Nonlinear excitonic absorption in (Zn,Mn)Se superlattices and ZnSe films

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Optical transmission studies have been performed on ZnSe thin films and two (Zn,Mn)Se superlattices ($E_g \simeq 2.8$ eV) of varying barrier compositions and well widths grown by molecular beam epitaxy. The excitons in these samples ranged in character from three dimensional to quasi two dimensional. The spectra, obtained at 77 K as a function of incident light intensity, clearly show the saturation of the excitonic resonance. This is the first demonstration of nonlinear excitonic absorption in the (Zn,Mn)Se system. Mechanisms for the saturation are discussed with estimates for the relative contributions from Coulombic screening and phase space filling.

Nonlinear optical absorption in semiconductors has been the subject of considerable current interest because of the possible application of the effect in bistable optical switches, modulators, and other novel nonlinear devices. In narrow gap semiconductors such as InSb[1,2] and (Cd,Hg)Te,[3] the nonlinearity arises from changes in the band to band absorption; the specific mechanisms which contribute to the nonlinearity are a dynamic Burstein–Moss shifting of the band edge, and a free-carrier Drude plasma contribution. For wider gap materials, bleaching of the free-exciton resonance gives rise to a significant nonlinear absorption. Much of the previous work on nonlinear absorption of the free exciton in both bulk and quantum well structures has focused on the (Al,Ga)As ($E_g \simeq 1.4$ eV) material system.[4–6] Recently, for example, Miller *et al.*[7] have demonstrated a saturation intensity of 580 W/cm^2 for quasi-two-dimensional (2-D) GaAs/(Al,Ga)As quantum wells at room temperature. Elsewhere, Dagenais[8] has studied a (3-D) bound exciton resonance in CdS platelets at low temperatures ($\sim$4 K). Two distinct physical processes have been discussed in attempts to explain the nonlinear absorption of the free exciton under resonant optical excitation.[9] These are a Coulombic screening of the excitonic states due to a free-carrier plasma, and a phase space filling (PSF) of the excitonic states. Recent work indicates that for the (Al,Ga)As system under resonant pumping conditions, the initially dominant mechanism is due to phase space filling of excitonic states.[9] However, the excitons are ionized rapidly ($\tau = 0.3$ ps) into free electron-hole pairs by interaction with longitudinal optical (LO) phonons; the dominant mechanism in steady state is attributed to Coulombic screening of the excitons. In the letter, we report nonlinear excitonic absorption in the (Zn,Mn)Se ($E_g \sim 2.8$ eV) system, both for molecular beam epitaxially (MBE) grown ZnSe films and ZnSe/(Zn,Mn)Se superlattices. This provides an opportunity to study a system with larger exciton binding energies (> 20 meV) than the (Al,Ga)As system. Additionally, due to the fact that in ZnSe/(Zn,Mn)Se superlattices the valence-band offset is believed to be small (on the scale of the exciton binding energy),[10] this material provides an opportunity to examine an unusual exciton composed of a quasi-2-D electron and a 3-D hole. The present work is also significant from an applied point of view as nonlinear excitonic absorption in the (Zn,Mn)Se system has potential for device applications in the blue region of the visible spectrum.

Transmission spectra discussed here were obtained from three samples: (1) a 1.3-μm-thick ZnSe film, (2) a superlattice with 73 Å ZnSe wells denoted ZSL-4, and (3) a superlattice with 24 Å ZnSe wells denoted ZSL-11. Thus, a substantial variation from a 3-D exciton (electron) to a quasi-2-D exciton was available, permitting the study of nonlinear saturation intensity as a function of the dimensional nature of the exciton (the exciton Bohr radius a_x in 3-D ZnSe is approximately 28 Å). The exact dimensions for each sample are listed in Table I. Details of the growth process and microstructural evaluation have been discussed elsewhere[11,12]; transmission electron microscopy and photoluminescence[10] measurements indicate that the samples used possess a high degree of crystal quality. The samples were mounted on clear glass microscope slides with Crystalbond so that the

TABLE I. Dimensions for the three samples on which the absorption experiments were performed.

	ZnSe film	ZSL-4	ZSL-11
ZnSe buffer thickness	1.3 μm	0.7363 μm	0.0720 μm
(Zn,Mn)Se buffer thickness	···	···	0.4457 μm
ZnSe well thickness	···	73 Å	24 Å
(Zn,Mn)Se barrier thickness	···	180 Å	160 Å
Mn concentration	0.00	0.51	0.26
Number of periods	1	67	76

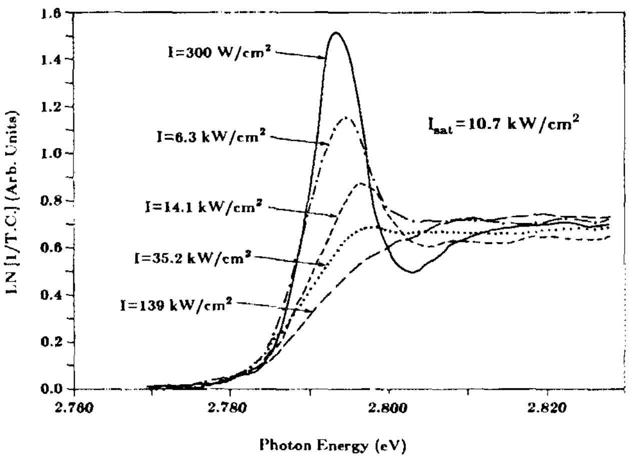

FIG. 1. Change in the excitonic absorption as a function of intensity for the 1.3-μm ZnSe film at $T = 77$ K. T.C. on the ordinate axis is the transmission coefficient and is defined as output power divided by input power.

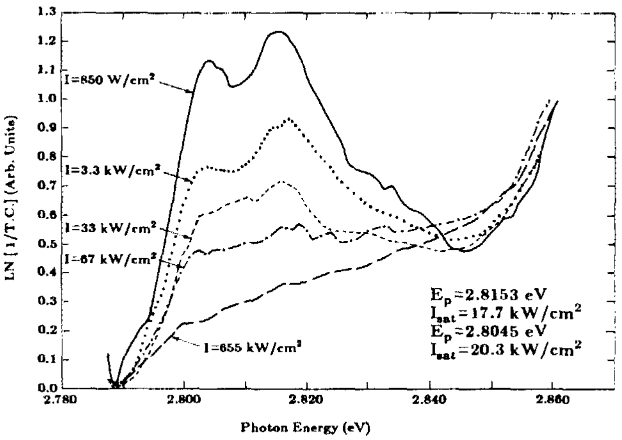

FIG. 3. Change in the excitonic absorption as a function of intensity for ZSL-11 at $T = 77$ K. The inset specifies the saturation intensity and energy for the two resonances. T.C. on the ordinate axis is the transmission coefficient and is defined as output power divided by input power.

GaAs substrate material was exposed and the MBE grown films were adjacent to the glass. The GaAs substrate was mechanically lapped to a thickness of 50–100 μm and then etched with a selective chemical etch.

The transmission experiments were carried out using an EG&G model 2100 pulsed dye laser system with Coumarin 440 and 460 dyes. Peak powers of approximately 10 kW were available, and neutral density filters were used to limit the power of the beam passing through the sample. Signal recovery was performed with the aid of a boxcar averaging system. The transmission experiments for the film and the superlattices were performed at 77 K, maintained by immersion in LN_2.

A pronounced absorption resonance was evident in the transmission spectra of the ZnSe film and was associated with the heavy hole exciton (see Fig. 1). This absorption was observed to be intensity dependent with a saturation intensity[13] of 10.7 kW/cm^2. An excitonic resonance is seen in the transmission spectra (Fig. 2) of the wide well superlattice sample ZSL-4. (For the well width $L_w = 73$ Å this is a near-by 3-D exciton.) The saturation intensity in this case corresponds to $I_{\rm sat} = 1.3$ kW/cm^2. The peak observed in transmission is attributed to the light hole exciton[10] since for the ZnSe/(Zn,Mn)Se superlattice, the compressive uniaxial component of the lattice mismatch strain in the ZnSe layers results in a splitting of the valence-band degeneracy, shifting the light hole towards the conduction band with respect to the heavy hole.[14] The heavy hole peak was not observed because of the masking of this resonance by buffer layer absorption. The third sample (ZSL-11) described here is expected to exhibit a particular form of quasi-2-D excitonic behavior with strong electron confinement and relatively weak hole confinement. As a result, the amount and nature of the 2-D behavior will be different in the (Zn,Mn)Se than in (Al,Ga)As, for example. Nevertheless, enhanced exciton binding energy is expected.[15] The transmission spectra (Fig. 3) in this case exhibit a double peaked resonance associated with the strain induced valence-band splitting; however, identifying these peaks as due strictly to light or heavy hole excitons is complicated by the strain induced coupling which occurs in the quantum well structure. The saturation intensities for the two peaks are each found to be approximately $I_{\rm sat} = 20$ kW/cm^2.

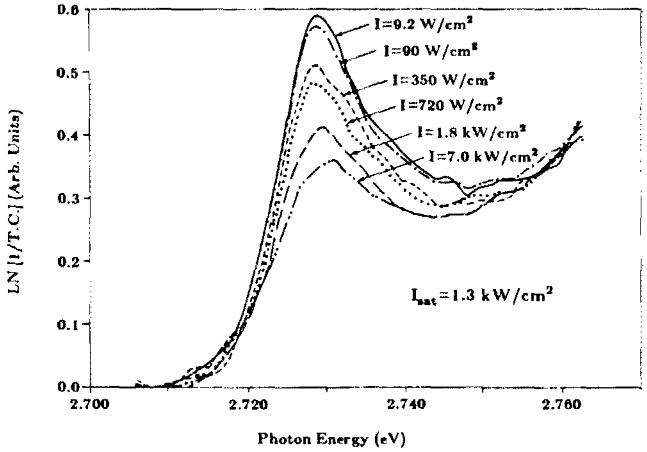

FIG. 2. Change in the excitonic absorption as a function of intensity for ZSL-4 at $T = 77$ K. T.C. on the ordinate axis is the transmission coefficient and is defined as output power divided by input power.

Using equilibrium statistics to estimate the relative free electron-hole pair and exciton densities,[16] we obtain some insight into the mechanisms which contribute to the observed absorption saturation in the three samples discussed. We emphasize, however, that thermal equilibrium based estimates may need to be modified to include here, e.g., the short lifetimes associated with these materials (sample dependent, but roughly ~200 ps).[17,18] We first consider the case of exciton screening by a co-existing electron-hole gas at $I_{\rm incident} = I_{\rm sat}$ by comparing the photogenerated densities with the Mott density (the density for which the Debye screening length equals the Bohr radius of the exciton in question). For the ZnSe films, where spatial diffusion must also be accounted for, the Mott density for heavy excitons at 77 K is estimated to be is $n_{mi} = 3 \times 10^{17}$ cm^{-3} whereas the generated free electron-hole pair density is 9×10^{16} cm^{-3}. For the wide quantum well sample ZSL-4 (nearly 3-D light hole excitons) $n_{mi} = 7 \times 10^{16}$ cm^{-3} while the estimated free electron-hole pair density for this sample at $I_{\rm incident} = I_{\rm sat}$ is

$2\times10^{16}\,\mathrm{cm}^{-3}$. Thus in both cases, the estimated carrier density at $I_{\mathrm{incident}} = I_{\mathrm{sat}}$ is only about a factor of 3 or 4 less than the Mott density, suggesting that Coulomb screening is an important mechanism for the 3-D absorption saturation. In the case of the narrow well sample (ZSL-11), the saturation mechanisms become more complex. For a strictly 2-D exciton, the effects of screening are negligible and the dominant nonlinear absorption mechanism at low temperatures is due to phase space filling.[19] We note again the unusual character of excitons in the ZnSe/(Zn,Mn)Se quantum wells due to the weak confinement of the hole. Converting the PSF argument to an elementary estimate of exciton occupancy in real crystal space we note that the area density for $I_{\mathrm{incident}} = I_{\mathrm{sat}}$ corresponds to $n_x \simeq 6\times10^{12}\,\mathrm{cm}^{-2}$. The implication is that the PSF occupancy is reaching completion (within a factor of 2 or so) under our experimental conditions. On the other hand, the density of thermally ionized free electron-hole pairs is estimated to be a factor of 2 less than the Mott density in this case. Thus, while PSF must be a contributing mechanism for the narrow well sample, screening may play a role as well (at 77 K).

In conclusion, saturation of the excitonic resonance in ZnSe signal crystal films and (Zn,Mn)Se superlattices has been observed. Rough estimates indicate that for the case of the (bulklike) ZnSe film or a wide-well (Zn,Mn)Se quantum well structure, Coulombic screening is the major mechanism for the nonlinearity at 77 K. For a narrow-well structure, the mechanism appears to be a combination of Coulombic screening and PSF, the actual contribution from each depending on the still uncertain degree of 2-D character associated with the exciton. Clearly, additional theory and experiment are required to detail this further.

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