

MULTIPHONON IMPURITY-MEDIATED RESONANT RAMAN SCATTERING FROM HIGHLY CONDUCTIVE ZnO LAYERS

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Abstract

Resonant Raman scattering (RRS) excited by the 351.1 and 363.8 nm lines of an Ar⁺ laser was studied in the temperature interval from 10 to 300 K in highly conductive ZnO layers deposited by thermal decomposition of Zn(C₅H₇O₂)₂ metalorganic compound on porous InP substrates. The occurrence of RRS is attributed to the resonance of outgoing photons scattered in multiphonon processes with electronic transitions involving an impurity (native defects) band.

ZnO is a wide band gap (3.37 eV at 300 K) semiconductor material promising for applications in light emitting diodes, photodetectors, transparent field effect transistors, etc. [1-3]. Along with semiconducting and semiinsulating materials, transparent conductive oxide (TCO) thin-film semiconductors are used in many technically significant applications [4]. Transparent conductive oxide (TCO) films consisting of ZnO offer a number of important advantages in comparison with conventionally used In, Sn, and Cd oxides coatings: they consist of cheap elements in contrast with In containing films; they are non-toxic in comparison with Cd containing films; the fundamental band gap of ZnO lies just at the end of the luminous spectrum therefore allowing the tailoring of the ultraviolet absorption. ZnO TCO films are usually prepared by doping with III-group and IV-group impurities as well as by deviation from stoichiometry assuring a high concentration of donor-type intrinsic defects. Previous work on conducting ZnO films fabricated using a number of technological approaches (see for instance [5] and refs. therein) focused mainly at the investigation of the influence of technological parameters on the morphology of layers, their electrical parameters, optical transmittance, chemisorption and desorption of oxygen at grain boundaries. As to the radiative properties of highly doped ZnO films, they are practically unexplored.

The goal of this work is to study the influence of temperature and excitation photon energy on RRS from ZnO films with high conductivity determined by donor-type intrinsic defects. We show that the obtained results indicate on a resonance of the outgoing photons scattered by LO phonons with electronic transitions involving an energy band related to the high concentration of these defects.

Transparent conductive ZnO films with electron concentration of $9 \times 10^{19} \text{ cm}^{-3}$ were prepared by means of a technique derived from chemical vapour deposition and comprising two processes: thermal decomposition of a metalorganic compound and oxidation [6]. The deposition process was carried out in a horizontal reactor. A mixture of argon and oxygen gases at a flux of $200 \text{ cm}^3/\text{min}$ passes through the Zn acetylacetonate source maintained at a fixed temperature of 100 °C. During the deposition process the substrate temperature was maintained at 400 °C. The composition of the gas mixture was adjusted to assure the deviation from stoichiometry towards the oxygen deficiency determining the high electron concentration in the layer. In order to reduce the influence of strains in ZnO layers we used

porous InP substrates prepared by photoelectrochemical dissolution [7] following the concept of nanoheteroepitaxy [8,9].

The ZnO layers were excited by the 351.1 and 363.8 nm line of an Ar⁺ SpectraPhysics laser and the emission was analyzed in a quasi-backscattering geometry through a double spectrometer with 1200 grooves/mm gratings assuring a linear dispersion of 0.8 nm/mm. The signal from a FEU-106 photomultiplier with SbKNaCs photocathode working in a photon counting mode was introduced in an IBM computer via the IEEE-488 interface. The spectral resolution was better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 workhorse-type optical cryogenic system. The excitation laser beam at 30-mW power was focused to a spot of about 2 mm in diameter resulting in the excitation power density of about 1 W/cm².

Fig. 1 illustrates the emission spectra of a ZnO layer with electron concentration $9 \times 10^{19} \text{ cm}^{-3}$ excited by 351.1 nm (a) and 363.8 nm (b) laser lines measured at 10 K (solid line) and 300 K (dashed line). The spectra excited by 351.1 nm laser line consist of resonant Raman scattering lines superimposed on a broad asymmetric PL band with the maximum at 3.355 eV at 10 K and 3.265 eV at 300 K. The emission excited by 363.8 nm laser line is dominated by RRS at both the temperatures.

The large full width at half maximum (FWHM) of the luminescence band (80 meV at 10 K and 130 meV at 300K) along with its broadening towards the Stokes part of the emission is a clear indicative of the participation of an impurity band in the electronic transitions responsible for this near band edge luminescence. The formation of an impurity band at doping levels higher than 10^{20} cm^{-3} is highly probable. Taking into account the high electron concentration of $9 \times 10^{19} \text{ cm}^{-3}$ and a possible partial compensation effect one should also consider the possibility of merging of the impurity and conduction bands. As concerned the origin of the impurity band, taking into account the deviation from stoichiometry towards the oxygen deficiency assured by the technology and confirmed by the energy dispersive X-ray analysis of the layers, one can suggest its connection with intrinsic defects related to the oxygen deficiency. Oxygen vacancy and zinc interstitial are the most probable donor-type intrinsic defects, since their formation enthalpy is low and they are abundant in Zn-rich conditions as shown recently [10]. Oxygen vacancy is a deep donor, while zinc interstitial is a shallow donor [10]. Thus, one can suggest that the luminescence band involved originates from electronic transitions between an impurity band associated with Zn_i defects and the valence band. The electronic states of this impurity band seem to mediate the resonant Raman scattering observed in our ZnO layers.

Resonant Raman scattering from solids can be observed if the energy of the incoming or scattered photons matches real electronic states in the material. This results from the denominator in the Raman scattering cross section tending to zero. One refers to incoming and outgoing resonance (see, e.g., [11]). Multiphonon scattering processes were previously reported for single crystalline bulk ZnO [12], and recently for ZnO films [13] and ZnO nanowires [14]. In all these cases the samples were excited by the 325 nm line of a He-Cd laser. The energy of this line is about 440 meV higher than the band gap of ZnO. It means that there is a case of incoming resonance, where the laser line is in resonance with an intrinsic interband electronic transition. Recently, we have investigated the outgoing excitonic resonant Raman scattering in non-doped ZnO layers excited by the 351.1 nm laser line [15]. In highly conductive ZnO layers excited by the 351.1 and 363.8 nm laser lines most probably we deal also with the outgoing resonant Raman scattering but the energy of the outgoing photons in this case is in resonance with the electronic transitions from the impurity band responsible for the near band gap luminescence to the valence band.

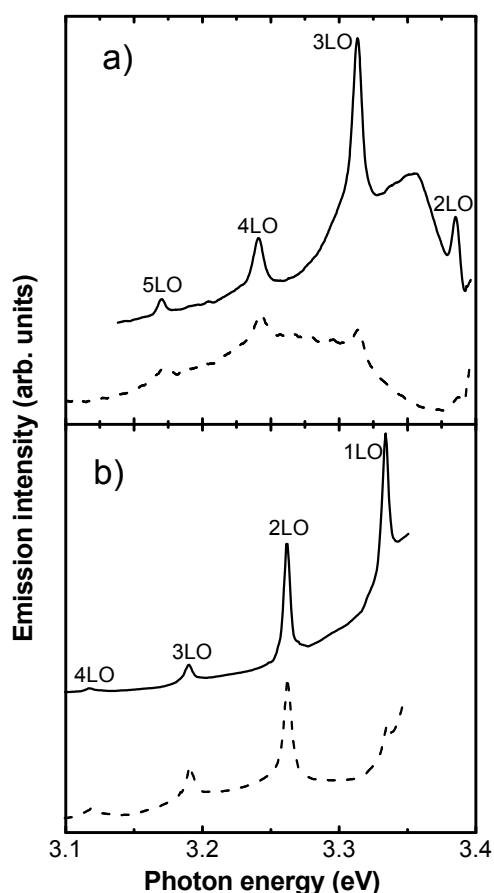


Fig. 1 Emission spectra from ZnO layer excited by 351.1 nm (a) and 363.8 nm (b) laser lines measured at 10 K (solid line) and 300 K (dashed line)

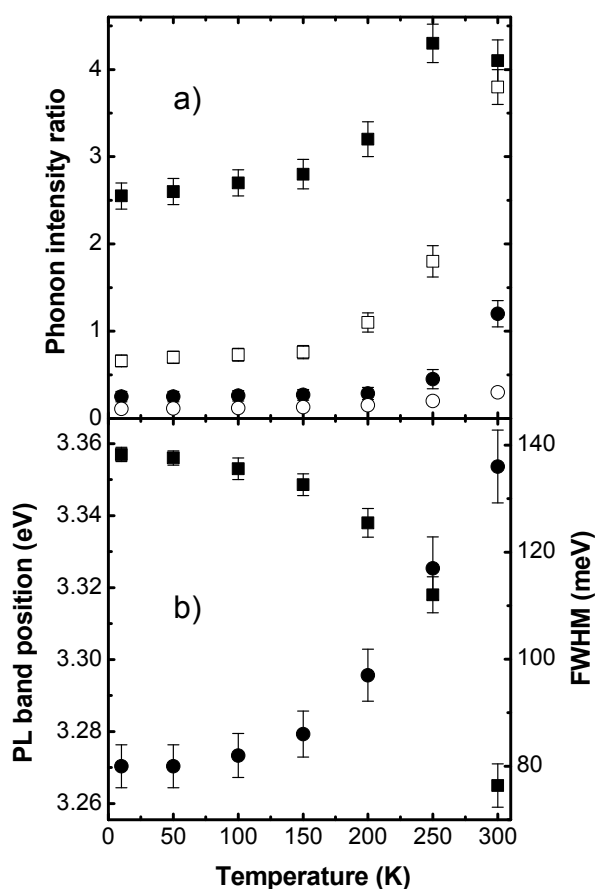


Fig. 2 Temperature dependence of RRS (a) and PL (b) for ZnO layer excited by 351.1 nm (full symbols) and 363.8 nm (open symbols) laser lines. In section (a) full squares stand for the intensity ratio (I_{3LO}/I_{2LO}), full circles correspond to I_{4LO}/I_{3LO} ratio, open squares stand for I_{2LO}/I_{1LO} , and open circles correspond to I_{3LO}/I_{2LO} . In section (b) squares stand for the PL band position (lefthand axis), and circles correspond to FWHM (righthand axis).

Fig. 2 presents the temperature dependence of the intensity ratio of phonon lines along with the temperature dependence of the position and the FWHM of the luminescence band. One can see that with increasing temperature the PL band shifts towards lower energies and broadens. At the same time, the temperature increase leads to the redistribution in the intensity of lines in the RRS in favour of the lines where the energy better matches the position of the luminescence band at the respective temperature. At low temperature, the position of the PL band is more appropriate to the energy of photons scattered by 3LO phonons when excited by the 351.1 nm laser line, and to the energy of photons scattered by 1LO phonon when excited by the 363.8 nm laser line. One can observe from Fig. 1 that the respective RRS lines are more intensive at low temperature. With the temperature increase, the PL band shifts towards the position of the 4LO RRS line under the 351.1 nm laser line

excitation, and towards the position of the 2LO RRS line under the 363.8 nm laser line excitation. The results presented in Fig. 2a clearly demonstrate the redistribution in favour of those RRS lines with increasing temperature. At room temperature the position of the 2LO RRS line under the 363.8 nm laser line excitation coincides exactly with the maximum of the PL band at 300 K, which results in a predominant income from 2LO scattering as illustrated by the dashed curve in Fig. 1b.

In conclusion, the results of this study demonstrate the relation between the outgoing multiphonon RRS and the impurity band responsible for the near band gap luminescence in highly conductive ZnO layers.

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