phys. stat. sol. (b) **156**, 371 (1989)

Subject classification: 71.25 and 78.20; 77.20; 88.15

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Interband Critical Point Parameters Determined by Ellipsometry in $Cd_xHg_{1-x}Se$

By

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The dielectric function of $Cd_xHg_{1-x}Se$ crystals, with $x = 0$ to 0.30, is measured by ellipsometry at room temperature between 1.8 and 5.5 eV. The E_1 and $E_1 + \Delta_1$ gaps and the Δ_1 spin–orbit splitting show a upwards quadratic dependence on composition. The broadening of the observed structures increases with x due to alloying effects and disorder or to the difference in chemical activity of the surfaces. The results are discussed in comparison with those obtained for $Zn_xHg_{1-x}Se$ and $Cd_xHg_{1-x}Te$.

Die dieelektrische Funktion von $Cd_xHg_{1-x}Se$-Kristallen mit $x = 0$ bis 0,30 wird mittels Ellipsometrie bei Raumtemperatur im Bereich von 1,8 bis 5,5 eV gemessen. Die E_1- und $E_1 + \Delta_1$-Lücke sowie die Δ_1-Spin–Bahnaufspaltung zeigen eine steigende quadratische Abhängigkeit von der Zusammensetzung. Die Verbreiterung der beobachteten Strukturen nimmt mit x infolge der Legierungseinflüsse und Fehlordnung oder infolge der Differenz der chemischen Aktivität der Oberflächen zu. Die Ergebnisse werden im Vergleich zu denen an $Zn_xHg_{1-x}Se$ und $Cd_xHg_{1-x}Te$ erhaltenen diskutiert.

1. Introduction

$Cd_xHg_{1-x}Se$(CdHgSe), one of narrow-gap semiconductors, is a mixture of a semimetal, HgSe, with inverted band structure and a semiconductor, CdSe. The transition from inverted to normal InSb-type band structure at the Γ point occurs, at room temperature, for $x = 0.05$ [1]. This semiconductor crystallizes in the zincblende structure for $0 < x < 0.77$ and in the wurtzite one for $x > 0.81$, while a mixed phase of both structures is observed for $0.77 < x < 0.81$ [2]. The value of the fundamental energy gap, E_0, of these crystals varies with x continuously from -0.06 eV for $x = 0$ to 1.07 eV for $x = 0.6$ at 300 K [1]. Many studies on this material have been done from the point of view of electrical [3] and optical measurements [4 to 7]. The first composition dependence of the critical point energies of CdHgSe with $0 < x < 0.8$ was obtained from the peak position in reflectivity over the range 2.0 to 5.6 eV at 300 K [4]. Recently the composition dependence of E_1 and $E_1 + \Delta_1$ gaps and Δ_1 spin–orbit splitting of $Zn_xHg_{1-x}Se$ (ZnHgSe) [8] and $Cd_xHg_{1-x}Te$ (CdHgTe) [9] was measured by ellipsometry at room temperature. The broadening of the critical points are also discussed by alloying effects.

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The optical properties at energies greater than those of E_0 are of interest because direct information about the band structure of the semiconductor alloys can be obtained from the Van-Hove singularities in the optical spectra. However, to our knowledge, there is no report on the optical properties and interband transitions, above the fundamental band gap, in CdHgSe obtained by ellipsometry. The purpose of this paper is to determine accurately higher energy gaps in CdHgSe crystals and to investigate the alloy-induced bowing and broadening effects.

2. Experimental Procedures

CdHgSe single crystals, with $x = 0$, 0.01, 0.03, 0.05, 0.07, 0.11, 0.20, and 0.30 were grown by a Bridgman method similar to that reported for CdHgSe [7, 10] and ZnHgSe [7, 8]. The composition of the samples was determined by an EPMA analysis. The electron concentration and Hall mobility were measured by the van der Pauw method.

The complex dielectric functions $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ were obtained at room temperature with an automatic rotating-analyzer ellipsometer [8, 9]. The (100) surfaces to be measured were mechanically polished with Syton (Monsanto trade mark). The samples, mounted in a windowless cell in flowing dry N_2, were etched prior to the measurement with bromine–methanol solutions and stripped with methanol and distilled water.

3. Result and Discussion

The electron concentration and Hall mobility of the samples at room temperature were 0.5 to 3.0 $\times$ 10^{18} cm^{-3} and 2 to 10 $\times$ 10^3 cm^2/Vs, respectively. The deviation of x was $\pm 10\%$.

Fig. 1 shows the real (ε_1) and imaginary (ε_2) parts of the pseudodielectric function of CdHgSe, at room temperature, for three selected compositions ($x = 0$, 0.03, and 0.11) as a function of photon energy. The values of ε_1 decrease rapidly from 9 to 2 as the photon energy increases from 2.5 to 3.5 eV. On the other hand, the ε_2's have a peak near 3 eV. The main peak in ε_2 corresponds to the E_1 singularity, while the $E_1 + \Delta_1$ gap is only seen as a shoulder at slightly larger energies. We observe a shift of the peak in ε_2 and the edge in ε_1 to higher energies with increasing x. A similar behavior was observed for the rest of the samples. In order to resolve the structure

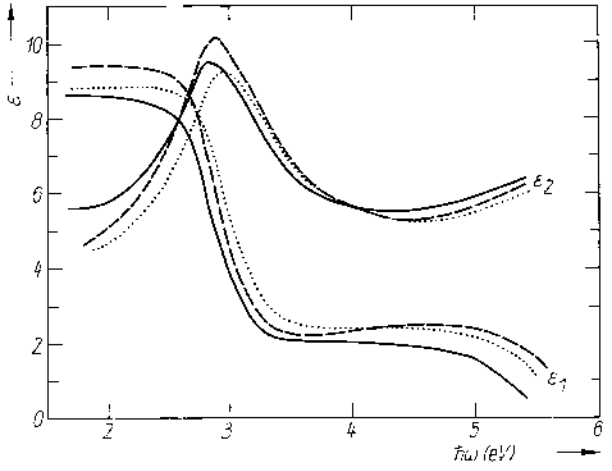

Fig. 1. Real (ε_1) and imaginary (ε_2) parts of the pseudodielectric function of CdHgSe with $x = 0$ (——), 0.03 (– – –), and 0.11 (·····) at room temperature, as a function of photon energy

present in the spectra and to obtain the critical point parameters we calculate numerically the second derivative spectra of the complex dielectric function from our ellipsometric data. The derivative spectra were fitted by assuming a mixture of contiguous two-dimensional critical points for the E_1 and $E_1 + \Delta_1$ singularities.

The critical point energies and spin–orbit splitting are shown in Fig. 2 as a function of x. The value of the spin–orbit splitting Δ_1 was obtained by subtraction of E_1 from $E_1 + \Delta_1$. The E_1 structure corresponds to transitions from the $\Lambda_{4,5}$ valence band to the Λ_6 conduction band, while $E_1 + \Delta_1$ is associated to transitions from the Λ_6 valence band to the Λ_6 conduction band in an extended region of the Brillouin zone. Our data are plotted as open marks. The solid points are taken from the values determined by the peak position of reflection measurements [4]. The results show a weakly quadratic dependence for the E_1 and $E_1 + \Delta_1$ gaps and the Δ_1 splitting on composition, as in many other semiconducting mixed crystals ([9] and references therein). For ZnHgSe [8] and CdHgTe [9], we also observed a quadratic dependence on x for the E_1 and $E_1 - \Delta_1$ gaps, however, an almost linear dependence was obtained for the Δ_1 splitting. The dotted lines correspond to the best fit of our data to the following expression:

$$E(x) = a + bx + cx^2 . \tag{1}$$

The values of a, b, and c for CdHgSe are listed in Table 1 together with those of CdHgSe calculated from the peak positions of reflection spectra [4] and those obtained from ellipsometric measurements for ZnHgSe [8] and CdHgTe [9].

The values for our samples are different from those calculated from reflection data and the sign of c is the opposite. The main cause for the opposite signs of c seems to arise from the existence of two different regions: the x-dependence of critical point energy is linear or weakly downwards quadratic for $0 < x < 0.5$, whereas a strong downwards quadratic dependence is obtained in the reflectivity results for $0.5 < x < 0.8$ [4]. Our coefficients obtained for $0 < x < 0.3$ fit well the results of reflectivity in the range $0 < x < 0.4$, as can be seen in Fig. 2, confirming the previous assumption of the existence of two different composition regions. On the other hand, the magnitude and sign of the coefficient a for the E_1 and $E_1 - \Delta_1$ gaps are similar in the three solid solutions, while those of the coefficients b and c are quite different. Namely, the magnitude of the coefficient b for the present results is about two or three times larger than that for the other compounds, having the same sign as CdHgTe but opposite to ZnHgSe. The value of c from our CdHgSe data is comparable with that of CdHgTe but is about twenty and six times smaller than that for ZnHgSe for E_1

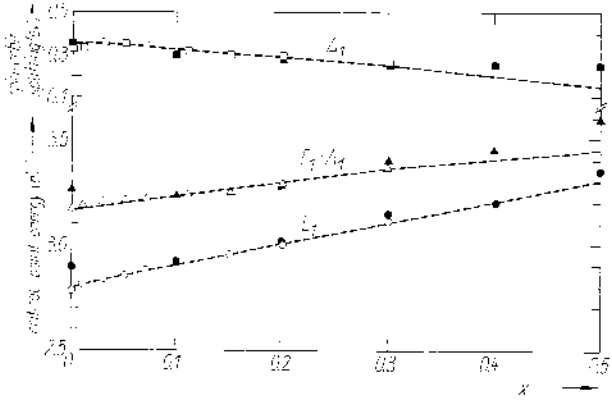

Fig. 2. Composition dependence of critical-point energies and spin–orbit splitting of CdHgSe. Open symbols are our data and closed ones are taken from [4]. The dashed lines represent the best fits of our data to a quadratic function

Table 1
Values of the parameters a, b, c obtained by fitting the critical-point energy E vs. composition x to the quadratic function (1)

critical point	compound	a (eV)	b (eV)	c (eV)
E_1	CdHgSe[a])	2.797	1.08	−0.12
	CdHgSe[b])	2.85	0.71	0.8
	ZnHgSe[c])	2.781	−0.31	2.3
	CdHgTe[d])	2.147	0.44	0.7
$E_1 + \Delta_1$	CdHgSe[a])	3.159	0.78	−0.41
	CdHgSe[b])	3.17	0.45	1.0
	ZnHgSe[c])	3.120	−0.41	2.4
	CdHgTe[d])	2.778	0.47	0.6
Δ_1	CdHgSe[a])	0.362	−0.293	−0.291
	CdHgSe[b])	0.34	−0.30	0.2
	ZnHgSe[c])	0.339	−0.101	0.062
	CdHgTe[d])	0.631	0.031	−0.079

[a]) This work ($0 < x < 0.30$).
[b]) Calculated from [4] ($0 < x < 0.8$).
[c]) Previous work [8] ($0 < x < 0.40$).
[d]) Ref. [9] ($0 < x < 1$).

and $E_1 + \Delta_1$, respectively. The sign of c for our CdHgSe is always negative. This upper bowing was also observed in CdHgTe for Δ_1 and E_2 [9]. The magnitude of b and c of Δ_1 for CdHgSe is three to ten times larger than that for the other compounds.

The bowing in the quadratic dependence of the energy thresholds on composition can be separated into two contributions. One is an intrinsic bowing, present already in the virtual crystal approximation of alloys, as a consequence of the dependence of the lattice constant on x [9]. The second is an extrinsic bowing, the difference between intrinsic and experimental bowing, being due to effects of the random potential of the alloy. The difference in lattice constant, $\Delta a/a$, is 29% for CdHgSe and 6.8% for ZnHgSe, but only 0.3% for CdHgTe. Generally the bowing parameter c in mixed crystals increases with the difference in lattice constant [11]. This trend is observed experimentally for the bowing parameter of the spin–orbit splitting, which decreases going from CdHgSe to ZnHgSe and to CdHgTe. However, in spite of the larger difference in the lattice constant, the magnitude of c for the E_1 and $E_1 + \Delta_1$ critical energies of CdHgSe is of the same order as those of CdHgTe. Although we cannot explain this fact at present, we believe that it is due to the contribution from the extrinsic bowing, for which there is no theoretical estimate for CdHgSe [12].

The Lorentzian broadening parameters Γ [9] for the E_1 and $E_1 + \Delta_1$ critical points are shown in Fig. 3 as a function of x. The crosses and triangles denote the broadening parameters taken from the ellipsometric data of ZnHgSe [8]. The dashed lines are drawn through the experimental points only to visualize the dependence on composition. The broadening of the $E_1 + \Delta_1$ critical point is about 50% larger than that of the E_1 structure, and the values of Γ increase with increasing x. The composition dependence looks quadratic for E_1 and almost linear for $E_1 + \Delta_1$. These features have been reported for CdHgTe and other ternary compounds ([9] and references therein). However, our values of Γ for the $E_1 + \Delta_1$ and E_1 critical points in HgSe ($x = 0$) are larger, by a factor of 1.9 and 3.1, respectively, than those obtained in HgTe [9]. This

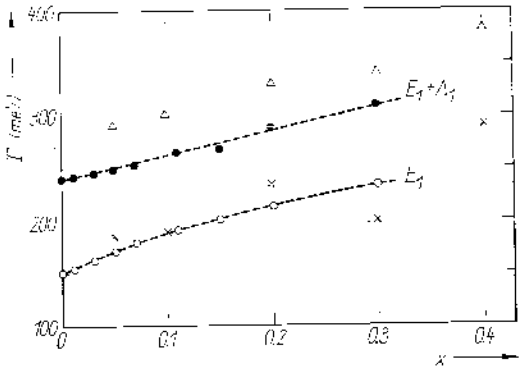

Fig. 3. Composition dependence of critical-point broadening parameters for CdHgSe. Circles are for CdHgSe and crosses (E_1) and triangles ($E_1 + \Delta_1$) are for ZnHgSe taken from the previous work [8]

large difference may be due to surface effects [8] originating from the following mechanisms.

One of them is the effect of inhomogeneities due to native defects or microscopic compositional disorder and to deviations in x. The existence of the former was established by the observation of symmetry-forbidden TO modes on the (100) surface in CdHgSe together with a peak due to clustering effects by Raman measurements [6]. The latter was observed in the plasmon-LO phonon coupling spectra of FIR reflection measurements in CdHgSe [7] and ZnHgSe [13]. The second mechanism is due to the difference in chemical activity of the surfaces as seen in the etching figures [14] and in FIR and Raman spectra for HgSe [15], CdHgSe [6, 7], HgTe [15], and CdHgTe [15 to 17]. We have also seen differences in the dielectric functions for the (100) and (111) surfaces in CdHgSe as shown in Fig. 4. We observe a slight increase of the real and imaginary part of the dielectric constants in the (111) surface compared with those in the (100) surface. A similar tendency was observed in HgSe. Thus we feel that the dielectric properties of narrow gap semiconductors, as measured by ellipsometry, are affected by surface effects due to etching or sample treatments.

We have tried to check the dependence on x of the difference between the experimental energy threshold values for the E_1 and $E_1 + \Delta_1$ singularities and the values obtained by linear interpolation between HgSe and CdSe. However, we could not find a parabolic dependence of composition, symmetric with respect to $x = 0.5$, observed in ZnHgSe [8] and other compounds (references in [9]). This may be related to the

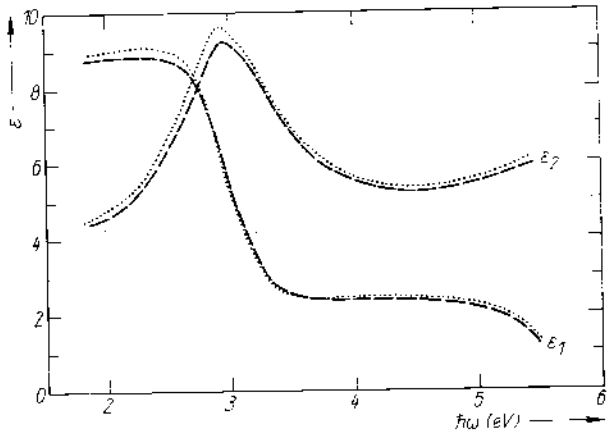

Fig. 4. Real (ε_1) and imaginary (ε_2) parts of the pseudodielectric function of CdHgSe with $x = 0.11$ on the (111) (.....) and (100) (— —) surfaces at room temperature, as a function of photon energy

existence of two different regions of composition dependence of the critical point energies or to inhomogeneities as mentioned above. We shall need more information about the x dependence of mixing of two-dimensional critical point and phase angle [9] to give a convincing discussion of this problem.

In conclusion, the critical point energies of the two structures E_1 and $E_1 + \Delta_1$ in CdHgSe have been measured as a function of the composition by means of ellipsometry. These critical points and the spin–orbit splitting (Δ_1) have a negative bowing parameter in our experimental region. In spite of large differences in the relative changes of the lattice constants with respect to the parent compounds, the dependence of the critical point energies on composition of CdHgSe is similar to that of CdHgTe and ZnHgSe. The larger broadening parameters for CdHgSe and ZnHgSe compared to those for CdHgTe may stem from inhomogeneities or larger surface effects.

Acknowledgements

One of the authors (K.K.) thanks the Max-Planck-Gesellschaft for the support during his stay. He is also grateful to the HIT special Foundation, the Private College Promotion Foundation and the grant of the Hitachi Microcomputer Eng. Ltd. for their financial support.

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(Received August 10, 1989)