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Abstract
ZnO layers doped simultaneously with Ga and N (codoping), and magnetic elements (V, Co) were characterized by Raman scattering to study their structural stability. Five impurity modes were observed in range 200–900 cm^{-1} in the doped samples, and showed characteristic variation with the doping level. It is shown that these modes can be used as a good measure of lattice defects induced by doping. The Raman spectra showed that the magnetic elements were incorporated up to 5 mol% without serious deterioration in crystallinity.

1. Introduction

ZnO doped with magnetic impurities is a highly promising candidate for a diluted magnetic semiconductor (DMS) showing ferromagnetism at above room temperature [1, 2]. To date, however, both positive [3, 4] and negative experimental results [5, 6] have appeared, suggesting that the sample performance is delicately dependent on the growth process, so careful inspection of the structural properties in each sample is indispensable for leading to a future consensus.

It has been predicted for some magnetic impurities that p-type doping is a necessary step to achieve room temperature ferromagnetism [1]. From this viewpoint, we investigated here by Raman scattering structural properties of ZnO layers codoped with Ga and N. This codoping technique was proposed to incorporate high concentration of acceptors in ZnO [7], and p-type conductivity was actually demonstrated using this technique [8]. The Raman spectra are compared with the results on Co- and V-doped samples. Characteristic impurity modes are observed in both cases, suggesting common structural defects induced by the doping process.

2. Experiment

The ZnO layers were grown by pulsed laser deposition (PLD) in oxygen atmosphere on glass (Corning 7059) for the Ga + N codoped samples, and on sapphire $(11\bar{2}0)$ for the V- and
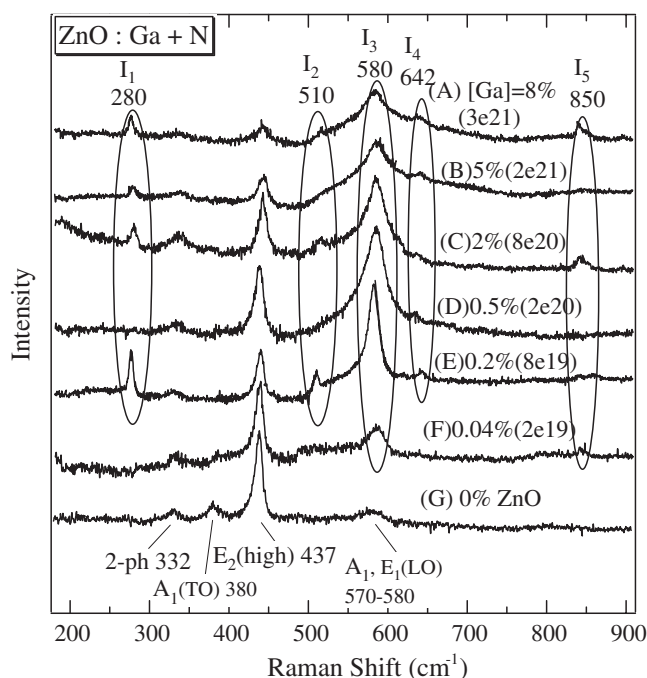
Figure 1. Raman spectra for the Ga + N codoped ZnO samples. The Ga concentration is denoted by mol% and density (3e21 means 3×10^{21} cm^{-3}).

Co-doped samples as described in detail elsewhere [9, 10]. The thickness was 100–300 nm. Nitrogen was supplied in the codoped samples through an RF radical source using N_2O. The dopant concentration was evaluated by secondary ion mass spectrometry (SIMS). The Raman scattering was observed by a confocal microscope using an Ar laser at 514.5 nm and a double monochromator of focal length 85 cm.

3. Results and discussion

Figure 1 shows the Raman spectra for the codoped samples. ZnO crystal has C_{6v} symmetry and gives six Raman-active phonon modes in the first-order spectrum at 101, 381, 407, 437, 574 and 583 cm^{-1} for the E_2 (low), A_1 (TO), E_1 (TO), E_2 (high), A_1 (LO) and E_1 (LO) mode, respectively [11]. A unique feature of the ZnO spectrum is that its LO signal is weak [12], while its two-phonon signal is relatively strong [13]. The bottom trace (for the undoped sample G) shows ZnO signals at 332, 380, 437 cm^{-1} and at 570–580 cm^{-1}, corresponding to a second-order phonon signal, and first-order phonon signals of A_1 (TO), E_2 (high), and LO, respectively. Raman selection rules indicate that the sample is polycrystalline in the sense that it is mainly *c*-axis oriented (normal to the surface), but contains small domains with different orientations. The Ga content increases from bottom to top as denoted by each trace (here 1 mol% = 4×10^{20} cm^{-3}). It is easily observed that five impurity modes appear in the doped samples at 280, 510, 580, 642, and 850 cm^{-1} (I_1–I_5). The first-order phonons, E_2 (high) and A_1 (TO), clearly weaken with the increase in Ga content. These impurity modes are classified at least to three groups by the different variations with the Ga content: first, a major signal, I_3, grows in peak height from 0.04 to 0.2%, then slightly broadens from 0.5 to 2%, then finally severely broadens at 5–8%. The modes I_1, I_2 and I_4 belong to the second group; they are always sharp, have constant relative intensities, and can be observed in relatively lightly doped sample such as E. The mode I_5 belongs to the third group, which appear in relatively heavily doped samples such as A–C.
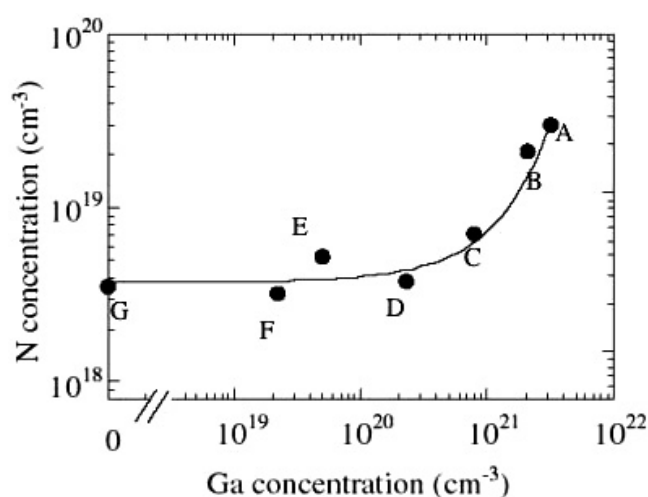
Figure 2. N and Ga concentrations evaluated by SIMS.

SIMS revealed that the N concentration increased nonlinearly with the Ga concentration as shown in figure 2, where the labels A–G correspond to the samples in figure 1. The N concentration begins to increase at $[Ga] > \sim 2 \times 10^{20}$ cm^{-3} (0.5%), then rises rapidly at $[Ga] > \sim 8 \times 10^{20}$ cm^{-3} (2%). Clearly, this variation is strongly correlated with the broadening of the main impurity peak I_3. Therefore, this broadening may correspond to the formation of complex centres with N or related defects. Kaschner *et al* [14] first observed the modes I_1 to I_5 in ZnO layers doped *only* with N ($<1.3 \times 10^{19}$ cm^{-3}). The mode intensities grew linearly with the N content, thus Kaschner *et al* assigned them to local vibrational modes (LVM) of N. Later, however, Bundesmann *et al* [15] observed these modes in ZnO layers doped with Fe, Sb and Al, but intentionally grown *without* N, and attributed them to host lattice defects. Our results suggest that the impurity modes are not LVM of N, because their intensities are uncorrelated with the N concentration. (The broadening of I_3 is correlated, though.) Figure 3 shows the Raman spectra of ZnO layers doped with V (upper) and Co (lower) in 0–15%. It is seen that the impurity modes I_1–I_5 in figure 1 appear in the doped samples. Since N is not included in the samples and the impurity modes appear for both dopants, the impurity modes are considered to derive from host lattice defects.

Figure 3 shows furthermore that sample M (doped with 5% Co) keeps better crystallinity than sample J (doped with 5% V), as evidenced by the sharp E_2-phonon peak. Thus, Co is more miscible than V. For higher Co concentrations such as 15% (sample L), the wurtzite crystalline structure is still retained, but the spectrum is overlaid with broad peaks extending from 400 to 700 cm^{-1}, probably indicating Co oxide precipitates. In the case of V doping, the wurtzite crystalline structure is retained up to 10% (sample I). However, new signals, probably due to some precipitates, appear at 650–850 cm^{-1}. At 15% of V concentration (sample H), the spectrum is completely overwhelmed by the secondary phase signals.

4. Conclusion

ZnO layers codoped with Ga and N, and those doped with magnetic impurities (Co and V) were characterized by Raman scattering. Five impurity modes were commonly observed in the range 200–900 cm^{-1}, showing that they derived essentially from host lattice defects induced by impurity doping. These modes were classified to about three groups corresponding to different origins for the defects. A major impurity signal at 580 cm^{-1} showed characteristic broadening
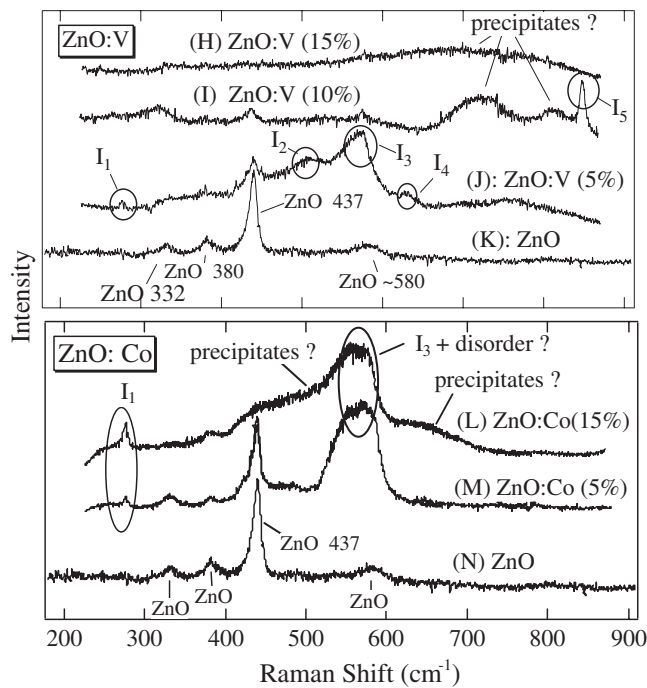
Figure 3. Raman spectra for the V-(upper) and Co-doped (lower) ZnO samples.

at high N concentrations. This suggests the formation of complex defects including N, or related defects. The magnetic elements were incorporated up to 5 mol% ($=2 \times 10^{21}$ cm^{-3}) without serious deterioration in crystallinity.

Acknowledgment

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