Silent Raman modes in zinc oxide and related nitrides

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Anomalous Raman modes have been reported in several recent papers dealing with doped- and undoped-ZnO layers grown by different methods. Most of these anomalous Raman modes have been attributed to local vibrational modes of impurities or defects. However, we will show that most of the observed modes correspond to wurtzite-ZnO silent modes allowed by the breakdown of the translational crystal symmetry induced by defects and impurities. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1856222]

I. INTRODUCTION

Wurtzite-type zinc oxide (*w*-ZnO) is a wide direct-gap II-VI semiconductor that is attracting the attention of many researchers in the last years because of its unique optoelectronic properties that are comparable and even better than GaN. In particular, ZnO is a brighter emitter than GaN because of its larger exciton energy, it possesses a lower threshold voltage for light-emitting diode (LED) and laser emission, amenability to wet chemical etching, and high radiation resistance. Besides, there are large-area substrates commercially available and the cost for fabrication of ZnO is relatively lower than for III-V nitrides.[1–3] These properties make ZnO a good candidate for applications in optics and optoelectronics, such as LEDs and lasers emitting in the blue and ultraviolet (UV) range, and transparent conducting electrodes for flat panel displays and solar cells.

ZnO is not widely used in these applications because it suffers from the "asymmetric doping" limitation that affects many other wide gap semiconductors; i.e., *n*-type doping is easily obtained, but it is very difficult to obtain *p*-type doping. Recent research interest is focused in obtaining *p*-type ZnO in a reproducible way. In this respect, ion implantation in ZnO and the growth of doped-ZnO films with different dopants by different techniques are intense fields of research where Raman scattering is one of the characterization methods usually employed.

II. OVERVIEW OF THE PROBLEM

In the last years, several works of undoped- and doped-ZnO thin films report on the observation of anomalous bands in the Raman spectra that seem not to correspond to first- or second-order modes of *w*-ZnO.[4–9] The anomalous Raman bands observed in Refs. 4–9 are summarized in Table I. Initially, anomalous Raman modes at 276 and 850 cm^{-1} in undoped-ZnO films and at 276, 516, 645, and 850 cm^{-1} in ZnO:Al thin films grown over silicon (001) and quartz by radio-frequency (rf) magnetron sputtering were reported by Tzolov *et al.*[4] These authors attributed the 276-cm^{-1} band to the inactive B_1 mode and explained the presence of the anomalous modes and of the anomalously high intensity of the longitudinal-optic (LO) mode at 570 cm^{-1} to electric-field-induced (EFI) Raman scattering. Also, anomalous Raman modes at 274, 508, 641.9, and 857 cm^{-1} in ZnO:N films grown over (0006) sapphire by metal-organic chemical-vapor deposition (MOCVD) were reported by Wang *et al.*,[5] while undoped-ZnO films did not show the anomalous bands. These authors attributed the anomalous bands to N doping but found no strong influence of the N doping on the photoluminescence (PL) spectra of the samples.

A deeper study on N doping was performed by Kaschner *et al.*[6] who reported anomalous Raman modes at 275, 510, 582, 643, and 856 cm^{-1} in ZnO:N films grown over GaN/sapphire templates by chemical-vapor deposition (CVD). These authors attributed the anomalous modes, in particular, those at 275 and 782 cm^{-1}, to local vibrational modes of N. This assignment is strange since local vibrational modes of N substituting O in ZnO should be located at longer wave numbers than those of O because of the smaller mass of N.[10] Similar anomalous bands at 273 and 580 cm^{-1} were observed by Wang *et al.* in N-doped ZnO films grown over silicon (001) and quartz glass substrates by filtered cathodic vacuum arc (FCVA).[7] These authors did not discuss in detail the nature of the bands, but correlated the increase of the N concentration with the decrease of the UV exciton emission and the increase of the deep emission in the PL spectra.

Bundesmann *et al.* have recently reported Raman-scattering spectra in ZnO thin films doped with Fe, Sb, Al, Ga, and Li and grown over *c*-plane sapphire by multistep pulsed laser deposition (PLD).[8] Anomalous Raman bands at

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TABLE I. Frequencies of the anomalous Raman modes measured in different samples grown under different conditions. The tentative assignment of these modes and their predicted frequencies from *ab initio* calculations are shown in the last rows.

ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	ω_4 (cm^{-1})	ω_5 (cm^{-1})	Sample type/substrate (growth method)	Ref.
276	516		645	850	ZnO, ZnO:Al/Si, SiO$_2$ (rf magnetron sputtering)	4
274	508		642	857	ZnO:N/sapphire (MOCVD)	5
275	510	582	643	856	ZnO:N/GaN-sapphire (CVD)	6
273		580			ZnO:N/Si, SiO$_2$ (FCVA)	7
277	511	584	644		ZnO:Fe,Sb,Al,N/sapphire (MS-PLD)	8
277			644		ZnO:Ga/sapphire (MS-PLD)	8
275	508	579	642		ZnO:N/GaN-sapphire (MOVPE)	9
B_1(low)	$2B_2$(low)	B_1(high)	TA+ B_1(high)	B_1(low)+ B_1(high)		
261	520	552	650	810	*Ab initio* calculations	11

277, 511, 584, and 644 cm^{-1} were observed in the spectra of Fe-, Sb-, and Al-doped ZnO thin films and in the spectra of the Ga-doped samples grown under N$_2$O atmosphere. However, ZnO:Ga samples show only the 277- and 644-cm^{-1} modes and ZnO:Li did not show any anomalous Raman band. These authors attributed the common anomalous bands to intrinsic host-lattice defects related to the doping because most of the bands observed under N doping were also observed in other doped samples. Furthermore, they commented that modes at 276, 511, and 581 cm^{-1} were already observed in undoped-ZnO films grown on *r*-plane sapphire, which exhibited a very low structural quality and concluded that the lack of observation of anomalous Raman modes in ZnO:Li thin films could be likely due to the higher quality of these samples.

Finally, recent work on gallium- and nitrogen-implanted ZnO has been reported by Reuss *et al.*[9] In this work, ZnO single crystals and thin-film layers grown over GaN/sapphire by metal-organic vapor phase epitaxy (MOVPE) have been implanted with Ga and N and studied under annealing. Anomalous Raman modes have been observed in both implanted samples. A mode near 580 cm^{-1} has been observed in Ga-implanted samples and four modes at 275, 508, 579, and 642 cm^{-1} have been observed in N-implanted samples. All the anomalous Raman modes of as-implanted samples decreased in intensity with increasing the annealing temperature. The 580-cm^{-1} mode in Ga-implanted ZnO was attributed to the one-phonon density of states (1-PDOS) of LO modes, and the modes seen in N-implanted ZnO have been attributed to local vibrational modes of N according to Ref. 6, despite the similar frequencies in both implanted samples and the recent work of Bundesmann *et al.*[8]

III. DISCUSSION

In order to explain the nature of the observed anomalous Raman modes, we have compared the previous experimental results with recently reported *ab initio* calculations of the lattice dynamics in *w*-ZnO.[11] Curiously enough, the anomalous Raman mode around 275 cm^{-1} reported by the previous authors falls near the position of the B_1(low) silent mode of *w*-ZnO, as already pointed by Tzolov *et al.*[4] *Ab initio* calculations locate this mode at 261 cm^{-1} and the B_1(high) silent mode at 552 cm^{-1} at the Γ point of the Brillouin zone (BZ). Taking into account that all LO modes were underestimated in the *ab initio* calculations, it is reasonable to assume that the B_1(high) silent mode is also underestimated and falls around 580 cm^{-1} near the A_1 and E_1 LO modes of ZnO.[12,13] In this respect, we think that the Raman modes around 275 and 580 cm^{-1} reported by the previous authors correspond to the B_1(low) and B_1(high) silent modes of *w*-ZnO. Both modes can be assigned to the B_1(low) and B_1(high) modes near the Γ point of the BZ due to the relatively small dispersion of these two modes along the Brillouin zone.[11]

There are several reasons that support our previous assignment: (i) the similar intensity and small width of these two peaks as observed in the high-quality Raman spectra of Ref. 6 and (ii) it is possible to assign other observed anomalous modes to second-order modes if the previous assignment is correct. With regard to the first point, the B_1 modes show the same scattering behavior as the E_2 modes in ZnO. Since both modes have small dispersion along the BZ we expect them to have a strong Raman contribution once Raman selection rules are broken and these modes can be observed along the whole BZ. Furthermore, the B_1(low) mode is located in a region of low two-phonon density of states (DOS) while the B_1(high) mode is located in a region of high two-phonon DOS so we expect the B_1(low) mode to be of much smaller width than the B_1(high) mode, as it is indeed experimentally found. The same situation holds for E_2 modes in ZnO.[14]

With regard to the second point, it is easy to check that the 510-cm^{-1} mode could be attributed to the $2B_1$(low)

second-order mode. The mode at 643 cm^{-1} can be assigned to the TA+B_1(high) second-order mode. Supporting this assignment, a mode near 640 cm^{-1} has been already assigned to the TA+LO second-order mode in Ref. 11 and LO and B_1(high) modes are thought to be near to each other. In fact, the mode at 643 cm^{-1} has been observed as a narrow peak in most of these thin films while in normal ZnO samples the mode at 640 cm^{-1} is observed as a broadband. The reason for the observation of this mode as a peak in the doped samples is likely related to the enhancement of the scattering of the B_1 modes. Furthermore, the 857-cm^{-1} mode can be attributed to the B_1(low)+B_1(high) second-order mode. With regard to the observation of the B_1(high)−B_1(low) second-order mode, which should also be observed around 307 cm^{-1} according to our assignment, we must recall that this mode is predicted to be observed around 290 cm^{-1} from *ab initio* calculations,[11] and has been indeed experimentally found in normal ZnO at 302 cm^{-1} as a low-energy shoulder of the second-order mode of 330 cm^{-1}, which corresponds to the $E2$(high)-$E2$(low).[11] Finally, the observation of the 2B_1(high) mode near 1164 cm^{-1} coincides with the position of the maximum of the 2LO band observed between 1000 and 1200 cm^{-1} in normal ZnO samples. The reason for the observation of the difference mode B_1(high)-B_1(low) and of the sum mode 2B_1(high) in normal ZnO samples is that the dispersion branches of the B_1(high) phonon modes occupy a narrow energy range along the Γ-A-L-M high-symmetry directions of the BZ. This can result in a strong singularity associated with this mode in the one- and two-phonon DOS.

The reason for the observation of the silent B_1 modes and the second-order modes in the Raman spectra of the previously commented ZnO films is likely disorder-activated Raman scattering (DARS). This scattering is induced by the breakdown of the translation symmetry of the lattice caused by defects or impurities either because of the dopant nature or because of the growth conditions, as it looks like the case of the undoped-ZnO film deposited by rf magnetron sputtering.[4] Support for this explanation is found in the works of Iwata *et al.*[15] and Nakahara *et al.*[16] who found defects in ZnO:N samples grown on *c* sapphire by molecular-beam epitaxy (MBE). They found rotational domains even at low N doping levels and that high N doping made the ZnO surface rough and faceted and the inner part of the samples contained 180° rotational twins. These authors also found a correlation between the increase of N doping and defects with the decrease of the UV exciton emission and the increase of the deep level emission. Furthermore, Guo *et al.*[17] have found that ZnO:N thin films grown on (11$\bar{2}$0) sapphire by pulsed laser reactive deposition do not show rotational domains and twinning characteristic of ZnO grown on *c*-plane sapphire or on other substrates such as LiNbO$_3$. On the other hand, reflection high-energy electron-diffraction (RHEED) patterns of undoped- and Al-doped ZnO thin films grown over silicon (001) and quartz by rf magnetron sputtering[4] show a diffuse halo, indicating the presence of a disordered phase at the surface of the samples.

The introduction of defects in ZnO:N films, being N$_O$ an acceptor in ZnO, could be understood on the base of the large Madelung energy contribution from N in the ZnO lattice (+0.79 eV).[18] This large contribution is coherent with the strong "chemical shift" of the electronic properties of impurities due to central-cell corrections affecting elements of the first row such as C, N, and O, and with the larger chemical shift of acceptor than of donor energies.[19] Consequently, the chemical shift should be much smaller for impurities substituting Zn than those substituting O, and the perturbation of the lattice should be almost negligible for impurities substituting Zn. This result could be related to the unobserved Raman anomalous modes in ZnO:Li films and the very poorly observed modes in ZnO:Ga films; however, this seems not to be the case of Fe- and Al-doped ZnO thin films.[8] Our explanation for these latter cases is that maybe the Zn site is not very stable in ZnO due to the fact that ZnO is a compound near the limit of the wurtzite-to-rocksalt transition according to Pauling's electronegativity scale. In this sense, it is well known that only a small fraction of Mg (10%–20%) substituting Zn in ZnO leads to the rocksalt modification.[20] Anyway, the most strange case is the observation of the Raman silent modes in ZnO:N thin films grown over (0006) sapphire by MOCVD in which the authors claim that the quality of the samples is very good.[5] We think that the quality of such doped samples is not as good as the authors claimed since the same authors have observed that the quality of undoped samples grown under the same conditions improves with thermal annealing.[21] A more detailed study of the surface and internal structure of ZnO:N thin films grown on sapphire by MOCVD ought to be performed.

Finally, support for our mode assignment comes from the observation of disorder-activated scattering of B_1 silent modes in other wurtzite-type materials such as InN, GaN, AlN, and Al$_{1-x}$Ga$_x$N samples. With regard to InN, two silent B_1 modes were observed at 200–220 and 540–565 cm^{-1} in InN films grown over *c*-plane sapphire by UV-assisted atomic layer epitaxy.[22] These frequencies correlate with the B_1(low) and B_1(high) calculated modes at 217 and 566 cm^{-1} with the adiabatic bond charge model[23] and at 225 and 576 cm^{-1} with the *ab initio* calculations.[24] Similarly, silent B_1 modes have been observed in Al$_{1-x}$Ga$_x$N solid solutions grown over (0001) sapphire by MOVPE (Ref. 25) and by MBE (Ref. 26) in several scattering configurations, in GaN pillar arrays grown over (0001) sapphire by MBE,[27] and in ion-implanted GaN layers.[28–30] Furthermore, the nature of the silent B_1 modes has been deduced from the isotropic shift of these modes in GaN samples mechanically damaged by ion implantation and in disordered AlGaN samples.[31]

With regard to GaN, the B_1(low) mode was observed around 300 cm^{-1} and the B_1(high) mode at 667 cm^{-1}.[31] Besides, weak bands near 360 and 420 cm^{-1} were also found in disordered samples[28–31] and in Mg-doped GaN.[32] On the assumption made to explain the anomalous Raman features in ZnO, the 360-cm^{-1} mode can be assigned to the B_1(high)-B_1(low) second-order mode in GaN and the 420-cm^{-1} mode can be assigned to the E_2(high)-E_2(low) [or TO-E_2(low)] second-order mode in GaN. We must note that both modes around 360 and 420 cm^{-1} have been observed in second-order Raman spectra of GaN thin films despite the fact that the weak 360 cm^{-1} has not been assigned.[33,34] The assignment of both second-order modes to a difference mode is

supported by the disappearance of both modes with decreasing temperature, as can be observed in Ref. 34. In that work, the mode around 415 cm^{-1} has been attributed to a second-order difference mode at the M point of the BZ in contrast with the previous work that assigned it to an overtone of acoustic phonons.[33] In GaN, also a 700-cm^{-1} mode has been identified as the B_1(high) mode.[27] Furthermore, the silent B_1(high) mode in GaN, AlN, and $Al_{1-x}Ga_xN$ has been reported along the full composition range.[26] From these measurements, values of 695 and 732 cm^{-1} can be extrapolated for the B_1(high) mode in GaN and AlN, respectively. All the B_1(low) and B_1(high) values reported are in good agreement with the observation of the B_1(low) and the B_1(high) at 329 and at 692 cm^{-1} in GaN (Ref. 35) and of the B_1(low) at 540 cm^{-1} in AlN by inelastic x-ray scattering.[36] Furthermore, they also agree with *ab initio* calculations that locate the B_1(low) and the B_1(high) modes around 336 ± 3 and 710 ± 10 cm^{-1} in GaN (Refs. 35 and 37) and around 544 ± 4 and 735 ± 15 cm^{-1} in AlN.[24,36,37]

IV. CONCLUSIONS

We have reviewed recent literature of undoped- and doped-ZnO thin films characterized by Raman spectroscopy. Many works have reported anomalous Raman bands, in many cases attributed to N local defects. In this work, we show that many of the anomalous bands correspond to silent Raman modes that are observed by disorder-activated Raman scattering due to the relaxation of the Raman selection rules produced by the breakdown of the translational symmetry of the crystal lattice. We have shown that the same silent modes are also seen in other wurtzite-type compounds, such as nitride films and alloys.

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