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Effect of temperature on Raman scattering in hexagonal ZnMgO for optoelectronic applications

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ABSTRACT

We have carried out a detailed investigation of temperature-dependent micro-Raman scattering on hexagonal ZnMgO films with different Mg compositions (0–0.323). The phonon frequencies downshift and linewidths broadening of A_1 [longitudinal optical (LO)] and E_1(LO) modes can be well explained by a model involving the contributions of thermal expansion, lattice-mismatch-induced strain, and anharmonic phonon processes. We have elucidated the variation with Mg composition of the contribution of the three- and four-phonon processes in the anharmonic effect. The present work establishes an experimental base for the micro-Raman technique to monitor the local temperature during the ZnMgO-based device operation with a submicrometer spatial resolution.

1. Introduction

Wurtzite ZnO-based materials and related heterostructures have attracted a great deal of attention for blue lasers, ultraviolet (UV) light-emitting diodes, and UV photodetectors [1] due to their superior properties of direct wide bandgaps and large exciton binding energies which give rise to excitonic emission up to room temperature [2]. GaN-based materials are well known for the tendency of luminescence efficiency to drop dramatically with decreasing wavelength [3]. However, higher luminescence efficiency can still be achieved for higher Mg composition of ZnMgO alloys [4], which indicates that ZnMgO has great potential for use in UV region optoelectronic devices. Most of the research efforts to date have concentrated on the growth and study of ZnMgO epitaxial films, heterostructures, and quantum wells, which have been mainly prepared by molecular beam epitaxy [1,4], metal-organic epitaxial methods [5], and pulsed laser deposition (PLD) [6,7].

Efficient electron-hole recombination in ZnMgO/ZnO heterostructures has been recently realized, and the exploitation of their UV device application is the focus of current optoelectronics [4]. For high-power ZnMgO-based light emission applications, it is essential to monitor and eliminate the facet degradation, which is triggered by strong facet surface heating due to any possible nonradiative carrier recombination [8]. Raman scattering, as a fast, nondestructive, and contactless technique, is highly sensitive to the lattice temperature which allows us to use Raman spectroscopy as a temperature probe [9]. Temperature dependence of E_2 phonon modes has been employed to determine the local temperature of GaN diodes as a function of the operating voltage [10]. Moreover, since the size of the recording laser beam spot is determined by the laser wavelength and the numerical aperture of the objective lens, the availability of Raman microprobes opens the possibility of using Raman scattering as a local temperature assessment of power devices under operation with submicrometer spatial resolution.

In this paper, we have presented a comprehensive micro-Raman investigation of temperature- dependent Raman spectra of A_1 [longitudinal optical (LO)] and E_1(LO) modes in hexagonal ZnMgO films with different Mg compositions (0–0.323) in the temperature range from 83 to 578 K. In combination with detailed theoretical modellings for the frequencies downshift and linewidths broadening, we have clearly illustrated the temperature effect on the phonon frequency and linewidth, which establishes

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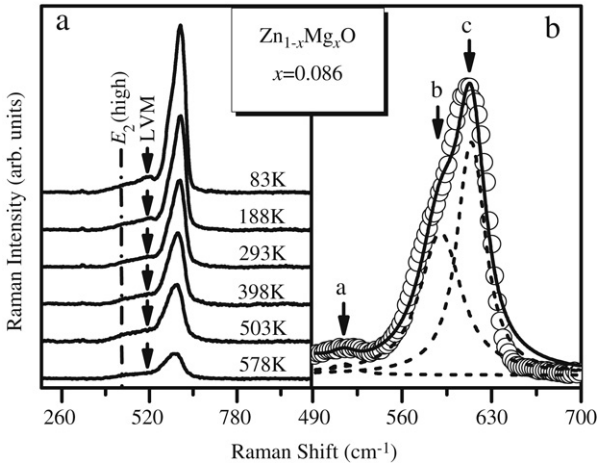

Fig. 1. (a) Temperature-dependent first-order micro-Raman spectra of $Zn_{0.914}Mg_{0.086}O$ and (b) Raman spectrum from $Zn_{0.914}Mg_{0.086}O$ at 83 K, where the solid curve fits results using three Lorentz peaks (dashed curves) with a: Mg-related LVM, b: A_1(LO), and c:E_1(LO).

an experimental base for monitoring the local temperature during the ZnMgO-based device operation.

2. Experiments

The studied $Zn_{1-x}Mg_xO$ thin films were deposited on (0001) α-Al_2O_3 substrates by PLD system employing a plasma oxygen or gaseous oxygen source at the temperature of 600 °C. During the deposition, the O plasma source was introduced by a plasma generator on the working voltage of 400 V and the current of 35 mA. Ceramic ZnMgO targets were ablated by a KrF excimer laser (Lambda Physik COMpex, wavelength of 248 nm, energy of 200 mJ/pulse, and repetition rate of 5 Hz). The crystallographic orientation was accessed by sharp and exclusive (0002) and (0004) x-ray diffraction peaks. The Mg composition was confirmed by x-ray photoelectron spectroscopy measurements (Quantum 2000). Temperature-dependent micro-Raman scattering spectra were recorded in a backscattering geometry of $z(x,-)\bar{z}$ configuration using a Jobin Yvon LabRAM HR 800UV system under the 325 nm line of a He–Cd laser. The employment of a 40 × optical microscopy objective with a numerical aperture of 0.5 will yield a laser spot size of ~0.8 μm.

3. Results and discussion

Fig. 1(a) presents the typical temperature-dependent first-order micro-Raman spectra of $Zn_{0.914}Mg_{0.086}O$. It is clear that the dominant peak can be attributed to the LO phonon mode, which shifts to high frequency and narrows with the decrease of temperature, accompanying the E_2 (high) mode [7] (dash-dotted curve) and the gradual appearance of an additional phonon mode centered at ~515 cm^{-1} (marked as arrows). In order to identify each part of the contribution, we have fitted the observed Raman spectra with Lorentz peaks. Fig. 1(b) shows the detailed analysis of the Raman spectrum for $Zn_{0.914}Mg_{0.086}O$ at 83 K (circles) with three peaks a, b, and c at about 515, 590, and 614 cm^{-1}, respectively. From the peak positions, we can assign peak a to the mixed mode of the ZnMgO, which originates from the Mg-related local vibrational mode (LVM) in ZnO [11], and peaks b and c to the A_1(LO)- and E_1(LO)-phonon modes of ZnMgO [12]. The above Lorentz fitting processes also help us obtain the detailed temperature and Mg-composition dependences of the phonon frequency and linewidth, and in the following we concentrate on the phonon characteristics of the A_1(LO) and E_1(LO) modes in the $Zn_{1-x}Mg_xO$ alloy.

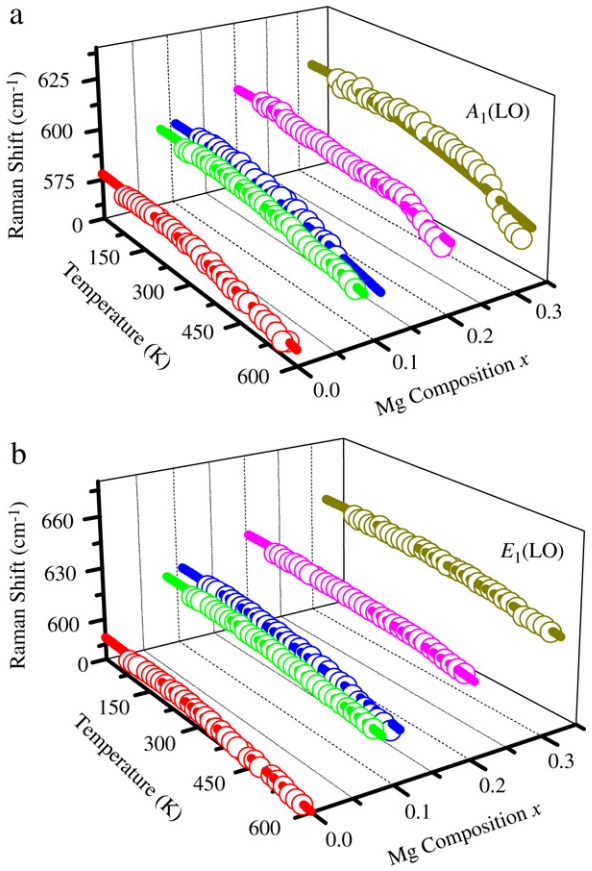

Fig. 2. Temperature-dependent Raman frequency of the (a) A_1(LO) and (b) E_1(LO) modes in ZnMgO with different Mg compositions. The solid curves are the theoretical calculation results with Eqs. (1) and (2).

Fig. 2(a) and 2(b) illustrate the frequencies of the A_1 (LO) and E_1(LO) modes with temperature. The downshift of the phonon frequency with the increase in temperature can be described by the perturbation model in which the frequency shift is mainly due to the effects of the thermal expansion, lattice-mismatch-induced strain, and the anharmonic coupling to other phonons [9,10]. The Raman frequency can be expressed as a function of the temperature as:

$$\omega(T) = \omega_0(T) + \Delta\omega_e(T) + \Delta\omega_s(T) + \Delta\omega_d(T) \quad (1)$$

with ω_0 the harmonic frequency of the optical mode, $\Delta\omega_e(T)$ the contribution of thermal expansion or volume change, $\Delta\omega_s(T)$ the lattice and thermal mismatch between the ZnMgO thin films and sapphire substrate, and $\Delta\omega_d(T)$ the one due to the anharmonic coupling to phonons of other branches. The term $\Delta\omega_e(T)$ can be written as $\Delta\omega_e(T) = -\omega_0\gamma\int_0^T[\alpha_c(T') + 2\alpha_a(T')]dT'$, where γ is the mode Grüneisen parameter [13], α_c and α_a are the temperature-dependent linear thermal expansion coefficients parallel and perpendicular to the c axis, respectively [14]. The strain-induced term $\Delta\omega_s(T)$ can be given by $\Delta\omega_s(T) = [2a - (2c_{13}/C_{33})b]\varepsilon(T)$, with $\varepsilon(T)$ a temperature dependence of in-plane strain for the different thermal expansion coefficients between thin films and substrates [15]. The phonon deformation potentials a and b are supposed to be the same as those of E_2 (high) in ZnO [16] since those of A_1(LO) and E_1(LO) are not available. The elastic constants C_{13} and C_{33} of ZnO are taken from Ref. [17].

Taking into account cubic and quartic terms in the anharmonic Hamiltonian, we have the term $\Delta\omega_d(T)$ as [9,10,15]:

$$\Delta\omega_d(T) = M_1[1 + n(T,\omega_1) + n(T,\omega_2)] + M_2[1 + 3n(T,\omega_0/3) + 3n^2(T,\omega_0/3)] \quad (2)$$