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ANOMALOUS WIDTH OF SOME PHOTOEXCITATION LINES OF IMPURITIES IN SILICON*

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The purpose of this Letter is to report experimental results on an unusual broadening of an excitation line of gallium acceptor and of bismuth donor in silicon. Experimental evidence is presented which suggests that the optical phonons play an important role in governing the lifetime of the excited states involved when the energy of the transition equals that of the optical phonons.

One of the remarkable features of the excitation spectrum of gallium acceptors in silicon[1,2] is that the excitation line with the second lowest energy, line 2, is at least an order of magnitude broader than any of the other lines of the spectrum. This is in contrast to the spectra of the other group-III impurities where line 2 is very prominent and just as sharp as the other lines. From the correspondence between the various acceptor spectra, line 2 of gallium is expected to occur at about 63 meV. In view of the proximity of this energy to the Raman energy of silicon, 64.8 meV,[3] we wish to suggest that the anomalous width of this transition is a consequence of a lifetime broadening of the excited state by the emission of an optical phonon of an energy close to that of the transition. It is significant that line 3 of aluminum acceptor in silicon is also expected to occur at ~63 meV; this line has not been observed. Another impurity in silicon whose excitation spectrum has lines with energies close to those of the optical phonons is the group-V donor, bismuth.[4-6] In particular, the $1s(A_1) \rightarrow 2p_\pm$ transition has an energy of 64.57 meV which is almost coincident with the Raman energy. However, as can be seen from Fig. 1, this line is sharp and shows no evidence of broadening. It is in fact found to be just as sharp as the $3p_0, 3p_\pm, \cdots$ lines. Per contra, the $2p_0$ line is anomalously broad and is asymmetric. The energy of this line is 59.51 meV, which is significantly close to the energy of the TO⟨100⟩ phonons of silicon, i.e., 58.7 ± 1.2 meV.[7] It is well known that for silicon the shallow acceptor states are constructed from the Bloch functions at the top of the valence band, while those of the shallow donors are associated with the conduction-band minima along ⟨100⟩. This might account for the difference in the optical-pho-

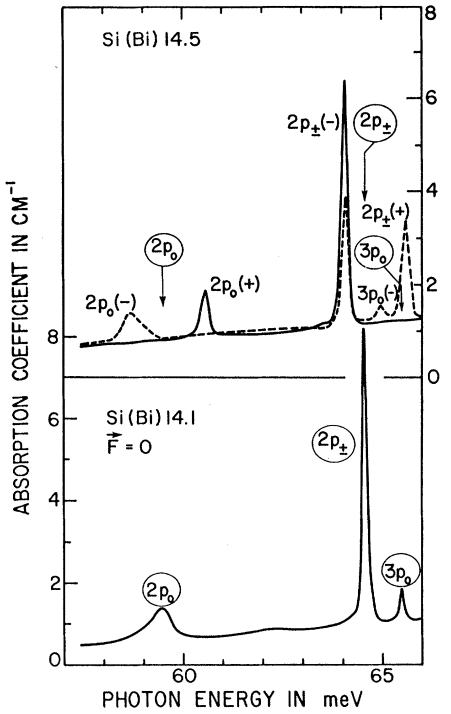

FIG. 1. Part of the excitation spectrum of bismuth impurity in silicon using liquid helium as coolant. Carrier concentration at room temperature = 4.5×10^{14} cm^{-3}. The upper curve is measured with a compressive force, $\vec{F}$, along [110] and the direction of propagation of the light, $\vec{q}$, along [1$\bar{1}$0]. The dashed curve is for the electric vector $\vec{E} \parallel \vec{F}$, while the full curve is for $\vec{E} \perp \vec{F}$. The vertical arrows together with their encircled labels indicate the zero-stress positions of the lines shown in the lower curve.

non energies which are postulated to give rise to the anomalous widths of the lines. In this connection it is interesting to note that line 1 of gallium acceptors in silicon occurs at 58.23 meV and is not broadened anomalously.

In order to test the above hypothesis for the broadening mechanism, the widths of the stress-induced components of the $1s(A_1) \rightarrow 2p_0$ transition of bismuth in silicon were investigated as a function of energy. It is known[8] that, under a uniaxial stress produced by a compressive force along $\langle 100 \rangle$ or $\langle 110 \rangle$, each of the $1s(A_1) \rightarrow np$ lines splits into two components, as can be seen in the upper part of Fig. 1. By varying the stress, the positions of the stress-induced components can be changed. It is evident that the $2p_0(+)$ component is markedly sharper than the $2p_0(-)$ component. This cannot be attributed to an inhomogeneity in the stress since this would result in $2p_0(+)$ being broader than $2p_0(-)$. In addition, the $2p_0(-)$ component, like the $2p_0$ line, shows a distinct asymmetry. However, unlike that of the $2p_0$ line, this asymmetry is to the high-energy side. It should be noted that the splitting of the $2p_0$ line is larger than that of the other lines. This is in contrast to the behavior of the $2p_0$ line of the other group-V impurities for which the splitting is the same for all lines, in agreement with the theory.[8] In Fig. 2 is shown the ratio of the half-widths of the corresponding components of $2p_0$ and $2p_\pm$ as a function of the energies of the former. The data have been plotted in this manner to eliminate any effects due to inhomogeneity in the stress. It is evident that the maximum half-width for the components would occur at about 59.2 meV; this, then, will be the energy of the optical phonon involved in the broadening mechanism proposed. This energy is very close to that quoted above for the TO$\langle 100 \rangle$ phonons.

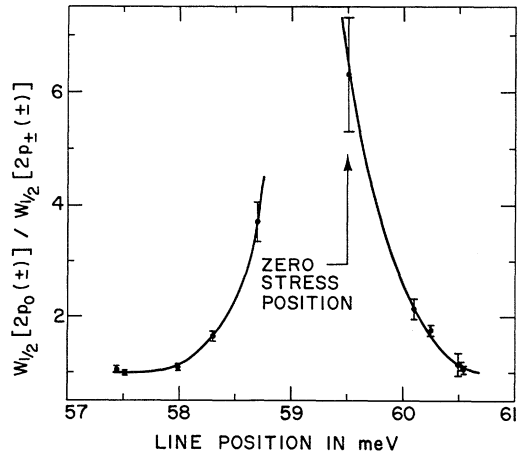

FIG. 2. The ratio of the half-widths of the corresponding components of the $2p_0$ and $2p_\pm$ lines of bismuth impurity in silicon as a function of the energies of the former. The data have been obtained with $\vec{F} \| \langle 100 \rangle$ and with $\vec{F} \| [110], \vec{q} \| [1\bar{1}0]$.

It is concluded that there is experimental evidence in support of the hypothesis that the lifetime of excited states can be limited by the emission of optical phonons. In case of aluminum acceptor in silicon,[2] line 4 at 64.08 meV is distinctly broader than lines 1 and 2. However, it is not clear why, as mentioned above, line 3 of aluminum should be completely missing whereas line 4, which presumably lies closer to the Raman energy, is still indentifiable; this is also the case for lines 4*A* and 4*B* whose energies are 64.96 and 65.16 meV, respectively.

Similar effects have not been observed for the shallow acceptors[9] and donors[10] in germanium presumably because the appropriate phonons have energies[11] different from those of the excitation lines. This is also true for the deeper acceptors zinc[12] and copper[13] in germanium. Of the excitation lines of these acceptor impurities, only the *G* line of copper, at 38.66 meV, is close to that of the optical phonons at the zone center, i.e., 37.2 meV.[11]

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EFFECT OF STRESS ON THE SUPERCONDUCTIVE TRANSITION TEMPERATURE OF STRONTIUM TITANATE

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The superconductive transition temperatures T_c of single-crystal specimens of reduced strontium titanate have been measured as functions of hydrostatic and uniaxial compressional stresses up to 1.5 kbar. The prominent features of the experimental results are a large, nonlinear, hydrostatic-pressure effect and an anisotropic uniaxial stress effect. The relative decrease of transition temperature with pressure $\Delta(\ln T_c)/\Delta p$ is about an order of magnitude larger than that seen in metallic superconductors.

The discovery[1,2] of a superconductive state in strontium titanate ($SrTiO_3$) occurred as a consequence of Cohen's[3,4] theory of superconductivity in many-valley semiconductors. A theoretical study of the energy-band structure of cubic $SrTiO_3$ by Kahn and Leyendecker[5] predicts a set of conduction-band minima located along the $\langle 100 \rangle$ axes near the Brillouin zone edge. Several relevant experiments[6,7] confirm this prediction, although the piezoresistance data of Tufte and Stelzer[8] are not entirely in agreement.

In the theory of superconductivity in many-valley semiconductors, the superconductive transition temperature is an explicit function of normal-state parameters. On the basis of the theoretical energy-gap expressions,[3,4] one therefore can predict that changes in T_c with crystal strain can result from variations in the dielectric function, the intervalley and intravalley phonon frequencies, the deformation potential, and the maximum phonon wave number, all of which result from a change in volume of the unit cell. Redistribution of electron population resulting from loss of degeneracy of the electron valleys also will change T_c.

In order to observe such effects, we have investigated the shift of T_c with both uniaxial and hydrostatic stress. The very low T_c of $SrTiO_3$ required that the experiments be carried out in an adiabatic demagnetization cryostat. The hydrostatic pressures were generated by using a modified version of the low-temperature ice-bomb technique of Alekseevskii and Gaidukov.[9] The pressure was varied from run to run by freezing various alcohol-water solutions.[10] The pressure was measured in each run by observing the shift in T_c of a 99.99% tin specimen which was located, along with the $SrTiO_3$, inside the ice bomb. Pressure values were calculated using the results of Jennings and Swenson.[11] The maximum pressure attainable in our stainless-steel ice bomb was about 1.5 kbar. In a separate series of experiments, uniaxial compressive stress was applied to oriented single-crystal specimens by a clamp assembly. The stress could be varied between runs at 1.2°K using a detachable screwdriver-gearbox device,[12] and was measured by observing the change of resistivity of a single-crystal specimen of antimony-doped germanium which was compressed along a $\langle 111 \rangle$ axis simultaneously with two $SrTiO_3$ specimens of different orientations. The stress values were calculated using the piezoresistance results of Fritzsche.[13]

All superconductive transitions were observed by measuring the ac mutual inductance of sets of coils surrounding the various specimens. Between 4.2 and 1°K the temperatures were determined from the T_{58} He^4 vapor pressure-temperature scale. Temperatures below 1°K were determined by measuring the ac magnetic susceptibility of a single crystal sphere of cerous magnesium nitrate (CMN) using the usual Curie-law extrapolation. In order to minimize errors resulting from uncertainties in absolute thermometry, unstressed reference specimens of $SrTiO_3$ were included in both experiments and a tin reference specimen was included in the ice-bomb sample holder so that an unstressed transition could be observed in