PHYSICAL REVIEW B VOLUME 61, NUMBER 23 15 JUNE 2000-I

Raman spectroscopy of heavily doped polycrystalline silicon thin films

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(Received 21 December 1999)

Raman backscattering measurements were performed on boron and phosphorous doped polycrystalline silicon films with an average grain size varying between 150 and 2500 nm. The B- and P-doped samples exhibit free hole and electron concentrations of up to 5×10^{20} and $2\times10^{21}\,\mathrm{cm}^{-3}$, respectively. The incorporation of dopants results in a shift of the Raman LO-TO line to smaller wave numbers. At B and P concentrations higher than mid $10^{19}\,\mathrm{cm}^{-3}$ the phonon lines are asymmetric. This is discussed in terms of a resonant interaction between optical phonons and direct intraband transitions known as a Fano resonance.

The fabrication of ultraheavily doped thin polycrystalline silicon (poly-Si) films for use as electrical contact material in device applications such as amorphous thin-film displays or solar cells is attracting a great deal of interest, recently. A wide variety of characterization methods is used to investigate the structure and electrical properties of these poly-Si films. One of the most powerful methods for studying the structure of disordered semiconductors is light scattering. For ultraheavily doped semiconductors Raman spectroscopy can be used to observe free-carrier excitation.[1] Intraband transitions in valence or conduction bands are of sufficiently low frequency to interfere with the optical phonon[2,3] and produce Fano line shapes.[4] Moreover, Raman spectroscopy can be used to detect amorphous and crystalline phases in a silicon film.[5] However, in ultraheavily doped silicon films the interpretation of Raman-backscattering spectra regarding an amorphous phase has to be done with great caution since interference of free carriers with optical phonons can result in a similar line shape.

Commonly, dopants are introduced by either ion implantation followed by a subsequent activation anneal, diffusion, or gas-phase doping. However, implantation and diffusion techniques require high temperatures that, depending on the device structures, may not be compatible with all processing steps and materials. On the other hand, the efficiency of gas-phase doping can be fairly poor, as in hydrogenated amorphous silicon (a-Si:H).[6] Previously, ion implantation, which produces some sort of alloy, and subsequent laser annealing was used to achieve ultraheavy doping in single-crystal silicon.[7] Recently, it has been suggested that laser doping has the potential of simplifying device fabrication processes. This technique uses a pulsed excimer laser to briefly melt a surface layer in a doping region of a device.[8,9] During this brief period, doping species are introduced into the molten material. However, this requires the crystallization to be performed in an atmosphere containing dopants such as phosphine or diborane or the utilization of a spin-on doping source.[9]

In this paper, we present a Raman spectroscopy study of ultraheavily boron and phosphorous doped poly-Si as a result of gas-phase doping of a-Si:H and subsequent laser crystallization. The incorporation of B and P concentrations results in a decrease of the Raman line to 514 and 511 cm^{-1}, respectively. For a given doping concentration an increase of the average grain size does not give rise to a shift of the Raman lines, however, in P-doped and -undoped specimens, the intensity of the Raman line increases with increasing grain size. The Raman lines in both, B- and P-doped specimens are asymmetric, which is indicative of the Fano effect.[4]

Polycrystalline silicon thin films were prepared by the following procedure. First, a-Si:H was deposited on quartz substrates to a thickness of 0.1 μm by decomposing silane in an rf glow discharge. Doping was achieved by premixing silane with PH_3 and B_2H_6 for n- and p-type doping, respectively. Then the a-Si:H samples were crystallized using an Excimer laser. Details of the crystallization process are described elsewhere.[10] Raman measurements were performed at room temperature using an excitation wavelength of 632.82 nm. Information on the grain size distribution was obtained from scanning electron microscopy (SEM) micrographs. Dopant concentrations were measured using secondary-ion-mass spectrometry and Hall-effect measurements were performed to determine free-carrier concentrations.

In Fig. 1, Raman-backscattering data of the LO-TO phonon mode in P-doped poly-Si are shown as a function of the phosphorous concentration. The average grain size amounted to $\langle x\rangle\approx400\,\mathrm{nm}$. In undoped laser crystallized poly-Si the LO-TO phonon line occurs at 517 cm^{-1} compared to 520 cm^{-1} in single-crystal silicon (c-Si). This indicates the presence of tensile strain. With increasing P concentration the LO-TO phonon line shifts to $\omega=511\,\mathrm{cm}^{-1}$. This shift is accompanied by the development of a broad low-energy tail that extends from 400–500 cm^{-1} for P concentrations larger than $4\times10^{19}\,\mathrm{cm}^{-3}$. In undoped microcrystalline silicon this broad low-energy tail is usually attributed to a residual amorphous phase. However, in laser crystallized poly-Si (laser fluence$\gg300\,\mathrm{mJ/cm}^2$ for 0.1 μm thick samples) there is no indication of an amorphous phase according to cross-sectional TEM and x-ray diffraction measurements. In fact, in undoped poly-Si the LO-TO phonon line can only be fitted with a Lorentzian line and there is no indication of a low-energy tail between 400 and 500 cm^{-1}. This suggests that the incorporation of P gives rise to this feature in ultraheavily P-doped poly-Si.

The average grain size varied from 89 to 330 nm. For samples with the same P concentration, the variation in grain

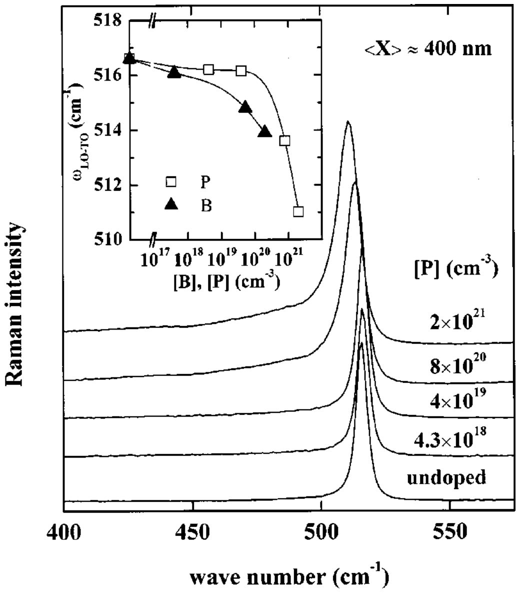

FIG. 1. Raman backscattering spectra measured on undoped and ultraheavily phosphorous doped poly-Si. The P concentrations are indicated in the plot. For clarity the spectra are shifted vertically. The inset shows the wave number of the LO-TO phonon line as a function of the P- (squares) and B- (triangles) doping concentrations.

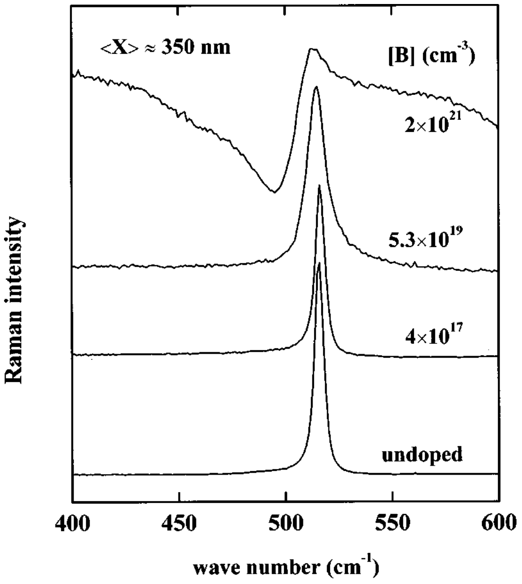

FIG. 3. Raman-backscattering spectra measured on undoped- and ultraheavily boron-doped poly-Si. The B concentrations are indicated in the plot. For clarity the spectra are shifted vertically.

size had no effect on the Raman spectrum except for the overall intensity shown in Fig. 2. The circles and diamonds represent undoped and P-doped poly-Si, respectively. For small grained poly-Si ($\langle x\rangle < 500\,\text{nm}$) the intensity of the LO-TO phonon line increases rapidly with increasing average grain size. Once the average grain size exceeds 500 nm, the increase of the Raman intensity becomes less pronounced. Eventually, when $\langle x\rangle$ becomes comparable or larger than the laser spot the Raman intensity should saturate.

Raman-backscattering data taken on boron-doped poly-Si are shown in Fig. 3 as a function of the B concentration. The spectra taken on samples with a B concentration of more than $5\times10^{19}\,\text{cm}^{-3}$ are distorted. Moreover, for $[\text{B}]=2\times10^{21}\,\text{cm}^{-3}$ the spectra exhibit a pronounced *minimum* centered at 494 cm^{-1} in addition to a maximum at approximately 514 cm^{-1}. This type of line shape is well known as a Fano resonance.[4] Similar data were reported on heavily p-type c-Si and c-Ge.[1,2] The variation of the average grain-size from 109 to 1040 nm had no effect on the Raman spectrum. The change of the wave number of the LO-TO phonon line with increasing B concentration is shown by the triangles in the inset of Fig. 1.

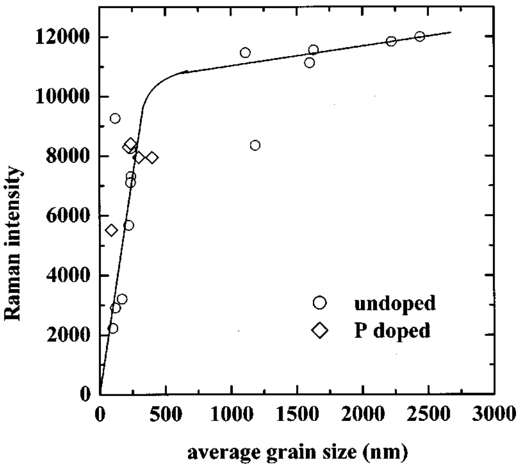

FIG. 2. Intensity of the LO-TO phonon line as a function of the average grain size determined from SEM micrographs. The circles and diamonds represent undoped- and phosphorus-doped poly Si, respectively.

Three mechanisms are contributing to the deviation and distortion of the LO-TO phonon vibrational modes in ultraheavily doped poly-Si from its value in c-Si: (i) tensile stress due to the laser-induced crystallization process, (ii) the incorporation of large concentrations of dopants (B, P) into the silicon host lattice, and (iii) the Fano effect. The first mechanism can be separated by crystallizing undoped a-Si:H. Independent of the average grain size the LO-TO phonon line is shifted by $\approx$3 cm^{-1} towards smaller wave numbers. In a pulsed excimer laser-crystallization experiment the entire energy is deposited in the sample surface within approximately 15–20 ns. The amorphous silicon layer liquefies for up to 200 ns and subsequently crystallizes with an average crystallization velocity of 15–20 m/s.[11] The tensile stress detected in the Raman spectra can either arise from the substrate/poly-Si interface or from grain boundaries. In the latter case one would expect that the shift of the LO-TO phonon line decreases as the average grain size increases from $\approx$150 nm to $\approx$2500 nm, which is accompanied by a significant reduction of the grain boundary volume. However, this is not the case. Therefore, it is more likely that the strain arises from the substrate/poly-Si interface. The magnitude of the stress can be estimated from the wave number shift of the LO-TO peak compared to the Raman line of stress free c-Si according to the following equation[12]

$$\sigma(\text{MPa}) = -250(\omega_s - \omega_0)(\text{cm}^{-1}), \tag{1}$$

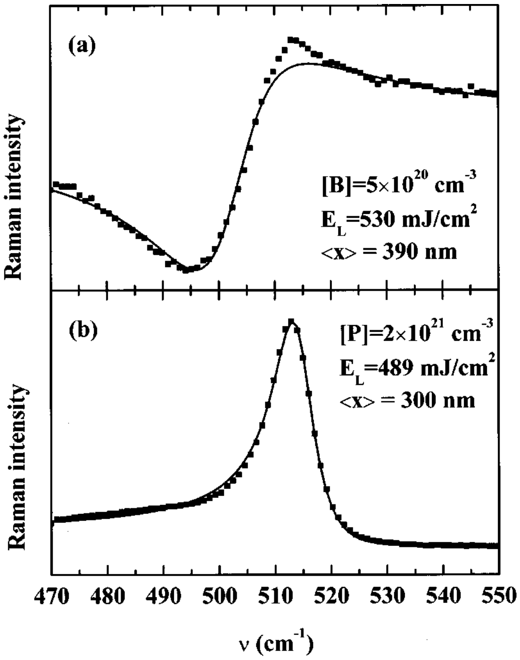

FIG. 4. Raman-backscattering spectra of (a) boron-doped and (b) phosphorous-doped poly-Si. The squares represent the data points and the curves represent least-squares fits to Eq. (2). $\langle x\rangle$ denotes the average grain size.

where ω_S is the wave number of the stressed sample and ω_0 is the wave number of the LO-TO phonon mode in stress free c-Si. The phonon shift corresponds to the isotropic part of the phonon shifts obtained in biaxial stress experiments.[12] According to Eq. (1) the observed shift of $-3\ \mathrm{cm}^{-1}$ in undoped poly-Si leads to a stress of 750 MPa.

The incorporation of high dopant concentrations causes a further decrease of the LO-TO phonon wave number. In B-doped poly-Si the LO-TO phonon line shifts monotonically towards smaller wave numbers with increasing B content (inset in Fig. 1). At boron concentrations larger than $3\times10^{19}\,\mathrm{cm}^{-3}$ the LO-TO phonon lines are distorted as shown in Fig. 3. Such Fano line shapes occur when the Fermi energy resides in the valence band. These resonances are due to a resonant interaction between optical phonons and direct intraband transitions of holes.[2] According to Hall-effect measurements the B-doped specimens exhibited a free hole concentration of $5\times10^{20}\,\mathrm{cm}^{-3}$, which is sufficient to move the Fermi energy into the valence band at room temperature. The Raman scattering cross section (Fano profile) can be described by[13,14]

$$\alpha(\omega)=\alpha_0\frac{(q+x)^2}{1+x^2}, \tag{2}$$

where ω is the wave number, α_0 the prefactor, q the symmetry parameter, and x is given by $x=2(\omega-\omega_P)/\gamma$, where ω_P is the phonon wave number and γ is the linewidth contribution to the total linewidth. Using Eq. (2) the Raman backscattering spectra shown in Figs. 1 and 3 can be fitted. In Fig. 4(a), a least-squares fit of the Raman spectrum for an ultraheavily B-doped poly-Si thin film is overplotted to the data.

TABLE I. Fitting parameters for the Fano line shapes shown in Fig. 4

	q	γ
B-doped poly-Si	0.7	19
P-doped poly-Si	−4.3	9

The fitting parameters are summarized in Table I. Data and fits are in good agreement. The Raman spectra of the heavily boron-doped specimens show, in addition to the Fano resonance, a residual nonresonant LO-TO phonon peak centered at $514\ \mathrm{cm}^{-1}$ [the data points that lie above the fitted curve in Fig. 4(a)]. Thus, an increase of the B concentration to $\approx5\times10^{20}\,\mathrm{cm}^{-3}$ results in a shift of the LO-TO phonon line of $-3\ \mathrm{cm}^{-1}$ with respect to undoped poly-Si ($\omega=517\,\mathrm{cm}^{-1}$). This corresponds to an increase in tensile stress by a factor of 2.

On the other hand, in P-doped poly-Si films the wave number of the LO-TO phonon line occurs at $517\ \mathrm{cm}^{-1}$ for P concentrations of up to $4\times10^{19}\,\mathrm{cm}^{-3}$. However, with a further increasing P concentration the LO-TO wave number shows a significant decreases to $511\ \mathrm{cm}^{-1}$ at $[\mathrm{P}]\approx2\times10^{21}\,\mathrm{cm}^{-3}$ (inset of Fig. 1). This cannot be explained with the buildup of tensile stress due to high concentrations of substitutional P atoms since one would expect that the incorporation of larger atoms such as P results in the formation of compressive stress. According to Hall-effect measurements performed on the sample with the highest P concentration, a free-electron concentration of $2\times10^{21}\,\mathrm{cm}^{-3}$ was measured, which is sufficient to shift the Fermi energy into the conduction band. Thus, the pronounced decrease of the phonon wave number should be due to a Fano interference.[15] Indeed, the Raman data of ultraheavily P-doped poly-Si can be described by Eq. (2). The Raman spectra of heavily P-doped specimens were fitted to a Fano line shape [solid curve in Fig. 4(b)] with symmetry parameter $q=-4.3$. Because of the negative value of q, the Raman scattering is enhanced on the low-energy side of the optical phonon peak (constructive interference) and suppressed on the high-energy side of the peak (destructive interference). Thus, the significant shift of the LO-TO phonon peak in ultraheavily P-doped poly-Si is not related to a doping induced increase of tensile stress. When q is positive, as in the boron-doped specimens, the reverse is true: the Raman scattering is suppressed on the low-energy side. (Note also that when the magnitude of q becomes large, for either positive or negative q, the Fano line shape approaches a symmetric Lorentzian.)

In summary, we have presented a detailed Raman spectroscopy study of ultraheavily P- and B-doped poly-Si. For a fixed doping concentration the position of the Raman phonon lines does not change with increasing grain size. In undoped poly-Si the LO-TO phonon line occurs at $517\ \mathrm{cm}^{-1}$, which corresponds to a tensile stress of 750 MPa. The incorporation of B and P dopants causes the phonon peak to shift towards smaller wave numbers. In B-doped samples this shift commences at low doping concentrations, while in n-type poly-Si a P concentration of more than $4\times10^{19}\,\mathrm{cm}^{-3}$ is required. In undoped and heavily P-doped poly-Si the Raman signal intensity increases with increasing grain size. The Raman spectra of ultraheavily doped poly-Si are distorted due to a resonant interaction between optical phonons and direct intraband transitions of electrons and holes in *n*-type and *p*-type specimens, respectively. The development of asymmetric line shapes at a B and P concentration larger than 10^{19} cm^{-3} indicates that the electronic structure changes from nongenerate to degenerate.

This work has been supported by the BMBF. The authors are grateful to G. Keiler, U. Mazur, D. Patzek, and M. Schmidt for technical support.

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