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Epitaxial $\text{GaN}_x\text{As}_{1-x}$ layer formed by pulsed-laser irradiation of GaAs in an ambient nitrogen gas

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Abstract. We report a novel method to synthesize $\text{GaN}_x\text{As}_{1-x}$ epitaxial films. The (001) GaAs substrates were irradiated by a pulsed laser in a nitrogen atmosphere at room temperature. High-resolution x-ray diffraction indicates the formation of an epitaxial $\text{GaN}_x\text{As}_{1-x}$ layer on the substrate. The effects of the ambient pressure and the laser parameters (fluence, repetition rate and number of shots) on the incorporated N content x and film quality are studied. A threshold laser fluence must be achieved in order that N can be incorporated. The maximum extent of x obtained is about 1%.

The ternary and quaternary III–N–V alloys, such as GaNAs and GaInNAs, have been intensively studied due to their potential applications in optoelectronic devices and interesting electronic properties [1–8]. The large difference between the atomic radii and electronegativities of nitrogen and arsenic makes the incorporation of N into III–V hosts difficult. Up to now, however, epitaxial GaNAs films have been synthesized by metal–organic chemical vapour deposition (MOCVD) [2], molecular beam epitaxy (MBE) [3, 4], pulsed laser deposition [5] etc. On the other hand, direct formation of a GaNAs layer by nitriding GaAs substrate seems an attractive alternative approach. In fact, nitridation of a GaAs surface under active nitrogen species has been an interesting topic of research because it is an important process prior to the growth of high-quality zinc blende GaN [9–11]. It was reported that a disordered GaNAs phase may form at the initial stage of nitridation. This phase may partly crystallize at an appropriate nitridation temperature, as observed from the results of reflection high-energy electron diffraction [11]. However, to the best of our knowledge, there is no x-ray diffraction (XRD) study to verify whether an epitaxial GaNAs can be formed on GaAs substrate.

Pulsed-laser irradiation on materials in vacuum or an ambient gas can induce structural and chemical changes of surface layers [12–17]. The most relevant examples are nitriding the surfaces of metal (Ti) and semiconductors (Si, Ge) [14, 16], and structural reordering of ion-implanted GaAs and InP due to the laser annealing effect [13, 14, 17]. Moreover, in the latter case, it was found that during the laser beam irradiation in the presence of a gas inlet into the annealing chamber, the ambient gas atoms diffused well into the target and changed the stoichiometry and electrical parameters [17].

In this work, we present the results of high-resolution XRD measurements on GaAs(001) substrates irradiated by a

pulsed laser in nitrogen ambient at room temperature. The XRD data indicate the formation of an epitaxial $\text{GaN}_x\text{As}_{1-x}$ layer on GaAs. The influences of the growth conditions on the incorporation of nitrogen into GaAs are studied. The details of the experimental procedures are described below.

Semi-insulating (001) GaAs substrates after degreasing and rinsing were placed in a chamber, which was evacuated to a base pressure of 2×10^{-6} Torr. Then high-purity N_2 gas was introduced into the chamber and a KrF excimer laser (LEXTRA 200, Lambda Physik) operating at a wavelength of 248 nm and a pulse duration of 23 ns was directed and focused onto the GaAs substrate at an inclined angle. The irradiated area was estimated to be $3 \times 4 \text{ mm}^2$. A series of samples was synthesized under various growth conditions. The controlled parameters were the N_2 pressure (ranging from 0 to 750 Torr), the laser fluence (ranging from 0.20 to 0.84 J cm^{-2}) and the number and repetition rate of the laser shots. Samples were examined *ex situ* with a high-resolution x-ray diffractometer using $\text{Cu K}\alpha_1$ line (wavelength = $1.541 \text{ \AA}$).

Figure 1 shows the conventional (004) XRD θ - 2θ scans of GaAs irradiated under different N_2 pressures (P_{N_2}) while the other parameters were kept the same. The XRD spectrum shows only the GaAs peak when GaAs was irradiated in vacuum ($P_{\text{N}_2} = 0$ Torr). An additional peak, which corresponds to an epitaxial $\text{GaN}_x\text{As}_{1-x}$ layer with a lattice constant smaller than GaAs, appears when there is an N_2 ambient. The peak position shifts with an increase of N_2 pressure, indicating an increase of the incorporated N atoms. Another effect of increasing nitrogen pressure is to reduce the degree of surface damage. The area of GaAs substrate irradiated in vacuum becomes milky, which indicates some modifications on the surface layers. With increasing P_{N_2} , the surface changes less. For the sample prepared under $P_{\text{N}_2} = 750$ Torr, the surface damage is nearly invisible.

Although the nitrogen depth profile of the film should not be exactly homogeneous, the average N composition

Figure 1. High-resolution (004) XRD spectra of (001) GaAs substrates irradiated by a KrF excimer laser under various nitrogen pressures. The laser fluence, repetition rate and shot number, kept the same for all the samples, were 0.53 J cm^{-2} , 0.2 Hz and 50 pulses, respectively.

can still be estimated from the XRD peak position. From Bragg's law the lattice constant $a_{\perp}$ perpendicular to the (001) GaAs surface can be determined. According to the solution of Hooke's law with biaxial stress, the perpendicular lattice constant $a_{\perp}$ and the parallel lattice constant $a_{\parallel}$ are related by

$$\frac{a_{\perp} - a_f}{a_f} = -\frac{2\nu}{1 - \nu} \frac{a_{\parallel} - a_f}{a_f}, \quad (1)$$

where ν is the Poisson ratio and a_f the lattice constant of the film material in the bulk state. ν and a_f of GaN_xAs_{1-x} can be expressed as linear interpolations of those of GaAs and cubic GaN (Vegard's law). We further assume that the GaNAs film is coherently strained on GaAs ($a_{\parallel}$ is the same as the lattice constant of GaAs). Then the nitrogen composition x can be solved from equation (1). The lattice constants of GaAs and cubic GaN used are 5.654 and $4.506 \text{ \AA}$, respectively. The Poisson ratios of GaAs and cubic GaN are taken to be 0.310 and 0.366 , respectively. The determined composition x , specified as atomic percentages, is plotted as a function of P_{N_2} in figure 2. The N concentration varies quite smoothly with the N_2 pressure in the range studied.

The film thickness t can be roughly estimated by the well known Scherrer formula, which relates the full width at half maximum (FWHM) W of the XRD peak to the finiteness of the film thickness:

$$t = \frac{0.9\lambda}{2W \cos \theta_B}, \quad (2)$$

where λ is the wavelength of the x-rays, and θ_B is the Bragg angle of the film. The thicknesses thus estimated are 480 , 730 and $880 \text{ \AA}$ for the film grown under $P_{\text{N}_2} = 50$, 250 and 750 Torr , respectively. However, such an estimation does not consider the broadening of the XRD peak due to the nitrogen compositional profile and should only be viewed as an average.

Figure 2. Dependence of the average N composition x in GaN_xAs_{1-x} on the pressure of N_2 .

Figure 3. High-resolution (004) XRD spectra for samples grown with increasing laser pulses (n). The laser fluence and repetition rate were 0.53 J cm^{-2} and 0.2 Hz , respectively. The N_2 pressure was 750 Torr . The inset shows the average N composition x in GaN_xAs_{1-x} as a function of laser shot number n .

The progressive incorporation of nitrogen into GaAs was followed by studying samples synthesized with increasing laser shot number (n), as presented in figure 3. Again, the average nitrogen composition is calculated and plotted versus the shot number n , as shown in the inset of figure 3. It is seen that nitrogen concentration increases rapidly in the first few to several tens of laser pulses. After that, the evolution becomes less pronounced. It is not clear whether a saturation will be reached. The effect of increasing n on the film thickness should be similar, as observed in an earlier study on the nitridation of titanium surface by similar treatment [16].

Pulsed laser irradiation instantaneously raises the surface temperature, which makes the surface layers active to interact

Table 1. The angular separation $\Delta\theta$ between the peaks of substrate and epilayer and the FWHM of the peak of the epilayer in the XRD curves for samples prepared under various conditions.

Fluence (J cm^{-2})	Repetition rate (Hz)	P_{N_2} (Torr)	Number of pulses n	$\Delta\theta$ (arcsec)	FWHM (arcsec)
0.20	1	750	500–5000	0	—
0.42	1	500	500	570	220
0.84	0.2	500	500	560	220
0.84	1	500	500	530	200
0.84	5	500	500	540	310
0.84	20	500	500	270	560

with nitrogen. Vitali *et al* [18] estimated the maximum surface temperature to be 728 K for GaAs irradiated at 5 MW cm^{-2} and 853 K at 5.5 MW cm^{-2} . They obtained these values by numerically solving the one-dimensional heat diffusion equation. In the following, we study the influence of the laser fluence (and thus the surface temperature) on the incorporation of nitrogen.

The effects of the laser fluence and the repetition rate of laser pulses on the resulting films are listed in table 1. The first point to be noted is the existence of a threshold fluence between 0.20 and 0.42 J cm^{-2} , below which the nitrogen incorporation cannot occur. For the fluence from above the threshold up to 0.84 J cm^{-2} , there is no essential difference observed. The fluence 0.20 J cm^{-2} corresponds to a power density of 8.7 MW cm^{-2} for the laser used. This value is very close to the critical power density (9 MW cm^{-2}) of micromelting of the GaAs surface [17]. Thus the formation of an epitaxial GaNAs layer is strongly correlated to the instantaneous melting of the GaAs surface layers during the laser irradiation. The nitrogen atoms may diffuse into the melted layers and replace the arsenic atoms. However, in the present study, the possibility of redeposition from the laser induced plasma of nitrogen atoms and evaporated GaAs species cannot be ruled out.

Also noted from table 1 is the increase of FWHM of the XRD curve when the sample was synthesized at higher repetition rates. The immediate laser shots on the sample may result in heat accumulation (high surface temperature), which will in turn cause the nitrogen atoms to migrate and result in degradation of the film. The sample made at 20 Hz even shows a decrease in the incorporated nitrogen concentration (smaller peak separation $\Delta\theta$), implying the decomposition of the metastable GaNAs phase at high temperature.

Compared to the conventional deposition methods for the GaNAs growth, the present technique is attractive in that it is not necessary to heat the whole substrate, the process time is short and it is spatially selective [15]. The maximum nitrogen content achieved in the present study is about 1.0%. To enhance the nitrogen content and improve the film quality, higher nitrogen pressure and optimized laser fluence should be acquired. Furthermore, a perfectly homogenized spatial distribution of the laser intensity across the beam will be very important for obtaining high-quality films [13, 14].

To summarize, we have demonstrated the possibility of forming directly an epitaxial $\text{GaN}_x\text{As}_{1-x}$

layer on a GaAs substrate by pulsed-laser irradiation of the substrate in a nitrogen ambient. The nitrogen composition and the film quality are affected by the ambient pressure and the laser parameters (fluence, repetition rate and total shot number). We point out that the simple method presented here provides a novel way to synthesize $\text{GaN}_x\text{As}_{1-x}$ films.

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