PHYSICAL REVIEW B VOLUME 32, NUMBER 8 15 OCTOBER 1985

Raman scattering in ultraheavily doped silicon

K. P. Jain, A. K. Shukla, and S. C. Abbi
Laser Technology Research Programme, Indian Institute of Technology, New Delhi 110016, India

M. Balkanski
Laboratoire de Physique des Solides, Université Pierre et Marie Curie, 4 Place Jussieu, F-75230 Paris, Cedex 05, France

(Received 4 February 1985)

Raman spectroscopy has been used to study compositional disorder in ultraheavily doped silicon. The disorder is characterized by line-shape asymmetry of the one-phonon mode and the scattering amplitude of the two-phonon transverse acoustic and transverse optic modes. For implantation doses exceeding the solubility limit, topological disorder also becomes important in determining the phonon correlation length.

Ion implantation in semiconductors has attracted a great deal of attention in recent years,[1] particularly due to device applications of the implanted materials. The high-energy impurity ions produce topological disorder in the host crystal, which may be partially or wholly removed either by thermal or laser annealing. In the limit of ultraheavy doping, it is possible to exceed the solubility limit by ion implantation, and this produces a sort of alloy in which compositional disorder[2] also exists in addition to the ordinary topological disorder. Pulsed laser annealing (PLA) of the ultraheavily doped sample is expected to repair the radiation damage due to the implantation process, the threshold power for which depends upon the dosage. Consequently, one expects to retrieve the crystalline properties of lightly or moderately ion-implanted samples after PLA. But the central question for ultraheavily doped samples is what happens to the compositional disorder after PLA and how it manifests itself in Raman spectroscopy.

Raman scattering[3,4] on ultraheavily doped PLA n-type Si, $N_e \sim 5\times10^{21}$ As ions/cm^3 reveals a doublet between 500 and 520 cm^{-1}. The lower-energy component of this doublet has been attributed to a large phonon softening $\Delta\omega \sim 10$ cm^{-1} of the 520 cm^{-1} silicon line due to many-body effects, arising from the electron-phonon interaction between the discrete phonon line and the continuum of virtual electronic transitions in the conduction band of the heavily doped n-type Si.[5] Recently,[6] alloying effects have also been invoked along many-body electron-phonon interaction effects to explain this doublet.

Light scattering is one of the most powerful methods for studying structure of disordered solids. Zone-center phonons (ZCP) reflect their sensitivity to disorder by asymmetry of the one-phonon mode as well as anharmonic effects.[7,8] Zone-edge phonons,[9] on the other hand, show up in two-phonon Raman scattering and correspond to large wave vectors, which are sensitive to short-range disorder. The short-range order is expected to persist even in highly disordered solids, and this would be reflected in the rather weak overdamped two-phonon spectra.

In this paper we present a Raman spectroscopy study of ultraheavily doped silicon as a result of ion implantation with arsenic ions and subsequent pulsed laser annealing. It emerges from an analysis of the asymmetry of the one-phonon line that this situation occurs whenever supersaturated substitutional alloys are formed by ion implantation and PLA. The asymmetric line shape can be correlated to the compositional disorder prevalent in alloys for very large dopant concentration. This conclusion is corroborated by the disappearance of the weak two-phonon LO and LA combination modes and the heavy damping of the 2TA and 2TO modes. For the supersaturated alloys in which the dopant ions exceed the solubility limit, the 2TA and the 2TO modes become overdamped leaving behind only residual scattering. For the unannealed specimens, the heavy implantation produces amorphous silicon, which yields the characteristic Raman spectrum of the amorphous material.

EXPERIMENTAL PROCEDURE AND RESULTS

Raman scattering experiments from ion-implanted and PLA silicon were performed in the backscattering geometry at room temperature using various lines of the argon-ion laser, Ramanor double monochromator, and photon counting electronics. Four silicon ⟨100⟩ samples, ion implanted with different doses of arsenic at 100 keV with fluences ranging from 10^{15} to 6×10^{16} ions/cm^2 and subsequently annealed with a ruby laser with energy density ~ 1.3–1.5 J/cm^2 were used in this study. The doping profiles of the samples, as measured after laser annealing by Rutherford backscattering, were essentially flat over a depth of 0.175 μm, falling off rapidly thereafter.

Figure 1(b) shows the Raman spectra of silicon implanted with arsenic ions at an energy of 100 keV and fluence of 10^{15} ions/cm^2 and then PLA with a ruby laser with annealing energy density ~ 1.3 J/cm^2. One can see that the spectrum is quite similar to the reference spectrum of unimplanted silicon Fig. 1(a). There are important differences, however, in the line shape and asymmetry of the 520 cm^{-1} line, which exhibits a tail on the low-energy side. In fact, denoting the half-widths on the low- and high-energy side of the maximum by Γ_a and Γ_b, respectively, the ratio Γ_a/Γ_b for this is about 1.44, while the line shape for the unimplanted silicon is symmetric. The two-phonon combination spectra remain very much the same as that for crystalline silicon.

Increasing the fluence of implanted ions to 10^{16} ions/cm^2 and then PLA further increases the asymmetry of the 520

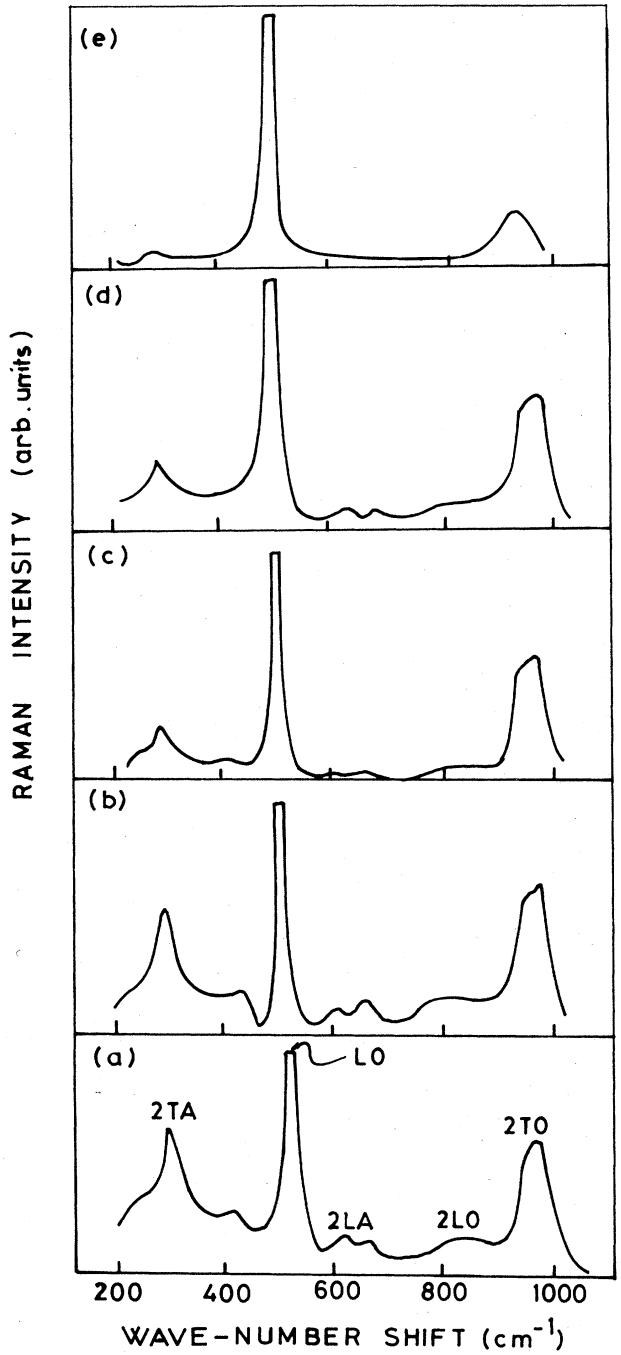

FIG. 1. Room-temperature backscattering Raman spectra with the 514.5-nm laser line. (a) is the spectrum of the pure silicon while (b), (c), (d), and (e) are the spectra of silicon samples implanted with arsenic atoms with fluences of 10^{15}, 10^{16}, 2.5×10^{16}, and 6×10^{16} ions/cm^2, respectively. The spectra are arbitrarily cut off at the top of the one-phonon line to focus attention on second-order spectra.

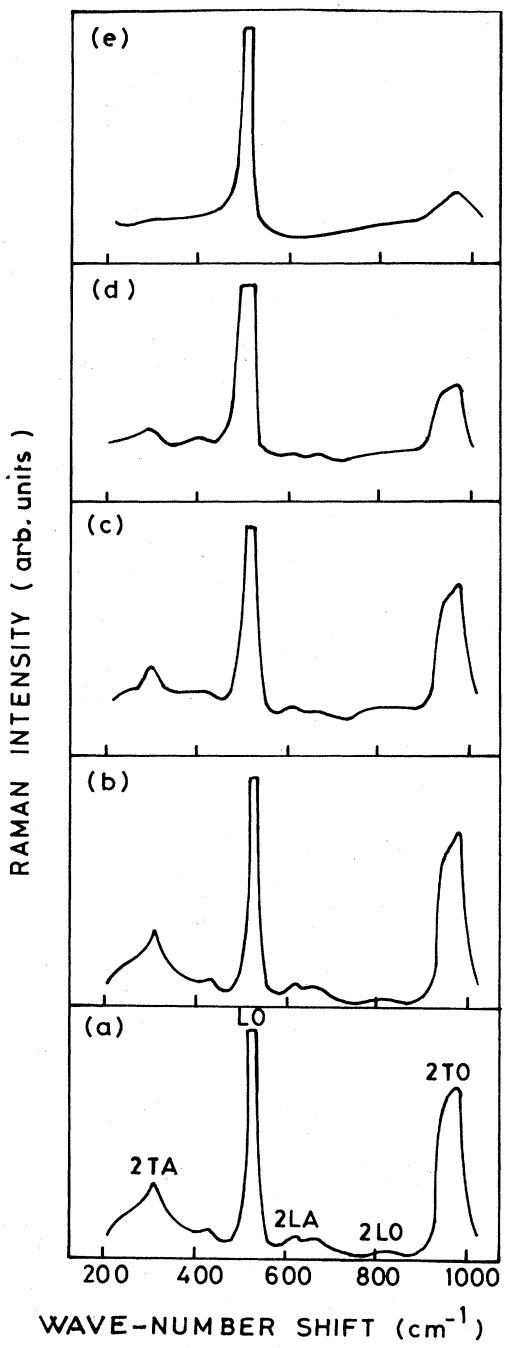

FIG. 2. Room-temperature backscattering Raman spectra with the 488-nm laser line of the same samples as in Fig. 1. Again, the spectra are arbitrarily cut off at the top of the one-phonon line to focus attention on second-order spectra.

cm^{-1} line, as shown in Fig. 1(c), so that in this case $\Gamma_a/\Gamma_b \sim 1.75$, leaving the second-order spectra more or less the same.

The situation changes significantly on further increasing the fluence to 2.5×10^{16} ions/cm^2 and PLA, when a doublet appears between 500 and 520 cm^{-1}, with increased asymmetry on the low-energy side of the doublet as shown in Fig. 1(d). Furthermore, the two-phonon combination modes begin to appear with diminished oscillator strength and are broader than their counterparts in crystalline silicon. This development progresses by further increasing the fluence to 6×10^{16} ions/cm^2 and then PLA with annealing energy density 1.5 J/cm^2. Figure 1(e) shows what happens in this case when the structures corresponding to 2LO and 2LA scattering disappear, leaving behind only residual

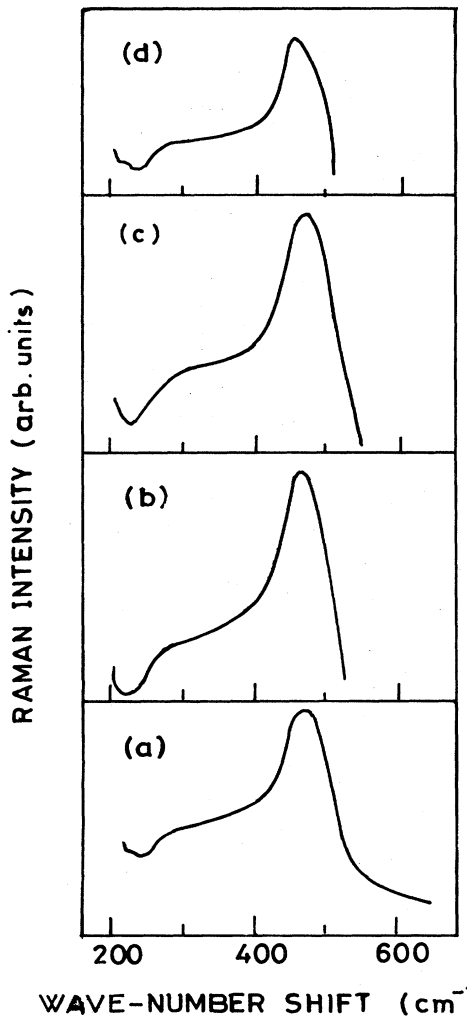

FIG. 3. Room-temperature backscattering Raman spectra with the 514.5-nm laser line. (a), (b), (c), and (d) are the spectra of the implanted but unannealed parts of the samples corresponding to fluences of 10^{15}, 10^{16}, 2.5×10^{16}, and 6×10^{16} ions/cm^2, respectively, of arsenic atoms.

scattering from the 2TA and 2TO combination modes. The asymmetry of the doublet structure is even more pronounced in this case. It should be noted that the doublet structure, which has been discussed previously,[3,4] does not appear in Figs. 1(c) and 1(d), since the structure has been truncated arbitrarily to focus attention on the two-phonon spectra.

The spectra for 514.5 nm, as given in Fig. 1, shows considerable wavelength dependence as the photon energy is increased to 488 nm, as shown in Fig. 2. For instance, the relative oscillator strengths of the doublet between 500 and 520 cm^{-1} depend upon the exciting laser wavelength: the strength of the 510-cm^{-1} satellite increases over the 520-cm^{-1} line on decreasing the wavelength, since the penetration depth decreases in this case. Furthermore, the asymmetry parameter Γ_a/Γ_b of the zone-center optic phonon mode decreases to 1.33 and 1.66 in Figs. 2(b) and 2(c), respectively, for the 488 nm exciting photon energy, i.e., the asymmetry decreases on increasing the photon energy for all the samples. Both the zone-center phonon and the two-phonon combination 2TA and 2TO modes show resonant Raman behavior for crystalline as well as implanted and PLA samples. The 2TO combination mode shows rapid resonance enhancement on increasing the photon energy compared to either the zone-center of 2TA modes. The latter are damped out more rapidly as the implantation fluence is increased: For very large fluences over the solubility limit, as in Figs. 1(e) and 2(e), both the 2TA and 2TO modes are damped out.

The corresponding spectra for the four samples mentioned above in the unannealed state are given in Fig. 3. From this one can see that the spectra of heavily implanted silicon is very similar to the spectra of the amorphous phase of this material. No second-order spectra were seen, due to the diffused scattering from the damaged surface of the semiconductor as a result of heavy implantation.

DISCUSSION

Very heavy implantation doses of group-III and group-V dopants in silicon followed by pulsed laser annealing leads to the formation of supersaturated substitutional alloys.[2] The degree of compositional disorder increases with the degree of supersaturation in these ultraheavily doped samples. Rutherford backscattering and ion channeling evidence shows that most of the impurity ions go to substitutional sites after laser annealing, which implies the existence of long-range single-crystal order.[2] But with increasing doping there is compositional disorder, which affects the Raman scattering.

The asymmetry of the zone-center one-phonon mode in heavily doped n-type Si has been studied previously.[5,10,11] A long tail on the low-energy side of the resonance is seen in this case. The Fano interaction between the phonon (discrete) state and the inter-conduction-band electronic (continuum) excitations has been invoked to explain the line-shape asymmetry. The asymmetry is both wavelength and carrier-concentration dependent: The longer the wavelength and larger the carrier concentration, the greater is the asymmetry. Figures 1(a) and 1(b) are very similar, as are Figs. 2(a) and 2(b), apart from the line-shape asymmetry, which implies that the dominant effect for silicon samples implanted with arsenic with a fluence of 10^{15} ions/cm^2, corresponding to $N_e \sim 5\times10^{19}$ cm^{-3}, is the Fano interaction, which distorts the line shape. This observation is consistent with the wavelength dependence of the asymmetry, since Γ_a/Γ_b goes from 1 to 1.44 as λ goes from 457 to 541.5 nm. In this case the effect of disorder on the line shape is rather small.

For higher doping fluences $\sim 10^{16}$ ion/cm^2, the effect of compositional disorder becomes evident in the damping of the 2TA modes, as shown in Figs. 1(c) and 2(c). This disorder also contributes to the distortion of the zone-center one-phonon line along with the interference effect alluded to before. A simple spatial correlation model has been introduced recently[7,8] to take into account the effect of spatial inhomogeneity on the scattering line shapes. In this phenomenological model, a tail emerges on the low-energy side of the resonance as a result of the disorder. Again Γ_a/Γ_b goes from 1.28 to 1.75 as λ goes from 457.9 to 541.5 nm, implying greater line-shape asymmetry than before, due

to the combined effects of the Fano interaction and compositional disorder.

For still higher doping fluence $\sim 2.5\times10^{16}$ ions/cm^2 the 2TA structure is all but damped out, while the 2TO structure appears with much reduced oscillator strength, as shown in Figs. 1(d) and 2(d). Zone-edge phonons, which show up in two-phonon Raman scattering, correspond to short wavelength displacements, which are sensitive to structural disorder. As the coherence length of phonons decreases due to increasing disorder, the two-phonon Raman amplitude becomes damped. The above-mentioned fluence corresponds roughly to the solubility limit of arsenic atoms implanted in silicon, and it is for this reason that there is substantial disorder, which is reflected in the damping of two-phonon structures.

As the doping is increased beyond the solubility limit, as shown in Figs. 1(e) and 2(e), both the 2TA and 2TO combination modes almost disappear, leaving behind only residual scattering. In this case there is large compositional and topological disorder even after laser annealing, which much reduces the phonon correlation length resulting in highly damped two-phonon scattering.

ACKNOWLEDGMENT

We would like to thank Professor A. Compaan, who provided the samples that were used in this study.

[1]See for example, *Laser and Electron Beam Processing of Materials,* edited by C. W. White (Academic, New York, 1980).

[2]C. W. White, S. R. Wilson, B. R. Appleton, and F. W. Young, Jr., J. Appl. Phys. **51**, 738 (1980).

[3]G. Contreras, A. K. Sood, M. Cardona, and A. Compaan, Solid State Commun. **49**, 303 (1984).

[4]M. Jouanne, M. A. Kanehisa, J. F. Morhange, N. M. Ravindra, and M. Balkanski, in Proceedings of the International Conference on Heavy Doping and the Metal-Insulator Transition in Semiconductors, Santa Cruz, California, 1984 (unpublished).

[5]M. Chandrasekhar, J. B. Renucci, and M. Cardona, Phys. Rev. B **17**, 1623 (1978).

[6]Rita Gupta, K. P. Jain, S. C. Abbi, and M. Balkanski, Solid State Commun. (to be published).

[7]P. Parayanthal and F. H. Pollak, Phys. Rev. Lett. **52**, 1822 (1984).

[8]K. K. Tiong, P. M. Amritharaj, and F. H. Pollak, Appl. Phys. Lett. **44**, 122 (1984).

[9]M. Teicher, R. Beserman, M. V. Klein, and M. Morkoc, Phys. Rev. B **29**, 4652 (1984).

[10]M. Jouanne, R. Beserman, I. Ipatova, and A. Subashiev, Solid State Commun. **16**, 1047 (1975).

[11]M. Cardona, in *Proceedings of the 15th International Conference on Physics of Semiconductors, Kyoto, 1980,* edited by S. Tanaka and Y. Toyozawa [J. Phys. Soc. Jpn. **49**, Suppl. A, 23 (1980)].