Nonparabolic Conduction Band in HgSe and $HgSe_{0.5}Te_{0.5}$

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The dependence of electron effective mass (m^*) on carrier concentration (N) has been determined for samples of n-type HgSe ($N=5\times10^{17}$ to 3×10^{19} cm^{-3}) and $HgSe_{0.5}Te_{0.5}$ alloy ($N=9\times10^{17}$ to 9×10^{18} cm^{-3}) by means of infrared reflectivity and magnetoreflectivity measurements. In both cases, m^* increases markedly with N. For HgSe, the variation of m^* with N is quantitatively consistent with the conduction band model derived by Kane for InSb. The band parameters derived from the data are $P=8\times10^{-8}$ ev-cm, in close agreement with the values determined for InSb and other III-V compounds, and $\epsilon_g\sim0.2$ ev. The data for $HgSe_{0.5}Te_{0.5}$ appear to be qualitatively consistent with Kane's model, although they exhibit too much scatter for quantitative comparison.

INTRODUCTION

THE conduction bands of a number of III-V compounds with zinc-blende structure are spherically symmetric and nonparabolic. For each of these compounds, the electron effective mass varies with energy in the manner derived theoretically for InSb by Kane.[1,2] The conduction band of HgSe, a II-VI compound with zinc-blende structure, is also spherically symmetric,[3] and previous studies of the reflectivity[4] and thermomagnetic properties[5] have indicated that the conduction band is nonparabolic. In view of the qualitative similarity between HgSe and the III-V compounds, the present detailed investigation of the infrared reflectivity of HgSe at zero magnetic field and as a function of field was undertaken to determine the quantitative dependence of effective mass on energy and to compare the measured dependence with the predictions of Kane's model. A similar investigation has also been made for the alloy $HgSe_{0.5}Te_{0.5}$.

THEORY

The nonparabolic character of the conduction band in InSb arises mainly from the interaction of the conduction band with the threefold degenerate valence band. Considering only this interaction, Kane[1] derived the following expression for the conduction band energy, ϵ_c:

$$\epsilon_c=\tfrac{1}{2}[\hbar^2k^2/m+\epsilon_g+(\epsilon_g^2+8k^2P^2/3)^{\frac{1}{2}}], \tag{1}$$

where ϵ_g is the energy gap between the conduction and valence bands, k is the wave vector of the energy eigenstate, and P is a constant proportional to the matrix component of momentum between conduction and valence band Bloch functions at $k=0$. This expression is valid if the spin-orbit splitting of the valence band is much greater than ϵ_g and kP.

The susceptibility effective mass, m_s, obtained from infrared reflectivity data is defined by[6,7]

$$\frac{1}{m_s}=\frac{1}{\hbar^2k}\left(\frac{d\epsilon_c}{dk}\right). \tag{2}$$

For convenience we shall use a reduced effective mass $m^*=m_s/m$, where m is the free electron mass. From Eqs. (1) and (2),

$$\frac{1}{m^*}=1+\frac{4}{3}\frac{P^2}{\hbar^2}[\epsilon_g^2+(8k^2P^2)/3]^{-\frac{1}{2}}. \tag{3}$$

In the case of sharp degeneracy, the free electron concentration N is equal to $k^3/3\pi^2$, and consequently

$$\left(\frac{m^*}{1-m^*}\right)^2=32.5\times10^{-32}\frac{\epsilon_g^2}{P^4}+8.27\times10^{-30}\frac{N^{\frac{2}{3}}}{P^2}, \tag{4}$$

where the dimensions of ϵ_g, P, and N are ev, ev-cm, and cm^{-3}, respectively. If Kane's model is applicable, a plot of $[m^*/(1-m^*)]^2$ vs $N^{\frac{2}{3}}$ will therefore give a straight line with slope proportional to $1/P^2$ and intercept proportional to ϵ_g^2/P^4.

The susceptibility effective mass of free charge carriers in a semiconductor may be found by measuring the infrared reflectivity at zero magnetic field, as shown by Spitzer and Fan.[6] The reflectivity R and complex index of refraction $(n-ik)$ are related by the usual expression $R=[(n-1)^2+k^2]/[(n+1)^2+k^2]$. For a semiconductor containing charge carriers, $(n-ik)$ exhibits the following dependence on frequency, ω:

$$(n-ik)^2=\kappa'\left[1-\frac{\omega_p^2}{\omega^2-i\omega\nu}\right], \tag{5}$$

where κ' is the dielectric constant of the material in the absence of charge carriers, ω_p is the plasma frequency, and ν is the carrier scattering frequency. It is assumed that κ' is real and constant over the frequency range considered. If $\nu\ll\omega_p$, it follows from Eq. (5) that in the vicinity of ω_p there will be a deep minimum in

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[7] M. J. Stephen and A. B. Lidiard, J. Phys. Chem. Solids 9, 43 (1958).

R, followed by a sharp rise. Since $\omega_p^2=(Ne^2/m_s\kappa'\epsilon_0)$, in mks units,

$$m^*=\left(\frac{e^2}{4\pi^2c^2m\epsilon_0}\right)\frac{N\lambda_{\min}^2}{\kappa'-1}, \quad (6)$$

where $\lambda_{\min}$ is the wavelength of the reflectivity minimum.

In the presence of a magnetic field transverse to the infrared electric vector and direction of propagation, if carrier scattering losses are negligible Eq. (5) becomes[8]

$$n^2=\kappa'\left[1-\frac{\omega_p^2}{\omega^2}\frac{(\omega^2-\omega_p^2)}{(\omega^2-\omega_p^2-\omega_c^2)}\right], \quad (7)$$

where $\omega_c=eB/m_s$ is the cyclotron frequency. In this case, there will be two reflectivity minima separated by ω_c, and it is therefore possible to determine m_s without independent measurements of N or κ'. In the usual case, where losses are appreciable, the expression for $(n-ik)$ is much more complicated. By fitting the data to numerically computed theoretical curves, however, one obtains values for m^*, N, ν, and κ' from the reflectivity data alone.

EXPERIMENTAL

Large-grained samples of HgSe and $HgSe_{0.5}Te_{0.5}$ were cut from ingots prepared from the elements ("99.999%" purity) by a modified Bridgman method.[9] The Hall coefficient (R_H) of each sample was measured at room temperature by conventional dc potentiometric techniques, and the free electron concentration was calculated according to the expression $N=1/R_He$. The concentrations ranged from 5×10^{17} to 3×10^{19} cm^{-3} for HgSe and from 9×10^{17} to 9×10^{18} cm^{-3} for $HgSe_{0.5}Te_{0.5}$. Samples with low concentrations were cut from undoped ingots, in which interstitial mercury atoms were probably the major ionized donors,[9] while samples with higher concentrations were obtained from ingots doped with aluminum. The carrier concentrations of undoped HgSe samples often changed appreciably not only during sample preparation, which involved heating the material above room temperature, but also during storage at room temperature. The changes were probably associated with diffusion of interstitial mercury atoms into and out of the samples, which has been shown to occur at an appreciable rate even at room temperature.[9] Samples of $HgSe_{0.5}Te_{0.5}$ and highly doped samples of HgSe were much more stable. To obtain carrier concentrations appropriate for analysis of the reflectivity data, Hall measurements on all samples were made immediately after the optical measurements, with a point-contact device which made soldering unnecessary.

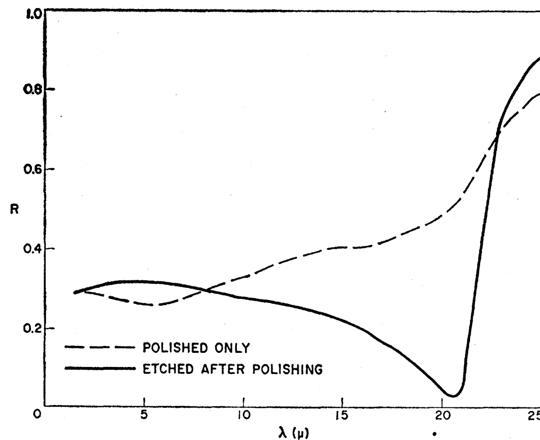

Fig. 1. Reflectivity of HgSe ($N=1.2\times10^{18}$ cm^{-3}) before and after etching.

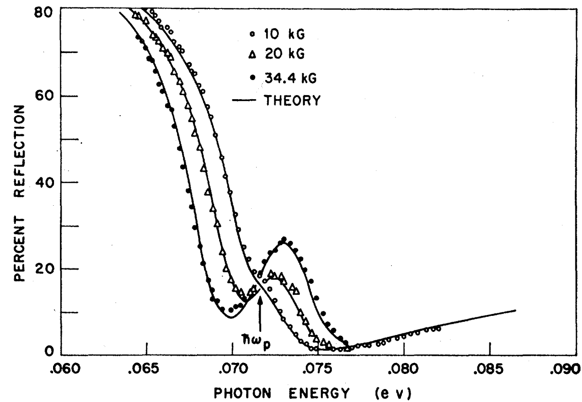

Fig. 2. Reflectivity of HgSe ($N=2.5\times10^{18}$ cm^{-3}) as a function of magnetic field.

After the samples for reflectivity measurements had been ground flat and polished to an optical finish, they were etched to remove work damage.[10] The necessity for etching is illustrated by Fig. 1, which shows that the work damage resulting from grinding and polishing could even cause the plasma reflectivity minimum to disappear.

Reflectivity at zero magnetic field was measured relative to an evaporated aluminum standard with a Perkin Elmer Model 221 double-beam spectrophotometer. The magnetoreflection data were taken with a single-beam magnetospectrometer at fixed photon energies. With an aluminum mirror in the beam, the recorder deflection was first standardized at 100%. The sample was then substituted for the mirror, and the magnetic field was swept from 0 to 39 kilogauss in a period of 5 min. This method was chosen because the reflectivity as a function of field is given directly by the recorder trace. If, instead, the photon energy is swept at fixed magnetic field, it is necessary to reduce

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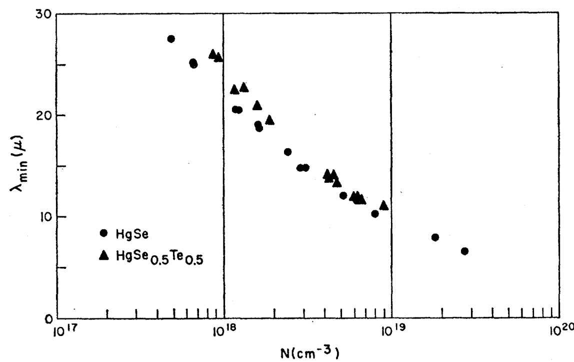

FIG. 3. Wavelength of minimum reflectivity (λ_{min}) vs carrier concentration (N) for HgSe and $HgSe_{0.5}Te_{0.5}$.

the recorder data point by point to compensate for the variation of incident energy with wavelength, and the requirements for equipment stability are much more severe.

RESULTS AND DISCUSSION

Magnetoreflection measurements were made on a sample of HgSe with $N=2.5\times10^{18}$ cm^{-3} as determined by Hall measurements. The data are shown in Fig. 2, together with theoretical curves computed on an IBM 7090 computer with a program which takes account of carrier scattering losses. The parameters determined by fitting the data are $m^*=0.050\pm0.003$, $\kappa'=12\pm1$, $\omega_p=1.09\pm0.05$, and $\nu=(4.6\pm0.4)\times10^{12}$.

For the remaining samples of HgSe and $HgSe_{0.5}Te_{0.5}$, the experimental values of λ_{min} at zero magnetic field (as shown in Fig. 3) were used to calculate m^* as a function of N (as shown in Fig. 4) according to Eq. (6). The value of κ' used was 12, as determined from the magnetoreflection data. For carrier concentrations exceeding 10^{18} cm^{-3}, the reflectivity at λ_{min} was 3% or less for HgSe and 5% or less for $HgSe_{0.5}Te_{0.5}$. Such deep minima imply that carrier scattering losses were very small and consequently that Eq. (6) is valid for

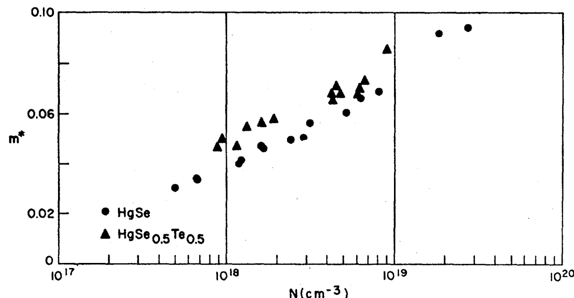

FIG. 4. Effective mass (m^*) vs carrier concentration (N) for HgSe and $HgSe_{0.5}Te_{0.5}$.

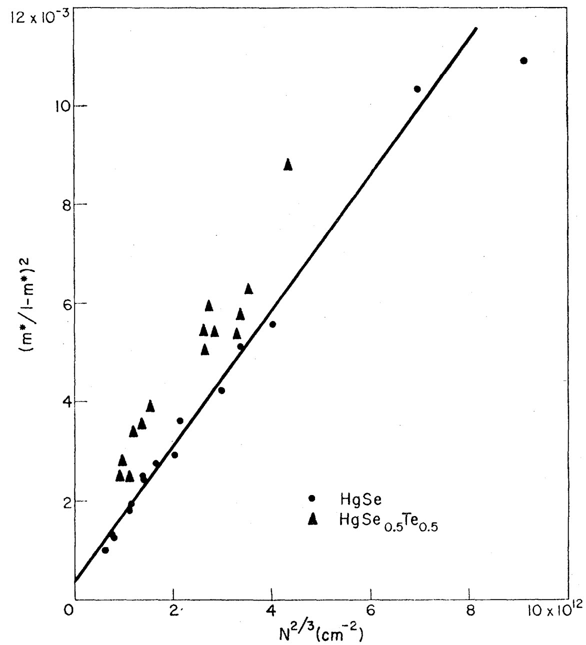

FIG. 5. Comparison of Kane's nonparabolic band model with results for HgSe and $HgSe_{0.5}Te_{0.5}$.

these samples. The values of m^* for lower carrier concentrations are somewhat less accurate, since the minimum reflectivities for these samples were approximately 10%.

The data for m^* are compared with Kane's theory in Fig. 5, where $[m^*/(1-m^*)]^2$ is plotted vs $N^{\frac{2}{3}}$. As predicted by Eq. (4), a straight line is obtained for HgSe. Therefore, Kane's model is valid for HgSe as well as for the III-V compounds. The value of P derived from the slope is 8×10^{-8} ev-cm, the same within experimental error as the value of 8.7×10^{-8} ev-cm obtained for InSb.[11] Very similar values of P have also been obtained for the III-V compounds InAs, GaAs, GaSb, and InP.[2] The value of ϵ_g calculated from the intercept is 0.2 ev. Although the data for $HgSe_{0.5}Te_{0.5}$ exhibit too much scatter to justify drawing a line through them, they also appear to be qualitatively consistent with Kane's model.

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