Photoluminescence of $Zn_xCd_yMg_{1-x-y}Se$ alloys as a manifestation of the breakdown of "common-anion rule"

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We have systematically studied the optical properties of $Zn_xCd_yMg_{1-x-y}Se$ alloys using photoluminescence (PL) and photoluminescence excitation. It is shown that, at low temperatures, PL is dominated by excitons localized by potential fluctuations, which become stronger with increasing Mg concentration. Such potential fluctuations are discussed in terms of a large valence band offset in Zn(Cd)Se/MgSe systems, which serves as a manifestation of the breakdown of "common-anion rule". © *2003 American Institute of Physics.* [DOI: 10.1063/1.1625096]

I. INTRODUCTION

Semiconductor alloys have been widely used for light emitting devices largely due to the flexibility to control changes in the band gap energy and lattice constant. Specifically, ZnCdMgSe-based light emitting diodes[1,2] and optically pumped laser structures[3,4] operating in the visible range of the spectrum have been reported by several research groups. Such structures are usually grown on InP substrates. Thus, by choosing appropriate composition of Zn, Cd, and Mg, emissions at different wavelengths can be achieved while lattice matching to InP is maintained. Therefore, $Zn_xCd_yMg_{1-x-y}Se$ alloys with high crystal quality are crucial for the fabrication of long-lived devices. Furthermore, the knowledge about the optical properties of such alloys is very important for proper device fabrication.

It has been reported[5,6] that band edge photoluminescence (PL) from $Zn_xCd_yMg_{1-x-y}Se$ alloys is relatively broad. We note that other Mg containing alloys also exhibit broad low temperature PL.[7] This differs from most II–VI common-anion alloys, where the band edge PL is quite narrow, in the alloys with common cation the PL is usually broad and relatively deep (for good discussion see Refs. 8 and 9). Indeed, in the case of common anions the fluctuations are associated with the conduction band and thus exciton localization occurs via electron trapping, which requires strong fluctuations. For instance, it has been shown that the PL from ZnCdSe is dominated by free excitons, and that the potential fluctuations only limit the free exciton diffusion length and do not affect the PL emission significantly.[9] On the other hand, when the potential fluctuations arise from the valence band, the localization is quite probable because of large hole mass,

and the localized excitons have been readily observed (see, e.g., Ref. 10 and references therein).

Thus, the origin of broad low temperature PL from $Zn_xCd_yMg_{1-x-y}Se$ requires a careful investigation. Previously,[5] this has been explained by the sum of free and localized exciton recombinations, with the former dominating the PL. The presence of both free and localized exciton transitions was postulated based on the assumptions that the asymmetric PL can be fitted by two Gaussians and that the observed nonexponential PL decay can be fitted by two exponentials.[5] However, it is also well known that such asymmetric line shapes with tail on the low energy side as well as a nonexponential PL decay are the hallmarks of systems with potential fluctuations.[11,12]

Therefore, we systematically investigate optical properties of high quality $Zn_xCd_yMg_{1-x-y}Se$ alloys grown nearly lattice matched on InP[13] to clarify the origin of this PL. We shall definitely show by photoluminescence excitation (PLE) as well as by temperature and excitation dependent PL that the excitons localized by potential fluctuations, which arise from incorporation of Mg, play a dominant role in the low temperature PL emission. We shall discuss this phenomenon in terms of a large valence band offset (VBO) in Zn(Cd)Se/MgSe systems, which is anomalous for common-anion alloys.

II. EXPERIMENTAL DETAILS

The samples were grown on epiready (001) InP substrate by molecular beam epitaxy, in a Riber 2300 system, which includes a III–V growth chamber and a II–VI growth chamber connected by ultrahigh vacuum (UHV) modules. Oxide desorption of the InP substrate was performed in the III–V chamber by heating to ~490 °C with an As flux impingent on the InP surface, after which a 120 nm lattice matched InGaAs buffer layer was grown. Then the substrate with the

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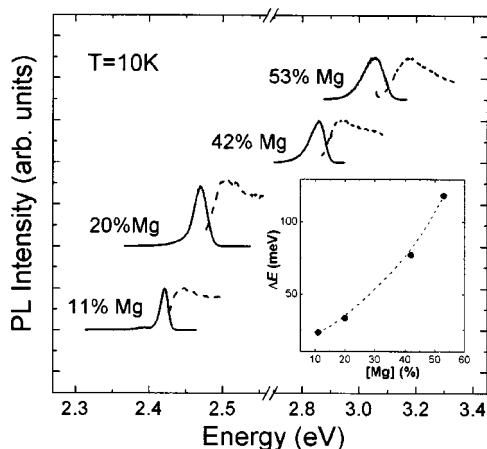[b)]Author to whom correspondence should be addressed; electronic mail: tamar@sci.ccny.cuny.edu

FIG. 1. PLE (dashed lines) and PL (solid lines) of $Zn_xCd_yMg_{1-x-y}Se$ alloys with various Mg concentrations at $T = 10$ K. The inset: the energy difference (ΔE) between PL and PLE peaks as a function of Mg concentration; the dotted line is a guide for eyes.
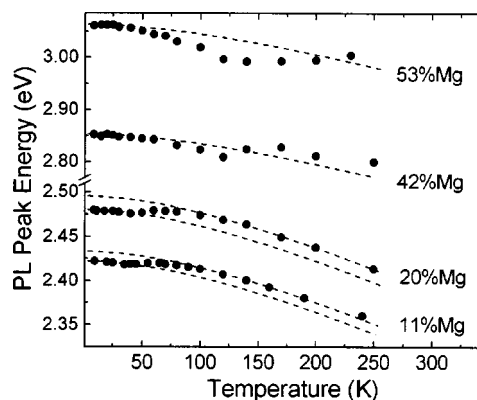

FIG. 2. PL peak energies (solid circles) as a function of temperature for samples with various Mg concentrations. The dashed lines represent the temperature dependence of the CdSe band gap energy (shifted for easier comparison).

buffer layer was transferred in UHV to the II–VI chamber for the ZnCdMgSe alloy growth. Prior to the growth of quaternary ZnCdMgSe, a Zn irradiation of the InGaAs buffer layer surface was performed and a 10-nm-thick low temperature ZnCdSe interfacial layer was grown at 170 °C in order to improve the crystalline quality.[14] The growth was initiated at a low temperature of 170 °C for 1 min. Then the substrate temperature was raised to the typical II–VI growth temperature of 270 °C and a 1-μm-high band gap ZnCdMgSe epilayer was grown, followed by a 10 nm ZnCdSe cap layer to protect the ZnCdMgSe from oxidation by atmospheric oxygen. All the $Zn_xCd_yMg_{1-x-y}Se$ epilayers were nearly lattice matched to InP substrate ($\Delta a/a < 0.2\%$) as confirmed by x-ray diffraction studies.[14]

Photoluminescence measurements were performed between 10 and 296 K, using a closed cycle refrigerator system. Samples were excited by the 325 nm continuous wave emission from a He–Cd laser with a maximum intensity $\sim$28 W/cm^2. The PL was recorded with a 3/4 m monochromator, a thermoelectrically cooled GaAs photomultiplier tube, and a SR400 photon counter. For PLE measurements, a 300 W xenon lamp, coupled with a 1/4 m monochromator, was used.

III. RESULTS AND DISCUSSION

We show in Fig. 1 the low temperature ($T = 10$ K) PLE spectra detected at the PL peak energy as well as corresponding PL spectra for samples with various Mg concentrations ([Mg]). All the samples exhibit a single asymmetric PL peak, whose width increases with increasing Mg concentration. The PLE spectra for the alloys with low [Mg] exhibit a relatively flat initial base line, as expected for the above band gap excitation, which is followed by the peak with a relatively sharp low energy side. For samples with high [Mg] this peak merges with the band edge and becomes less distinguishable; also the lower energy tail becomes longer.

It has to be noted that if free excitons (FX) are to dominate the PL as suggested in Ref. 5, no such peak should be observed in PLE. However, if the PL is dominated by local-

ized excitons, one would expect to see a FX line in PLE spectra. Thus we attribute the observed PLE peak to a free excitonic transition and the low temperature PL to excitons localized by the potential fluctuations. Consequently, the energy difference (ΔE) between PLE and PL peaks would correspond to an average localization energy and thus ΔE should increase with increasing magnitude of the potential fluctuations. Indeed, as seen from the inset in Fig. 1, ΔE increases from 24 meV in the sample with [Mg]=11% to 120 meV in the sample with [Mg]=53%. Therefore, we conclude that the potential fluctuations become stronger with larger [Mg], resulting from increased compositional disorder. This also explains the broadening of the PL with increasing [Mg].

Studies on the temperature-dependent PL further confirm our conclusions. In Fig. 2, we plot the PL peak position as a function of temperature for samples with various [Mg]. It is interesting that for samples with lower [Mg] (the lower two curves), the PL peak first follows the temperature dependence of the band gap (the CdSe band gap[15] in this case) up to $T = 40$ K, then it shifts to higher energies up to $T = 80$ K, and afterwards it starts following the band gap again. For the samples with higher [Mg] (the upper two curves), the PL peak first shows a redshift relative to the band gap, then it shifts to higher energies, exhibiting a so-called "inverted-S" shape that has been routinely observed in disordered systems.[16,17] We note that such a behavior cannot be explained within the model proposed in Ref. 5, since if FXs dominate, the PL would closely follow the band gap as a function of temperature. On the other hand, such a behavior is easily explained within the model of localized excitons as follows. The PL blueshift of samples with lower [Mg] is due to ionization of excitons localized by rather shallow potentials, after which FXs dominate the PL, and then follow the temperature dependence of the band gap. For samples with higher [Mg] (stronger potential fluctuations), the ionization of excitons localized by shallow potentials also occurs as the temperature increases; however, excitons localized by deep potentials start to dominate at intermediate temperatures, which contributes to the redshift of the PL. As the temperature increases further, almost all the localized excitons are
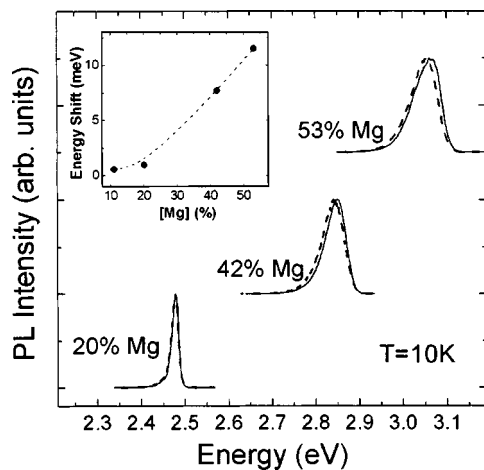
FIG. 3. PL spectra of $Zn_xCd_yMg_{1-x-y}Se$ alloys with various Mg concentrations as functions of excitation intensity at $T = 10$ K (solid lines represent the highest excitation intensity, and dashed lines represent the excitation intensity about two orders of magnitude lower). The inset: the peak shift as a function of [Mg]; the dotted line is a guide for eyes.

ionized and become free excitons, which results in the blueshift of the PL.

Studies of PL as a function of excitation intensity also corroborate our model. In Fig. 3 we plot PL of various $Zn_xCd_yMg_{1-x-y}Se$ alloys under two different excitation intensities; all the samples[18] exhibit a blueshift with increasing excitation intensity and the magnitude of the shift is larger in samples with higher [Mg] (see the inset in Fig. 3). Such a behavior is attributed to the effect of filling of shallower localized states as the quasi-Fermi levels move closer to the corresponding band edges.[11,19]

Therefore, based on the above, we conclude that the low temperature PL of ZnCdMgSe alloys is primarily due to excitons localized at the potential fluctuations arising from compositional disorder. Having established the PL emission mechanism, we then proceed to explain the origin of the exciton localization in this common-anion alloy. As mentioned above, it has been argued that in alloys with cation substitution the potential fluctuations are associated mostly with the conduction band, and thus exciton localization occurs via electron trapping, which requires very large fluctuations. On the other hand, when the potential fluctuations are associated with the valence band, the localization is quite probable because of large hole mass. Thus the appearance of the localized excitons in ZnCdMgSe suggests that the presence of Mg breaks down the "common-anion rule". Indeed, this alloy differs from many other II–VI common-anion systems by the fact that the VBO between MgSe and Zn(Cd)Se is rather large (0.8–1 eV).[20,21] This has also been observed in some other common-anion systems (e.g., AlAs/GaAs,[22] CdTe/HgTe,[23] and AlN/GaN[24]), which contain cations with and without d orbitals. It has been shown[25] that the cation d orbitals can interact with anion p orbitals, and such an interaction modifies valence band maximum. As a result, the VBOs between materials containing cations with (Zn(Cd)Se) and without (MgSe) d orbitals are enhanced.

The VBO values in Zn(Cd)Se/MgSe are comparable to those of common-cation systems. Thus, even relatively small quantities of Mg added to ZnCdSe will lead to significant modifications in the PL properties due to the appearance of rather strong potential fluctuations associated with the valence band, which we indeed have observed.

In summary, we have shown that, at low temperatures ($T = 10$ K), PL from $Zn_xCd_yMg_{1-x-y}Se$ is dominated by excitons localized by the potential fluctuations due to compositional disorder and that the magnitude of the fluctuations increases with increasing Mg concentration. Such potential fluctuations serve as a manifestation of breakdown of the "common-anion rule" in some Mg-containing alloys.

ACKNOWLEDGMENTS

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