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Raman spectrum of a ZnSe/GaAs heterostructure

D. Walsh, K. Mazuruk, and M. Benzaquen
Physics Department, McGill University, 3600 University Street, Montreal, Quebec, Canada H3A 2T8
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With the use of below-band-gap laser light to generate bound holes, light scattering from an undoped n-type ZnSe epitaxial layer on GaAs (100) shows evidence for a Γ_8 ground-state splitting of 52 cm^{-1} in agreement with predictions involving the lattice mismatch. The $1S \rightarrow 2S$ excitation energy of 511 ± 2 cm^{-1} identifies P as the dominant acceptor impurity.

Although electronic Raman scattering from localized electronic states in a semiconducting crystal is a weaker process than the corresponding photoluminescence after laser excitation, its singular advantage is that the initial electronic state is known at low temperatures. Well-resolved electronic Raman spectra in compound semiconductors have been obtained from bound holes in GaP,[1,2] GaAs,[3,4] and ZnTe.[5] Because of the lower growth temperatures for ZnSe epitaxial layers grown by either molecular-beam epitaxy[6,7] (MBE) or metal-organic chemical-vapor deposition,[8,9] (MOCVD), high-quality ZnSe epilayers on semi-insulating GaAs substrates are now available. Consequently, background photoluminescence is less pervasive, making light scattering more attractive in this potentially useful optoelectronic material.

We report here an electronic Raman spectrum for a phosphorus acceptor impurity in an undoped, high-resistivity n-type ZnSe sample grown by MOCVD on a (100) semi-insulating GaAs substrate. The ZnSe epilayer (thickness $t = 0.35$ μm) was grown at 300 °C on a 1-μm-thick buffer layer of undoped n-type GaAs grown in a separate adjoining reactor by MOCVD. The nonequilibrium population of bound holes in an n-type crystal is generated by below-ZnSe-band-gap laser light, a technique which has been exploited recently to obtain the corresponding electronic Raman spectra of shallow acceptors in semi-insulating GaAs.[4] In addition, this laser light is strongly absorbed in the GaAs buffer layer and recent transport measurements, undertaken to illuminate the band offset at the interface,[9] indicate that holes can tunnel into the ZnSe epilayer producing a nonequilibrium population of neutral acceptors. The depolarized Raman spectrum at 8 K of Fig. 1 was obtained by backscattering from the (100) ZnSe/GaAs sample using 200 mW of the 482.5 nm Kr$^+$ laser line, a cylindrical lens slightly defocused to minimize heating, and an Anaspec prism filter assembly to remove unwanted plasma lines. The sample was mounted in a Janis variable-temperature optical Dewar and the collected light was diffracted in a Jobin-Yvon 1-m double monochromator using photon-counting techniques and an automated data-acquisition system. For comparison purposes, Fig. 2 shows an identical spectrum (apart from the background photoluminescence) at 8 K using the 476.2-nm Kr$^+$ line. The spectrum contains the LO-phonon line of both the ZnSe and the GaAs buffer layers, the latter being enhanced by the presence of the ZnSe epilayer; in this configuration the TO-phonon Raman line is absent for high-quality crystals. The two-LO-phonon line of ZnSe at 415 cm^{-1} is too weak at these low temperatures to be observed unambiguously, although there is some structure in that spectral region. The A and B spectral lines have characteristic features observed in inelastically scattered laser light from a bound hole at a neutral acceptor,[2] the B line corresponding to the dominant $1S \rightarrow 2S$ excitation of the acceptor bound hole; however, the relatively narrow width of the A line, due to the splitting of the four-fold-degenerate Γ_8 ground state into two doublets, indicates a fairly uniform tetragonal distortion due to the lattice mismatch between GaAs and ZnSe (the lattice constants are 5.653 and 5.667 Å, respectively)

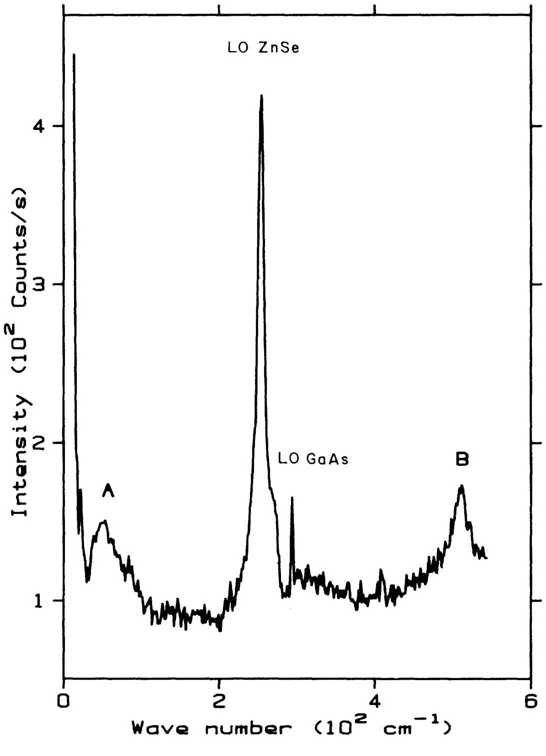

FIG. 1. Raman spectrum at 8 K of ZnSe on (100) GaAs; laser power was 10 W cm^{-2} at 482.5 nm.

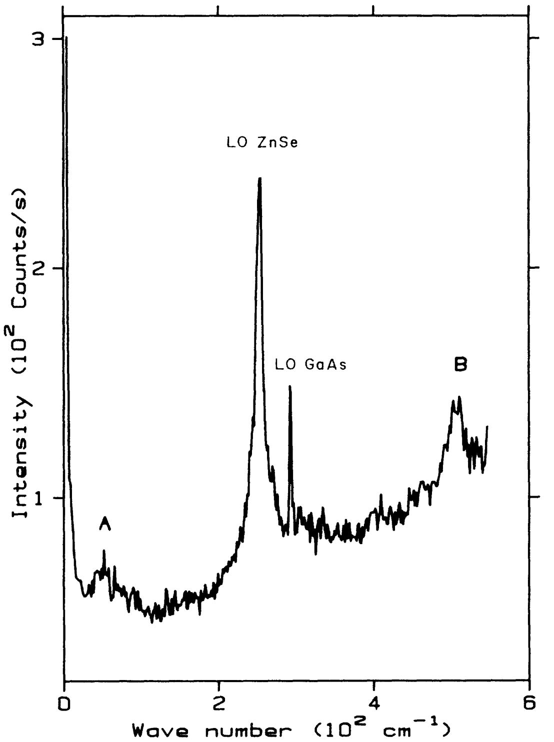

FIG. 2. Raman spectrum at 8 K of sample in Fig. 1; laser power was 5 W cm^{-2} at 476.2 nm.

and the low density of misfit dislocations. At 20 K the LO-phonon spectrum is preserved but the A and B spectral lines are broadened beyond recognition due to phonon coupling with the acceptor state,[3] a property which compels one to do electronic Raman measurements at very low T^2.

We obtain a $1S \rightarrow 2S$ excitation energy of 63.4 meV, quoted in Table I, which can be compared with the theoretical value of 77.1 meV obtained by using the effective-mass approximation for a shallow acceptor,[10] the difference being due to central core corrections. We identify this acceptor impurity with P, whose binding energy from donor-acceptor pair photoluminescence of liquid-phase-epitaxially grown ZnSe containing P was estimated to be between 85 and 90 meV.[11,12] The position of the A line is consistent with the expected splitting of the Γ_8 state under a tetragonal strain, due to the 0.24% mismatch and a valence-band deformation potential of 3.6 eV.[13] This potential for acceptor states is known to be slightly less than that for the valence band; for instance, the deformation potential for a Zn acceptor in GaP was 72% of the valence-band value,[2] similar to the situation for a B acceptor in Si.[14] Using this reduction we estimate the Γ_8 splitting to be 6.2 meV, in very good agreement with the A values of Table I.

TABLE I. Energy ±2 cm^{-1} of the LO-phonon excitations, the acceptor excitation within the strain-split Γ_8 ground state (A) and the corresponding $1S \rightarrow 2S$ excitation (B). The LO-phonon energies reported previously are 295 cm^{-1} for GaAs at 10 K [A. Pinczuk, J. Shah, A. C. Gossard, and W. Wiegman, Phys. Rev. Lett. **46**, 1341 (1981)] and 253 cm^{-1} for ZnSe and 90 K [W. Taylor, Phys. Lett. **24A**, 556 (1967)].

	E (cm^{-1})			
	A	LO ZnSe	LO GaAs	B
Fig. 1	51	255	294	512
Fig. 2	53	255	293	510

In conclusion, we have observed the low-T electronic Raman spectrum of a bound hole in an undoped, high-resistivity n-type ZnSe epitaxial layer grown by MOCVD on semi-insulating GaAs using an undoped n-type GaAs epilayer as a buffer. The $1S \rightarrow 2S$ excitation energy was 511±2 cm^{-1} and the acceptor impurity was identified to be P. The Raman line at 52 cm^{-1} corresponding to the strain-split Γ_8 ground state was in very good agreement with that deduced from the corresponding tetragonal distortion in a submicrometer-thick ZnSe epilayer due to the lattice mismatch. The LO-phonon energies of both the ZnSe epilayer and GaAs buffer layer agree with previous reports (see Table I). Since it was first proposed in 1978,[15] light scattering by two-dimensional electron systems in semiconductors has become a very useful spectroscopic tool for studying heterostructures. Light scattering from neutral acceptors is also well known and this report shows that accommodation of the lattice mismatch in a submicron epitaxial crystal can be revealed by the electronic Raman spectrum of the dominant acceptor impurity in the corresponding epilayer. It would be very instructive to examine in this way GaAs-lattice-matched $ZnSe_{0.95}S_{0.05}$ epilayers reported recently.[16] Work is underway to observe light scattering from our ZnSe epilayers using uniaxial-stress techniques.[17]

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