

RAMAN SPECTROSCOPY OF ION-IMPLANTED SILICON

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ABSTRACT

Raman spectroscopy is used to characterize silicon implanted with boron at a dose of $10^{14}/\text{cm}^2$ or less and thermally annealed. The Raman scattering strengths and band shapes of the first-order optical mode at 520 cm^{-1} and of the second-order phonon modes are investigated to determine which modes are sensitive to the boron implant. The as-implanted samples show diminishing Raman scattering strength as the boron dose increases when the incident laser beam is 60° with respect to the sample normal. Thermal annealing restores some of the Raman scattering strength. Three excitation wavelengths are used and the shortest, 457.9 nm, yields the greatest spectral differences from unimplanted silicon. The backscattering geometry shows a variety of changes in the Raman spectrum upon boron implantation. These involve band shifts of the first-order optical mode, bandwidth variations of the first-order optical mode, and the intensity of the second-order mode at 620 cm^{-1} .

INTRODUCTION

Ion implantation is a critical step in the fabrication of semiconductor devices. Most processes involve several implants, so the effects of implantation are a prime concern. Raman spectroscopy is frequently used to investigate as-implanted and annealed samples [1]. Implant dose series and Raman spectra have been reported for Si in silicon [2,3], phosphorus in silicon [4], and arsenic in silicon [5]. A detailed study of a high-dose boron implant in silicon has appeared [6,7]. The present work is concerned with boron implants into silicon at doses of 10^{13} and 10^{14} boron atoms/ cm^2 . Both macro-Raman and micro-Raman are used to characterize the boron-implanted and the annealed silicon wafers. The macro-Raman studies use three different excitation wavelengths and have the incident

laser beam at an angle of 60° with respect to the sample normal. The micro-Raman is done at 457.9 nm in a backscattering configuration. The micro- and macro-Raman arrangements are used to determine which approach provides a more sensitive measure of lattice damage due to the boron implant.

The second section describes the sample preparation and the Raman measurements. The third section presents and discusses the experimental data. The final section has the conclusions.

EXPERIMENTAL PROCEDURES

Lightly doped, n-type, $\langle 100 \rangle$ silicon wafers were implanted with 30 keV boron ions through a $0.0785 \mu\text{m}$ thick thermal oxide. The boron dose was either 1×10^{13} or $1 \times 10^{14}/\text{cm}^2$. Selected wafers received a post-implant furnace anneal at 1000°C for 30 minutes in nitrogen. The oxide was then etched off all the samples.

The macro-Raman spectroscopy is done with a SPEX 1403 double monochromator. An Ar^+ laser provided the excitation at 457.9, 488.0, and 514.5 nm. The Raman shift spectra are obtained over 100 to 1100 cm^{-1} , and are collected in increments of 1 cm^{-1} at an integration time of 2 seconds per increment. The monochromator's entrance and exit slits are set to $400 \mu\text{m}$, while its middle slits are set to $480 \mu\text{m}$. Additional data are collected over 500 to 540 cm^{-1} in increments of 0.2 cm^{-1} at an integration time of 3.0 seconds per increment with the successive slit widths set to 200, 280, 280, and $200 \mu\text{m}$. The samples are held in a holder such that there is a 60° angle between the incident beam and the normal to the sample surface. A 90° geometry is used for the collection of the scattered light.

The micro-Raman spectra are obtained with an ISA S3000 spectrometer at an excitation wavelength of 457.9 nm. The spectrometer is coupled to an Olympus MSPlan 100 (0.95 NA) microscope objective, which is also used to collect the light.

An unimplanted, 10-30 Ohm-cm, n-type, $\langle 100 \rangle$ silicon wafer serves as a crystalline silicon reference. The assignment of the Raman bands of silicon is discussed in Refs. [2,8-12].

RESULTS

The macro-Raman spectra obtained with 457.9 nm excitation show the

greatest deviation from the reference silicon spectrum. The boron implant reduces the intensity of the first-order 520 cm^{-1} optical phonon band and of the second-order transverse optical mode (TO) near 970 cm^{-1} . The effects on the first- and second-order optical modes of silicon for the 10^{14} B/cm^2 dose are shown in Figures 1 and 2. Implantation attenuates the Raman scattering strength, but subsequent annealing causes a partial recovery of the Raman signal. It is noteworthy that, in the present studies, annealing does not lead to a full recovery of the Raman signal.

Figure 3 displays the integrated intensity of the 520 cm^{-1} peak for the three excitation wavelengths. The integrals are normalized at each wavelength by those for the reference silicon sample. The higher dose produces less Raman scattering at each excitation wavelength. In addition, the 457.9 and 488.0 nm laser excitations yield weaker Raman scattering relative to the reference silicon than does the 514.5 nm excitation. The macro-Raman spectra for the second-order 970 cm^{-1} show a similar trend. Raman spectra, obtained using 514.5 nm excitation, for the $10^{14}\text{ B atoms/cm}^2$ case are shown in Figure 4. There is less attenuation than in Figure 1 of the 970 cm^{-1} band because of the greater depth of penetration. However, a weak broadening on the low-energy side of the 520 cm^{-1} band is observed in the spectra of the as-implanted samples.

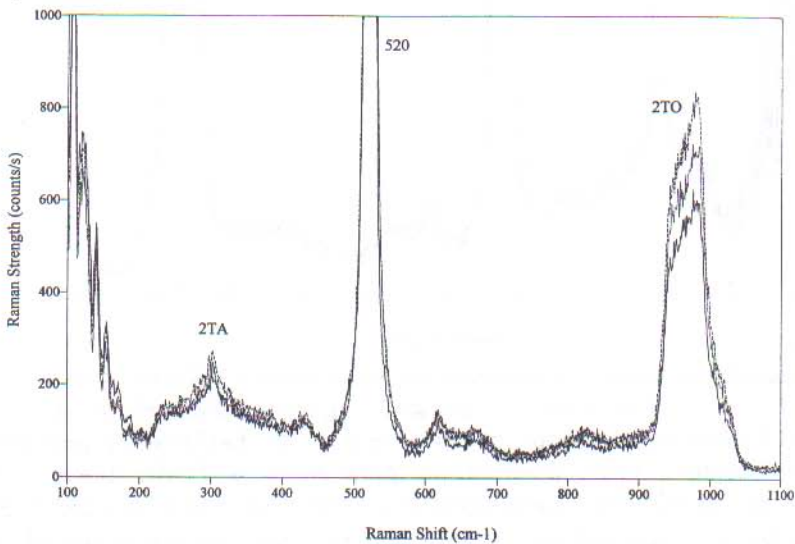


Fig. 1. Macro-Raman spectra of implanted silicon with excitation at 457.9 nm. Dose of $1 \times 10^{14}\text{ B/cm}^2$. As-implanted (—), annealed (.....), and reference wafer (---).

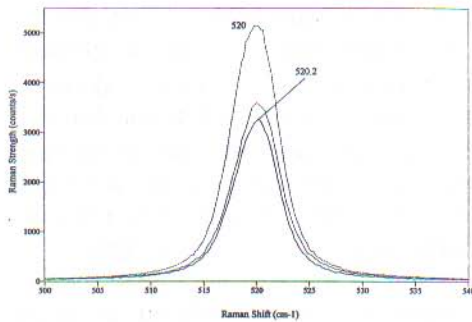


Fig. 2. Macro-Raman spectra of implanted silicon with excitation at 457.9 nm. Dose of 1×10^{14} B/cm². As-implanted (—), annealed (.....), and reference wafer (---).

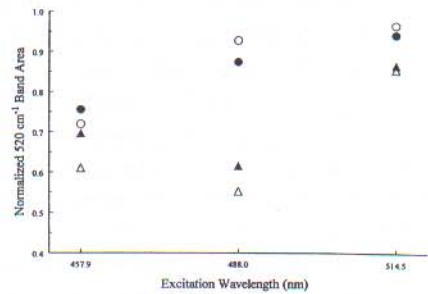


Fig. 3. Area of the 520 cm^{-1} peak normalized by the area for the reference wafer versus the laser excitation wavelength. As-implanted 1×10^{13} B/cm² (○), plus anneal (●), as-implanted 1×10^{14} B/cm² (Δ), plus anneal (▲).

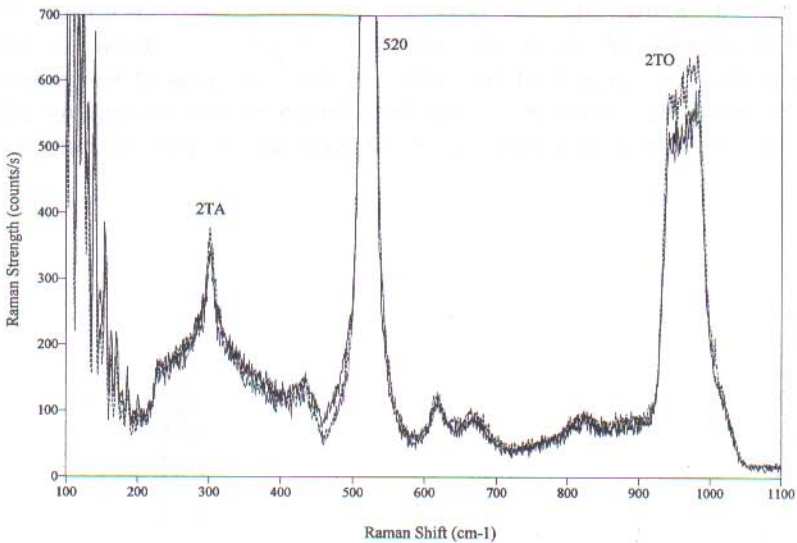


Fig. 4. Macro-Raman spectra of implanted silicon with excitation at 514.5 nm. Dose of 1×10^{14} B/cm². As-implanted (—), annealed (.....), and reference wafer (---).

Micro-Raman spectroscopy is performed in the backscatter geometry with the incident laser polarization parallel to a (100) plane. The maximum of the 520 cm^{-1} band shifts from 520.4 cm^{-1} to 519.4 and 519.6 cm^{-1} for the as-implanted, and 519.8 and 519.6 cm^{-1} for the annealed, for doses of 10^{13} and 10^{14} B/cm², respectively. The micro-Raman spectra are compared with that for the reference silicon sample in Figures 5 and 6 for

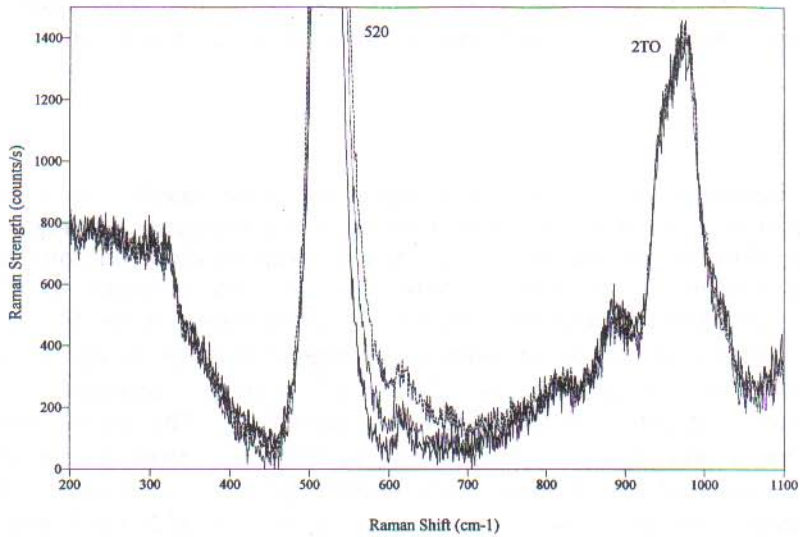


Fig. 5. Micro-Raman spectra of implanted silicon with excitation at 457.9 nm. Dose of 1×10^{13} B/cm². As-implanted (—), annealed (.....), and reference wafer (----).

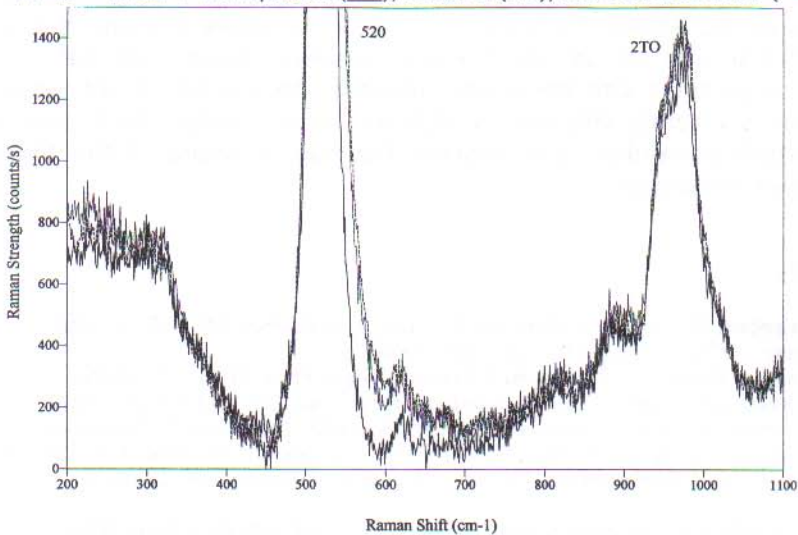


Fig. 6. Micro-Raman spectra of implanted silicon with excitation at 457.9 nm. Dose of 1×10^{14} B/cm². As-implanted (—), annealed (.....), and reference wafer (----). implant doses of 10^{13} and 10^{14} B/cm², respectively. The lower dose implant shows a narrower peak at 520 cm⁻¹, which is broadened by the anneal. Both doses show a reduced width and less intensity at 620 cm⁻¹ with respect to the reference sample. Figure 6 demonstrates that the

annealed sample for the higher dose implant has nearly the same width as the reference sample at 520 cm^{-1} and a similar intensity at 620 cm^{-1} .

CONCLUSIONS

The macro-Raman spectra of the implanted silicon samples show less deviation from the reference silicon sample as the excitation wavelength increases. With longer wavelength excitation, most incident photons are absorbed deeper in the silicon where there is less influence of the implant. The spectra obtained with 457.9 nm excitation show that the 970 cm^{-1} 2TO peak can be an indicator of implant damage, in agreement with [6]. The strength of the 520 cm^{-1} peak is attenuated by implantation and only partially restored by annealing. The micro-Raman spectra show less effect of the implant at 970 cm^{-1} than the macro-Raman, because of the different experimental geometry. However, the micro-Raman spectra show more band narrowing at 520 cm^{-1} and a sensitivity to the implant at 620 cm^{-1} . The implants also induce a band shift to lower wave number of the first-order mode that is not completely recovered by the anneal. The boron implants do not cause as many changes in the Raman spectra as the low-dose arsenic implants of Ref. [5]. However, in common with the arsenic implants, the anneals do not restore the Raman scattering strength to that of the reference silicon sample. Further study is needed to understand the microstructure of the silicon that follows the anneal.

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