MnSe: Rocksalt versus zinc-blende structure

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MnSe epilayers are grown on (001) GaAs substrates by molecular beam epitaxy (MBE), which exhibit NaCl structure as shown by x-ray diffraction. Their zone-center transverse optic (TO) and longitudinal optic (LO) phonons have been observed as minima in infrared transmission with oblique incidence, i.e., in the Berreman geometry, using Fourier transform infrared spectroscopy. In contrast, they are absent in the Raman spectrum, consistent with the rule of mutual exclusion. The TO and LO frequencies thus deduced, 139 and 239 cm^{-1}, respectively, differ significantly from the corresponding values of 219.5 and 257 cm^{-1} obtained for zinc-blende MnSe. The latter were deduced from the $x \rightarrow 1$ values of the TO and LO frequencies from a Raman study of MBE-grown $Cd_{1-x}Mn_xSe$ epilayers. A similar study of ZnTe/MnSe multiple quantum well structure also yielded the LO at 249 cm^{-1}, compatible with the zinc-blende character of MnSe in such structures, combined with the strain experienced by them. [S0163-1829(98)01136-9]

I. INTRODUCTION

II-VI semiconductors and the fascinating subset of ternaries in which the group-II sublattices are partially populated with $3d$-transition metal ions, i.e., the *diluted magnetic semiconductors* (DMS), continue to be intensely investigated, thanks to their unique physical properties[1] and the current interest in blue/green light emitters.[2] The DMSs, in particular, display striking magnetic properties. Among the DMSs, the Mn-based II-VI ternaries are the most extensively studied and understood. The successful fabrication of epilayers, heterostructures, and multiple quantum well structures, which include DMS layers achieved with nonequilibrium growth techniques such as molecular beam epitaxy (MBE) and metalorganic chemical-vapor deposition, has significantly expanded II-VI investigations.[1-5] These techniques have also led to the growth of materials with a structure different from that of the stable forms occurring as bulk crystals, viz., zincblende MnSe,[6] MnTe,[7] and $Cd_{1-x}Mn_xSe$.[8]

Bulk Mn chalcogenides have been reported[9] with either octahedral coordination (i.e., with NaCl or NiAs structure) or with tetrahedral coordination (i.e., with zinc-blende or wurtzite structure). It appears that the zinc-blende and wurtzite forms of these compounds are metastable. In this context, their MBE growth on (001) GaAs substrates are of considerable interest. Kolodziejski *et al.*[6] fabricated zinc-blende MnSe as a constituent of ZnSe/MnSe superlattices; they were also successful in achieving epilayer thicknesses reaching 400 Å and even 1000 Å (Refs. 3 and 10). Similarly MnTe epilayers, also with zinc-blende structure, were grown by Durbin *et al.*[7] using the MBE technique, reaching a thickness of $0.5 \mu m$ and more recently by Janik *et al.*[11] up to thicknesses of as much as $8 \mu m$.

The zone-center transverse-optical (TO) and longitudinal-optical (LO) phonons in crystals with NaCl (O_h^5:$F4/m\bar{3}2/m$) structure differ significantly from those with the zinc-blende (T_d^2:$F\bar{4}3m$) form. In the former, they are forbidden in the Raman effect but occur prominently as a reststrahlen band in the infrared, thanks to the rule of mutual exclusion. In the latter, the absence of center of inversion permits the LO and TO phonons to appear in *both* Raman and infrared spectra.

For the III-V and II-VI semiconductors, three spectroscopic techniques are available for observing the zone-center optical phonons: (1) The TO and the LO modes can be deduced from the infrared reflectivity (reststrahlen) spectrum of a polar crystal by a curve-fitting procedure,[12] which is computer intensive. (2) The TO and LO modes in the zinc-blende structure can be observed as Raman lines.[13] One should note here, however, that Raman scattering from a MBE-grown film can be very weak or forbidden by symmetry for specific scattering geometries except under resonance conditions. For example, Raman selection rules allow the observation of only LO phonons for backscattering along [001], the typical growth axis employed in MBE of zinc-blende semiconductors. As mentioned above, both LO and TO lines are forbidden in the Raman effect for the rocksalt (NaCl) structure. (3) With specimens significantly smaller than the reststrahlen wavelength, the infrared absorption spectrum of a very thin film recorded in normal incidence, can reveal only TO polar modes directly as shown by Barnes and Czerny for NaCl films,[14] whereas for oblique incidence *both* TO and LO modes are manifested as transmission minima in the infrared, as first predicted and verified by Berreman.[15] Thus, for a crystalline film with NaCl structure, the Berreman technique is a very powerful way for investigating both LO and TO frequencies. In particular, for MBE-grown zinc-blende epilayers, the Berreman effect allows one to observe both TO and LO modes, irrespective of their orientations.

In this paper, we report the investigation of TO and LO phonons in MBE-grown MnSe films with rocksalt structure, as seen in the infrared transmission employing the Berreman geometry. The observed values are compared with the TO and LO frequencies of the ''hypothetical'' zinc-blende MnSe
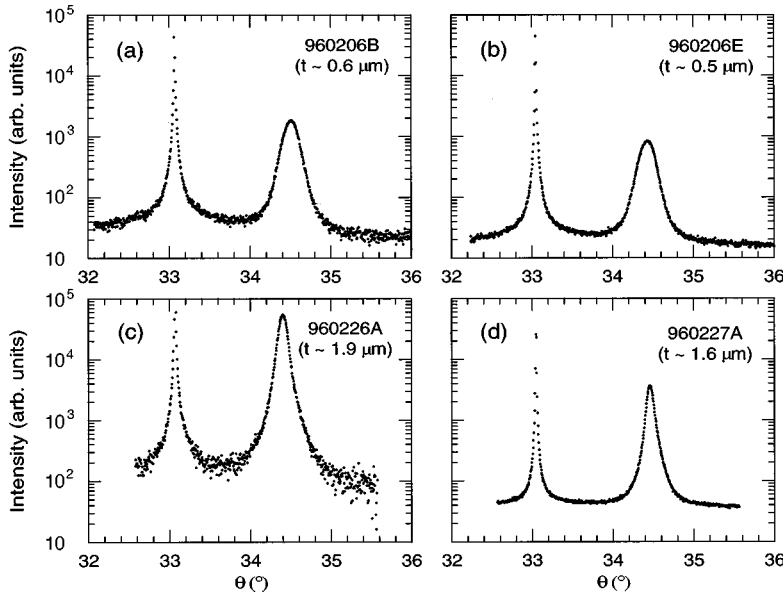
FIG. 1. The θ-2θ x-ray diffraction from MnSe epilayers with NaCl structure of (a) 0.6 μm thickness on tilted GaAs, (b) 0.5 μm on standard GaAs, (c) 1.9 μm on tilted GaAs, and (d) 1.6 μm on standard GaAs substrate. The thicknesses of MnSe epilayers were measured with scanning electron microscope.

as deduced from the $x \to 1$ values from $Cd_{1-x}Mn_xSe$ epilayers,[16] as well as with those from ZnTe/MnSe MQW[17] determined from Raman scattering.

II. EXPERIMENT

A. Sample growth and x-ray diffraction

The MnSe epilayers were grown by MBE on (001) GaAs substrates. The surface reconstructions were monitored using reflection high-energy electron diffraction, which indicated a ''spotty'' pattern almost from the inception of growth. The films were deposited approximately at 300 nm/h, and were grown for 2 h (960206B and 960206E) and 6 h (960226A and 960227A). Two of the samples (960206B and 960226A) were grown on tilted (4°) GaAs (001) substrates, and the other two on standard GaAs (001).

X-ray measurements were made using a double crystal diffractometer with Cu $K\alpha_1$ radiation. As shown in Fig. 1, the θ-2θ scans on each of the samples clearly show an epilayer peak yielding the corresponding lattice parameter of ~ 5.45 Å. On the basis of this lattice parameter of MnSe in the rocksalt structure, distinctly smaller than 5.90 Å, the lattice parameter of zinc-blende MnSe,[18] we attribute the rocksalt structure to the epilayer. The full width at half maximum of the epilayer peak decreases with increasing epilayer thickness; this signals an improvement of crystal quality with increasing sample thickness—a result supported by observations on a scanning electron microscope, which reveal better surface quality in the thicker samples. Since the rocksalt structure is observed in even 10 nm thick samples, the critical thickness of zinc-blende MnSe on GaAs substrates should be below this value, a conclusion consistent with studies of Heimbrodt et al.[19]

B. Infrared transmission

The infrared transmission spectra were recorded with a BOMEM DA3 Fourier transform infrared spectrometer,[20] employing a Globar source and a mylar beam splitter. The

resolution in the transmission experiment is 0.5 cm^{-1}. Typical spectra were obtained with 50 co-added scans. A composite Si bolometer[21] operating at 4.2 K with a long-pass cold filter and cone optics was used as a detector. The samples were cooled to 5 K in a Janis Supervaritemp 10DT optical cryostat[22] with polypropylene windows.
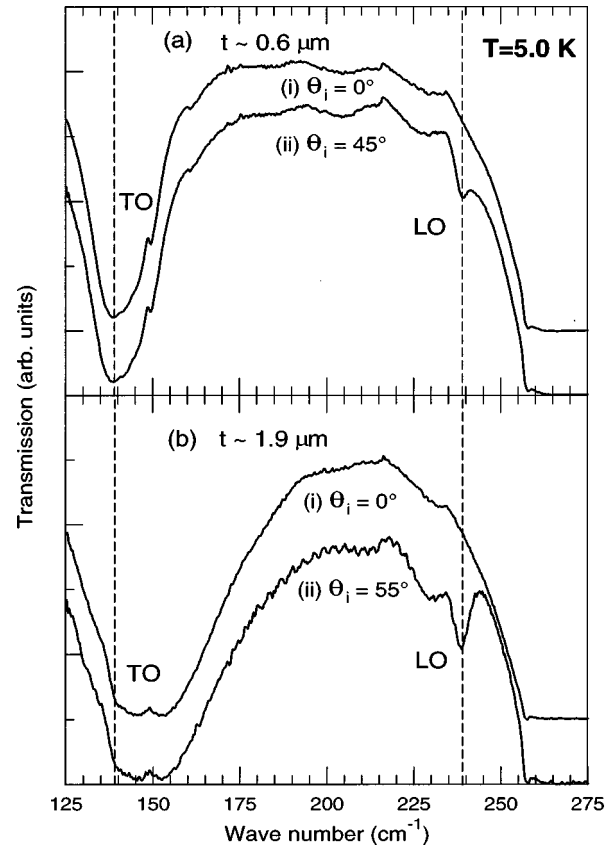

FIG. 2. The infrared transmission spectra of (a) 0.6 μm and (b) 1.9 μm MnSe epilayers with NaCl structure. Each figure shows spectra for (i) normal and (ii) oblique incidence. Note that the thickness of the film in (b) precluded the precise determination of the TO frequency.

TABLE I. The TO and LO frequencies (in cm^{-1}) for the different structures in which MnSe and MnTe occur.

	Structure		TO	LO	Temperature
MnSe	NaCl[a]		139	239	5 K
	NaCl[b]		141	237	300 K
	zinc-blende[c]		219.5	257	5 K
	wurtzite[d]	A_1	219	256	5 K
		E_1	220	258	
MnTe	NiAs[e]	$\mathbf{E} \perp \hat{c}$	131	191	300 K
		$\mathbf{E} \| \hat{c}$	115	170	
	zinc-blende[f]		189.7	218.5	5 K

[a]MBE (present).
[b]Bulk (Ref. 23).
[c]MBE (Refs. 16 and 24).
[d]Bulk (Ref. 26).
[e]Bulk (Ref. 27), $\mathbf{E}$, electric vector; $\hat{c}$, optic axis.
[f]MBE (Ref. 24).

III. RESULTS AND DISCUSSIONS

The infrared transmission spectra of (a) 0.6 μm and (b) 1.9 μm MnSe epilayers with NaCl structure, recorded at 5 K, are displayed in Fig. 2. Each figure shows the spectrum (i) for normal and (ii) oblique incidence, the angle of incidence θ_i being 45° in (a) and 55° in (b). As can be seen, only TO is observed at normal incidence, while both TO and LO appear in oblique incidence. We thus obtain TO and LO phonon frequencies for the MnSe epilayers with NaCl structure as 139 and 239 cm^{-1}, respectively. These values are in good agreement with those deduced by Decker and Wild[23] from the analysis of the reststrahlen band of a MnSe film produced by flash sublimation. From the channeled spectrum observed in the transmission spectrum of the thickest sample in the frequency range higher than that of the LO, we deduce $\epsilon_\infty = 8.6 \pm 0.2$; combined with the Lyddane-Sachs-Teller relation, i.e., $\omega_{LO}/\omega_{TO} = (\epsilon_0/\epsilon_\infty)^{1/2}$, we finally obtain $\epsilon_0 = 25.4 \pm 0.6$ at $T = 5.0$ K. The values of ϵ_0 and ϵ_∞ deduced in this manner agree well with those given by Decker and Wild.[23] Thinner samples give higher values of ϵ_∞ for reasons not yet fully understood.

As is to be expected for MnSe with NaCl structure, its LO and TO lines were absent in the Raman spectrum of the epilayer, while the LO of the underlying GaAs substrate appeared distinctly.

IV. CONCLUDING REMARKS

The TO (139 cm^{-1}) and LO (239 cm^{-1}) modes for MnSe with NaCl structure investigated in the present study differ significantly from the corresponding values of 219.5 and 257 cm^{-1} obtained for zinc-blende MnSe. The latter were deduced from the $x \to 1$ values of the TO and LO frequencies from a Raman study of MBE-grown Cd$_{1-x}$Mn$_x$Se epilayers.[16] The Berreman effect investigated on the same series of samples[24] yielded phonon frequencies in excellent agreement with the Raman values. Oh et al.[17] have also reported the observation of confined LO phonons in MBE-grown ZnTe/MnSe multiple quantum wells on a (001) GaAs substrate. From Fig. 6 in their paper, a value of 249 cm^{-1} can be deduced for the zone-center LO phonon. The lower value of the LO frequency has been attributed to a strain-induced frequency shift caused by the $\sim 3\%$ lattice mismatch between MnSe and ZnTe. The larger ionicity of MnSe with NaCl structure than that in the zinc-blende form clearly emerges from the comparison of the corresponding frequencies of the TO and the LO modes in the two structures.[25] From an extrapolation of the Raman frequencies observed in bulk Cd$_{1-x}$Mn$_x$Se with wurtzite structure to $x \to 1$, one can deduce the zone-center TO and LO modes of MnSe with wurtzite structure.[26] The comparison of the TO and LO values of MnSe with NaCl structure obtained from Pb$_{1-x}$Mn$_x$Se ($x \to 1$) will be of interest in this context. In a similar fashion, the LO and TO values of MnTe with NaCl structure can be established from $x \to 1$ values of the phonon frequencies in Pb$_{1-x}$Mn$_x$Te. In Table I we list the TO and LO frequencies of MnSe with NaCl (Ref. 23) and wurtzite[26] structures, and of MnTe with NiAs structure,[27] along with the corresponding values obtained on MBE-grown epilayers with structures appropriately noted.

It is interesting to note that zinc-blende MnTe can be grown on (001) GaAs substrates with thicknesses as high as 10^4 nm, whereas zinc-blende MnSe occurs only for thicknesses of at most a few tens of nm. While Heimbrodt et al.[19] report the limit of zinc-blende MnSe to be 3-5 nm, Chang et al.[10] have observed zinc-blende MnSe up to 100 nm. The MnSe epilayers with NaCl structure studied in the present investigation are characterized by thicknesses one order of magnitude larger.

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