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Size dependent electron–phonon coupling in N, Li, In, Ga, F and Ag doped ZnO thin films

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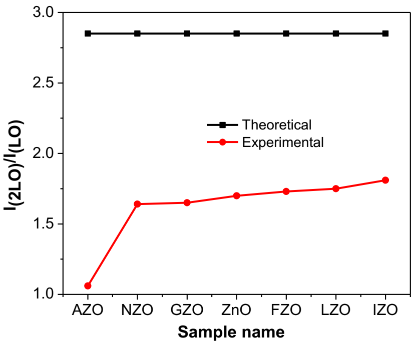
HIGHLIGHTS

- ▶ Raman spectra of N, Li, In, Ga, F and Ag doped ZnO thin films.
- ▶ Second-order Raman features are discussed in the light of DFT calculations.
- ▶ A visible line-shape asymmetry is observed for the E_2^{high} mode.
- ▶ Size dependent electron and phonon coupling strength.

GRAPHICAL ABSTRACT



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ABSTRACT

Polarized micro-Raman measurements are performed to study the phonon modes of N, Li, In, Ga, F and Ag doped ZnO thin films, grown by spray pyrolysis on corning glass substrates. The E_2^{high} mode displays a visible asymmetric line shape. The size and dopant dependence onto coupling strength between electron and LO phonon is experimentally estimated.

Introduction

The Wurtzite-type ZnO and its compounds are interesting materials for potential applications in transparent electronics and UV optoelectronic devices. Good understanding of the vibrational properties of this material is essential to recognize transport properties and phonon interaction with free carriers, because it has huge impact on optoelectronic device performance. Coupling between electron and phonon is a significant issue in semiconductor materials because it has significant influence on the optical and electrical properties of semiconductors, such as the energy relaxation rate of excited carriers and phonon replicas of excitons. Displacement of the partially ionic nuclei is accompanied by a radial electric field enlarging over various unit cells and potential of the displacement is proportional to the amplitude of phonon. This electric field interacts coulombically with the exciton and strength of exciton–phonon coupling can be enhanced when wavelength of the phonon vibration is comparable to spatial extent of the exciton [1–4]. So far, development in material science made it possible to prepare nanostructured semiconductor that occupy volumes comparable to size of the bulk exciton. Such quantum confined electronic systems should vary strongly from their bulk counterpart in their optical and electronic properties. Therefore, an efficient study of the size dependence of the electron–phonon coupling

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strength is of meticulous attention for understanding the fundamental physics and application to functional devices.

However, there are few efforts to study the electron–phonon coupling by Raman scattering measurements, which in principle can probe the electron–phonon coupling strength directly [5,6]. On the other hand, the emission properties of ZnO are found to be very sensitive to the structural quality of the films though the origin and mechanism of the emission properties are still a matter of controversy. Moreover, the ZnO films are usually deposited on lattice-mismatched substrates such as sapphire, silicon, etc. showing stress in the lattice [7]. The analysis of Raman scattering results is very difficult because shifting of the phonon due to stress. To avoid this problem, we focused on preparation of nanostructured ZnO thin films by spray pyrolysis technique. Recent research interest is focused on p-type ZnO, because reproducibility of p-type doping is a great challenge. In this work, we present a study of the first- and second order Raman spectra of N, Li, In, Ga, F and Ag doped ZnO thin films. Second-order Raman features are discussed in the light of recently available DFT calculations of phonon DOS. A visible line-shape asymmetry is observed for the E_2^{high} mode, which can be explained by the features of the two-phonon DOS around the E_2^{high} frequency. The size and dopant dependence of the coupling strength between electron and longitudinal optical (LO) phonon is experimentally estimated.

Experimental

All thin films were prepared by spray pyrolysis technique onto corning glass substrates. To deposit N, Li, In, Ga, F and Ag doped ZnO thin films, zinc acetate and *N*,*N*- Dimethylformamide, Lithium nitrate, Indium trichloride, Gallium nitrate, Ammonium fluoride and Silver nitrate were used as initial ingredients, respectively. The typical film thickness lies between 115–300 nm. The physicochemical properties of deposited thin films were reported elsewhere [8–12]. The typical dopant concentration of the N, Li, In, Ga, F and Ag doped thin films was 10, 1, 3, 2, 15 and 3 at.%, respectively. Raman-scattering experiments were performed in air at room temperature with micro Raman system from Jobin Yvon Horibra LABRAM-HR visible within 200–1400 cm^{-1}. The Raman spectra were excited with the Argon 488 nm laser source for different catalyst. The 600 and 1800 lines/mm gratings – Detector: CCD detector were used. The spectra were recorded in the x(zy)x' backscattering configuration. The letters before and after the parentheses show the direction of an incident and scattered light, while the letters within the parentheses show their polarization [13].

Results and discussion

Wurtzite-type ZnO belongs to the space group C^4_{6v} with two formula units in the primitive cell. The zone-center optical phonons can be classified according to the following irreducible representations,

$$\Gamma_{opt} = A_1 + E_1 + 2B_1 + 2E_2 \tag{1}$$

Both A_1 and E_1 modes are polar and split into transverse (TO) and longitudinal optical (LO) phonons, all being Raman and infrared active. The two non-polar E_2 modes ($E_2^{(1)}$, $E_2^{(2)}$) are Raman active only and B_1 modes are infrared and Raman inactive (silent modes). Raman scattering experiments are performed at room temperature in quasi-backscattering geometry with parallel polarized incident light. Fig. 1 shows Raman spectra in the x(yy)x' scattering configuration of pure, N, Li, In, Ga, F and Ag doped ZnO thin films. We used the phonon dispersion calculated by DFT [14] and the symmetry selection rules for two-phonon Raman scattering [15] to serve the detection of the second-order features. The results as well as a comparison with the previous works are listed in Table 1 showing good agreement between observed and calculated values of modes. The peaks from 90–540 cm^{-1} are clearly observed in the low wavenumber region having acoustic overtones, 540–820 cm^{-1} are found in intermediate-frequency region having optical and acoustic phonon combinations and 820–1200 cm^{-1} observed in high-frequency region with optical overtones and combinations. No any other higher order peaks are observed at the region over 1200 cm^{-1}.

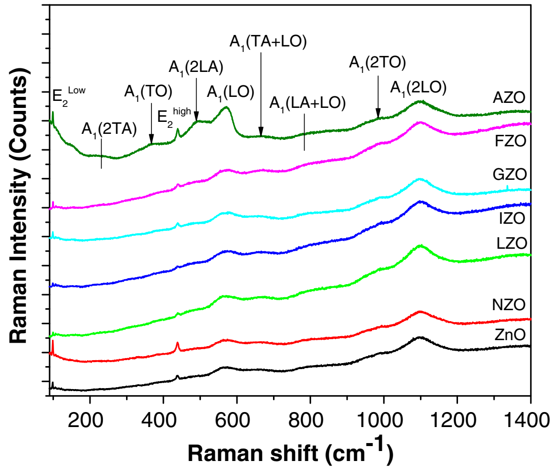

Fig. 1. Polarized micro-Raman spectra in the x(yy)x′ scattering configuration for pure, N, Li, In, Ga, F and Ag doped ZnO thin films.

The most prominent second-order features occur in the high-frequency region and correspond to LO overtones and combinations involving LO modes. The broad, intense peak at 1098 cm^{-1} contains contributions of $2A_1$(LO) and $2E_1$(LO) modes at the H, K points of the Brillouin zone. The weak mode at about ≈1160 cm^{-1} is attributed to $2A_1$(LO), $2E_1$(LO), 2LO at Γ; A–L–M point. The mode in the low-frequency region is observed at 332 cm^{-1} assigned to transverse acoustic overtone scattering at *M* [16]. Optical phonon mode observed at ≈572 cm^{-1} is assigned to the A_1(LO) and which shows the presence of resonance of exciting phonon energy with that of electronic interband transition within the ZnO lattice. The ≈214–239 cm^{-1} peaks could also have a significant contribution of 2TA scattering at the *H* point. TA + LO combinations give rise to the doublet observed at 660–668 cm^{-1}. The band at 478–497 cm^{-1} is assigned to modes highly localized near the grain boundaries because of the reason that they are located in the spectral region where interface and surface phonon modes are expected [17]. It exhibits A_1 symmetry and assigned to LA overtones along M–K, where phonon dispersion is less intense and hence the DOS is very high. The mode observed at ≈802 cm^{-1} assigned to LO + LA combinations with A_1 symmetry at the L and M points. The E_2^{low} and E_2^{high} peak positions shift with low wave number by 2 cm^{-1}, respectively due to dopant incorporation. Variation of the E_2^{low} phonon mode as a function of dopant is considered to explain with three possible reasons. First one is the mass effect due to the difference in the mass of dopant and host atoms, second one is the size effect due to the difference in ionic radius of dopant and host atoms and third one is the variation in force-constant or bond strength due to the difference in chemical states of dopant and host atoms [18]. Due to dopant incorporation intrinsic lattice defects are related to local vibrational modes. Because of the large differences in mass of dopant N, Li, In, Ga, F and Ag, we expect that the shifting of phonons discussed are due to intrinsic host lattice defects, which either become activated as vibrating complexes or their concentration increases upon dopant incorporation. The intensities of all observed vibrational modes decrease and their line shapes become asymmetric and some