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Novel Optical Properties of ZnTe/CdSe Superlattice

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Type II ZnTe/CdSe superlattices were grown by molecular beam epitaxy on a GaAs substrate. Radiative type II transitions between electrons confined in the CdSe and holes confined in the ZnTe were observed in the photoluminescence spectra. For samples with thin CdSe layer, strong absorptive and weak emissive type I transitions, which involves both electrons and holes confined in the CdSe layer, were also found. For the radiative type II transitions, the excitonic activation energy decreases with CdSe layer thickness. While, for the type I emissive transitions, the excitonic activation energy increases with the CdSe layer thickness.

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I. Introduction

ZnTe/CdSe is an interesting heterostructure due to its unique structure and optical properties. This structure is unique among the II-VI heterostructure, in that the lattice match is obtained between two binary compounds where neither the anion nor the cation is common [1]. The band alignment of this superlattice system is type II. However, both type I and type II excitonic transitions are observed optically [2-4]. A radiative type II excitonic transition involving electrons confined in the CdSe well and holes confined in the ZnTe well is observed in the photoluminescence (PL) spectra near 1.0 eV. For the type I transition, the electron is confined in the CdSe conduction band well the hole is localized in the CdSe valence band barrier. The electron in the CdSe conduction band well creates a shallow Coulombic potential well on top of the CdSe valence band barrier. It makes hole localization in the CdSe layer possible [3]. Both strong absorptive and weak emissive excitonic transitions are observed in the transmission (T) and PL spectra, respectively. This type of optical transition, above-barrier exciton, was also observed in type I $Zn_{0.86}Cd_{0.14}Se/Zn_{0.75}Mn_{0.25}Se$ [5] and $Al_xGa_{1-x}As/Al_yGa_{1-y}As$ [6] quantum well structures. It is interesting to study the relative strength against temperature activation of the above-barrier exciton before further device applications.

In this study, reflectivity (R), transmission and photoluminescence spectra were measured to identify the type I and type II excitonic transitions. Temperature dependent PL spectra were

TABLE I. Sample parameters of ZnTe/CdSe superlattices

Sample	Buffer layer (^{1}m)	ZnTe (nm)	CdSe (nm)	Capping layer (^{1}m)
1	2	15	7	0.1
2	2	15	9	0.1
3	2	15	12	0.1
4	2	15	21	0.1
5	2	4.5	9	0.1

studied to measure the excitonic activation energy for both type I and type II transitions. The excitonic activation energy is studied as a function of the CdSe layer thickness.

II. Experiments

Type II ZnTe/CdSe superlattices were grown by molecular beam epitaxy on a GaAs substrate. Elemental solid sources Zn, Cd, Se and Te were used. The substrate temperature was at 300$^{\pm}$C. Before the growth of the ZnTe/CdSe superlattices, a ZnTe buffer layer of 2 ^{1}m was grown. Sample parameters are listed in Table I. To study the energy shift as a function of CdSe layer thickness, samples 1, 2, 3 and 4 were grown with the ZnTe layer thickness fixed at 15 nm, while the CdSe layer thickness varies from 7, 9, 12 to 21 nm. For sample 5, the CdSe layer thickness was 9 nm, while the ZnTe layer thickness decreases from 15 nm (sample 1 to 4) to 4.5 nm, in order to investigate the effect of ZnTe layer thickness on quantum confinement. For all samples, a ZnTe capping layer of 0.1 ^{1}m was grown on top of the ZnTe/CdSe superlattices.

A tungsten halogen lamp was used as the white light source for the R and T experiments. To excite the PL spectra, the 488.0 nm line from an Argon ion laser was used. For the R, T and PL experiments in the visible light region of the type I transition, SPEX 1403 was used to analyze the spectra with spectra resolution much better than 1 meV. While, for the missive type II transition near 1.1 eV, SPEX 270M was used to analyze the spectra. For the T experiment, samples were mechanically ground and chemically etched to remove the GaAs substrate.

III. Result and discussion

In Fig. 1, the type II band alignment of the ZnTe/CdSe superlattices is shown. The conduction and valence band offset is 1.29 eV and 0.64 eV, respectively [3]. Electrons are confined in the CdSe layers, while holes are confined in the ZnTe layers. A radiative type II transition, labeled as A, involving a confined electron and a hole can be observed at a photon energy near 1.0 eV, as shown in Fig. 2. In addition, a type I exciton composed of a confined electron and an above-barrier hole, indicated by B [1-4], and type I exciton consisting of an above-barrier electron and confined hole [5, 7], shown as C, are also observed. In the current study, only the thermal activation of the A and B exciton is discussed. In Fig. 2, the PL spectra of both the A and B

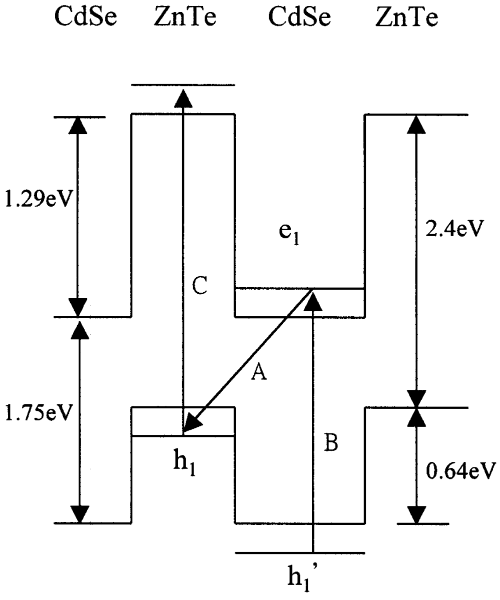


FIG. 1. Schematic band diagram of type II ZnTe/CdSe superlattices.

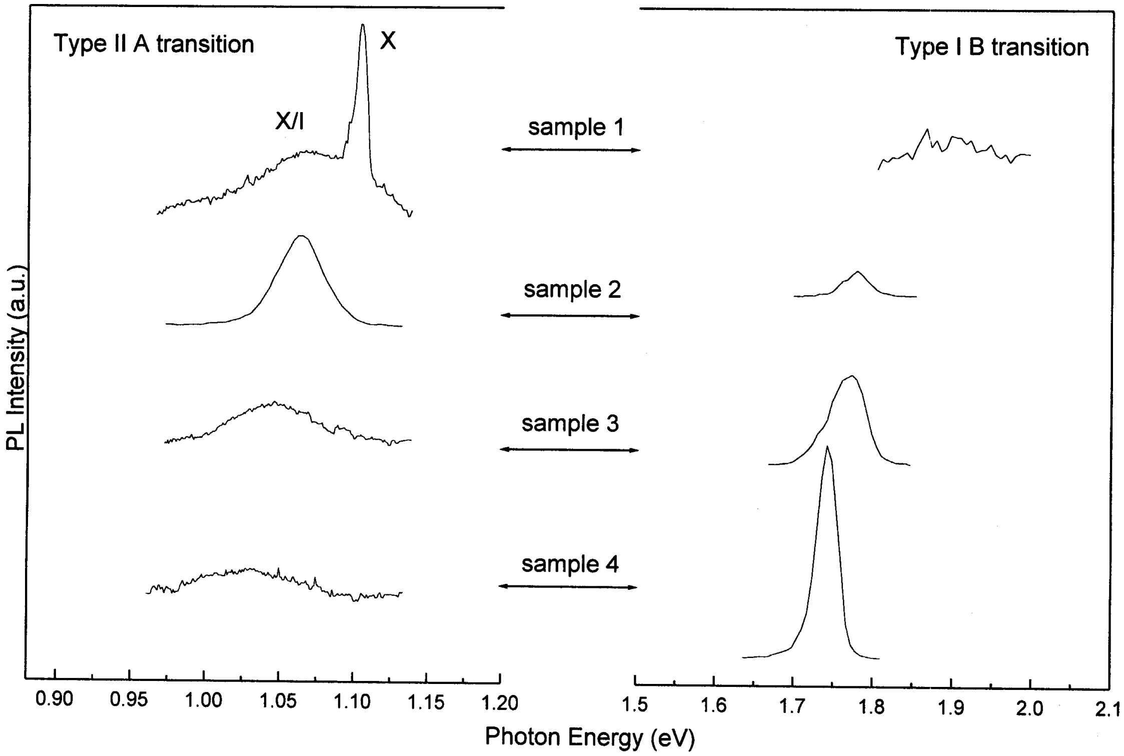


FIG. 2. Photoluminescence spectra of A and B transitions for samples 1 to 4.

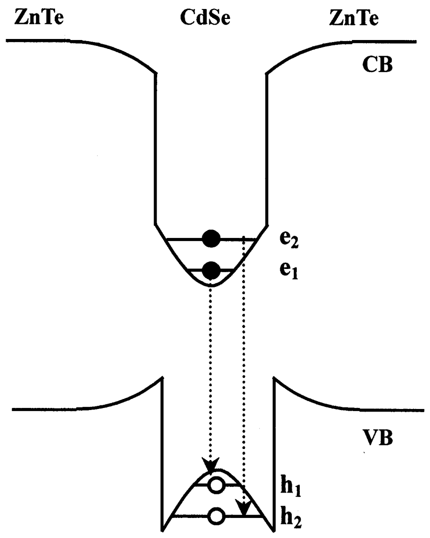


FIG. 3. Schematic diagram of the modified band structure for type II ZnTe/CdSe superlattices. The shallow (Coulombic) potential well (in the valence band barrier) is created by an electron confined in the CdSe conduction band wells.

transitions are shown for samples 1 to 4. The transition intensity of A decreases with the sample number, i.e. the CdSe layer thickness, due to a decrease in wave-function over-lapping of the confined electron and hole. The lower energy peak of sample A is due to an impurity related transition (acceptor or donor bound exciton, X/I), which will be ionized by temperature faster than the higher energy peak (free exciton, X), as shown in the temperature dependent PL spectra described later.

On the other hand, the transition intensity of B increases with CdSe layer thickness. For sample 1, the CdSe layer is thin. The optically pumped hole drops easily into the ZnTe valence band well. As a result, the B transition is weak. As the CdSe layer thickness increases with the sample number, electrons (confined in the conduction band well) create a shallow Coulombic potential well in the CdSe valence band barrier, as shown in Fig. 3. Optically pumped holes can be localized in the shallow Coulombic potential well to form the above CdSe valence band barrier state as well as a confined hole state in the ZnTe valence band well. As the CdSe layer thickness increases, the localization of the above-barrier state is enhanced. As a result, the PL intensity increases with the CdSe layer. The decrease/increase in PL intensity of typeII/type I exciton with the CdSe layer is significant.

In addition to the PL work, R and T spectra of sample 5 are shown in Fig. 4. The optical interference pattern shown in the R spectrum of Fig. 4 screens the B transition near 1.8 eV. The B transition becomes more visible in the T spectrum. For the T spectrum, the GaAs substrate and a part of the ZnTe buffer layer are removed. This weakens the optical interference effect. The strong B absorption observed near 1.8 eV sits on the broad spectrum, which is a characteristic of the tungsten-halogen lamp and spectrometer. The absorption coefficient of the B transition is as large as 10^4 $\mathrm{cm}^{\mathrm{i}\ 1}$ which is comparable to that of a GaAs/AlGaAs quantum well of type I band alignment [7, 8]. The T spectra of sample 1 to 4 are shown in Fig. 5. The transition energy

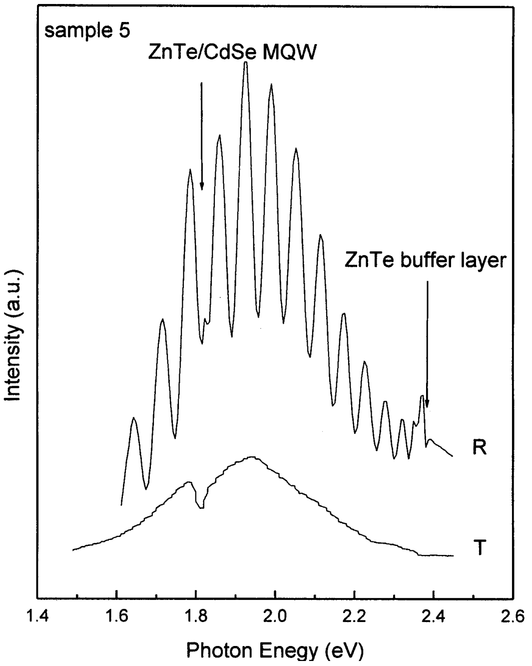


FIG. 4. Reflectance (R) and Transmission (T) spectra of sample 5.

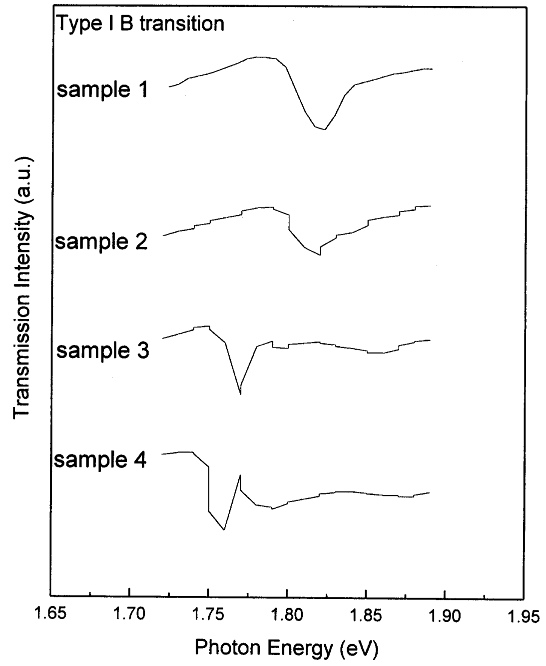


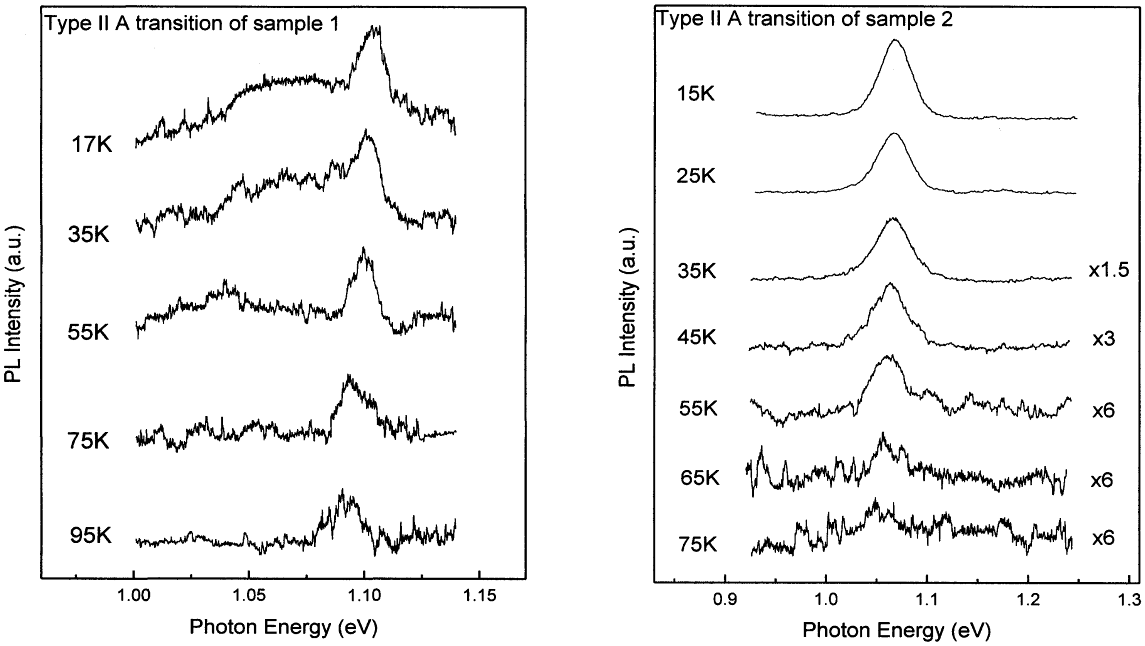
FIG. 5. Transmission spectra of sample 1 to 4.

decreases with the CdSe layer thickness due to the decreases in the quantum confinement energy of electron. For sample 3, the CdSe layer thickness is large enough to have a second electron confined state in the CdSe conduction band well and a second hole state localized in the above CdSe barrier Coulombic potential well, an additional absorption peak is observed near 1.860 eV. The absorption intensity involved in the second hole above the barrier state and second electron confinement state is weaker. As the CdSe layer thickness increases further, both absorption peaks exhibit a red shift in energy. Also the peak separation becomes smaller due to the decrease in the difference of confinement energy between the ground electron/hole and the first excited electron/hole state.

Temperature dependent PL spectra of a type II A excitonic transition from sample 1 and 2 are shown in Fig. 6(a) and (b). The PL intensity drops fast with temperature. This type of thermal carrier emission has been discussed in GaAs/AlGaAs and InGaAs/InP quantum well systems [9]. The Arrhenius plot of the logarithmic integrated PL intensity versus inverse temperature for sample 1 is shown in Fig. 7. By using equation [10]

$$I(T) = I_0/[1 + D\exp(-E_a/kT)];$$

the activation energy E_a = 13.2 meV responsible for ionizing the exciton (quenching the PL intensity) can be determined from the slope (at the high temperature limit) of Fig. 7. Where I and I_0 are the PL intensity at temperature T and near 0 K, respectively. D is a fitting constant and k is the Boltzmann constant. The binding energy obtained by this method is usually considered as the total binding energy, which includes the confinement energy and the exciton binding energy [9, 11]. As the CdSe layer thickness increases, the electron and hole wave-function overlapping



(a) (b)

FIG. 6. Temperature dependent photoluminescence spectra of type II A excitonic transition from (a) sample 1 and (b) sample 2.

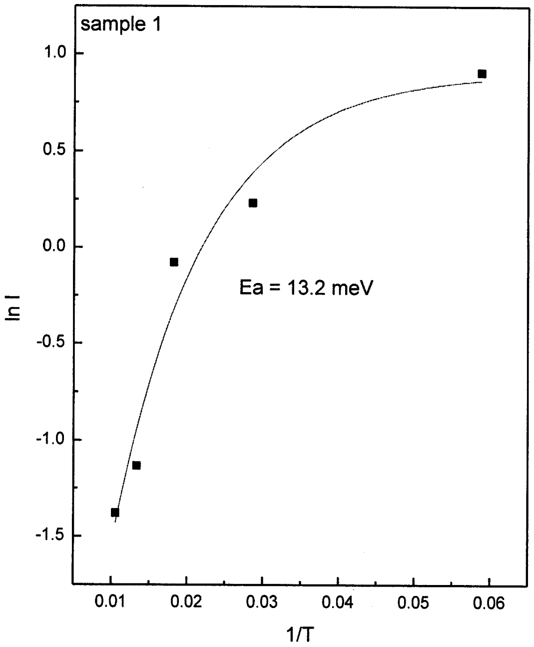
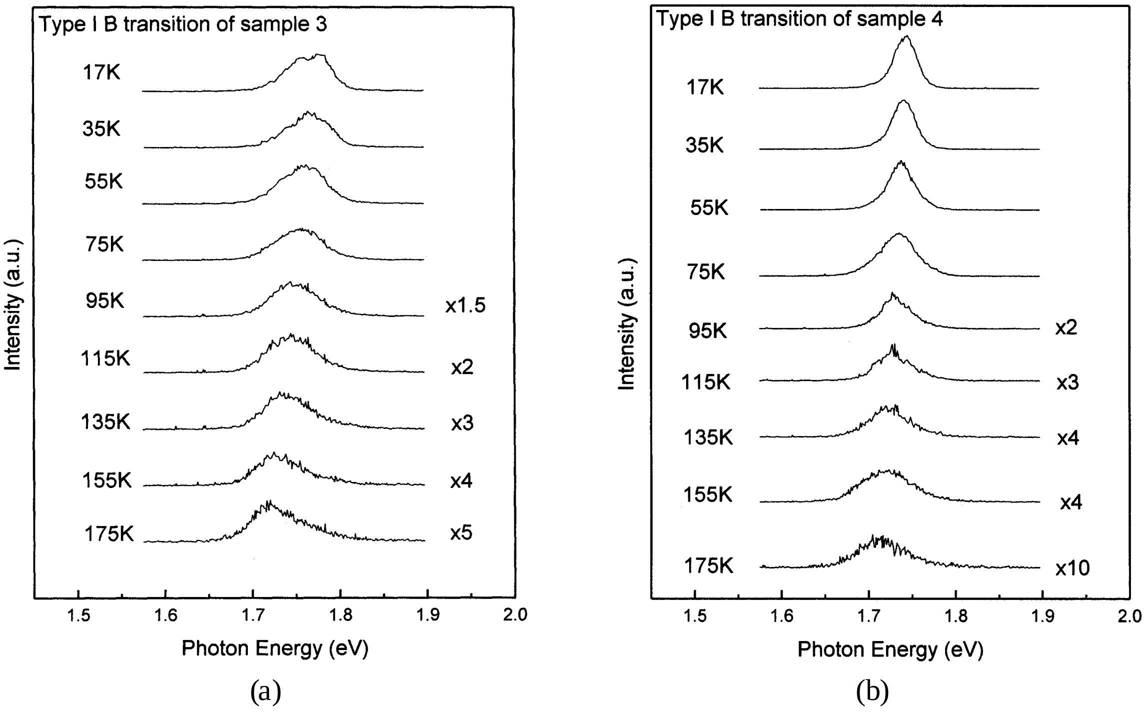


FIG. 7. Arrhenius plot of the logarithmic integrated photoluminescence intensity versus inverse temperature for sample 1.

of type II A exciton decreases. As a result, the exciton binding energy drops from 13.2 meV to 11.5 meV, 7.1 meV and 3.9 meV as the CdSe layer thickness increases from 7 nm (sample 1) to 9nm (sample 2), 12 nm (sample 3) and 21 nm (sample 4), respectively.

The temperature dependent PL of a type I B excitonic transition from samples 3 and 4 are shown in Fig. 8(a) and 8(b), respectively. A red shift in energy is observed as the temperature increases. The PL intensity does not drop as fast as that of a type II A exciton, as shown in Fig. 6. This implies a larger exciton binding energy than that of a type II A exciton. The exciton binding energy of a type I B exciton, which involves both an electron and a hole in the CdSe layer, can be obtained from the Arrhenius plot of the integrated PL intensity versus inverse temperature similar to Fig. 7. The obtained values are 7.6 meV, 11.8 meV, 19.3 meV and 27.9 meV for samples 1, 2, 3 and 4, respectively. In contrast to the type II A exciton, the binding energy (activation energy) of a type I B exciton increases with the CdSe layer thickness. It is understandable that for a type I B exciton the above barrier hole wavefunction tunneling from the Coulombic potential well into the ZnTe valence band well becomes less pronounced as the CdSe layer thickness increases. This enhances the electron-hole Coulomb interaction, which in turns results in an increase in type I B exciton binding energy (activation energy). The variation of the activation energy with the CdSe layer thickness for both type II A exciton and type I B exciton was shown in Fig. 9.



(a) (b)

FIG. 8. Temperature dependent photoluminescence spectra of type I B excitonic transition from (a) sample 3 and (b) sample 4.

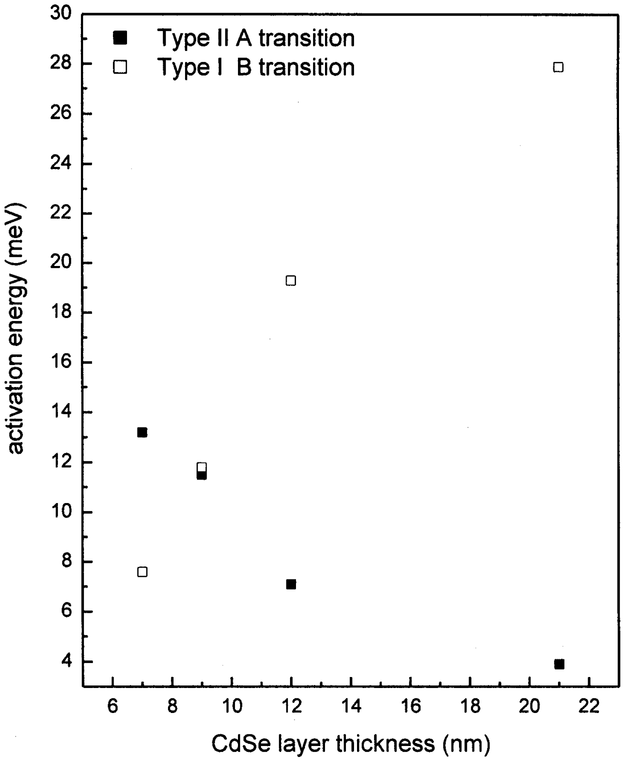


FIG. 9. CdSe layer thickness dependence of the activation energy for both a type II A exciton and a type I B exciton.

IV. Conclusion

Both type II and type I optical transitions were observed in a ZnTe/CdSe superlattice, which has type II band alignment. The binding energy of the type II exciton decreases with CdSe layer thickness due to the decrease in electron hole wavefunction overlap. While the binding energy of the type I exciton, which involves an electron confined in the CdSe well and a hole localized in the electron, created Coulombic potential well of the CdSe valence band barrier, increases with CdSe layer thickness.

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