Exciton luminescence and resonant Raman scattering of CdTe submonolayers in ZnTe films grown by molecular beam epitaxy

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When submonolayers of CdTe, with a thickness amounting to ≈ 0.25 of a monolayer, are introduced in ZnTe, some intense spectral lines appear in the emission, Raman scattering, and reflection. They stem from the onset of new exciton states.

The properties of ultrathin quantum wells consisting of ultrathin layers of one semiconductor in another semiconductor have recently attracted much research interest.[1–5] The thickness of the layers is typically from one to a few monolayers. In this case it is possible to grow high-quality structures without misfit dislocations, even if there is a large lattice mismatch between the materials of the well and the barrier. In this letter we are reporting a study of the structures shown schematically in Fig. 1: "pure" ZnTe films (W_0) and ZnTe films containing one (W_1) or two (W_2) submonolayers of CdTe. We studied the structures by low-temperature optical spectroscopy and transmission electron microscopy.

The structures were grown by molecular beam epitaxy from separate sources. The deposition of the layers was monitored on the basis of oscillations in the intensity of reflection high-energy electron diffraction. Spectra of the photoluminescence, Raman scattering, and optical reflection [$R(\lambda)$] were measured over the temperature range 5–80 K on a double monochromator with a resolution no worse than 0.5 Å. The samples were excited by an ILA-120 argon laser operated to emit individual lines. The study by transmission electron microscopy was carried out in a cross-section configuration on a Philips SM-30 microscope with an accelerating voltage of 300 kV and a resolution of 2 Å.

As will be shown below, the new spectral lines which appear in the photoluminescence and Raman scattering because of the CdTe submonolayers fall in the region of edge emission of ZnTe. We will accordingly begin with a discussion of the spectra of pure ZnTe (W_0). Figure 2 shows photoluminescence and Raman spectra (1 and 2) for two excitation frequencies, along with $R(\lambda)$ spectra (3) of W_0 structures at $T=5$ K. Our results are similar to those reported in several previous studies.[6–8] However, analysis of many spectra recorded at various excitation frequencies and various temperatures led us to an interpretation of lines X, $\tilde{X}$, I_0, and I_0–LO in the photoluminescence spectra slightly different from that of Refs. 6–8. Line X (2.3783 eV) coincides with the strongest minimum in the reflection, which is known[9] to be close to the

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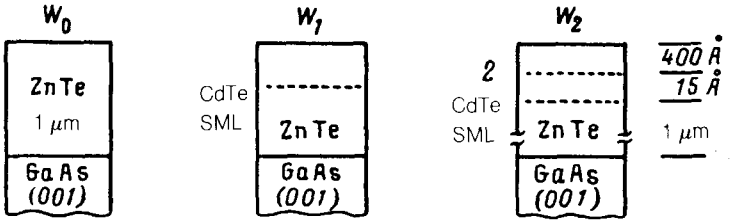

FIG. 1. Schematic diagrams of the structures studied (W_0, W_1, and W_2). Here SML stands for "submonolayer."

bottom of the exciton band along the energy scale. The appearance of the second line, $\tilde{X}$ (2.3734 eV), besides the bottom of the exciton band is a consequence of polaritons emerging from the interior of the film. Lines I_0 and I_0–LO are due to emission from the peak of the polariton distribution involving the emission of, respectively, one and two LO phonons. The intense line A^0X ($\hbar\omega$=2.368 eV) is due to the emission of an exciton trapped at a neutral As[6] acceptor. Raman scattering by phonons is manifested by narrow lines in the spectra. In order of decreasing energy, they correspond to

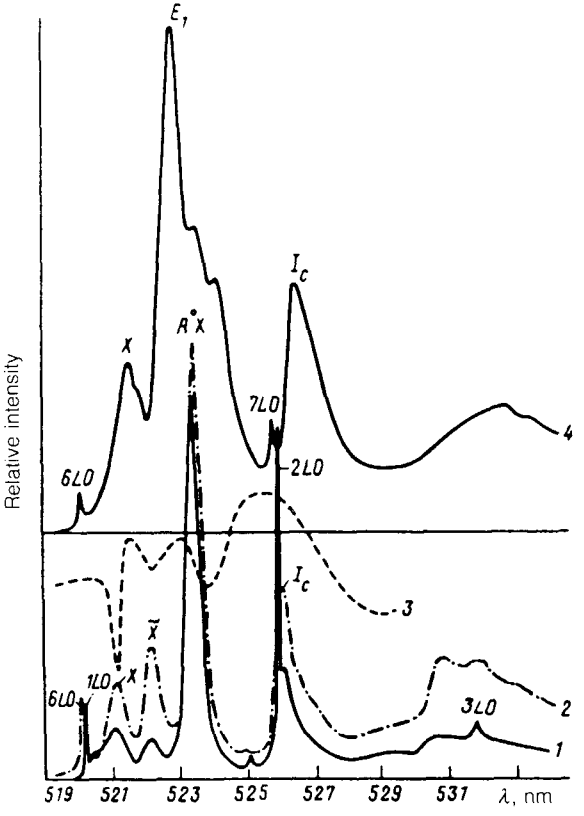

FIG. 2. Spectra at T=5 K. 1—W_0, photoluminescence and Raman scattering, λ_L=4880 Å; 2—λ_L=5145 Å; 3—optical reflection $R(\lambda)$; 4—W_1, photoluminescence and Raman scattering, λ_L=4880 Å.

Raman scattering accompanied by the emission of, respectively, LO, $LO+TO$, $2LO$, and $3LO$ photons during excitation at $\lambda_L=5145$ Å (spectrum 1) and $6LO$ and $7LO$ during excitation at $\lambda_L=4880$ Å (spectrum 2). The interpretation of the ZnTe photoluminescence spectrum outlined above will be rendered, and a corresponding theory derived, in a separate paper.

Study of the W_1 and W_2 structures by high-resolution transmission electron microscopy led to the following conclusions about their structure: 1) The submonolayers constitute a system of isolated islands with lateral dimensions of 40–60 Å spaced at a period of 140–180 Å. 2) The CdTe/ZnTe interfaces are free of extended defects associated with the relaxation of large misfit stresses.

A new line, E_1 ($\hbar\omega=2.371$ eV at $T=5$ K), appears in the photoluminescence spectra of sample W_1 (spectrum 4 in Fig. 2) on the short-wave side of line A^0X. Lines of approximately the same energy are seen in sample W_2 and also in other structures containing submonolayers of CdTe which we studied. One might naturally suggest that E_1 stems from an exciton trapped by a CdTe submonolayer. This suggestion is supported by a calculation which we carried out. According to this calculation, the energy of an exciton trapped by a CdTe submonolayer should lie in the region of the edge photoluminescence of ZnTe. Further evidence that lines A^0X and E_1 differ in nature comes from the circumstance that they differ in the temperature dependence of their intensity I: $I(A^0X)\to 0$ at $T>30$ K, while $I(E_1)\to 0$ at $T>70$ K. Perhaps the most obvious manifestations of a CdTe submonolayer is a multiphonon resonant Raman scattering which we observed in W_1, accompanied by the emission of 9 and $13LO$ phonons during excitation by the lines 4765 and 4579 Å, respectively. The Raman lines $9LO$ and $13LO$ lie a bit below E_1 in energy and are not observed in ZnTe films. An intense new line, E_2, with $\hbar\omega=2.338$ eV at $T=5$ K, appears in the photoluminescence spectra of W_2. Figure 3 shows photoluminescence and Raman spectra of a W_2 sample at $T=5$ K during excitation by the lines 5145 (spectrum 1) and 4880 Å (spectrum 2). Also shown here is an $R(\lambda)$ spectrum (3). There is a minimum in the $R(\lambda)$ spectrum at approximately the energy of E_2 (Ref. 1). This fact indicates that E_2 is of an excitonic nature.[1] The existence of an exciton state $|E_2\rangle$ is also manifested in the resonance Raman spectra. The appearance in spectrum 1 of the $3LO$ Raman line, which is anomalously intense here in comparison with the other samples, is due to the approximate agreement of the energies of the $3LO$ Raman scattering and E_2. This is a typical manifestation of a resonant effect in Raman scattering.[10] For the same reason, we see the Raman line $8LO$ in spectrum 2, which is not seen in the ZnTe film. It is natural to suggest that E_2 stems from the emission of an exciton trapped by two CdTe submonolayers which are close together (separated by ≈ 5 ZnTe monolayers). A calculation using the approximation of planar CdTe wells shows that the difference between the energies of excitons in an isolated monolayer quantum well and in two coupled (in the quantum-mechanical sense) such wells agrees within 10 meV with the difference between the E_1 and E_2 emission energies. This fact can be taken as a further argument in favor of the interpretation of these lines offered above. The small discrepancy (≈ 40 meV) between the theoretical and experimental values of E_1 and E_2, which is small in comparison with the large observed shifts of exciton energies (>750 meV) with respect to the bulk value in CdTe, may be due to two factors. First, there

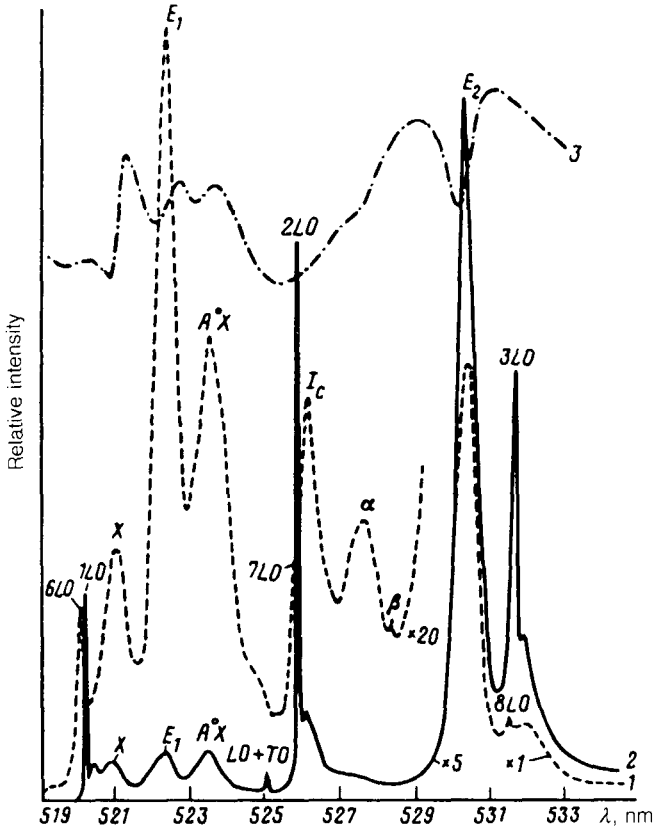

FIG. 3. Spectra at $T=5$ K. 1—W_2, photoluminescence and Raman scattering, $\lambda_L=4880$ Å; 2—$\lambda_L=5145$ Å; 3—$R(\lambda)$.

is a scatter in the values reported in the literature for ΔE_c and ΔE_v and also the parameters characterizing the deformation shifts in CdTe. Second, the model used in the calculations incorporates some simplifications (it assumes ideally planar rectangular quantum wells). Our calculations show that incorporating the additional quantization due to the small values of the lateral dimensions of the CdTe islands leads to a short-wave shift of 20–30 meV. As a result, the calculated energies come very close to the experimental ones. Line β in Fig. 3 (spectrum 2) is equivalent in nature to E_2, except that the thickness of the ZnTe barrier is one monolayer greater in this case. This conclusion is based on the agreement of the experimental and theoretical energies of the E_2 and β lines. Line α apparently corresponds to CdTe inclusions shifted with respect to each other in the lateral direction. Calculations are difficult to carry out in this case, but it is clear that the energy of an exciton in this model should be larger than in the case corresponding to line E_2. The reason for the appearance of α and β in the spectrum in the case $\lambda_L=5145$ Å (a resonant excitation of an exciton) and for their absence in the case $\lambda_L=4880$ Å is the difference in the kinetics of the trapping of excitons and electron–hole pairs by quantum wells. This effect has been observed in several structures, with various types of quantum wells. We are currently studying it.

The exciton energies were calculated in the approximation of envelope wave

functions and also by a method similar to that used in calculating the energies of excitons trapped by isoelectronic impurities in bulk semiconductors.[11] The results are nearly the same. We should point out in this connection that the unusual fact that the method of envelope wave functions gives a good description of experimental results in the case of ultrathin layers was also pointed out in Refs. 1, 2, and 5, which were studies of isolated and coupled multilayer InAs quantum wells in GaAs.

In summary, it has been shown that when CdTe submonolayers are added to ZnTe, some CdTe islands form. These islands give rise to new exciton states, which are manifested in the spectra of the photoluminescence, the Raman scattering and the optical reflection $R(\lambda)$. The exciton energies can be described well in a model of multilayer islands.

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