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Strain property studies of GaN:Mg films grown by MOCVD

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Abstract. The influence of Mg doping on structural and strain properties in GaN layers grown on sapphire substrates by metalorganic chemical vapor deposition was studied by means of high resolution X-ray diffraction and Raman scattering. The results showed that the disorder of GaN films aggravated and the quality reduced as Mg doping rate increasing. However, according to the theoretic calculation, the compressive stress determined by the Raman shift of the E2 mode was not due to the substitution of Mg atoms for Ga. Furthermore, the SEM measurements indicated that some Mg atoms substituted Ga to become acceptors, while most of them existed as Mg interstitials(Mgi) and aggregated at defects and dislocation, hence a great deal of cracks are introduced during decreasing temperature process for inhomogeneous strain distribution.

Introduction

Wide band-gap III-V nitride semiconductors have attracted intense interests because of their tremendous applications for short wavelength optoelectronic devices[1].Rapid advancements in p-type technologies for GaN epitaxial layers have made possible the fabrication of blue and ultraviolet light-emitting diodes and of high-power laser diodes.

In this letter, we report the High-resolution X-ray diffraction(HRXRD), Raman scattering and scanning electron microscope(SEM)study of a set of GaN:Mg layers grown on Al_2O_3 substrates. We discuss the influence of Mg doping on the crystalline quality and stress state of GaN films, furthermore, the character of Mg atoms in GaN films.

Experiments

The GaN:Mg samples used in this study were grown by MOCVD at 150Torr on sapphire substrate . Trimethylgallium (TMGa) and NH_3 were used as precursors. To improve the structural properties of the film, the deposition of the GaN active epilayer on the 25nm thick GaN buffer layer grown at 540°C was done at a substrate temperature of 1040°C. After growth, the samples were annealed at 780°C for 20min in N_2 ambient. The thickness of the samples were about 2.2μm ~2.4μm. All the samples had exactly the same growth conditions except for the CP_2Mg flow rate.

Raman scattering measurements were carried out in a quasibackscattering geometry in which the incident as well as the scattered light was almost normal to the Al_2O_3 substrate surface. The spectra were excited by the 488 line of an Ar^+ laser and the average laser power was about 200mW. No analyzer was used. The Raman signal was collected and analyzed by a standard Raman system. All the Raman spectra were recorded at room temperature. The c-lattice constant was obtained in $\theta/2\theta$ scan mode of x-ray diffractometry to measure the residual strain. The full width at half maximum(FWHM) for a symmetric(0002) reflection of the GaN:Mg was also measured with double-crystal x-ray diffractometry to asses the crystalline quality of the epitaxial GaN film.

Results and Discussion

Fig.1 shows XRD pattern measured with $\theta/2\theta$ scan mode.As the Mg doping concentration increases, the 2θ position shifts to the lower angle, indicating that the c-lattice becomes longer. From the 2θ value the residual strain and stress were analyzed, where C_0 is the lattice constant along c axis for strain-free bulk (0.5185nm)[2], B is the bulk modulus (200GPa) and ν is the Poisson ratio (0.23)[3]. The biaxial stress in four samples is 0.637GPa, 0.671GPa, 0.755GPa and 0.855GPa respectively. So with the Mg doping concentration increasing, the

$$\varepsilon = \frac{c - c_0}{c_0}$$

$$\sigma = \varepsilon \cdot \frac{B}{\nu}$$

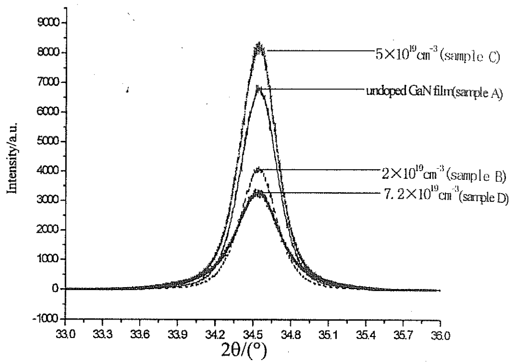


Fig.1 XRD curves for samples

compressive stress increases gradually. On the other hand, the FWHM of sample increases from 8.8 arcmin to 10.2arcmin, 10.8arcmin and 12.6arcmin(not shown in this paper), furthermore, we obtain the screw dislocation density of $2.70\times10^8/cm^2$, $3.63\times10^8/cm^2$, $4.07\times10^8/cm^2$, $5.53\times10^8/cm^2$ for samples[4]. Hence, we conclude as the flow rate of CP_2Mg increasing, the quality of film decreased gradually.

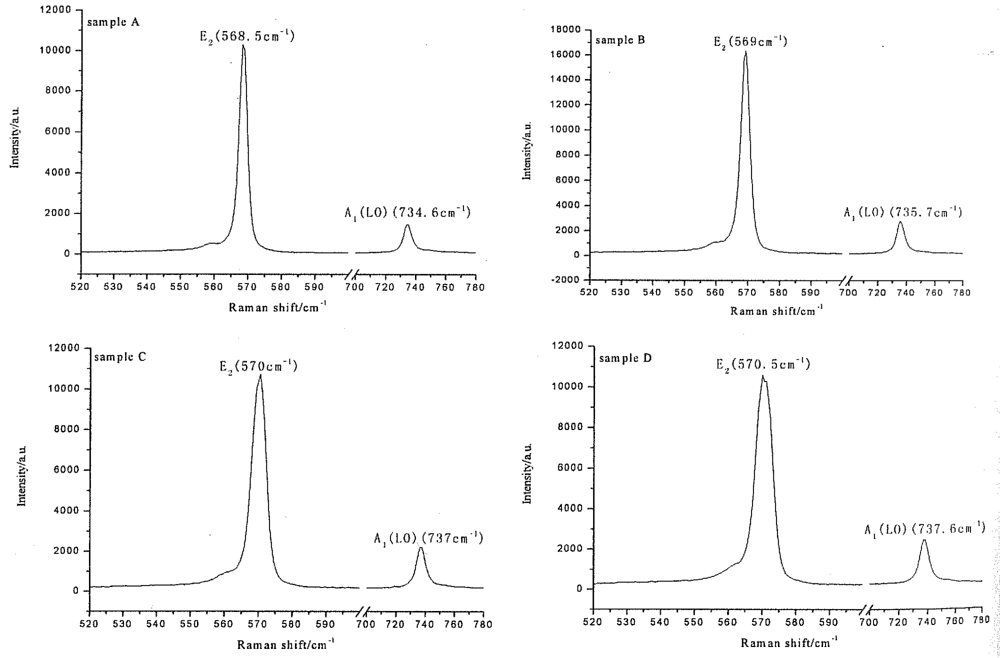


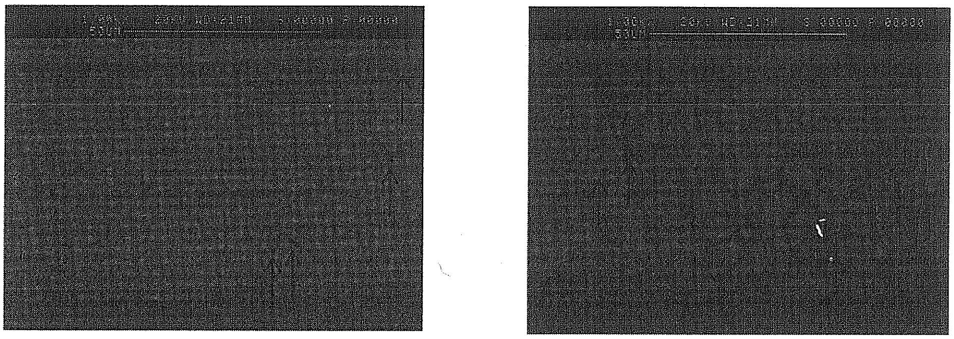
Fig.2 Raman spectrum of samples

To make further comprehension about the influence of the Mg incorporation on the structure of the GaN film, we performed the Raman scattering experiments(as shown in Fig.2). In our scattering configuration with incident and scattered light propagating along the z-axis, A_1(LO)and E_2 are allowed to participate in the scattering[5]. However, the weak shoulder on the left side of E2 was observed and defined as E_1(TO)(556cm-1), the reason for which is that the Raman spectra active was altered and the peak shifted for the changing strain when the film is decreased from growth temperature to room temperature because of the difference in lattice constants and expansion coefficients among Al_2O_3 substrate and GaN epilayer. With the concentration of Mg increasing, the shift of E2 line towards higher frequency as compared to its position for a strain-free sample(which in this case was a "bulk" GaN sample grown by HVPE with E2 mode peak at 568cm-1)[6]points out to a compressive character of the in-plain stress in the samples studied, whereas the substrate mode remains at the same energy. Since the source and carrier gas were highly purified, the change of stress was due to the incorporation of Mg. If we assume that all Mg atoms substitute Ga position, the compressive stress alteration in GaN:Mg samples can be explained by the different size of the dopant atom(r_{Mg}=0.14nm) and the replaced host atom(r_{Ga}=0.126nm),we can use the following equation to calculate the influence of this effect on the strain[7,8]

$$\varepsilon = \frac{c - c_0}{c_0} = \frac{\left[1 - \left(\frac{r_{Mg}}{r_{Ga}}\right)^3\right] \cdot C}{3N}$$

$$\sigma = \varepsilon \cdot \frac{B}{\nu}$$

Here, N is the number of lattice sites of the host matrix($8.8\times10^{22}cm^{-3}$),C the dopant concentration, c and c_0 the doped and undoped lattice constant, respectively. Therefore the compressive stress introduced by the incorporation of Mg was about 0.122GPa, where the Magnesium concentration is less than $10^{20}cm^{-3}$.This value is less than 0.218GPa, the compressive stress alteration attained from the frequency shift of the E_2 mode for sample D. Hence the change of strain is not due to the substitution of Mg for Ga. At the same time, the A_1(LO) mode appears in all sample, with full widths at half maximum of 5.92, 5.93, 6.63 and 7.06 cm^{-1}.For the hole concentration of $10^{18}cm^{-3}$,the LPP mode shifts $1cm^{-1}$ towards high frequency. Thus, within the range of hole concentration in our samples(about $10^{17}cm^{-3}$), the phonon-plasmon interactions can be neglected, which suggests that crystalline quality is responsible for shift and broadening of the A_1(LO) line.Furthermore, in SEM experiments. there exists big cracks in GaN:Mg film, between which the angles are about 60° and still lots of small irregular cracks in the local domain(as shown in Fig.3).



a b

Fig.3 Surface morphology of GaN samples(a:undoped-GaN films,b:GaN:Mg films)

Thus we consider some Mg atoms substitute for Ga to show acceptor character ,the rest atoms existing as interstitials(Mg_i) to aggregate at defects and dislocation and accordingly lots of cracks are produced in some area for inhomogeneous stress distribution as the GaN:Mg sample decreased from high temperature to room temperature.

Summary

Scanning electron microscope(SEM), Raman scattering and x-ray diffraction(XRD) measurements were taken on the GaN:Mg epilayers grown on Al2O3 substrate. In conclusion, the compressive stress determined by the Raman shift of the E_2 mode is not to the substitution of the Mg atoms for Ga. Furthermore, some Mg atoms substitute Ga to become acceptors, while most of them exist as Mg interstitials(Mgi) and aggregate at defects and dislocation, hence a great deal of cracks are introduced during decreasing temperature process for inhomogeneous strain distribution.

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