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Growth Temperature Reduction for Isoelectronic As-Doped GaN

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As-doped GaN films were grown at different temperatures by atmospheric metalorganic chemical vapor deposition. A higher electron Hall mobility, narrower line width in photoluminescence, and longer spatial correlation length of the filmes were obtainable at low growth temperatures compared to undoped GaN grown at the same temperatures as a result of isoelectronic As-doping. [DOI: 10.1143/JJAP.42.L239]

KEYWORDS: GaN, isoelectronic As-doping, Raman scattering, spatial correlation length, photoluminescence, Hall mobility

In the past few years, nitride-based materials drew public attention and were ripe for applications such as blue light-emitting diodes, blue-ultraviolet laser diodes, and high-temperature electronic devices.[1,2] Owing to the isoelectronic doping technique, the crystalline quality, electrical mobility, and luminescence emission efficiency of the majority of compound semiconductors could be improved.[3,4] Recently, different research groups have reported that In-isoelectronic doping improves the optical and electrical properties of GaN, and these positive effects were attributed to the surfactant effects.[5–8] The group-V elements, such as phosphorus (P), arsenic (As) and antimony (Sb), can also possibly be used as isoelectronic dopants for GaN to improve its optoelectronic properties. For examples, Guido *et al.* reported the increase of electron mobility[9] and the suppression of yellow luminescence[10] by As-doping, and Li *et al.*[11] found an As-related deep-level emission peak around 450–480 nm.

Because of the high bonding energy between Ga and N atoms in GaN, and the low NH_3 decomposition efficiency at a low temperature, a high growth temperature is necessary for growing high-quality GaN. Several research groups have found the optimal growth temperature for GaN to be in the range from 1000°C to 1080°C.[12–15] However, high growth temperature also induces various parasitic reactions and layer interdiffusion that cause a reduced growth rate, low dopant incorporation efficiency, and degraded device performance. In this study, we investigated the electrical and optical properties of lightly As-doped GaN grown at various temperatures from 900°C to 1050°C, and found that the growth temperature can be reduced down below 950°C without marked degradation by isoelectronic As-doping as compared with undoped GaN.

GaN:As samples were grown on sapphire (0001) by the atmospheric pressure metalorganic vapor deposition (AP-MOVPE) method using trimethylgallium (TMGa), ammonia (NH_3), and tertiarybutylarsine (TBAs) as Ga, N, and As precursors, respectively. The ratio of group-III to group-V components in the vapor phase was 3068. An about 35 nm thick GaN buffer layer was deposited at 520°C followed by 1 hr. deposition of As-doped GaN epilayer grown at a temperature range from 900°C to 1050°C in three divisions. During the GaN:As layer growth, the molar flow rates of TMGa, NH_3 and TBAs were 14, 42400, and 225 μmole/min, respectively. By secondary ion mass spectrometry measurements, the detected As/N content ratio was found to be less than 0.2%. Although we expected more As atoms to be incorporated into the GaN film at a low growth temperature, the solubility of As in our samples was still limited in the range of isoelectronic doping.

The room-temperature Hall measurement was conducted using the van der Pauw scheme with In contacts under a 5000 gauss magnetic field. For the photoluminescence (PL) experiments, we utilized a single monochromator (ARC Spectro PRO-500), a photomultiplier detector (Hamamatsu R-955), and a He–Cd laser (Kimmon IK5552R-F) operating at the 325 nm line for the above band gap excitation. The samples were kept at 18 K with a closed-cycle helium cryogenic system (APD HC-2). The Raman scattering system consisted of a double monochromator (JOBIN-YVON U1000), a multichannel photodiode array detector (PI IRY 1024G), and a mixed Ar^+/Kr^+ ion laser operating at 488 nm (Coherent Spectrum Innova-70).

The results of Hall concentration and mobility measurements for As-doped and undoped GaN are shown in Fig. 1. As the growth temperature was decreased from 1050°C to 950°C, the carrier concentration was maintained at about $8 \times 10^{18}\,\mathrm{cm}^{-3}$, and the mobility was decreased from $150\,\mathrm{cm}^2/\mathrm{V\text{-}s}$ to $30\,\mathrm{cm}^2/\mathrm{V\text{-}s}$ for undoped GaN. On the other hand, by introducing As atoms into GaN, the carrier concentration was rapidly reduced from $3 \times 10^{18}\,\mathrm{cm}^{-3}$ to $6 \times 10^{17}\,\mathrm{cm}^{-3}$ but the mobility remained almost unchanged at $135\,\mathrm{cm}^2/\mathrm{V\text{-}s}$. It is well known that a nitrogen vacancy (V_N) increases the background electron concentration in GaN. The decrease in carrier concentration may be attributed to filling of V_N sites by As atoms, because more As atoms can be incorporated into GaN at a low temperature.[16] Our results showed that such an effect was more pronounced at 950°C than at 1050°C. As the growth temperature was further decreased to 900°C, the carrier concentration still remained low but the mobility sharply dropped to $50\,\mathrm{cm}^2/\mathrm{V\text{-}s}$, even though more As atoms could be incorporated into GaN. Apparently, the sample degradation was related to the fact that more structural defects were formed at a low growth temperature, which will be addressed in detail later. These results indicate that As-isoelectronic doping in GaN can effectively decrease the background carrier concentration by compensating V_N formed at a growth temperature above 950°C. During the sample growth, there were two mechanisms competing with each other. First, the solubility of As atoms into GaN was increased as the temperature decreased, hence more V_N sites could be filled by As atoms, reducing

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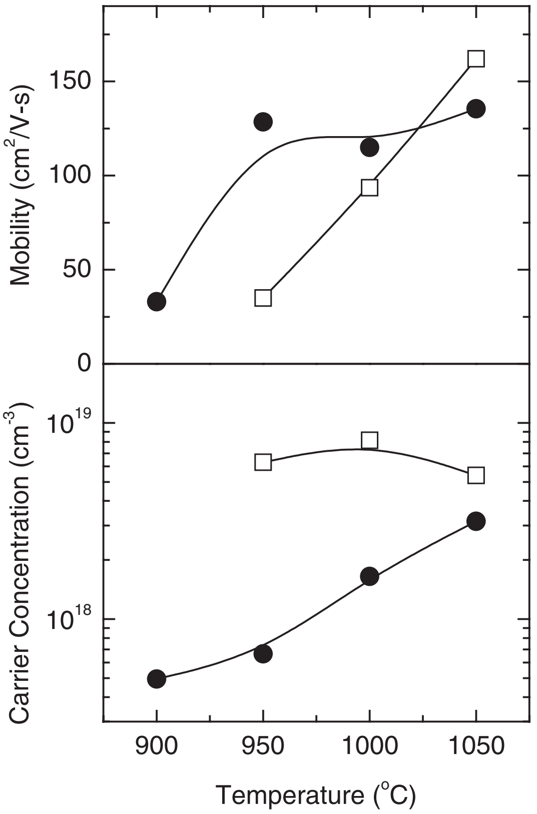

Fig. 1. Growth temperature dependence of Hall concentration and mobility for As-doped and undoped GaN. (●: As-doped GaN; □: undoped GaN.)

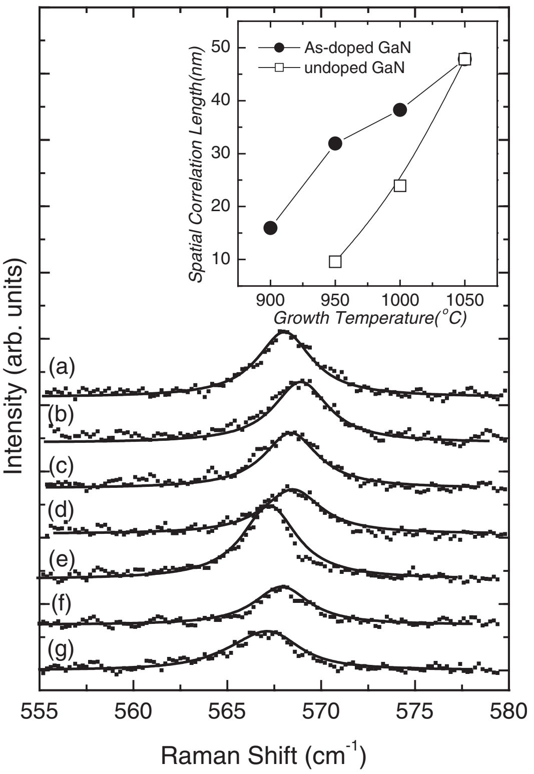

Fig. 2. (a), (b), (c), (d) are Raman spectra of GaN:As grown at 1050°C, 1000°C, 950°C and 900°C, respectively. (e), (f), (g) are those of undoped GaN grown at 1050°C, 1000°C and 950°C, respectively. The dots indicate the Raman spectra, and the solid lines, the fittings with the spatial coherence length shown in the inset. (●: As-doped GaN; □: undoped GaN.)

the point defects. Second, more structural defects could be formed at low growth temperatures, because NH_3 was decomposed less completely into N radicals. As the temperature continuously decreased to 900°C, the deterioration of sample quality due to defects was even more severe than the improvement by As-doping alone.

To further investigate the As-doping effects on the crystalline structure of GaN, we performed Raman scattering to examine its hexagonal symmetry (i.e., the E_2 mode behavior). As shown in Fig. 2, the intensity variation of the E_2 mode is within a factor of 2 and the center frequency shift is less than $2\,\mathrm{cm}^{-1}$, but its line shape is clearly asymmetric. This asymmertry was likely due to the phonon propagation being interrupted over a finite distance, which led to the relaxation of the selection rule during the scattering process, in which the phonon momentum was no longer sharply confined. To correlate the crystalline quality with the Raman spectrum, we adopted the spatial correlation model,[17] in which the Raman intensity at the frequency ω is given by a Lorentzian function presumably modified by a Gaussian distribution as follows,

$$I(\omega) \propto \int \frac{\exp\left(-\frac{q^2L^2}{4}\right)}{\{\omega - \omega(q)\}^2 + \left(\frac{\Gamma_0}{2}\right)^2} d^3q. \tag{1}$$

In eq. (1), L is the correlation length in the unit of lattice constant a, q is the wave vector expressed in the unit of $2\pi/a$, and Γ_0 is the spectral width of the Raman line of undoped GaN (typical width is $4\,\mathrm{cm}^{-1}$). The lattice constant, a, along the a-axis of GaN is 3.189 Å. The dispersion curve $\omega(q)$ for the E_2 phonon mode is assumed to be in the following analytical form.

$$\omega = A + B\cos(C\pi q). \tag{2}$$

Equation (2) has been shown to be in good agreement with empirical results along the $\Gamma - K$ (T line) axis of GaN,[18] with the parameters $A = 551\,\mathrm{cm}^{-1}$, $B = 18\,\mathrm{cm}^{-1}$, and $C = 1.45$.[19] By fitting eq. (1) to the line-shape of E_2, the correlation length was evaluated. As shown in the inset, the correlation length for As-doped GaN varied from 46 nm to 15 nm as the growth temperature decreased from 1050°C to 900°C. On the other hand, though the correlation length for undoped GaN was also 46 nm at 1050°C, it dropped rapidly to 10 nm at 950°C. The correlation length for As-doped GaN is hence longer than that for undoped GaN at different growth temperatures. Since the correlation length represents an average range of undisturbed phonon propagation without interruption by various kinds of defects, the longer correlation length reflects fewer defects in the samples. Taking into account the results of Hall measurements, it is evident that As-doping had reduced point defects to a certain extent by filling As atoms into V_N sites even at a low growth temperature.

Because the radius of As atoms is larger than that of N, the inclusion of As in the GaN lattice would induce a compressive stress, causing a higher Raman peak shift of As-doped GaN by about $1\,\mathrm{cm}^{-1}$ than that of undoped GaN. According to the relationship between the stress and strain,[20)] we estimated that the As concentration is less than $10^{16}\,\mathrm{cm}^{-3}$. On the other hand, as the growth temperature was decreased, the peak position changes were similar for both As-doped and undoped GaN. There are probably two driving forces for the peak shift. First, the more the Raman mode leans to the higher frequency, the shorter correlation length would be. Second, the crystalline grain size is smaller at a lower growth temperature, resulting in a smaller compressive stress,[21)] hence the peak position can also have a red shift.

As far as the optical property is concerned, we have also carried out PL measurements. In Fig. 3, all the samples showed a strong near band edge emission (I_2) at ~357 nm and a negligible yellow emission at 18 K, which indicated not much deep level concentration present in the samples. For all of the samples, the I_2 peak position was the same, but the line shape broadening with the decreasing growth temperature was different for As-doped and undoped GaN. As shown in the inset of Fig. 3, the full width at half maximum (FWHM) of I_2 for GaN:As slowly increased from 27 meV to 40 meV as the growth temperature decreased from 1050°C to 900°C, while that for undoped GaN rapidly increased from 33 meV to 70 meV. The FWHM of As-doped GaN was always narrower than that of undoped GaN for all the growth temperatures. This reflects that As doping had somewhat redistributed the energy levels and improved the optical quality even at low growth temperatures. In the spectra of As-doped GaN, there appeared some minor peaks around 380 nm corresponding to the donor-to-acceptor pair (DAP) emissions also seen by Jin *et al.*[10)] Theoretical calculations showed that, As atoms on the nitrogen sites in GaN are neutral isoelectronic impurities and behave as shallow acceptor centers.[22)] This means that an electrically neutral As atom is less electronegative than the host N atom to trap a hole. Such an isoelectronic center may trap a hole first and then bind to an electron through a Coulombic field which results in an isoelectronic bound excitonic emission.[11)] Because the intensity of DAP is weak, we believed that our samples were lightly As-doped in which As atoms were mostly filled into the nitrogen sites of GaN, reducing the concentration of V_N.

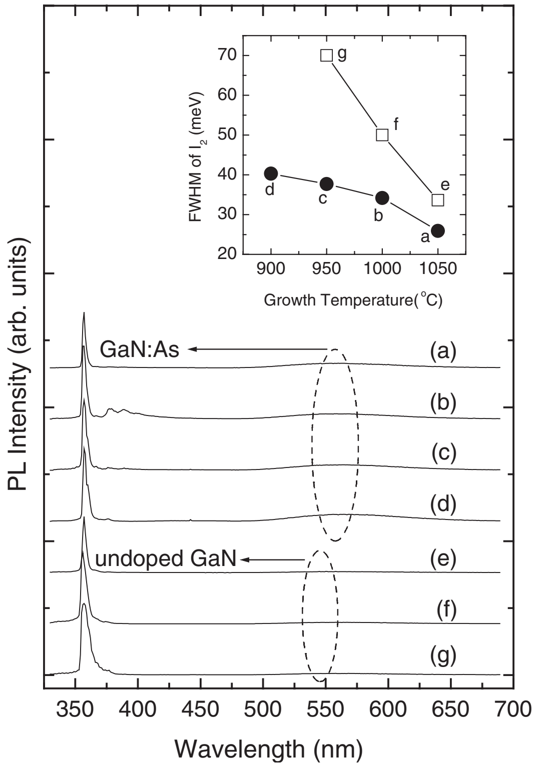

Fig. 3. (a), (b), (c), (d) are PL spectra of GaN:As grown at 1050°C, 1000°C, 950°C and 900°C, respectively. (e), (f), (g) are those of undoped GaN grown at 1050°C, 1000°C and 950°C, respectively. The spectra cover the range of YL to show their insignificance.

The growth temperature reduction of GaN by As-isoelectronic doping is studied. Without As doping, the electrical, crystalline, and optical properties of GaN were deteriorated severely at a low growth temperature. The As doping reduced the Hall concentration by an order of magnitude but the mobility remained essentially the same at growth temperatures between 950°C and 1050°C. For the crystalline structure, the As-doped GaN had a longer spatial coherence length than undoped GaN, indicating fewer defects in As-doped GaN. Moreover, the optical property in terms of the linewidth of GaN grown at a low temperature was improved by As-doping. All these results show that, by isoelectronic As-doping, we can effectively reduce the growth temperature of GaN.

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