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RAMAN STUDIES OF THE P LOCAL MODE VIBRATION IN P IMPLANTED, LASER ANNEALED Ge

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Abstract - We report the first observation by Raman scattering by the localized vibrational mode of P in P implanted and pulsed laser annealed Ge. The heavy dose ion implantation followed by pulsed laser annealing have allowed us to achieve P densities exceeding the normal solid solubility limits in Ge, a fact which is essential for the local mode observations. We have obtained information about the position and intensity of the P local mode as a function of the implantations dose and its resonant Raman behavior as a function of laser photon energy.

The band structure of semiconductors is changed little by the presence of high concentrations hydrogenic donor or acceptor atoms /1,2/. However, if these atoms are lighter than the host atoms, localized vibrational modes can appear at frequencies above that of the Raman phonons /3/. Many of these local modes have been observed by means of ir absorption, Raman observations have been limited to boron in Si /4/.

In this paper we report the first observation by Raman spectroscopy of a vibrational local mode in germanium, namely that of substitutional phosphorus. The samples were P-implanted (at 190 keV) and excimer laser annealed /5/ to produce germanium layers of an estimated thickness ~300 nm and dopant concentrations N_p between 2 x 10^{20} and 1 x 10^{21} cm^{-3}. Doping by implantation was found to be absolutely necessary for this work; previous attempts to observe the local mode in bulk doped samples failed on account of the small solubility of P in Ge (~4 x 10^{19} cm^{-3}).

Figure 1 shows the room temperature Stokes spectra of the Raman phonons and the local mode of P for three samples with different implantation doses. For these samples the phonon obeyed T_{25}; (T_{2g}) selection rules for the orientation of the substrates, thus indicating good epitaxy. The local symmetry around the impurity atom is T_{2d} (tetrahedral). Thus the local mode should have T_{1g}(T_{1}) symmetry. The Raman selection rules for this mode are the same as those for the T_{25}, phonon. The local

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mode, however, is ir-active \cite{6} while the phonon is not. For the two samples with the lowest doses the local mode peaks at $336 \pm 1 \text{ cm}^{-1}$. It shifts to $342 \pm 1 \text{ cm}^{-1}$ for the sample with $6 \times 10^{16} \text{ cm}^{-2} \text{ P/cm}^{2}$. Infrared spectra of Li-compensated P-doped Ge show a local mode at $343 \text{ cm}^{-1}$ at liquid nitrogen temperature \cite{6}. We note that the three spectra of Fig. 1 show no shift in the phonon frequency of the doped layer with respect to that of pure Ge ($300 \text{ cm}^{-1}$), in agreement with previous work at lower densities \cite{7}. The local mode frequency can be obtained from the simplified mass defect secular equation \cite{6}:

$$\omega_{p} = \omega_{M} \left( 1 - 0.64 \varepsilon \right)^{1/2},$$

which assumes that the force constants are the same for P-Ge as for Ge-Ge pairs. In Eq. (1) $\omega_{M} = 280 \text{ cm}^{-1}$ is the frequency of the maximum in the density of TO phonons and $\varepsilon = 1 - M_{p}/M_{Ge} = 0.57$ the mass defect parameter. Equation (1) yields for the local mode frequency of P in Ge $\omega_{p} = 340 \text{ cm}^{-1}$ in rather good agreement with the experiments. The increase of $\omega_{p}$ for the highest implantation dosage may be due to deviation from the isolated P-atom model implicit in Eq. (1), i.e., to the presence of P-P pairs.

\[\text{Fig. 1 - Raman spectra of the P local mode for the } 1 \times 10^{16}/\text{cm}^{2}, 2 \times 10^{16}/\text{cm}^{2} \text{ and } 6 \times 10^{16}/\text{cm}^{2} \text{ P implanted and pulse laser annealed Ge. Exciting laser line } \lambda = 5682 \text{ Å.}\]
We have measured the spectra of Fig. 1 for various laser frequencies between 1.8 and 3.1 eV. Figure 2 shows the ratio of the integrated strength of the phonon to that of the local mode versus laser photon energy. The maximum seen in Fig. 2.2 eV corresponds to the resonance of the phonon between the $E_1$ and the $E_1 + \Delta_1$ gaps /9/. Thus the phonon resonates much more strongly than the local mode, a fact which must be attributed to k-nonconservation in the Raman scattering mechanism of the local mode.

![Graph showing the ratio of the integrated Raman intensity of the zone center optical phonon of Ge to the P local mode for different photon energies.](image)

**Fig. 2** - Ratio of the integrated Raman intensity of the zone center optical phonon of Ge to the P local mode for different photon energies of the exciting laser line. The sample used was P implanted (dose $6 \times 10^{16}$ cm$^{-2}$) and laser annealed Ge.

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