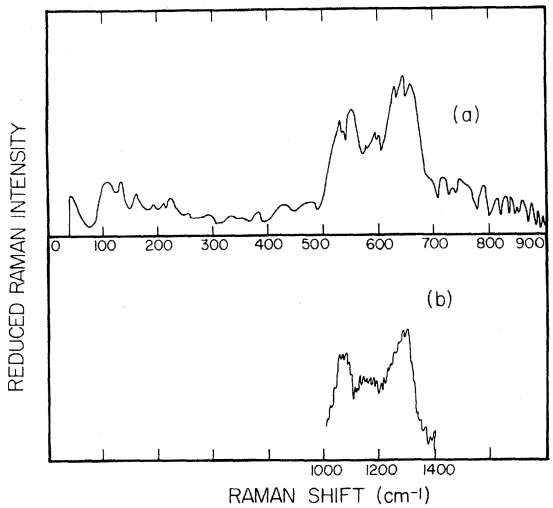

FIG. 3. Trace a: Reduced Raman spectrum as described in the text; Cd-ion dose 1.5×10^{15} ions/cm^2; 4880-Å excitation. A constant background of 50 counts/sec was subtracted before reduction to correct for dark count and elastically scattered light in the spectrometer. Trace b: Reduced second-order spectrum from pure Cu_2O as described in the text; 4880-Å excitation. Note that the horizontal scale is compressed by a factor of 2.

Δk is the difference between scattered- and incident-photon momenta, i.e., little contribution arises from combination scattering from mixtures of two different-symmetry phonons. Second, there appears to be little shift of vibrational frequencies from the pure crystal to the heavily damaged crystal. Both of these characteristics have been noted previously in observations on silicon, germanium, and some III-V semiconductors.[6]

To examine in more detail the intensity behavior of the zone-center features, we show in Fig. 4 the peak intensity of the 154-, 218-, and 515-cm^{-1} lines for both 4880- and 4765-Å excitation for all samples used. We shall focus on understanding two principal damage-related features: (i) Using 4880-Å radiation, very low damage produces a factor of 10 increase in the 154-cm^{-1} line, with only about a factor of 3 increase for the 515-cm^{-1} line. (ii) Moderate amounts of damage (doses from 1.5×10^{12} to 5×10^{14}) greatly weaken all three lines in the 4765-Å spectra, with a more gradual weakening apparent in the 4880-Å results. We believe that both effects can be understood in terms of damage-induced broadening of the excitonic structure of Cu_2O. Although no absorption or reflectivity measurements have been done on these implanted samples, the measurements of Daunois *et al.*,[14] and of Williams and Porto[2] show that the intrinsic 1*S* blue exciton linewidth (full width at half maximum) broadens from ~ 140 cm^{-1} in high-quality bulk samples to as much as 500 cm^{-1} in ~ 10-μm-thick samples or poor-quality bulk samples. In addition, resonance Raman measurements on high-purity Cu_2O samples with poorly prepared surfaces show indirectly that the exciton structure is greatly broadened by surface damage introduced during mechanical polishing.[3] Ion implantation almost certainly produces similar effects. Broadening of the exciton features can arise either from a reduced exciton lifetime due to scattering from damage sites, or from a distribution of exciton energies arising from variations in the local-crystal environment due to lattice damage. The former mechanism would produce a Lorentzian-shaped line while the latter would likely produce a Gaussian distribution. Undoubtedly, both effects occur; however, for illustration we shall consider the effects arising from Gaussian broadening.

Raman scattering in semiconductors is generally described in terms of a third-order scattering process. Near resonance with an electronic state the scattering-matrix element is dominated by terms of the form[15]

$$M\sim\frac{M_{0\beta}M_{\beta\alpha}M_{\alpha 0}}{(\omega_s-\omega_\beta-i\Gamma_\beta)(\omega_L-\omega_\alpha-i\Gamma_\alpha)},$$

where $M_{\alpha 0}$ and $M_{0\beta}$ are exciton-radiation field-matrix elements, $M_{\beta\alpha}$ is the exciton-lattice matrix element which scatters the exciton from state α with energy $\hbar\omega_\alpha$ to state β with energy $\hbar\omega_\beta$, and ω_s and ω_L are the scattered and (incident) laser frequencies, respectively. In the absence of any direct evidence to the contrary, we shall assume that the three matrix elements in Eq. (1) are not strongly damage dependent. The effects of damage-induced broadening of the exciton states arise through the linewidth parameters Γ in the case of additional Lorentzian broadening. Gaussian broadening can be introduced by assuming a distribution of central frequencies ω_α and ω_β and a probability of occurrence given by $P(\omega_\alpha)\sim\exp[-(\omega_{\alpha 0}-\omega_\alpha)^2/\sigma_\alpha^2]$, where $\omega_{\alpha 0}$ is the resonant frequency with no damage-induced broadening, and σ_α is the characteristic width of the broadening. Because first-order Raman scattering involves coupling through two intermediate electronic states, two situations that have been shown to be operative for phonon-Raman scattering in Cu_2O must be carefully distinguished[3]: (i) If the exciton-lattice operator produces *inter*-band scattering (sometimes called a three-band Raman term), then one intermediate electronic state may be resonant but the other state will be far off resonance. That is, if $\omega_L-\omega_\alpha$ is comparable to Γ_α or σ_α, then $\omega_s-\omega_\beta$ will greatly exceed Γ_β or σ_β, and only one term in the denominator of the scattering-matrix element will be resonant. For this experiment in Cu_2O, the Raman-allowed 515-cm^{-1} phonon is produced by inter-band scattering via the deformation potential interaction, and the intensity should be

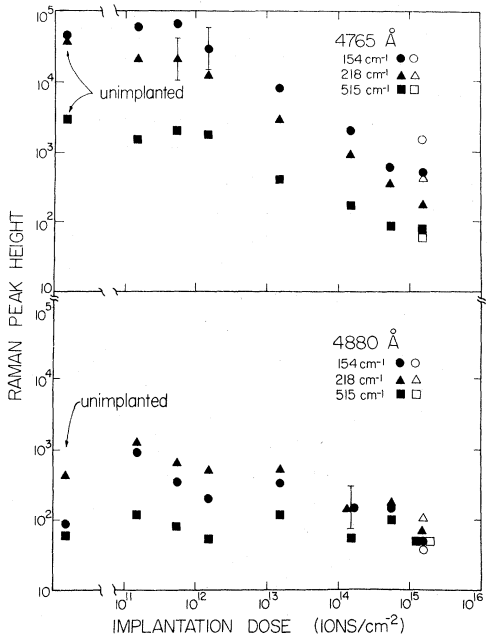

FIG. 4. Peak intensities of three Raman features with 4880- and 4765-Å excitation for all implanted samples. Open symbols correspond to the sample implanted with 90-keV rather than 180-keV Cd ions.

examined in light of this mechanism. (ii) If *intra*-band exciton-phonon scattering is involved (two-band Raman term), then the two electronic states may be members of the same exciton series, and both states are likely to be nearly resonant, i.e., $\omega_L - \omega_\alpha \simeq \omega_s - \omega_\alpha \simeq \Gamma_\alpha \simeq \sigma_\alpha$ and similarly for state β. In Cu_2O, the 154 cm^{-1} longitudinal-optical mode appears to be activated near resonance by an intra-band Fröhlich mechanism as described by Martin.[2,16] In this case, it is possible for a double resonance to occur in which both terms in the denominator of the matrix element become small simultaneously.

The intensity behavior of these phonons in damaged Cu_2O is consistent with these scattering mechanisms. The 4765-Å laser line (20 986 cm^{-1}) lies near an absorption minimum midway between the 1*S* (20 850 cm^{-1}) and 2*S* (21 130 cm^{-1}) blue exciton states, and for the 154-cm^{-1} line the outgoing photon lies near the peak of the 1*S* blue resonance. Slight damage-induced broadening decreases the strength of the out resonance but increases the strength of coupling of the incident laser field to the 2*S* state, so that little change in the Raman intensity occurs (see Fig. 4). For greater broadening, ($\sigma \gtrsim 200$ cm^{-1}) however, the Raman intensity should fall in proportion to the square of the peak-absorption strength or like σ^{-2}. For the slightly off resonance case with 4880-Å excitation (20 492 cm^{-1}), the 154-cm^{-1} line should increase strongly for low damage as the coupling with both broadened exciton states become resonant and the intensity should decrease only after σ exceeds 500 cm^{-1}. This agrees well with the observations; an increase of a factor of 10 in intensity occurs when slight damage is introduced with the lowest dose implantation, and this is followed by a very slow decrease in intensity with increasing dose as seen in Fig. 4. In contrast with the 154 cm^{-1} line, the 515-cm^{-1} line increases in intensity by a factor of about 3 with 4880-Å excitation for very low damage, and this is quite consistent with a singly resonant process. With 4765-Å excitation, a similar effect of damage-induced broadening of the blue exciton states on this singly resonant process would be expected to give an initial rise in intensity for low dose followed by weakening as the implantation dose increases. The observed behavior, however, is that the intensity of this allowed line is nearly constant for low dose, and we suggest that this result from a slightly broadened exciton structure of our unimplanted crystal over that shown in the insert of Fig. 1. Also, we emphasize that the intensity data has not been adjusted to account for absorption corrections which will influence the quantitative results. This will be especially important very near resonance (4765 Å) in the crystals with sharp excitonic structure, i.e., the pure and lightly damaged crystals. In addition, the penetration of the laser through the depth distribution of the 90-keV implant may account for slightly stronger zone-center peaks than those observed with the 180-keV implant. This effect is small, and gives us confidence in our interpretation of the variation of intensity with dose.

Of considerable interest is the relationship between changes in the Raman spectra and a plausible model of damage distribution in Cu_2O. The nuclear-energy loss calculated for 180-keV Cd in Cu_2O using the method of Lindhard *et al.*[11] averages 1.6 keV per lattice plane. If this is taken as the energy E of a primary recoil (e.g., a Cu ion), its range would be of the order of 15 Å. The Kinchin-Pease relation[17] gives approximately 80 displaced atoms for each primary recoil, and the picture which emerges is one with each Cd track surrounded by a heavily damaged region roughly 15 Å wide.[18] Thus, at a dose of 1.5×10^{11} cm^{-2} roughly 0.3% of the surface is heavily damaged, and the remainder is completely undamaged. At a dose of 1.5×10^{13} cm^{-2}, nearly 30% of the implanted region should be heavily damaged and damage saturation should occur near 5×10^{13} cm^{-2}. However, if one regards the Raman spectra simply as a superposition of pure-crystal and heavily damaged crystal spectra in proportion to their relative volumes, the data show some important inconsistencies. First, the 4880-Å spectra show a strong *increase* in intensity of the pure-crystal (zone-center) Raman lines for very low dose. We have suggested an interpretation based on damage-induced broadening of the intrinsic exciton states, and this is plausible even at low doses since the excitons are made up from valence and conduction *band* states which are extended through the entire crystal. Thus, the electronic states in the undamaged regions are affected by nearby damage tracks. Second, the intensity vs dose data of Fig. 4 does not saturate near a dose of 5×10^{13} cm^{-2} expected on the basis of the diameter of the heavily damaged region surrounding each damage track. The peak heights continue to decrease to doses of approximately 1.5×10^{15} cm^{-2}. This behavior suggests that either the damage has not yet saturated within each damage track or the diameter of the damage tracks are considerably less than we have estimated. Because the implantation was done at room temperature, partial self-annealing during implantation may account for this result.

IV. SUMMARY

In conclusion, we believe that these results show that phonon-Raman scattering, especially when carried out near resonance with sharp excitonic structure, can be a useful tool in studying lattice damage in semiconductors over a wide range of

damage levels. In particular, the technique shows promise of yielding a semiquantitative measure of the amount of ion-implantation-produced damage or, correspondingly, a measure of the success of various annealing cycles in removing this damage.

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