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Determination of the fundamental and split-off band gaps in zinc-blende CdSe by photomodulation spectroscopy

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We present the results of experimental determination of the fundamental band gap (E_0) and the spin-orbit split-off energy gap (Δ_0) of zinc-blende CdSe using photomodulation spectroscopy. The single-crystal CdSe film was grown by molecular-beam epitaxy on a (100) GaAs substrate with a ZnTe buffer layer. Photoreflectance (PR) measurements were performed on the sample at various temperatures from 10 K to room temperature. The sharp derivativelike spectral features associated with the interband Γ_8^V-Γ_6^C and Γ_7^V-Γ_6^C transitions in PR spectra allow us to determine the E_0 and $E_0+\Delta_0$ band-gap energies. We found that zinc-blende CdSe has a fundamental band gap E_0 of 1.661 eV and a spin-orbit split-off gap Δ_0 of 0.42 eV at room temperature (295 K). The fundamental band gap E_0 of zinc-blende CdSe has been mapped out as a function of temperature and the Varshni thermal coefficients have been determined for this material. The results yield $E_0(T)=1.766-6.96\times10^{-4}\ T^2/(281+T)$ eV.

In recent years, much effort has been devoted to the study of wide band-gap II-VI compound semiconductors and their multilayer heterostructures for optoelectronic device applications, such as laser diodes and light-emitting diodes operating in the blue-green range. The $Cd_xZn_{1-x}Se$/ZnSe quantum-well and superlattice structures are among the most extensively studied heterostructure materials. The ternary II-VI compound $Cd_{1-x}Zn_xSe$ with zinc-blende structure has been grown by molecular-beam epitaxy (MBE) over the entire range of compositions by Samarth *et al.*[1] Blue laser action and electroluminescence have been successfully achieved from the ZnSe-based quantum-well devices using $Cd_{1-x}Zn_xSe$ as quantum-well materials.[2-4] The success of these developments has partially been attributed to the quality and properties of $Cd_xZn_{1-x}Se$ alloys which proved to be particularly useful for electron-hole pair confinement in the $Cd_xZn_{1-x}Se$/ZnSe heterostructures.[5,6] However, there has been relatively little work on the electronic band structure of the binary zinc-blende CdSe itself (which is one of the end points of the alloy just mentioned), especially for such important parameters as the fundamental band gap E_0 and the spin-orbit split-off band gap Δ_0.

In this paper we present the results of a photomodulation spectroscopy study of optical transitions between the bottom of the Γ_6^C conduction band and the tops of the Γ_8^V valence band and the Γ_7^V spin-orbit split-off band in a zinc-blende CdSe single-crystal epilayer. Photoreflectance (PR) measurements were performed on the sample at different temperatures from 10 K to room temperature (295 K). The sharp spectral features related to Γ_8^V-$\Gamma_6^C(E_0)$ and $\Gamma_7^V-\Gamma_6^C(E_0+\Delta_0)$ transitions due to the derivative nature of photoreflectance spectra allow us to determine the transition energies precisely. The fundamental band gap E_0 of zinc-blende CdSe is found to be 1.661 eV at room temperature (295 K). The spin-orbit split-off band gap Δ_0 is determined to be ~0.42 eV. The dependence of the fundamental band gap E_0 on temperature has been mapped out by fitting the experimental data to the Varshni empirical equation,[7] yielding $E_0(T=0)=1.766\pm0.003$ eV, and Varshni thermal coefficients $\alpha=6.96\times10^{-4}$ eV/K and $\beta=281$ K.

The CdSe epilayer used in this work was grown by MBE on a semi-insulating (100) GaAs substrate. The substrate was pretreated by chemical etching using H_2SO_4:H_2O_2:H_2O (5:1:1) mixture at room temperature for 1 min. Before the growth of CdSe film, a ZnTe buffer layer with a thickness of 1 μm was deposited on the GaAs substrate at the growth temperature of 315 °C to provide a clean and defect-free surface for CdSe deposition. The CdSe epilayer of ~1 μm was then grown at 300 °C. It has been previously demonstrated that, although the normal (i.e., bulk) crystal structure of CdSe is hexagonal (wurtzite), CdSe single-crystal epilayers with cubic (zinc blende) structure can be formed by MBE growth on zinc-blende substrates.[1,8,9] The zinc-blende crystal structure of the CdSe epilayer used in this study was verified by x-ray double-crystal rocking curves. The lattice parameter of the MBE-grown CdSe directly on GaAs substrate was previously determined to be 6.077 Å,[8] very close to the ZnTe lattice constant of 6.099 Å.[10] The CdSe epilayer may thus be considered to be nearly lattice matched to the ZnTe buffer.

PR spectroscopy was carried out on the CdSe sample at a temperature range from 10 K up to room temperature (295 K). The sample was attached to a cold finger of a closed-cycle refrigerator by vacuum grease and cooled down to the desired temperatures for PR measurements. Quasimonochromatic light dispersed by a 0.5-m monochromator from a halogen tungsten lamp was focused on the sample as the probe beam, and a chopped HeCd laser beam was used to provide the photomodulation. The reflectance signals were detected by a Si photodiode using

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lock-in amplification and computer-controlled data acquisition.

Photoreflectance spectroscopy is a differential method utilizing modulation of the built-in electric field through photoinjected carriers by a periodically modulated light beam, such as the chopped laser beam used in this work. A change in reflectivity $\Delta R/R$ due to the modulation may be expressed as[11]

$$\Delta R/R = a\Delta\epsilon_1 + b\Delta\epsilon_2 , \tag{1}$$

where a and b are referred to as Seraphin coefficients and are related to the unperturbed dielectric function $\epsilon=\epsilon_1+i\epsilon_2$, while $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are the changes in the real and the imaginary parts of the modulated dielectric function.[11] The differential changes in the reflectance appear as sharp derivativelike line shapes in the modulated reflectance spectrum, corresponding to specific transitions in the Brillouin zone. In this work, the photoreflectance spectra obtained on the CdSe epilayer at various temperatures consist of two derivativelike spectral signatures in the visible range, as illustrated in Fig. 1.

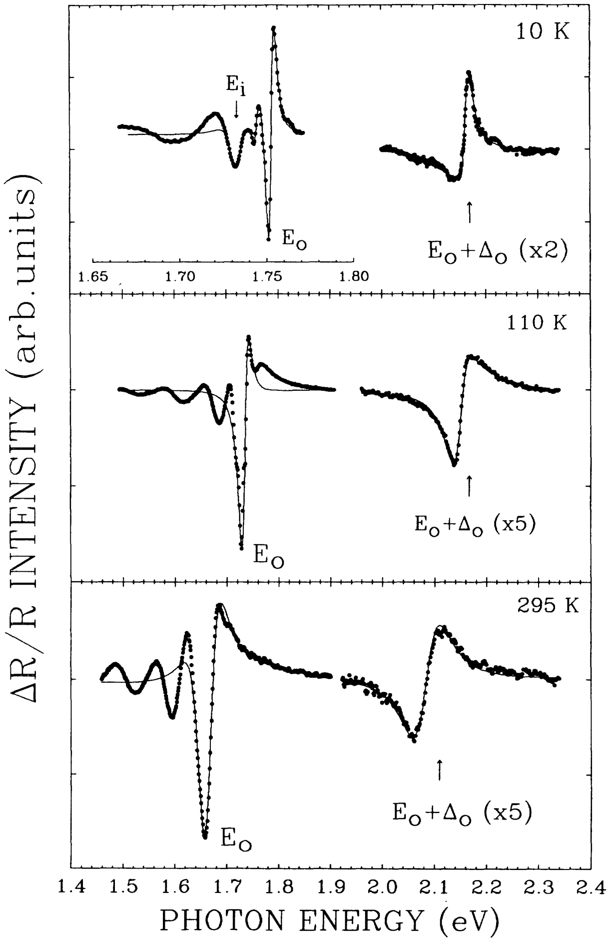

FIG. 1. Photoreflectance spectra taken at 10, 110, and 295 K. The E_0 spectral feature at 10 K is horizontally expanded for clarity. Solid circles are experimental data and solid lines represent the least-squares fit to the data.

The features marked by E_0 and $E_0+\Delta_0$ correspond to the Γ_8^V-Γ_6^C and Γ_7^V-Γ_6^C transitions, respectively. The oscillations at the energy below the Γ_8^V-$\Gamma_6^C(E_0)$ transition are interference effects caused by the heterointerface.

In order to determine the energy positions associated with the optical transitions, the PR spectra are fitted to the functional form[11-13]

$$\Delta R/R = Re[Ce^{i\theta}(E-E_0+i\Gamma)^{-n}] , \tag{2}$$

where C and θ are the amplitude and phase of the line shape, and E_0 and Γ are the energy and the empirical broadening parameter of the transitions, respectively. The exponent n is a characteristic parameter which depends on the type of the critical point and the order of the derivative. The values of $n=\frac{5}{2}$ and 2, which correspond to the three-dimensional interband and excitonic transitions, respectively,[11,14] are used to fit the derivativelike spectral structures. We found that the line positions and widths of the PR spectra taken at low temperatures (≤ 140 K) could be fit using $n=2$ due to the excitonic nature of these features. The $n=\frac{5}{2}$ (which simulates band-to-band line shapes) was found to be more appropriate for fitting the spectra obtained at high temperatures (≥ 150 K), where excitons are expected to dissociate via strong exciton-phonon coupling and inhomogeneous perturbations.[11] The broadening parameter Γ was indeed found to increase significantly with temperature in the numerical fits to the spectra taken at temperatures higher than 150 K. The solid lines in Fig. 1 are the least-squares fits to the experimental data using Eq. (2).

As shown in Fig. 1, the portion of PR spectra at 10 K in the region of the Γ_8^V-$\Gamma_6^C(E_0)$ transition is quite complicated even excluding the interference effect. It is necessary to fit the experimental data with two oscillators using a first-derivative line shape for the spectral feature E_0 and a third-derivative line shape for the feature denoted by E_i. The excellent agreement between the theoretical fit and the observed spectrum indicates that the E_i feature corresponds to a real transition rather than an oscillatory interference signature. The transition energies for E_0 and E_i are 1.752 and 1.732 eV, respectively. While the E_0 feature can be identified as the excitonic Γ_8^V-Γ_6^C transition for its predominant feature in the PR spectra taken at various temperatures, the origin of the E_i feature is not immediately clear. It is known that for such a heterostructure as CdSe epilayer grown on ZnTe, although the two constituents are nearly lattice matched, the difference in the thermal expansion coefficients of lattice constants could introduce an additional temperature-dependent built-in strain. The strain will shift the center of gravity of the entire Γ_8^V band and split the fourfold degeneracy of the top of the Γ_8^V band into two twofold degenerate $|\frac{3}{2},\pm\frac{3}{2}\rangle$ and $|\frac{3}{2},\pm\frac{1}{2}\rangle$ states, i.e., the heavy-hole band and the light-hold band. As a result, two distinct spectral features associated with these two states could be observed if the strain-induced splitting is large enough. It seems that this could be a plausible interpretation for the E_i feature as it is an excitonic transition associated with either the heavy-hole or the light-hole band edge. However, this is not the case in this study, as can be elucidated from studying temperature dependence of the relative intensity and energy separation between the E_i and E_0 features. If the strain induced by the difference in thermal expansion were used to account for the 20-meV separation between the E_i and E_0 features at 10 K, one would expect the relative intensity of the E_i and E_0 features to be insensitive to temperature and the energy separation of these two features to change with temperature. But the intensity of the E_i feature was found to decrease much faster than that of the E_0 feature as temperature increases, and completely disappear with temperature above 100 K. The energy separation between two features was found to be temperature independent while the E_i feature is still observable. Thus, the aforementioned interpretation for the E_i feature can be ruled out since it is inconsistent with the experimental observations. We find that, provided the CdSe epilayer is thick enough, the built-in strain induced by the overall lattice mismatch between CdSe and ZnTe including the effect of different thermal expansions is fully relaxed in the CdSe layer, so that the maxima of the heavy- and light-hole valence bands remain degenerate, and the optical response of the sample is essentially that of unperturbed bulk CdSe. The photoluminescence spectrum of a zinc-blende CdSe sample cut from the same wafer as the samples used in this work exhibits a strong dominant emission peak at 1.73 eV at 10 K (Ref. 9), which is very close to the transition energy of the E_i feature observed in this work. Note that low-temperature PL spectra are generally dominated by radiative recombinations associated with impurity states.[15] The carriers trapped by impurities can recombine through interaction with free carriers and carriers bound to other impurities, and excitons can be bound to those impurities before annihilation. The E_i feature therefore can be attributed to a near band-edge impurity transition due to its significant decrease in intensity caused by thermal ionization with increasing temperature. It also needs to use two oscillators to fit the line shape of spectral features corresponding to the Γ_7^V-$\Gamma_6^C(E_0+\Delta_0)$ transition at 10 K though the spectrum does not explicitly exhibit that. The best fit yields a 2.168 eV for the transition at 10 K. The fitting also indicates that the second oscillator has an energy position ~ 10 meV below the $E_0+\Delta_0$ transition, which suggests that there might be an impurity state closely associated with the Δ_0 band edge.

For the fitting to the PR spectra taken at temperatures ≥ 80 K, all line shapes can be fit well using only one oscillator in Eq. (2), except the oscillatory shoulder on the high-energy side of the E_0 feature (see Fig. 1). The oscillatory line shape is most likely due to a Franz-Keldysh oscillation induced by a built-in electric field.[16,17] It is well known that the mechanism of photoreflectance, whether in the low-field regime or the Franz-Keldysh regime, depends on the presence of a built-in electric field. Usually, the appearance of Franz-Keldysh oscillations is the indication of the presence of a built-in field which is above the low-field limit. As a result, PR line shapes are related to the magnitude of the field and to the interband effective mass along the field direction.[11,16] Equation (2) used to fit PR line shapes is, strictly speaking, only valid in the low-field limit, where the PR line shapes are independent of electric field.[11] However, the fact that there is only one small Franz-Keldysh oscillatory signature on the high-energy side of the E_0 feature suggests that it is just above the low-field limit, and therefore Eq. (2) can still be used to fit the PR line shapes in this case. The direct band-to-band transitions E_0 and $E_0+\Delta_0$ at room temperature (295 K) are evaluated by using $n=\frac{5}{2}$ (the third-derivative line shape), since they are of three-dimensional interband nature, to be 1.661 and 2.082 eV, respectively. As a result, we can determine that in zinc-blende CdSe the Γ_7^V split-off valence band has an energy gap Δ_0 of 0.42 eV below the Γ_8^V valence band at the center of the Brillouin zone.

The change of the fundamental band gap E_0 with temperature is of considerable importance both for basic science and for technological applications. It is well known that the temperature dependence of the fundamental band gap in a semiconductor can be described by the Varshni empirical equation[7]

$$E_0(T)=E_0(0)-\alpha T^2/(\beta+T) , \tag{3}$$

where $E_0(0)$ is the band-gap value at 0 K, and α and β are constants (referred to as Varshni thermal coefficients). In Fig. 2 we plot the values of the E_0 band gap of zinc-blende CdSe as a function of temperature. The solid line represents the best fit to the data using Eq. (3). The parameters obtained from the fit are $E_0(0)=1.766$ eV, $\alpha=6.96\times 10^{-4}$ eV/K, and $\beta=281$ K. To the best of our knowledge, these are the first values ever reported for zinc-blende CdSe. A free exciton binding energy of 13 meV has been added to Γ_8^V-Γ_6^C transition energies obtained at low temperatures (<150 K), as plotted in Fig. 2, due to the excitonic origin of the spectral features associated with the transition observed in that temperature range. The exciton effect has to be taken into account so as to obtain the temperature dependence of the actual fundamental band gap E_0 (band-to-band transition instead of excitonic transition). The exciton binding energy was estimated using the effective masses for zinc-blende

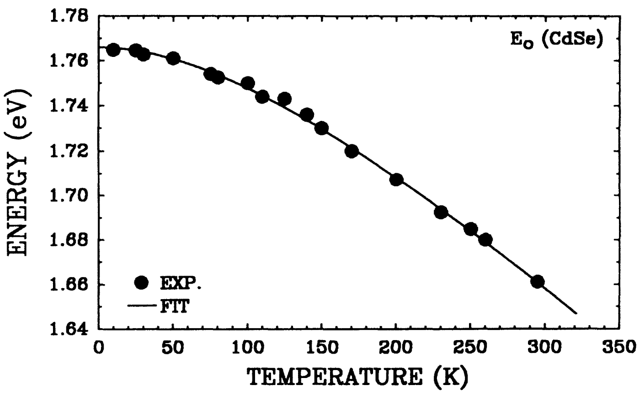

FIG. 2. Variation of the E_0 energy gap with temperature, with the exciton binding energy taken into account. The curve represents the best fit to the Varshni equation.

CdSe at the Γ point calculated by Kim *et al.*[18] ($m_n=0.12m_0$ and $m_p\approx1.16m_0$) and an average dielectric constant of wurtzite CdSe (Ref. 19) [$\epsilon(0)\approx9.5$], because this value for zinc-blende CdSe is not available at present. The uncertainty in this estimate of the exciton binding energy is ~3 meV, primarily coming from the value of the dielectric constant. At higher temperatures, since the E_0 band gap is directly determined by fitting Eq. (2) to the experimental data due to the PR spectral features originating from band-to-band transition rather than excitonic transition, the uncertainty in determination of E_0 mainly results from the fitting to the complicated line shape at the lower energy side of the E_0 feature, where the spectral structure related to the Γ_8^V-Γ_6^C transition overlaps with the interference oscillations. The largest deviation of E_0 energy obtained by using different amplitude and phase parameters in the fittings is found to be around 3 meV in the fit to the experimental data of room temperature (295 K). We have also fitted the energies of $E_0+\Delta_0$ (the Γ_7^V-Γ_6^C transition) at different temperatures to Eq. (3), obtaining Varshni coefficients $\alpha=5.63\times10^{-4}$ eV/K and $\beta=288$ K, respectively. The result suggests that Δ_0 is weakly temperature dependent.

Finally, we note that recently Kim *et al.* reported $E_0=1.66$ eV and $\Delta_0=0.39$ eV for zinc-blende CdSe obtained from their room-temperature ellipsometric measurements of the dielectric function of $Zn_xCd_{1-x}Se$ single-crystal films, from which the band structure of cubic CdSe was calculated using a nonlocal empirical pseudopotential method.[18] Compared with these values, the energy of E_0 obtained in this work is in excellent agreement, whereas there is a ~30-meV deviation in the energy of Δ_0. Since the E_0 and $E_0+\Delta_0$ are the lowest direct band gaps located at the center of the Brillouin zone, with a relatively small density of states in ellipsometric measurements, they appeared only as small spectral features sitting on a slowly varying large background of the dielectric function.[18] By contrast, the spectral features associated with these two transitions are greatly enhanced in PR measurements, appearing as sharp peaks on a featureless background in the modulated spectrum. This results in a much better spectral resolution and allows a more precise determination of the actual transition energy. We therefore regard $\Delta_0=0.42$ eV as a more accurate result.

In summary, the E_0 and $E_0+\Delta_0$ band-gap energies of zinc-blende CdSe were measured as a function of temperature using photomodulation spectroscopy. The room-temperature value of the fundamental band gap E_0 of zinc-blende CdSe obtained from these measurements is 1.661 eV, and the spin-orbit split-off gap Δ_0 is 0.42 eV. By fitting the temperature-dependent energy value of E_0 to the Varshni empirical relation, we have determined the fundamental band gap $E_0=1.766\pm0.003$ eV at 0 K, with the thermal coefficients $\alpha=6.96\times10^{-4}$ eV/K and $\beta=281$ K.

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