Optical properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ ($x \leq 0.78$) epilayersW.K. Hung^{a,*}, M.Y. Chern^a, Y.F. Chen^a, W.C. Chou^b, C.S. Yang^b,
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Abstract

The optical properties of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ with x up to 0.78 grown by molecular beam epitaxy on GaAs (001) substrates are reported. The complex dielectric functions $\epsilon = \epsilon_1 + i\epsilon_2$ are obtained by spectroscopic ellipsometry in the photon range from 3.5 to 5.5 eV at room temperature. The critical-point energies E_1 and $E_1 + \Delta_1$ for $x \leq 0.52$ are determined by fitting the calculated second-derivative spectra of ϵ to the standard line shape. For the sample with $x = 0.78$, the peak position in the ϵ_2 spectrum is taken as an estimate for E_1 . While the fundamental band gap E_0 increases with x , the E_1 and $E_1 + \Delta_1$ energies decrease almost linearly with x . Comparing our results with those of the other experimental and theoretical studies, we consider the sp–d hybridization between the Mn 3d level and the sp band states to be an important factor affecting the band structures at the L point in the Brillouin zone over the whole range of Mn concentration. © 2001 Published by Elsevier Science Ltd.

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Diluted magnetic semiconductors (DMS) are formed by randomly replacing a fraction of the cations in compound semiconductor alloys with magnetic ions. DMS have attracted a great deal of attention due to their unique electronic and magnetic properties [1,2]. In particular, the sp–d interaction between the magnetic ions and band electrons leads to many interesting physical effects, such as extremely large Faraday rotation [3], giant negative magnetoresistance [4], and the magnetic polaron [5]. The fact that their electronic properties are tunable both by composition and magnetic field has made DMS candidates for novel optoelectronic devices [6]. The $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ alloy is one of the most extensively studied DMS compounds [1,2]. Bulk $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ has been synthesized previously by the Bridgman method with a zinc-blende structure for $x < 0.35$ and a wurtzite structure for $0.35 < x < 0.57$ [7]. Using the molecular beam epitaxy (MBE) technique, thick ZnMnSe epilayers with zinc-blende structure over the $0 \leq$

$x \leq 0.66$ composition range have also been successfully grown [8]. Due to the large difference between the atomic radii of Mn (1.79 Å) and Zn (1.53 Å), high quality ZnMnSe epitaxial layers with high Mn content would be difficult to prepare. Thus most epitaxial ZnMnSe films (and microstructures) reported in recent years were focused on low Mn concentrations [9–11]. Furthermore, most optical studies have been focused on the effects of sp–d interaction on the fundamental band gap region. On the other hand, knowledge of the optical response properties of ZnMnSe and other DMS at higher photon energies are useful for device applications and for the investigations on the band structures. However, there have been few studies on this topic [11,12]. Kim et al. reported the dielectric function spectra of epitaxial $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ films between 3.5 and 5.5 eV using spectroscopic ellipsometry (SE) measurements [11]. They found that the E_1 and $E_1 + \Delta_1$ band gap energies, which correspond to the direct interband transitions at the L point of the Brillouin zone (BZ), decrease with increasing x . On the contrary, the fundamental band gap E_0 increases with x . Such an ‘anomaly’, as compared with most other zinc-blende semiconductor alloys (their E_1 and E_0 have the same trends with x), was explained by the repulsive interactions

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Fig. 1. High-resolution (004) XRD spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ grown on (001) GaAs substrates for $x = 0.05, 0.31, 0.52$, and 0.78 .

between the L band states and the Mn d levels (sp–d hybridization model) [11–13].

SE is a powerful technique that gives information on dielectric functions and band-structure critical points (CPs). In the present work, SE measurements of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ epilayers were performed in the spectral range 3.5–5.5 eV at room temperature. We extend the previous work on low Mn concentrations [11] to systems with Mn concentration up to $x \approx 0.78$. The dielectric

Fig. 2. Composition dependence of the band-gap energy E_0 of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$, determined from reflectivity and photoluminescence measurements at low temperature (10 K).

functions and the E_1 , $E_1 + \Delta_1$ energies were obtained as functions of the composition. We found that E_1 decreases monotonically from ≈ 4.75 (ZnSe) to ≈ 4.04 eV (maximum Mn content) and qualitatively follows the predictions of the sp–d hybridization model. Also pointed out is that, the theory which ignores the correlation between the localized d states, fails to explain our experimental result. Our measurement therefore calls for more detailed theoretical work.

The ZnMnSe epilayers (0.5–1 μm thick) were grown on GaAs(001) substrates by solid-source MBE. The details of the growth were published elsewhere [14,15]. The Mn concentration was determined by energy-dispersive X-ray (EDX) measurements to range from 0.05 to 0.78. High-resolution X-ray diffraction (XRD) was performed to evaluate the crystalline properties of the samples. Fig. 1 shows the (004) XRD spectra for four samples. For samples with $x \leq 0.52$, the position of the X-ray peak for the epilayer is consistent with a fully relaxed film if the Vegard's law is assumed and the lattice constants of ZnSe and zinc-blende (ZB) MnSe are taken to be 5.668 and 5.903 Å, respectively [2]. The crystalline quality of the films degrades with increasing Mn content, as evidenced by the broadening and weakening of the peak structure. For the sample with the highest Mn concentration ($x = 0.78$), the peak structure is so weak and broad that we may regard this sample to be nearly amorphous.

The photoluminescence (PL) and optical reflectivity measurements were used to measure the energy gap of the epilayers [14]. A He–Cd laser (with 325 nm line) was used for the excitation of the PL and the SPEX 1403 double grating spectrometer equipped with a thermal electric cooled photomultiplier was used to analyze the PL spectrum. For the reflectivity experiments, the tungsten halogen lamp was used as the light source. Both the measurements were done at $T = 10$ K. Fig. 2 summarizes the composition dependence of the fundamental band gap E_0 determined from PL and reflectivity measurements. For samples with larger Mn content ($x \geq 0.4$), the PL signals are undetectable due to the degradation of crystalline quality. It should be noted, however, that the energies obtained from PL and reflectivity are lightly smaller than the optical band gap by the bound exciton energy and free exciton energy, respectively. The energy obtained from PL is smaller than that obtained from reflectivity, since the binding energy of the bound exciton is larger than the binding energy of the free excitons. It is seen that the band gap increases with the incorporated Mn concentration, consistent with the earlier reports [1,2,7]. At low x , the initial red shift in energy was attributed to the sp–d exchange interaction between the Mn d electrons and the band electrons [7].

SE measurements on the samples were performed using an automatic spectroscopic ellipsometer Sopra GESP5. The system uses a 75 W xenon lamp, a rotating polarizer, an autotracking analyzer, a double monochromator, and a

Fig. 3. Real (a) and imaginary (b) parts of the dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$. Spectra have been offset by amounts indicated in the brackets.

single-photon-counting photomultiplier detector. Data were collected in the 3.5–5.5 photon energy region with the energy interval of 10–20 meV, at an incident angle of 68.5°. Before measurements, samples were etched in a 1:3 mixture of NH_4OH (29%)/methanol to remove the natural oxide overlayer [11]. Although it was reported that such an etching process may roughen the sample surface [16], we will not make corrections for this, since neither the real microstructure nor the composition of the residual overlayer is known. The dielectric function ϵ is obtained by reducing the ellipsometric data with the two-phase (ambient- ZnMnSe) model. The GaAs substrate can be ignored in

Fig. 4. Fits to the second derivatives of the real (solid line) and the imaginary (dashed line) parts of the dielectric function of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$. The dots represent experimental data for $d^2\epsilon_1/dE^2$. The fit for the imaginary part is of the same quality. The number of data points is reduced for clarity.

the model, since the penetration depth in this spectral region is far less than the film thickness.

The real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ are shown in Fig. 3. The spectra have been offset as indicated. The structures corresponding to the E_1 and $E_1 + \Delta_1$ transitions can be clearly observed in the spectra for the sample with $x = 0.05$. For the samples with higher x these structures broaden to merge into a single peak, which clearly shifts to the lower energy side as x increases. Also, the peak amplitude decreases as its broadening increases. The fact that the dielectric function spectra become more featureless when more Mn atoms are incorporated in ZnSe is probably due to the crystalline degradation (as shown by the XRD results) or the sp–d hybridization [12].

We obtain the values of the CP energies by fitting the numerically calculated second-derivative spectra of ϵ to the standard analytical line shapes developed by Cardona and Aspnes [17,18]

$$\frac{d^2\epsilon}{d\omega^2} = \frac{n(n-1)A e^{i\phi}(\omega - E + i\Gamma)^{n-2}}{A e^{i\phi}(\omega - E + i\Gamma)^{-2}}, \quad n \neq 0 \quad (1)$$

$$A e^{i\phi}(\omega - E + i\Gamma)^{-2}, \quad n = 0,$$

where A , E , Γ , and ϕ are the amplitude, threshold energy, broadening parameter, and excitonic phase angle, respectively. The exponent n has the values $-1/2$, 0 , and $+1/2$ for one-, two- (logarithmic), and three-dimensional CPs, respectively. Discrete excitons are represented by $n = -1$. Fig. 4 shows the calculated derivative spectra together

Fig. 5. Composition dependence of the E_1 and $E_1 + \Delta_1$ energies of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$. The data from this work are shown as closed circles. Also shown are the experimental data from Ref. 11. The dashed lines represent an extrapolation from the theoretically calculated results from Ref. 13.

with the best-fit curves for four of our ZnMnSe samples. The excitonic line shape was found to give a better fit than the one-, two-, or three-dimensional CP line shapes for ZnMnSe [11]. Although the E_1 and $E_1 + \Delta_1$ splitting are not visible in the derivative spectra for samples with $x \geq 0.20$, we still fit them with double peak structures. This is justified by the facts that both E_1 and $E_1 + \Delta_1$ transitions are expected to exist and that the line shape with two peak structures give a better fit. The method of standard line shape is not suitable for the $x = 0.78$ sample due to the rather broad and weak structure in its ϵ spectra. For this sample, the center energy position of the peak structure in the ϵ_2 spectrum is taken as an estimate for the E_1 energy.

The energies of E_1 and $E_1 + \Delta_1$ thus determined are plotted as functions of the Mn composition x in Fig. 5. It is seen that both transition energies decrease with increasing x , in contrast to the E_0 transition which increases with x . The latter result is expected from the viewpoint of alloying, since ZB MnSe was reported to have a larger fundamental band gap than ZnSe [2]. On the other hand, the former result was viewed as 'anomalous' if one assumes that the E_1 energy of ZB MnSe should also be larger than that of ZnSe. This anomaly can be resolved if one includes the repulsive interactions between the Mn d levels and the L band states (consisting of the sp orbitals from Zn and Se) of ZnSe host [11–13]. The occupied d levels are located below the valence bands ($L_{4,5}$ and L_6) while the unoccupied d levels are located above the conduction band (L_6) [11,19]. Thus the sp–d hybridization will push the valence bands upward and the conduction band downward, resulting in the reduction of the E_1 and $E_1 + \Delta_1$ transition energies.

Kim et al. studied this hybridization effect for $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ quantitatively by perturbative semiempirical tight-binding calculations in the range of low Mn concentrations [13]. They assumed that the correlation between the localized d states can be ignored. A linear term proportional to x was added to account for the normal alloying effect. The E_1 and $E_1 + \Delta_1$ energies thus estimated agree quite well with their experimental data for $x \leq 14.4\%$, as is also shown in Fig. 5.

We extend the experimental data to high Mn concentrations and find that $E_1(E_1 + \Delta_1)$ energy decreases almost linearly with x through the whole range of x studied. Similar behavior was found in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($0 \leq x \leq 0.7$) alloys [12], in which E_0 and E_1 also show different trends with x . The substitution of Mn for the cations Zn (or Cd) seems to affect the band structure at L point in the following manner. The energy difference between Zn (Cd) and Mn 4s orbitals increases the L band gaps ('normal' alloying effect), while the sp–d hybridization decreases them, both in a smooth way with increasing Mn concentration. The net effect is the reduction in E_1 and $E_1 + \Delta_1$ energies. The linear dependence of energy gaps on the Mn concentration implies the validity of the 'virtual crystal' approximation. That is, the $E_1(E_1 + \Delta_1)$ energy of ZB MnSe is smaller than that of ZnSe and the energy of $\text{ZnMn}_x\text{Se}_{1-x}$ is approximately the linear interpolation of the energies of ZnSe and ZB MnSe. In fact, theoretical studies showed that the E_0 and E_1 energies of the ZB MnTe with type I antiferromagnetic order are larger and smaller than those of CdTe, respectively [20]. Again, the sp–d hybridization plays a central role. The electronic structure of ZB MnSe was reported to be similar to that of ZB MnTe [21]. Thus we believe that the sp–d hybridization model provides a unified description on the $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ band structure at the L point over the x range from the dilute limit to the end compound ZB MnSe.

Finally, our results for the composition dependence of E_1 and $E_1 + \Delta_1$ energies deviates from the theoretical lines obtained by extrapolating the calculations of Kim et al. [13] as seen in Fig. 5. Such a deviation is not surprising. We consider the sp–d hybridisation to be the most important factor affecting the band structure near the L point. However, the theory of Kim et al. is based upon a perturbation calculation on the sp–d hybridisation [13]. In their calculations, the correlation between any two localized d states is ignored and a supercell approach is applied. The magnetic impurities of the same spin are assumed to distribute periodically to simplify the calculations. When the Mn content becomes large, such an approach is not well justified. The electronic structures of DMS alloys usually depend on the magnetic structures (for example, ferromagnetic or antiferromagnetic phase), that is, the correlation between the Mn d states [20,21]. Thus, a more detailed theoretical work is required to evaluate the optical properties of $\text{ZnMn}_x\text{Se}_{1-x}$ alloys at high Mn content x .

In summary, we have reported optical studies of the dielectric functions of $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ epilayers for x up to

0.78. The dielectric functions and the CP energies of the 3.5–5.5 eV region have been determined using room-temperature SE measurements. The E_1 and $E_1 + \Delta_1$ transitions were found to shift toward lower photon energies with increasing x over the whole composition range studied. The sp–d hybridization model was considered to be an important factor affecting the band states at the L point in BZ.

Acknowledgements

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