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Raman study of $In_xGa_{1-x}N$ (x = 0.32–0.9) films irradiated with Xe ions at room temperature and 773 K

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ABSTRACT

Wurtzite $In_xGa_{1-x}N$ (x = 0.32, 0.47, 0.7, 0.8, and 0.9) films grown on the GaN epilayers were irradiated with 5 MeV Xe ions to fluences of 3×10^{13} and 6×10^{13} cm^{-2} at room temperature (RT) and 773 K. Raman spectroscopy was used to study the effects on structure and electron carrier concentration in the irradiated materials. The results show that the irradiation induces lattice relaxation and reduction of the electron carrier concentration in the films, the extent of which increases and decreases, respectively, with increasing In content x in $In_xGa_{1-x}N$. Compared to RT irradiation, significant simultaneous defect recovery was observed during irradiation at 773 K up to a fluence of 3×10^{13} cm^{-2}. Further irradiation to 6×10^{13} cm^{-2} leads to delamination of the In-rich $In_xGa_{1-x}N$ films (x = 0.7, 0.8 and 0.9) from the GaN epilayers.

1. Introduction

Indium gallium nitride [$In_xGa_{1-x}N$ ($0 < x < 1$)] is an important ternary semiconductor material with bandgap from 3.4 to 0.7 eV for In content x from 0.0 to 1.0, which covers nearly the whole solar spectrum [1,2]. This favorable property is well suited for development of tandem photovoltaic devices. Ion implantation technique has been widely used for elemental doping in semiconductors, because it can precisely control the number and penetration depth of implanted ions and achieve ion doping without thermal and soluble constraints. However, it inevitably produces lattice defects during the implantation process. Extensive studies have been devoted over the past decades to ion-beam-induced radiation effects in GaN, AlN, InN and their alloys [3–15]. At present, it is known that in contrast to Al atom doping [8,9], In atom incorporation in GaN can dramatically reduce the resistance of the material to irradiation-induced damage [10–15]. For heavy ion irradiation at room temperature (RT), the critical dose needed to amorphize or break down the lattice structure of $In_xGa_{1-x}N$ decreases from ~90 to 0.05 displacements per atom (dpa) as x increases from 0.0 to 1.0 [3,10,12,15]. This enhanced irradiation-induced disordering processes, especially in high In-content $In_xGa_{1-x}N$ ($x > 0.2$), are not yet fully understood to date primarily because of the difficulties in growing high-quality large-area $In_xGa_{1-x}N$ single crystals [1]. We recently reported the structural and compositional changes in $In_xGa_{1-x}N$ ($0.32 \le x \le 1.0$) irradiated with Xe ions at RT using Rutherford backscattering spectrometry (RBS) under ion channeling conditions (RBS/C) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) [15]. The results from the study indicated that in contrast to Ga-rich $In_xGa_{1-x}N$, significant volume swelling and oxidation occurred in In-rich $In_xGa_{1-x}N$ ($x > 0.5$) after irradiation even to a very low dose of ~0.1 dpa. In order to reduce defect production rate, irradiation at elevated temperatures needs to be investigated, where simultaneous defect recovery process is expedited during ion irradiation.

Raman spectroscopy is a powerful technique that provides non-destructive characterizations of structural, optical and electrical properties of semiconductor materials. Raman peak intensity, width and position are subject to change with the irradiation-induced variation in lattice structure, stress, carrier concentration etc. Raman spectroscopy also detects local structural and chemical defects induced by irradiation. In addition, the forbidden Raman modes for a perfect lattice structure could be activated and detected after irradiation. Because of those capabilities, Raman spectroscopy has been extensively used to study radiation effects in semiconductors [16–21]. This work reports on the Raman results of $In_xGa_{1-x}N$ ($0.32 \le x \le 0.9$) films irradiated with 5 MeV Xe ions at RT and 773 K.

2. Experimental details

Wurtzite $In_xGa_{1-x}N$ films of 200–350 nm in thickness deposited on ~2 μm thick GaN epilayers were grown on c-plane sapphire

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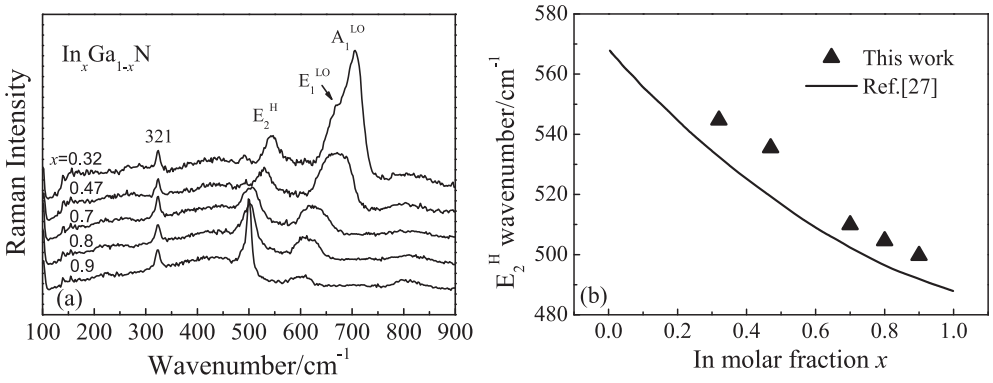

Fig. 1. (a) Raman spectra for as-grown $In_xGa_{1-x}N$ (x = 0.32–0.9) films. (b) E_2^H wavenumbers as a function of In concentration (triangles). Also included is a calculated curve for E_2^H wavenumbers of strain-free $In_xGa_{1-x}N$ from Ref. [27].

substrates by metal-organic chemical vapor deposition (MOCVD). Based on RBS measurements, the In contents x in the $In_xGa_{1-x}N$ films of this study were determined to be 0.32, 0.47, 0.7, 0.8 and 0.9 ± 0.01, respectively. All the films are of n-type without intentional doping. Ion-irradiation experiments were carried out at the 320 kV platform for multidisciplinary research with highly charged ions at the Institute of Modern Physics, Chinese Academy of Sciences. The samples were irradiated with 5 MeV $^{129}Xe^{q+}$ (q = 20, 23) ions at RT and 773 K, respectively. An annular heater around the sample holder was used during irradiation at elevated temperatures, and a moderately high temperature of 773 K was applied to prevent possible thermal decomposition of $In_xGa_{1-x}N$ [22,23]. The irradiation was conducted with the incident ion beam close to the sample surface normal (no more than 5° off the surface normal). The effects of accidental ion channeling in the disordering process, if any, are assumed to be insignificant. Uniform irradiation over an area of 12 × 15 mm^2 was achieved using a rastering system. The samples were irradiated to ion fluences of 3×10^{13} and 6×10^{13} cm^{-2} at a beam flux of ~ 1×10^{11} cm^{-2} s^{-1}, which were measured via charge integration using a transmission Faraday cup located in front of the sample. According to the SRIM 2013 [24], the Xe ion projected range in the $In_xGa_{1-x}N$/GaN samples is ~1.1 μm, which is about 3–6 times larger than the film thickness values. Thus, a great majority of the incident Xe ions penetrated the films. The average electronic and nuclear stopping powers of the Xe ions in the films are 2.4 and 1.6 keV/nm, respectively. It should be noted that the SRIM database has been found to overestimate the electronic energy powers for slow heavy ions in nitride materials [7]. The average doses over the film thickness, estimated from the SRIM full-damage cascade calculation, are ~0.07–0.1 dpa for Xe ion fluence of 3×10^{13} cm^{-2} [15].

After irradiation, the samples were characterized by micro-Raman scattering at RT using a LabRAM HR 800UV spectrometer (Horiba Jobin-Yvon) equipped with a charge-coupled device (CCD) detector (Andor Technology). 325-nm line of a Cd-He laser was used for excitation of Raman yields from the $In_xGa_{1-x}N$ films without GaN sublayer contributions. Raman spectra were recorded in backscattering geometry with the laser beam propagating along the normal direction of the sample surface. Wurtzite $In_xGa_{1-x}N$ has many vibrational, rotational, and other low-wavenumber modes in principle, including one A_1 (LO/TO), one E_1 (LO/TO), two E_2 (H and L) and two B_1 (H and L) phonon modes. LO/TO denotes the longitudinal/transverse optical vibration, and H and L denote the high- and low-wavenumber modes. Only E_2 and A_1^{LO} modes are Raman active for backscattering geometry [25]. The laser beam was focused onto a spot with a diameter ~3 μm at the sample surface. To minimize thermal effects, the laser power was reduced to ~3 mW on the sample. The Raman spectral resolution was better than 1 cm^{-1} in this study.

3. Results and discussion

3.1. As-grown $In_xGa_{1-x}N$

Fig. 1 (a) shows Raman spectra for as-grown $In_xGa_{1-x}N$ (x = 0.32–0.9) films. There is an apparent shift of peaks E_2^H and A_1^{LO} to a lower wavenumber with increasing In content x. The peak at 321 cm^{-1} has been identified as a fluorescence-induced background peak [26]. Fig. 1 (b) shows In content dependence of E_2^H wavenumbers, together with the calculated wavenumber values (solid line) for strain-free $In_xGa_{1-x}N$ that is reported in Ref. [27]. The E_2^H wavenumbers from this study are systematically higher than the reported data, suggesting that there exists compressive strain in the films of this study, which is attributed to the large lattice mismatch between GaN and InN (~11%–13%) and also a film/substrate mismatch [1]. From Fig. 1 (a), the widths of the peak E_2^H for $In_xGa_{1-x}N$ (x = 0.32, 0.47, 0.7, and 0.8) are obviously larger than that for $In_{0.9}Ga_{0.1}N$, indicating the worse crystalline quality of the $In_xGa_{1-x}N$ with x between 0.32 and 0.8, which is also ascribed to the lattice mismatch between GaN and InN [1]. The intensity of peak A_1^{LO} decreases with increasing x because of the increasing electron carrier concentration [28,29]. As the free carrier concentration increases, the influence of the LO phonon-plasmon coupling in $In_xGa_{1-x}N$ becomes stronger, which damps the LO phonons and leads to an intensity reduction of peak A_1^{LO} [30]. For $In_{0.32}Ga_{0.68}N$ with a distinct peak A_1^{LO}, a shoulder is evident on the lower-wavenumber side of the peak, which has been assigned as a disorder-activated E_1^{LO} mode [31–33]. The poor crystal quality of the $In_xGa_{1-x}N$ films breaks down the Raman selection rules. Several other forbidden Raman modes (e.g., A_1^{TO}, E_1^{TO} and B_1) are also active in the as-grown films, as discussed below.

3.2. Irradiation at RT

Fig. 2 shows Raman spectra and their fitting results (dash lines) for $In_xGa_{1-x}N$ (x = 0.32–0.9) films before and after 5 MeV Xe ion irradiations to fluences of 3×10^{13} and 6×10^{13} cm^{-2} at RT. In addition to peaks E_2^H and A_1^{LO}, the disorder-activated peaks A_1^{TO}, E_1^{TO}, B_1^H and E_1^{LO} also need to be included for the data fitting [25,31–34]. Peak A_1^{TO} may contain a contribution from the LO phonon-plasmon coupled (LPP) mode [31], but will not affect any conclusions from this study. Gaussian peaks are assumed for all the fitting components. After irradiation, the intensities of peaks A_1^{TO}, E_1^{TO}, B_1^H and E_1^{LO} relative to those of peaks E_2^H and A_1^{LO} increase gradually with increasing ion fluence, indicating an increasing level of lattice disorder in the films. It is worth noting that compared to the Ga-rich $In_xGa_{1-x}N$ (Fig. 2 (a) and (b)), peak E_2^H of the In-rich $In_xGa_{1-x}N$ shifts to a lower wavenumber after irradiation (Fig. 2 (c)–(e)). The E_2^H wavenumbers from the In-rich $In_xGa_{1-x}N$ after irradiation are found to be closer to the values of the strain-free $In_xGa_{1-x}N$