MICRO-RAMAN CHARACTERIZATION OF UNUSUAL DEFECT STRUCTURE IN ARSENIC–IMPLANTED SILICON

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ABSTRACT

Raman spectroscopy has often been used to study the damage to semiconductors induced by ion implantation. Off-axis, macro-Raman spectra reveal extensive damage to the silicon lattice, consistent with many literature reports. However, when the same samples were analyzed in the backscattering mode by micro-Raman spectroscopy, evidence was found for orientational dependent lattice damage and an unusual defect structure. P/O micro-Raman spectra reveal the spatially-varying appearance of a band between 505 and 510 cm^{-1} always accompanied by that of the silicon optical mode at 520 cm^{-1}.

INTRODUCTION

Raman spectroscopy is useful for characterizing the chemical bonding and crystal structure of solids because Raman scattering depends not only on the atomic masses and bond force constants, but also on the polarization and direction of the incident light, the crystal symmetry, and the orientation of the sample. Consequently, it has often been used to study the damage to semiconductors induced by ion implantation [1-4]. The Raman selection rules, which for crystalline materials restrict spectroscopic activity to the Brillouin zone center, break down as lattice order is broken. The Raman spectrum of ion-implanted crystals increasingly mirrors a phonon density of states, no longer restricted to phonons of zero crystal momentum, as the lattice is disrupted by implantation.

We have previously studied and characterized by macro- and micro-Raman spectroscopy the type of lattice damage induced by arsenic implantation of silicon [5-6]. Raman spectroscopy is an effective probe of lattice damage because it is sensitive to changes in Si crystal structure following even low-dose As implantation. Depth profiles of lattice damage induced by As implants ranging from 2×10^{13} / cm^2 to 5×10^{15} / cm^2 were obtained by varying the excitation wavelength. Lattice damage is manifest in low dose implants by the emergence of a low energy shoulder to the 520 cm^{-1} band (first-order optical-mode) and the attenuation of the second-order transverse acoustic-mode and second-order transverse optical-mode. Here we report on the use of a micro-Raman technique that is particularly sensitive to crystallinity and spatial heterogeneity.

Polarization/orientation (P/O) micro-Raman spectroscopy is a technique developed to probe changes in chemical bonding and crystal structure, and it is based upon the dependence of Raman scattering strength on the incident electric field, the polarizability tensor dictated by the point group symmetry of the crystal, and the scattering vector [7]. The P/O micro-Raman method may be used to identify vibrational modes, distinguish allotropes and polymorphs, distinguish single from polycrystalline materials, and determine orientation of the crystal and degree of disorder, all on a micrometer scale. A program has been written to calculate normalized Raman intensities of

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single crystals, belonging to any crystal class, as a function of sample orientation for a given incident polarization and scattering vector [7].

Off-axis, macro-Raman spectra reveal extensive damage to the silicon lattice, consistent with many literature reports. However, when the same samples were analyzed in the backscattering mode by micro-Raman spectroscopy, evidence was found for spatially-varying lattice damage and an unusual defect structure. P/O micro-Raman spectra reveal the spatially-varying appearance of a band between 505 and 510 cm^{-1} always accompanied by that of the silicon optical mode at 520 cm^{-1}.

EXPERIMENT

Lightly-doped, (100), 100 mm silicon wafers were implanted with 150 keV ions through a 0.06 μm thick thermal oxide. The arsenic dose was varied from 2 x 10^{13} to 5 x $10^{15}/cm^2$ and the rate was approximately 1.4 x 10^{13} As/s-cm^2. Macro-Raman spectroscopy was performed using a SPEX 1403 double monochromator. The samples were mounted such that there was a 60° angle between the incident beam and the normal to the sample surface. A 90° geometry was used for the collection of the scattered light and the incident power level was 300 mW. The micro-Raman spectra were obtained using an Instruments SA S3000 spectrometer at excitation wavelengths of 488.0 nm and 514.5 nm with an incident power of 5 mW. The slits were set to 400 μm/4.05 mm/400 μm, and spectra were detected using an EEV Class One #15-11 CCD. The spectrometer is coupled to an Olympus MSPlan 100 (0.95 NA) microscope objective, which is used to focus the exciting laser beam and to collect the Raman scattered light. Consequently, a 180° (backscattering) geometry is used, thereby simplifying the calculations and interpretation of the response for the Polarization/Orientation Raman experiment. The P/O spectra are collected by rotating the crystal in 5° increments around a (100) axis with the collection polarization analyzer parallel to the incident polarization. A second set of spectra are then collected in the same fashion with the collection analyzer perpendicular to the incident polarization. Together, the two data sets constitute the P/O spectra for a given crystal face.

RESULTS AND DISCUSSION

The P/O micro-Raman spectra of Si (100), polarized parallel and perpendicular, consist of the single band at 520 cm^{-1} arising from the longitudinal optical (LO) phonon mode. The Si spectra in Figures 1 and 2 clearly show the dependence of Raman scattering strength on the orientation of the crystal lattice relative to the incident polarization. We note that the sample orientation in the P/O figures refers to a laboratory reference frame and not a crystallographic frame. The scattering strength of the Si 520 cm^{-1} band varies sinusoidally with respect to sample angle for both parallel and perpendicular polarizations, the responses for the two configurations being 45° out of phase with respect to each other. Such a P/O response is predicted for a cubic crystal of class O_h for the triply degenerate optical phonon whose Raman polarizability tensors are of the form

$$\alpha_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & a \\ 0 & a & 0 \end{bmatrix}, \alpha_y = \begin{bmatrix} 0 & 0 & a \\ 0 & 0 & 0 \\ a & 0 & 0 \end{bmatrix}, \alpha_z = \begin{bmatrix} 0 & a & 0 \\ a & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

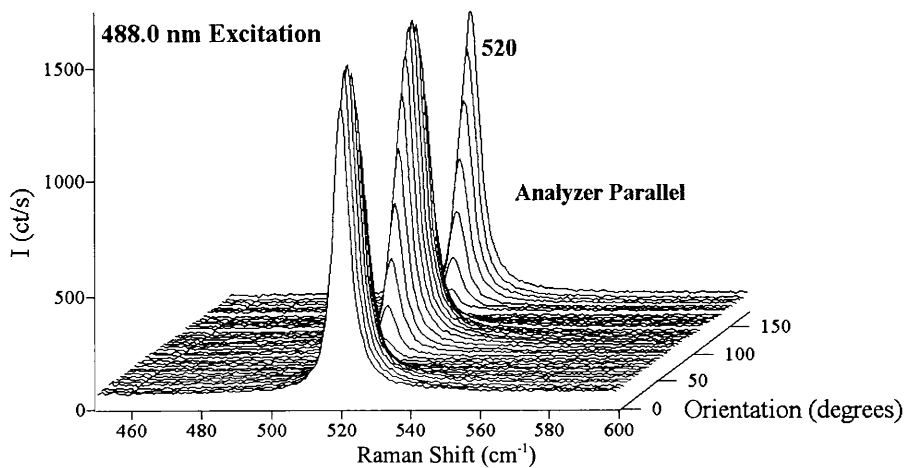

Figure 1. P/O micro-Raman spectra of Si (100). Analyzer parallel.

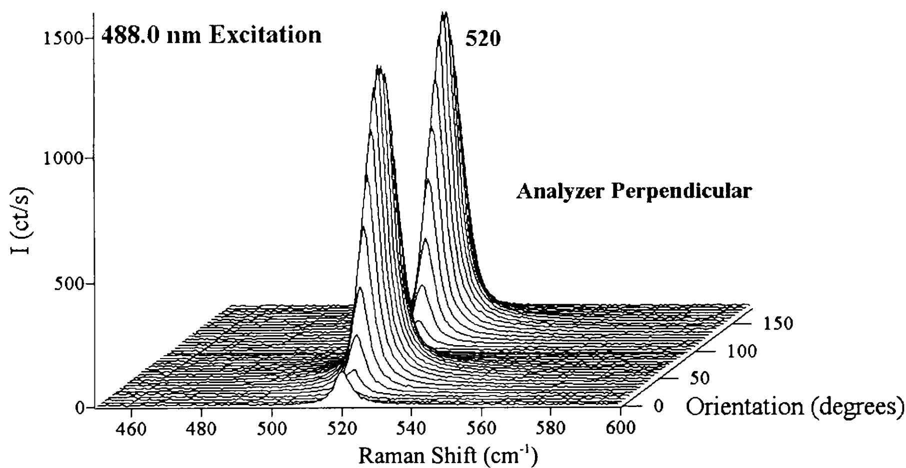

Figure 2. P/O micro-Raman spectra of Si (100). Analyzer perpendicular.

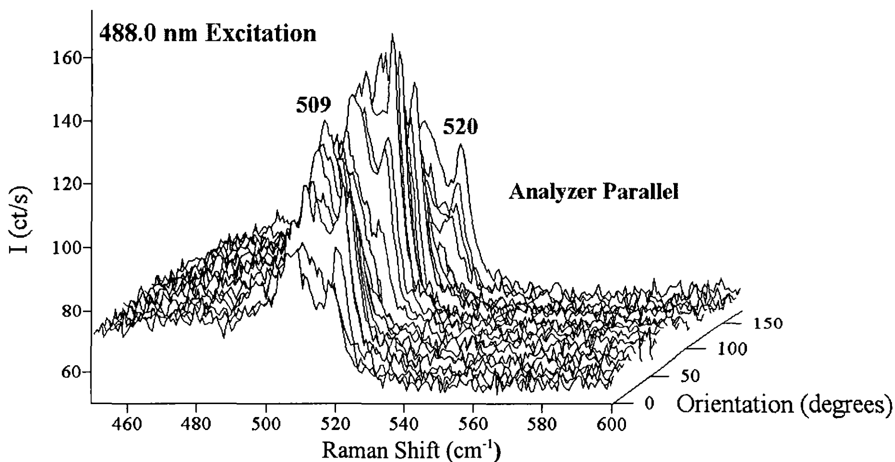

Figure 3. P/O micro-Raman spectra from irregular defect region of Si implanted with 2×10^{14} As/cm^2. Analyzer parallel.

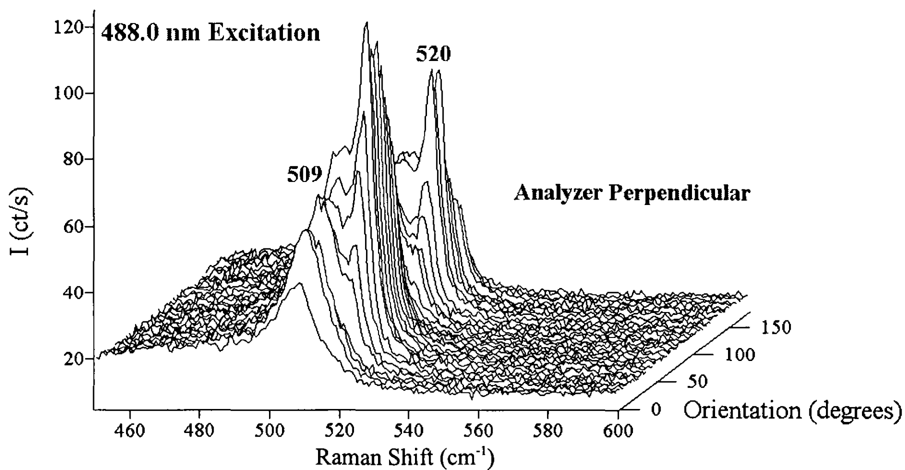

Figure 4. P/O micro-Raman spectra from irregular defect region of Si implanted with 2×10^{14} As/cm^2. Analyzer perpendicular

Ion implantation causes damage to the silicon lattice commensurate with the dose, mass, and energy of the implant. Macro-Raman spectra were acquired of a series of As implanted Si samples [8]. The optical phonon mode at 520 cm^{-1} is observed to diminish with increasing implant dose, giving way to a disorder-induced broad response below 500 cm^{-1}, indicative of amorphous silicon (α-Si). The Si most extensively damaged by As implantation yields a broad Raman band centered at ~470 cm^{-1}, matching that of α-Si. Such were the results of the macro-Raman analyses, for which the probe laser beam has a ~150 to 200 μm diameter. Our macro-Raman results are in good agreement with those of Raman studies of ion implanted Si reported elsewhere [1,2,9-11].

The beam diameter for the P/O micro-Raman arrangement is ~1 μm, thereby giving it a much higher spatial resolution than that of the macro-Raman analysis. Most positions analyzed by micro-Raman spectroscopy yielded results comparable to those of the macro-Raman measurements. However, there were some irregularly-shaped regions ranging from 1 to 10 μm that appeared only in samples with a dose $\geq 2 \times 10^{14}/cm^2$, which is above the reported amorphization threshold for arsenic implants into silicon at room temperature [12]. These regions could be observed by optical microscopy because of the contrast with the surrounding silicon when viewed with reflected white light. P/O micro-Raman spectra reveal the spatially-varying appearance of a band between 505 and 510 cm^{-1} always accompanied by that of the silicon optical mode at 520 cm^{-1}. Figures 3 and 4 show the P/O micro-Raman spectra obtained from one of these regions in a heavily-damaged sample. The macro-Raman spectra of Si implanted with 2×10^{14} As/cm^2 consist of a broad band centered at 470 cm^{-1} and a weaker band at 520 cm^{-1}, thereby indicating that the Si has been extensively amorphized in the optical sampling region. However, when the same samples were analyzed in the region of optical contrast by P/O micro-Raman spectroscopy, evidence was found for spatially-varying lattice damage and an unusual defect structure. A conventional interpretation of the P/O spectra is made problematic by the convolution of sample orientation with spatial variation of Si structure as the microscope stage is rotated.

The appearance of a band between 505 and 510 cm^{-1} suggests the presence of small, insufficiently damaged crystalline regions. However, a lower dose in irregular areas seems unlikely with implants on a production ion implanter. Also, our observation is that the scattering strength of the ~510 cm^{-1} band increases in the samples with higher implant dose. An alternative explanation may lie in the fact that these samples had been implanted five years prior to the most recent micro-Raman analyses. Mizoguchi and coworkers, in their micro-Raman study of phosphorus implanted and annealed silicon, have observed a 508-511 cm^{-1} Raman band in irregularly-shaped regions ranging from 2 to 10 μm [13]. However, in contrast with our unannealed samples, their ion implanted samples were subsequently treated to a rapid thermal anneal with a tungsten-halogen lamp for 10 s, during which time the temperature of the sample surface was controlled and maintained between 600 and 1100 °C.

Recently, a set of 12 Si wafers were implanted at 150 keV with arsenic doses ranging from 2×10^{13} to $5 \times 10^{15}/cm^2$. The investigation of these wafers by micro-Raman spectroscopy and optical microscopy was performed within weeks of the ion implantation. A Raman band between 505 and 510 cm^{-1} was not observed from any of the 12 freshly implanted samples. Also, no regions of optical contrast with the surrounding silicon were observed when the newly implanted wafers were viewed under an optical microscope with reflected white light. Therefore,

we postulate that room-temperature annealing has occurred in the wafers implanted five years ago, thereby converting small, irregularly shaped regions of α-Si to a modified crystalline Si.

CONCLUSIONS

A study was performed of silicon samples that were implanted with arsenic five years prior to this investigation. Macro- and micro-Raman spectroscopy, in conjunction with reflected light optical microscopy, yielded evidence for spatially-varying lattice damage and an unusual defect structure. Off-axis, macro-Raman spectra reveal extensive damage to the silicon lattice, consistent with many literature reports. However, when the same samples were analyzed at much higher spatial resolution by micro-Raman spectroscopy, evidence was found for spatially-varying lattice damage and an unusual defect structure. P/O micro-Raman spectra reveal the spatially-varying appearance of a band between 505 and 510 cm^{-1} always accompanied by that of the silicon optical mode at 520 cm^{-1}. We postulate that room-temperature annealing has occurred in the wafers implanted five years ago, thereby converting small, irregularly shaped regions of α-Si to a modified crystalline Si.

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