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Far infrared absorption in Sb-doped Ge epilayers near the metal insulator transition

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Epitaxial germanium layers doped near the metal insulator transition were grown by liquid phase epitaxy from a Pb melt. Far infrared absorption was measured between $\sim 20 \text{ cm}^{-1}$ and 150 cm^{-1} . Linear optical absorption coefficients were determined for Ge:Sb in the doping range of $9.0 \times 10^{14} \text{ cm}^{-3} < N_D < 6.7 \times 10^{16} \text{ cm}^{-3}$. The peak absorption was found to increase linearly with dopant concentration as expected. The absorption at $\sim 50 \text{ cm}^{-1}$ increased superlinearly with Sb concentration as a result of impurity banding. The optimal Sb concentration for extended far infrared photoconductive response ($\lambda > 200 \text{ }\mu\text{m}$) in blocked impurity band detectors is discussed.

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The evolution from localized to extended electronic states in semiconductors doped near the metal-insulator transition has been studied widely.^{1,2} For lightly doped n-type (p-type) semiconductors, electrons (holes) are localized on the dopants. Above a characteristic concentration they are delocalized as impurity banding occurs. Electrical conduction in this regime occurs by hopping between donor states. Above a still higher concentration the Fermi energy passes into the conduction (valence) band, and metallic behavior is observed. For antimony doped germanium (Ge:Sb) impurity banding is observed in the range $\sim 10^{16} \text{ cm}^{-3} < N_D < \sim 10^{17} \text{ cm}^{-3}$. Impurity band broadening leads to a reduction in donor binding energy, which can be taken advantage of in far infrared detectors. Lightly doped Ge:Sb detectors ($\sim 10^{14} \text{ cm}^{-3}$) exhibit an onset in photoconductivity at $\sim 75 \text{ cm}^{-1}$ which corresponds to the electron binding energy of an isolated Sb shallow donor.^{3,4} Impurity band broadening is expected to reduce the binding energy, thereby extending the photoconductive response to longer wavelengths. Detectors that employ this effect are known as Blocked Impurity Band (BIB) detectors and have been successfully implemented with Si:Sb and Si:As.⁵ Germanium BIB detectors are of interest since they are expected to extend photoconductive response to $\sim 250 \text{ }\mu\text{m}$, a feat currently achieved only by stressed Ge:Ga photoconductors.⁶ Previous Ge BIB detector efforts focused on photoconductivity as a measure of extended response due to impurity banding.⁷ However, such measurements are limited to the device depletion width, which is often small and could be dominated by charge accumulation at interfaces. In order to separate absorption from other device parameters, far infrared absorption as a function of Sb concentration should be carefully studied independently and directly. For this purpose, we have measured linear absorption coefficients for Ge:Sb in the range of $9.0 \times 10^{14} \text{ cm}^{-3} < N_D < 6.7 \times 10^{16} \text{ cm}^{-3}$.

Absorption has been measured by Reuszer and Fisher⁸ for lightly doped (Group V) bulk Ge. The concentration dependence of absorption in bulk Sb-doped Ge crystals between 6×10^{14} and $2 \times 10^{16} \text{ cm}^{-3}$ has been studied by Nisida and Horii.⁹ The bound excited states were found to broaden with increasing concentration, an effect more dominant for higher energy states with larger Bohr radii. It has been suggested by Pomerantz¹⁰ that the line broadening observed was due to strain produced by the donors, a theory which was refuted by Stoneham¹¹ who showed that strain broadening is too weak of an effect. Line broadening due to overlap of the wavefunctions with increasing concentration is the currently accepted theory.

In this work, epitaxial layers of Sb-doped Ge were grown from a Pb solvent by Liquid Phase Epitaxy in a tipping boat system. Pure $\langle 111 \rangle$ oriented Ge substrates ($n=2 \times 10^{12} \text{ cm}^{-3}$) were chosen for their far infrared transparency. The $8 \times 8 \times 0.5 \text{ mm}^3$ substrates were held by a graphite clip in a graphite crucible loaded into a single zone quartz tube furnace. LPE

growth was carried out in 1.3 atm of palladium diffusion purified H₂. Sb dopant concentration was controlled by the addition of a Pb-Sb master alloy to ~ 10g of 6N pure Pb solvent. The solvent was saturated with ultra-pure Ge at 655 °C and equilibrated for 5.5 hours. The system was tipped at an undercooling of 3 °C to begin growth. Layer growth occurred as the furnace temperature was ramped down to 340 °C over 12 hours. A typical epilayer thickness is 40 μm. With this technique, the terminating layer surfaces (~ 10 μm) were found to contain an excess concentration of Sb which was removed by chemical-mechanical polishing.

The Sb dopant concentration was determined by Hall Effect measurements using samples with pressed-on In contacts. All concentrations quoted in this work have been measured at 77K. Compensation, as determined by variable temperature Hall effect and BIB capacitance measurements, was ~ 10¹² cm⁻³.

Far infrared absorption was measured by Fourier Transform Infrared Spectroscopy (FTIR) using a Michelson interferometer with a mylar beamsplitter. The beamsplitter was ~ 25 μm thick with a first interference minimum at ~ 150 cm⁻¹. Light from a mercury arc lamp was chopped at ~ 20 Hz and phase sensitive detection with a lock-in amplifier was used. Six samples were mounted on a rotatable wheel in an Infrared Labs dewar cooled to 1.3 K by pumping on a liquid helium reservoir in contact with the sample cold stage. A cold black polyethylene filter was used to filter out bandgap light. The sample wheel was rotated to place one of six samples between the spectrometer light and a Neutron Transmutation Doped (NTD) Ge bolometric detector. Spectra were taken using the bolometer with each of the six samples in place. A bare Ge substrate, in which impurity absorption could be considered negligible, was used as a reference.

Absorption coefficients were obtained from transmitted intensities (I) taking into account multiple reflections in the samples described by:

$$T = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} = \frac{I}{I_0} \quad (1)$$

where T is the transmission, I is the transmitted intensity, I₀ is the incident intensity, R is the reflectivity (=0.36 for Ge), α is the linear absorption coefficient, and d is the layer thickness. I₀ was determined using the bare substrate with α=0. Although this equation is valid specifically for a single thickness of material, it can be used as a close approximation for the LPE layers since the substrate does not contribute to absorption and there is no change in refractive index at the interface. The absorption coefficient as a function of wavenumber for various Sb concentrations is shown in Figure 1. The oscillations in the

spectra are due to a combination of Fabry-Perot interference and electronic noise. Transitions from the ground state to bound excited states produce sharp absorption lines in samples with concentrations below 10^{14} cm^{-3} . Such transitions would still be visible for the $9 \times 10^{14} \text{ cm}^{-3}$ sample if the data were taken at higher resolution. Donor spectra for the more heavily doped samples of interest here are expected to show significant line broadening. A lower resolution was therefore chosen in favor of increased temperature stability of the bolometer that comes with shorter measuring times. The instrumental resolution of the spectra is 2 cm^{-1} . The bulk sample containing $9 \times 10^{14} \text{ cm}^{-3}$ Sb can be compared to the work of Reuszer and Fisher where a maximum absorption coefficient of $\sim 13 \text{ cm}^{-1}$ was found at $\sim 80 \text{ cm}^{-1}$ for a bulk Sb-doped Ge crystal $\sim 7 \times 10^{14} \text{ cm}^{-3}$. The spectra are in general agreement with the work of Nisida and Horii. It should be noted that concentration values were measured at 77K in this work and care must be taken in comparing the results to other works where concentrations are likely to be quoted at room temperature.

The absorption coefficient as a function of Sb concentration is shown in Figure 2 for 50 and 100 cm^{-1} . At 100 cm^{-1} the absorption coefficient is proportional to the dopant concentration as expected. At 50 cm^{-1} the onset in impurity banding causes a rapid rise in absorption up to $\sim 6 \times 10^{15} \text{ cm}^{-3}$ above which the absorption becomes proportional to Sb concentration and converges on the expected behavior. The ideal Sb concentration for a BIB detector will likely lie between 1 and $4 \times 10^{16} \text{ cm}^{-3}$ and will be determined to some extent by the achievable depletion width of the device. As a point of comparison, Ge:Sb bulk detectors doped to $2 \times 10^{14} \text{ cm}^{-3}$ have an absorption coefficient at 100 cm^{-1} of $\sim 3 \text{ cm}^{-1}$ and a volume of $0.15 \times 0.15 \times 0.1 \text{ cm}^3$. The same absorption could be achieved at 50 cm^{-1} in a $1 \times 10^{16} \text{ cm}^{-3}$ Ge:Sb BIB detector with a volume $\sim 50 \times$ smaller (due to the $50 \times$ larger absorption coefficient). For a $0.15 \times 0.15 \text{ cm}^2$ pixel size, this would translate into a depletion width of $\sim 20 \text{ }\mu\text{m}$. For a $4 \times 10^{16} \text{ cm}^{-3}$ sample, the required depletion width would be $\sim 10 \text{ }\mu\text{m}$. These values are achievable with minority acceptor concentrations which can be reached with current technology, leading to BIB detectors with significant long wavelength response.

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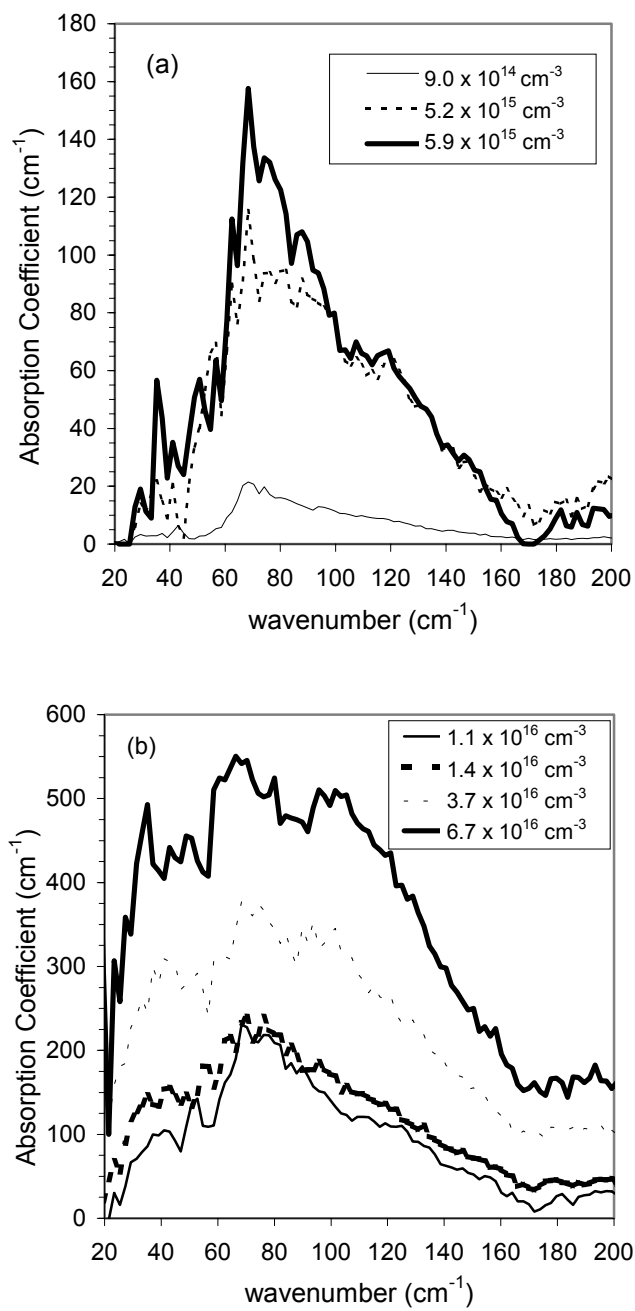


Figure 1
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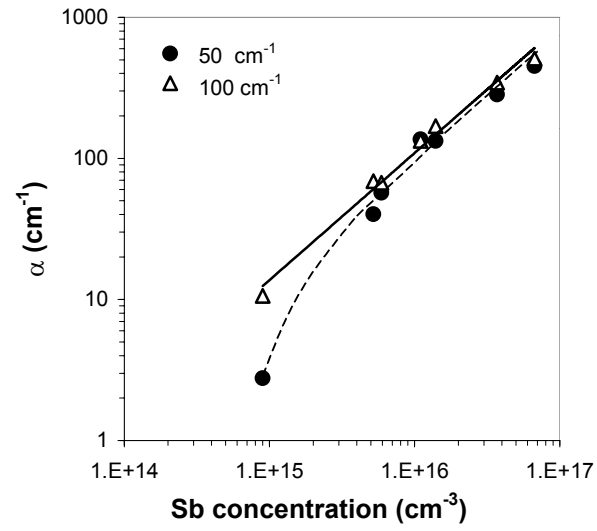


Figure 2
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Figure Captions

Figure 1. Absorption coefficient vs. wavenumber for Sb-doped Ge epilayers of given Sb concentration. Separate plots (a) and (b) are used for clarity. All samples were ~30 microns thick and were grown by liquid phase epitaxy with the exception of the $9 \times 10^{14} \text{ cm}^{-3}$ sample which was a 0.8 mm thick bulk Ge crystal.

Figure 2. Linear absorption coefficient (α) as a function of Sb concentration for 50 and 100 cm^{-1} radiation.

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