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Density-of-States Effective Mass in the System $(GeTe)_{1-x}(AgSbTe_2)_x$

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The compound $Ge_{1-y}Te_y$ is characterized by a wide homogeneity region shifted in the tellurium-rich side /1/, high carrier concentration ((0.4 to 2.5)x x10^{21} cm^{-3}), and reversible phase transition ferroelectric $\beta \rightarrow \alpha (y \leq 0.504)$ or antiferroelectric $\beta \rightarrow \gamma (y > 0.504)$. The high-temperature phase β-GeTe possesses a face-centered cubic lattice. The rhombohedral α-GeTe (or rhombic γ-GeTe) lattice distortion with the phase transition $\beta \rightarrow \alpha$, γ is accompanied by an energy band change comprising the splitting of the four equivalent L extrema of the first Brillouin zone of the cubic phase into 1:3 or 2:2 ratio for the α- and γ-phases, respectively /1/. The low-temperature modifications (α or γ) are narrow-band gap semiconductors. Tunneling experiments at 4.2 K have given 0.2 eV for the band gap width, which decreases linearly with temperature /2/.

The variation of the conductivity and density-of-states effective masses with temperature and carrier concentration has been studied for GeTe and some of its solid solutions /3 to 5/.

The physicochemical investigation of the system $(GeTe)_{1-x}(AgSbTe_2)_x$ has shown that there exists limited solid solubility at the GeTe side ($x \leq 0.63$ at 809 K).

The solubility region is narrowed with decreasing temperature and reaches $x \approx 0.30$ at 300 K /6/. These solid solutions undergo $\beta \rightarrow \alpha$ phase transitions. The phase transition temperature (T_c) and the rhombohedral distortion decrease upon increasing the $AgSbTe_2$ content /7/. Their band structure is similar to the GeTe one. The band gap of the α-phase at 300 K (determined from optical measurements) increases upon increasing x /8/.

The effective masses in the system $(GeTe)_{1-x}(AgSbTe_2)_x$ have not been studied.

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The scope of the present note is the density-of-states effective mass dependence on alloy composition in the $0 \leqq x \leqq 0.20$ range.

The band-edge density-of-states effective masses were calculated from the experimental values of the thermoelectric power and carrier concentration at 300 K utilizing the Kane model for IV-VI compounds /9/

$$n = \frac{(2m_d^* k_o T)^{3/2}}{3\pi^2 h^3} \; {}^{o}\mathfrak{L}_o^{3/2}, \tag{1}$$

$$\alpha = \frac{k_o}{e}\left(\frac{{}^{1}\mathfrak{L}_2^{1}}{{}^{o}\mathfrak{L}_2^{1}} - Z\right), \tag{2}$$

where ${}^{n}\mathfrak{L}_k^{m}(Z, \beta)$ are the modified two parameter Fermi integrals to include the energy dependence of the square of the transition probability matrix element /10/, and $Z = E_F/k_oT$ and $\beta = k_oT/E_g$ are the reduced Fermi energy and the non-parabolicity factor, respectively. E_g is taken from the optical measurements /8/. The Fermi energy calculated from (2) presumes that only the singlet valence valley in the α-phase is occupied by carriers, so the band-edge density-of-states effective mass computed from (1) refers only to that valley.

Results and discussion The alloying of $AgSbTe_2$ into GeTe leads to a decrease in m_d^* by about 2 times for $0 \leqq x \leqq 0.04$. At $x > 0.04$ m_d^* decreases slowly with increasing x (Fig. 1). The theory of the formation of solid solutions of substitution predicts a decrease of the effective mass /11/. An estimation of such a decrease can be done utilizing the formula /12/

$$m_{dx}^* = m_{do}^*\left(1 - \frac{2x(1-x)\delta^2 m_{do}^{*2}}{(2\pi N_o)^{4/3}\hbar^4}\right), \tag{3}$$

where N_o is the number of atoms per unit volume, δ is associated with the energy gap difference of the end compounds, and m_{dx}^* and m_{do}^* are the band-edge density-of-states effective masses of the solid solutions and the end compound, respectively.

Fig. 2 represents the plot of the ratio $\Delta m_d^*/m_o^*$ versus $x(1-x)$ (dashed line). From the linear part of the dependence $0.04 \leqq x \leqq 0.15$ was estimated the value $\delta = 2.7$ eV.

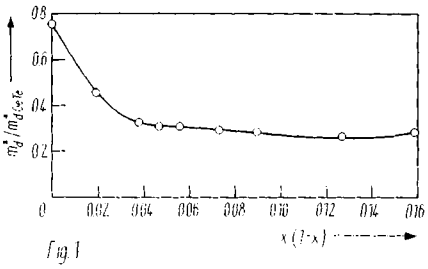

Fig. 1

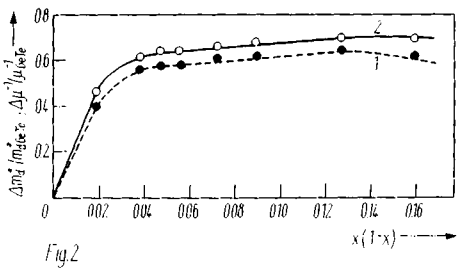

Fig. 2

Fig. 1. The density-of-states effective mass versus composition in the range $0 \leqq x \leqq 0.20$ at 300 K

Fig. 2. Relative change of the density-of-states effective mass $(m^*_{dGeTe} - m^*_{dx})/m^*_{dGeTe}$ (● and dashed line) and reverse mobility $(\mu^{-1}_{GeTe} - \mu^{-1}_{x})/\mu^{-1}_{GeTe}$ (o and solid line) versus $x(1 - x)$

On the assumption that the prevailing scattering mechanisms are acoustic phonon, ion core, and potential fluctuation and that Matthiessen's rule holds, one obtains for the reverse mobility /13/

$$\mu^{-1} = \frac{m_c \pi \varrho(E_F)}{e N \hbar} \left[\frac{\Xi^2 k_o T}{C} + p U_i^2 + \frac{x(1-x)\delta^2}{N_o} \right] |M|^{-2} , \qquad (4)$$

where $\varrho(E_F)$ is the density of states at the Fermi energy, Ξ accoustic phonon deformation potential, C a combination of the elastic moduli, N number of equivalent extrema, U_i potential well strength for the cation vacancies in the solid solutions, p hole concentration.

The estimation of the second and the third terms in the brackets of formula (4) has given

$$2 \times 10^{-29} > p U_i^2 > 2 \times 10^{-30} \quad (eV)^2 m^3 ,$$

$$8 \times 10^{-30} < \frac{x(1-x)\delta^2}{N_o} < 2 \times 10^{-29} \quad (eV)^2 m^3$$

as x varies from 0.04 to 0.15.

The value of $U_i = 2 \times 10^{-28}$ eV m^3 was taken to be as it was evaluated for Pb and Sn vacancies in $Pb_{1-x}Sn_xTe$ /13/ and $\delta = 2.7$ eV. If the first term does not change drastically with x (all solid solutions are in the rhombohedral phase) the variation of the mobility should be governed by the change in the effective

mass. This can be seen from the plot of $\Delta\mu^{-1}/\mu_o^{-1}$ versus $x(1 - x)$ (the solid line in Fig. 2). Note that both curves are in one and the same scale. The more rapid change of $\Delta\mu^{-1}/\mu_o^{-1}$ at $x \leqq 0.04$ compared with $\Delta m_d^*/m_{do}^*$ can be associated with the more abrupt change of the hole concentration in that region.

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