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Abnormal temperature behavior of photoluminescence in CdSe/ZnSe self-assembled quantum dots

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ABSTRACT

We report on the temperature dependence of photoluminescence (PL) of CdSe/ZnSe self-assembled quantum dots (QDs). In the temperature range of 19–120 K, although the energy gap of CdSe shrinks by 25 meV, the PL of CdSe QDs does not show any line shift or shape change. According to the equilibrium theories of heteroepitaxial growth, a model involving the presence of interface disorders is suggested to be responsible for this invariant PL. In the temperature range of 120–300 K, the PL peak of CdSe QDs initially blue-shifts and then red-shifts with increasing temperature arising from the thermally activated detrapping of carriers.

1. Introduction

II–VI self-assembled semiconductor quantum dots (QDs) have attracted great attention due to their fascinating optical properties, interesting growth dynamics, and potential application in light-emitting devices [1–5]. Over the last decade, studies of their optical properties have been extensively reported [6–10]. It is accepted that the temperature dependence of the photoluminescence (PL) is generally considered as an important method to reveal the luminescence mechanism of samples. Earlier studies of the temperature-dependent PL in CdSe-based QDs can be found in the following works. Strassburg et al. found the enhanced redshift of the PL emitted by CdSe QDs as function of temperature and explained by carrier localization effects involving thermal escape and recapture in lateral transfer processes [9]. While a blueshift of the CdSe QDs PL maximum and a significant broadening of the emission band above 50 K was reported by Tranitz et al. and the reason is a thermal activation of localized excitons and a redistribution of the occupation within the inhomogeneous QD ensemble [10]. Similarly, Park et al. reported a novel phenomenon that as the temperature increases, the PL peak of the CdSe QDs initially redshifts, then levels off, and finally continues to redshift which they ascribe to delocalization of carriers with increasing temperature [11]. These above references indicated that in such structures the PL line and peak energy always depend very much on the temperature and carrier localization effects play an important role.

In this paper, the temperature dependence of optical properties in CdSe/ZnSe self-assembled QDs is studied. In contrast to the existing reports, the spectra of CdSe QDs do not show any change in the PL line shape or its peak position when the temperature increasing from 19 to 120 K, even though the energy gap of CdSe redshifts by 25 meV at 120 K. This is an unusual phenomenon and has never been reported in II–VI semiconductors. Here we present a model with supporting evidence suggesting that the observed temperature-independent radiative recombination only occurs from the same localized state and the localization most probably result from heterointerfacial disorder.

2. Experimental

The sample used in the present study was grown by the MBE technique. A ZnSe buffer layer was first grown on (110) GaAs substrate to a thickness of 100 nm. Then the QDs were formed on

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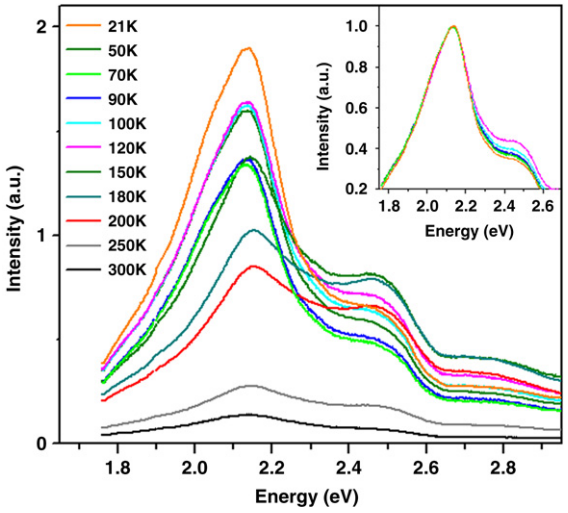

Fig. 1. (color online) PL spectra of the self-assembled CdSe/ZnSe QDs measured at different temperatures. The spectra in the inset are normalized to the PL maxima of CdSe QDs.

the top of ZnSe buffer layer by depositing 10 monolayers (ML) of CdSe, followed by a growth interruption for 30 s under vacuum at the growth temperature of 250 °C. Subsequently, the dot layer was covered by a ZnSe spacer of 50 nm. The beam equivalent pressure ratio $p(\mathrm{VI})/p(\mathrm{II})$ of 1.0, and growth rate of 0.1 mm/h. The growth mode was monitored from the observation of *in situ* reflection high-energy electron diffraction (RHEED) patterns with an electron acceleration voltage of 20 kV. The RHEED patterns changed from the streaky lines to spotty features after the deposition of about 3 ML CdSe indicate the critical thickness of the mode transition from 2D to 3D is about 3 ML in these growth conditions. For comparison, another sample was prepared by the same growth condition as above sample except no growth interruption. The steady state PL spectra were excited by the 325 nm line of a continuous-wave He–Cd laser and detected by a cooled charge-coupled device. The time-resolved PL measurements were carried out using a frequency-doubled beam of a mode-locked Al_2O_3:Ti laser pumped by an Ar^+ laser, and a photon-counting method with a synchroscan streak camera in conjunction with a single-grating monochromator. The wavelength, the pulse width, and the repetition rate of the excitation beam were 3800 Å, 2 ps, and 82 MHz, respectively. The temperature was controlled by a closed-cycle helium cryostat system with a programmable temperature controller.

3. Results and discussion

For the steady state PL spectra of CdSe/ZnSe self-assembled QDs obtained at different temperature ranging from 19 to 300 K, two main structured peaks are resolved at approximately 2.47 and 2.14 eV as indicated by Fig. 1. These bands could be ascribed to the emissions from CdSe quantum wells (QWs) acting as wetting layers and QDs, respectively. The inconspicuous appearance of a third band at about 2.8 eV is attributed to ZnSe barrier layer. As shown in the inset of Fig. 1, we clearly observed that the spectra show the remarkable temperature invariant PL line shape as well as its peak position when the temperature between 19 and 120 K.

The lack of a PL energy shift or line-shape change with increasing temperatures is very abnormal, because under these conditions, the CdSe band gap decreases according to the Varshni formula [12]:

$$E_G(T) = E_0(0) - aT^2/(T+b) \quad (1)$$

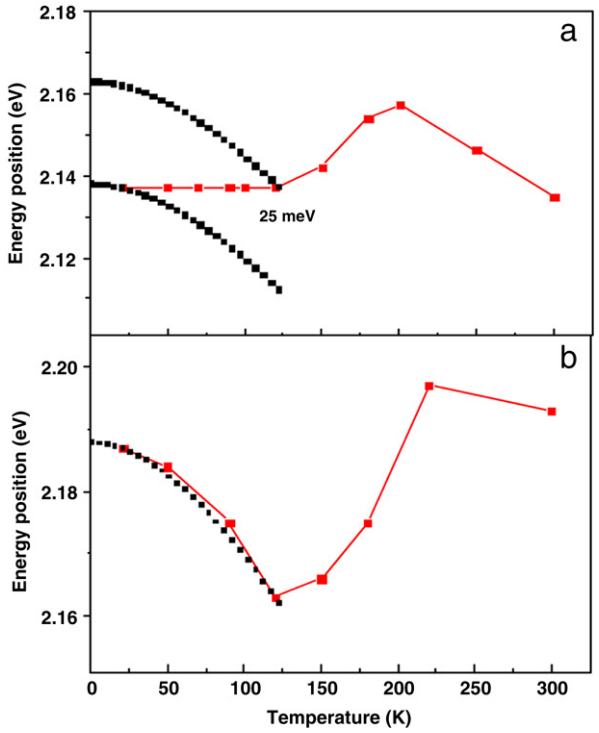

Fig. 2. (color online) Temperature dependence of the PL peak position for the CdSe QDs in the sample (a) with growth interruption time of 30 s and (b) Without growth interruption. Broken line shows the temperature dependence of the CdSe energy gap fitted by the Varshni function.

where T is the temperature, parameters $a = 6.96 \times 10^{-4}$ eV/K and $b = 281$ K given in Ref. [13] for zinc-blende CdSe. The CdSe energy gap, along with the PL energy of the CdSe QDs, is shown in Fig. 2 for the temperature range of interest. Clearly, in Fig. 2(a) for the sample with growth interruption, the PL does not track in any way with the expected shrinking of the CdSe gap. According to the general model [9–11], the interpretation for the invariant PL should be that the shift of peak position due to the delocalize of the excitons from deeply to weakly localized states just compensates the band-gap reduction with increasing temperature. However, even based on this assumption, the explanation as such can not explain the temperature invariance of the PL line-shape, as it should have larger full width at half maximum (FWHM) at higher temperature [11]. Furthermore, the following experiment results also exclude the possibility of this assumption. Fig. 3(a) shows the transient state time-resolved PL spectra of CdSe QDs at 19 K. It is clearly seen that the PL peak of CdSe QDs does not show any expected shift with increasing delay time. Similar phenomenon is observed at other temperature below 120 K. The temporal independent PL indicates that the radiative recombination only occurs from the same localized state [11]. This can be further confirmed by the analysis of the energy-dependent PL decay times of CdSe QDs, since the PL lifetime is also practically independent of energy at $T = 120$ K as shown in Fig. 3(b) as well as at any other temperature below 120 K (not shown) [11].

In order to explore the origin of this abnormal temperature behavior of CdSe QDs PL, a comparative analysis of two samples with and without growth interruption are presented. Fig. 2(b) shows the temperature dependence of the peak position of CdSe QDs in the sample without growth interruption. In sharp contrast to the previous sample, the shift of the peak energy is well tracked in the shrinking of energy-gap, without any anomaly. This quite different result provides a dramatic illustration of the sensitivity of the growth conditions. Namely, the growth interruption plays a decisive role in the PL characteristic. As

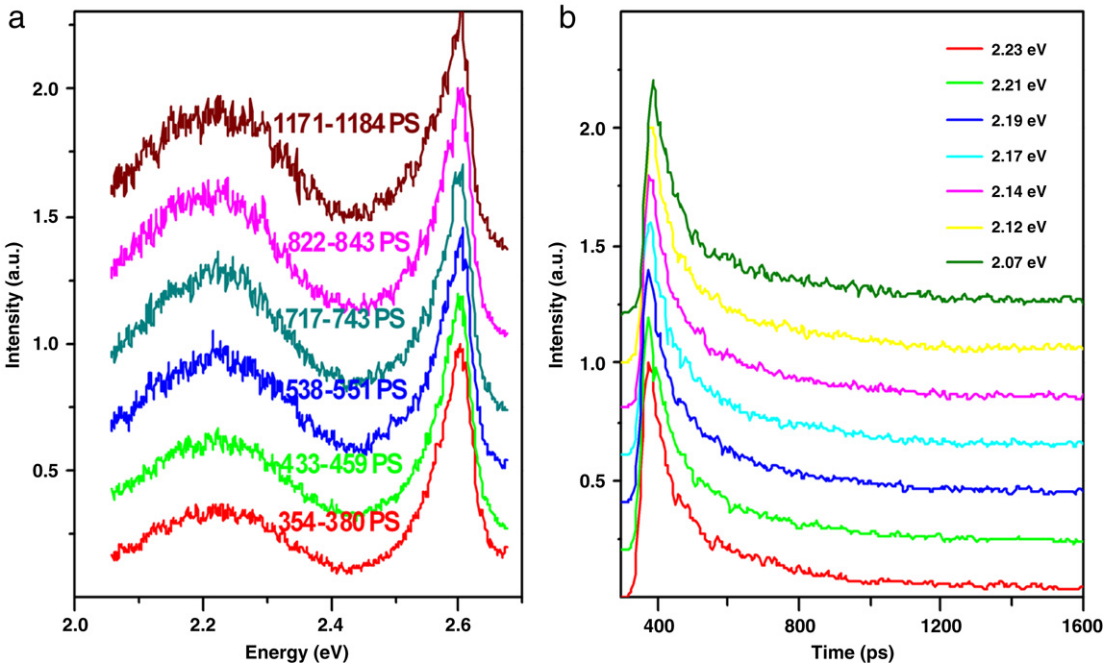

Fig. 3. (color online) Time-resolved PL spectra of the CdSe/ZnSe self-assembled QDs at 19 K. The spectra are normalized to the PL maxima of CdSe QWs (b) PL decay cures monitoring at different photon energies for CdSe QDs at 120 K.

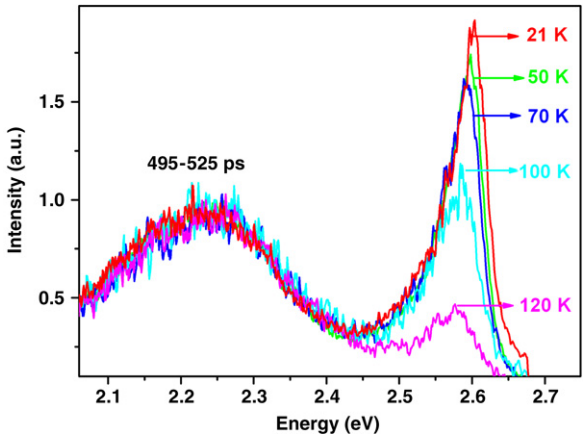

Fig. 4. (color online) Time-resolved PL spectra of the CdSe/ZnSe self-assembled QDs measured at same time intervals from 495 to 525 ps in the process of luminescence decay at selected temperature. The spectra are normalized to the PL maxima of CdSe QDs.

we know, in heteroepitaxial growth, strain in growing films can be relieved by the formation of coherent (dislocation free) island which elastically deform the substrate to relieve some of the mismatch [14]. Coherent islands are energetically favored over dislocated islands for islands smaller than some critical size. Further growth of these islands by ripening can cause a coherent-to-incoherent transition via the introduction of misfit dislocations [15]. An important step in this direction was taken by Kim et al. [16] who have investigated the evolution of CdSe self-assembled QDs on ZnSe surfaces with different interruption time. They have found the number density of CdSe QDs has a striking minimum at the sample with 5 s interruption [16,17]. The minimum number density is corresponding to the maximum of CdSe QDs size and stress field in ZnSe which will result in more defects in the interface. Additionally, the growth interruption will result in rough interface and bad crystal quality in the case of the (110)-oriented CdSe/ZnSe structure was also clarified by Ko [18]. In our cases, consider the 7% CdSe/ZnSe lattice mismatch and 10 ML nominal thickness of the deposited material (CdSe), according to the equilibrium theories of heteroepitaxial growth described in Ref. [19], the deposited material is distributed between a wetting film, finite (nonripening) islands, and ripened islands. In the growth interruption, the ripened islands will undergo the ripening process following misfit-dislocation introduction [15]. However, in the sample without growth interruption, capping the dots with a ZnSe layer immediately can "freeze" the ripening [16] and consequently all islands will be dislocation free. On basis of this, we have reason to suggest that the source of the invariant PL may be localized defects, which are very similar to the interface dislocations such as interface dangling bonds and broken bonds. During the preparation of the paper, we noticed that the similar invariant PL at $300 \leq T \leq 1107$ K from annealed porous silicon have been discovered by Prokes' group [20,21]. In their paper, a nonbridging oxygen hole centers (NBOHC) which might be caused by the strain of bonding at an interface was suggested to be responsible for the PL. The origin of the invariant PL is obviously similar to that of ours.

This model is further confirmed by the comparative analysis of the PL from CdSe QDs and QWs. The peak of the CdSe QWs PL can not definitely resolve due to rather weak emission intensity and the overlap of two emission bands in steady state spectral as shown in Fig. 1. In order to determine the temperature evolution of CdSe QWs PL, transient state time-resolved PL spectra at $19 \leq T \leq 120$ K is shown in Fig. 4. It is worth to mention that due to random distribution of size, shape and depth of QDs [22,23], different peak positions and PL line-shapes between steady state and transient state time-resolved PL are separatively observed. Here, obviously, the peak energy of CdSe QWs undergoes an expected redshift with increasing temperature while the PL of CdSe QDs still remains invariant. Why only the PL of CdSe QDs shows the characteristic of temperature-independent? It is well known that in heteroepitaxial growth, a thicker layer has larger strain energy and can lower its total energy by forming isolated islands in which strain is relaxed [14]. Accordingly, the interfacial zones between the CdSe QWs and ZnSe buffer layer will be almost free of defects. This is why the absence of an abnormal temperature-independent PL of QWs.

This experimental result is consistent with our above explanation for the origin of the invariant PL of CdSe QDs.

So far, we can conclude that in the sample with growth interruption there are many special defect states such as interface dangling bonds and broken bonds at the interface between the CdSe QDs and ZnSe buffer layer, which lead to introduce a localized energy level. The radiative recombination only occurs from this localized state below 120 K. From the results of the experiment, the PL origin from the localized center is insensitive to temperature which may be caused by the interaction of these defect states in this complicated system. Although the essential reason is not at present satisfactorily understood, this model explains all the experimental observations.

When the temperature increases from 120 to 200 K, the peak position of the PL maximum undergoes a blueshift of approximately 20 meV, while above 200 K the maximum emission again starts to shift to lower energy. Such a blueshift in an intermediate temperature range is attributed to a thermally induced redistribution of localized carriers from interface dangling bonds and broken bonds related defects to QDs with smaller localization energies. Above 200 K the band-gap reduction overcompensates the energy shift of the PL maximum due to the thermal rearrangement of the excitons in quantum QDs, leading to the observed redshift of the exciton emission.

4. Conclusion

In summary, the PL spectra of CdSe/ZnSe Self-assembled QDs were investigated in the temperature range of 19–300 K. Below 120 K, both the steady state and transient state time-resolved PL of CdSe QDs do not show any line shift or shape change at different temperatures. These experimental results suggest a new and interesting regime of PL for which there is as yet no theoretical prediction. According to the equilibrium theories of heteroepitaxial growth and by the comparative analysis of the PL from two different samples with and without growth interruption, a model involving the presence of heterointerfacial disorders has been suggested to be responsible for this PL. Above 120 K, the nonmonotonic temperature-dependent PL is ascribe to delocalization of carriers with increasing temperature.

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