

# Optical properties of amorphous GaAs<sub>1-x</sub>N<sub>x</sub> film sputtering with different N<sub>2</sub> partial pressures

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We study the optical properties of amorphous GaAs<sub>1-x</sub>N<sub>x</sub> films grown by radio frequency magnetron sputtering method with different N<sub>2</sub> partial pressures. The surface morphology, the optical absorption, the Raman spectra, and optical constants of the films with different N<sub>2</sub> partial pressures are reported. The appearance of the Raman peak at 245 cm<sup>-1</sup> of "GaAslike" and a shoulder at about 750 cm<sup>-1</sup> related to GaN indicates the formation of GaN clusters in GaAs matrix. The roughness decreases and the optical band gap of amorphous GaAs<sub>1-x</sub>N<sub>x</sub> films moves to short wavelength with increasing N<sub>2</sub> partial pressure. The refractive index and the extinction coefficient of the films decrease with increasing N<sub>2</sub> partial pressure, and it has been found that the amorphous GaAs<sub>1-x</sub>N<sub>x</sub> films with nonzero N<sub>2</sub> partial pressure are transparent in red and near infrared wavelength regions. © 2006 American Vacuum Society. [DOI: 10.1116/1.2217977]

## I. INTRODUCTION

Amorphous group-III nitrides and related ternary compounds are wide-gap materials with unique properties, which are promising for electronic and optoelectronic device technologies working in the visible wavelength zone. Amorphous GaAs<sub>1-x</sub>N<sub>x</sub> (*a*-GaAs<sub>1-x</sub>N<sub>x</sub>) is particularly interesting as it is expected to range from a GaAslike semiconductor to a GaN-like insulator according to the content of nitrogen. In this structure, some of the incorporated N atoms would fill in vacancy sites which can improve the GaAs network quality, and on the other hand, some other N atoms are believed to replace As ones thus giving rise to the formula of *a*-GaAs<sub>1-x</sub>N<sub>x</sub>.<sup>1</sup> There exists an everlasting interest in integrating semiconductor lasers with silicon electronic circuits for applications such as optical interconnect and communications, and thus the growth of high-quality film on Si substrate is a key technology for the realization of optoelectronic integrated circuits.<sup>2-4</sup> However, due to the large lattice mismatch between them, the large number of dislocation limits the material quality and consequently prevents them from practical using, and thus nitrogen-doped crystalline GaAs and amorphous GaAs (*a*-GaAs) have attracted much attention in recent years, partly due to the lattice matching with Si.<sup>1,5</sup>

Because of the low nitrogen solubility in the GaAs<sub>1-x</sub>N<sub>x</sub> alloys (<2% in the epilayers<sup>6</sup> and <10% in narrow quantum wells<sup>7</sup>) and phase separation with appreciable nitrogen concentrations,<sup>8</sup> the growth of GaAs<sub>1-x</sub>N<sub>x</sub> films have been limited to low nitrogen concentration except for few reports with heavily N-doped GaAs.<sup>9-12</sup> In this article, we present a study of *a*-GaAs<sub>1-x</sub>N<sub>x</sub> films deposited by sputtering with different N<sub>2</sub> partial pressures ( $P_{N_2}$ ). We found that the N composition (*x*) in *a*-GaAs<sub>1-x</sub>N<sub>x</sub> films is proportional to  $P_{N_2}$  in the plasma during deposition. The Raman spectra reveal sev-

eral features related to GaN and GaAs clusters, and the dependence of these features on  $P_{N_2}$  is presented and analyzed. The optical constants (*n*, *k*) of the *a*-GaAs<sub>1-x</sub>N<sub>x</sub> films with different  $P_{N_2}$  were firstly reported.

## II. EXPERIMENT

Amorphous GaAs<sub>1-x</sub>N<sub>x</sub> thin films were grown on Si wafers and glass by sputtering from a 60 mm in diameter GaAs target (99.999%) using a rf magnetron sputter system at 300 °C. In order to study the Raman spectrum of amorphous GaAs<sub>1-x</sub>N<sub>x</sub> thin films, crystalline GaAs thin film was also deposited at substrate temperature of 400 °C. Film growth was carried out in the growth ambient with N<sub>2</sub>/(N<sub>2</sub>+Ar) ratios ranging from 0 to 1 at a constant working pressure of 1 Pa and a rf power of 50 W and bias voltage of 50 V. The Si and glass wafers were ultrasonically washed in acetone, alcohol, and de-ionized water before being placed into a vacuum chamber. The sputtering chamber was evacuated up to 5 × 10<sup>-6</sup> Pa before the high-purity (99.999%) Ar and N<sub>2</sub> gases were introduced separately by two flow controllers.

The surface morphological features of the films were characterized by atomic force microscope (AFM) using Auto Probe CP Instrument. X-ray diffraction (XRD) was carried out on Philips X'Pert PRO diffractometer (40 KV, 40 mA) using Cu K $\alpha$  line ( $\lambda=0.154$  19 nm). Room temperature optical absorption spectra were measured with a Cary 5E UV-VIS-NIR spectrophotometer. The Raman spectra were recorded using LABRAM-HR spectrometer and excited with an argon ion laser of 514.5 nm in the backscattering geometry with the resolution of 1 cm<sup>-1</sup>; optical constants were determined with Jobin-Yvon ellipsometer over the spectral range of 190–1650 nm in steps of 5 nm at the angle of incidence of 70°.

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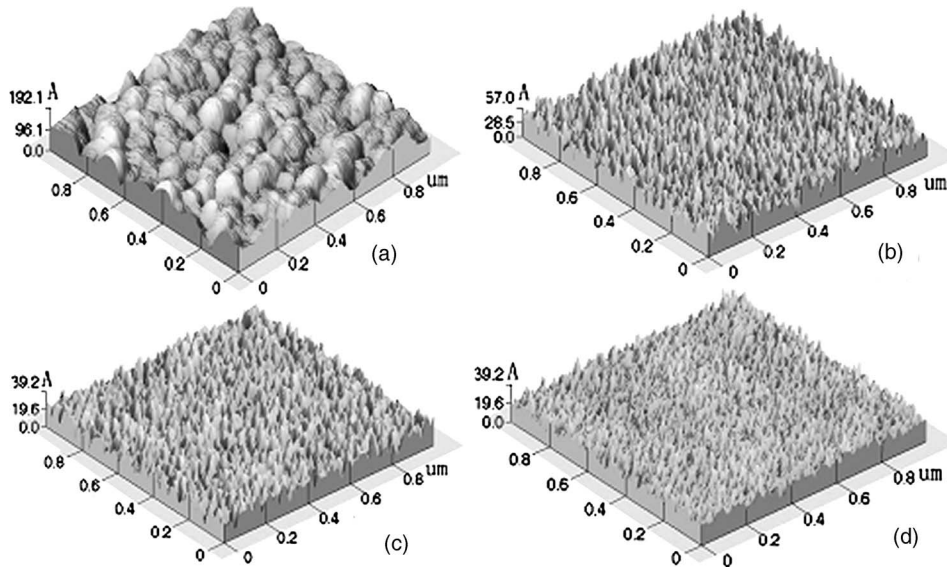


FIG. 1. AFM images of *a*-GaAs<sub>1-x</sub>N<sub>x</sub> films with different N<sub>2</sub> partial pressures: (a) 0%, (b) 8%, (c) 60%, and (d) 100%.

### III. RESULTS AND DISCUSSION

The XRD analyses indicate that all the GaAs<sub>1-x</sub>N<sub>x</sub> films with different  $P_{N_2}$  ( $>0$ ) are amorphous at substrate temperature of 300 °C, and even at 400 °C (the XRD patterns are not shown here). To avoid the loss of As in the films, GaAs<sub>1-x</sub>N<sub>x</sub> thin films were grown at substrate temperature of 300 °C. It was found that GaAs thin film with a amorphous structure was formed at 300 °C, while a crystalline was obtained at 400 °C. This result indicates that the prepared conditions used in this study are in favor of the formation of amorphous structure. Figure 1 shows the surface AFM images of *a*-GaAs<sub>1-x</sub>N<sub>x</sub> films grown on Si substrate with different  $P_{N_2}$ . As can be seen from Fig. 1(a), the surface roughness and the grains are in a globular state for *a*-GaAs film. A relative smooth surface with a whisker grains forms for *a*-GaAs<sub>1-x</sub>N<sub>x</sub> films, and the whisker density increases and the roughness decreases with increasing  $P_{N_2}$ , as shown in Figs. 1(b)–1(d) and Table I. A similar result has also been observed by Alvarez-Fregoso *et al.*<sup>13</sup> The formation of Ga–N and As–N species with the introduction of N ionic species in the sputtering process will interact with the surface of the substrate originating the activation of nucleation sites, with the consequent needlelike grain growth following the vapor liquid solid (VLS) process, the same phenomenon also has been observed in the growth of indium tin oxide (ITO) whiskers.<sup>14</sup> The introduction of N subsequently reduces the strain energy of GaAs grown on Si substrate,<sup>3</sup> and leads to a more uniform growth of *a*-GaAs<sub>1-x</sub>N<sub>x</sub> films.

The Raman spectrum of crystalline GaAs film deposited at substrate temperature of 400 °C was measured firstly, as

shown in Fig. 2(a). One can see that the spectrum is featured by a longitudinal-optic (LO) mode and a transverse-optic (TO) mode. Compared with bulk GaAs 265 cm<sup>-1</sup> (TO) and 290 cm<sup>-1</sup> (LO),<sup>15</sup> the peak positions shift to low frequencies by 5.0 cm<sup>-1</sup>, which might be due to the phonon confinement effect. The intensity of LO phonon mode is lower than that of TO phonon mode, which might be as a result of the higher

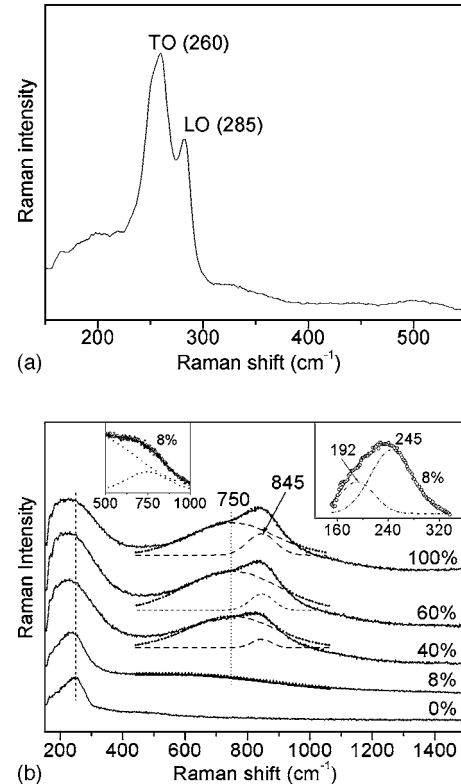


FIG. 2. Raman spectra of (a) crystalline GaAs film and (b) *a*-GaAs<sub>1-x</sub>N<sub>x</sub> films with different N<sub>2</sub> partial pressures. The left and right insets in (b) are the Gaussian fitting results of peaks at 750 and 245 cm<sup>-1</sup> of the sample with 8% N<sub>2</sub> partial pressure, respectively.

TABLE I. Roughness ( $R$ ) of *a*-GaAs<sub>1-x</sub>N<sub>x</sub> films with different N<sub>2</sub> partial pressures.

$P_{N_2}$ (%)	100	60	40	8	2	0
$R$ (nm)	4.68	5.86	6.32	10.7	12.1	20.4

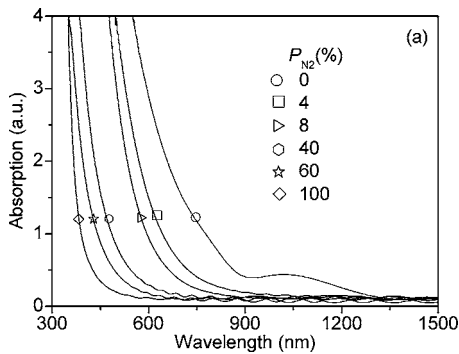


Fig. 3. (a) Optical absorption spectra and (b) plots of  $(h\nu\alpha)^2$  and  $(h\nu\alpha)^{1/2}$  (inset) vs  $h\nu$  of  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films with different N<sub>2</sub> partial pressures.

concentration of free carriers in the GaAs film deposited by sputtering. It is well known that Raman peak of materials with an amorphous structure tends to shift to low energy range as compared with the crystalline one. From Fig. 2(b), one can see that the Raman spectrum of the  $a$ -GaAs film is featured with a broadband at 250 cm<sup>-1</sup>. However, the Raman spectra of  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films consist of two broadbands at 245 and 845 cm<sup>-1</sup>, which are clearly different from that of the  $a$ -GaAs film. The first band fits with the Raman peak of  $a$ -GaAs, which is in agreement with Lollman's result,<sup>1</sup> meanwhile the peak positions have slightly redshift with increasing  $P_{N_2}$ . The Gaussian fitting of the first scattering band of sample with 8%  $P_{N_2}$  gives two peaks [the right inset in Fig. 2(b)], one is at 245 cm<sup>-1</sup> and the other is at 192 cm<sup>-1</sup>, the intensity of the former increases with  $P_{N_2}$  and might be due to the first-order scattering from both GaAslike and GaNlike disorder modes of GaAs,<sup>16,17</sup> and intensity of the latter almost does not change and is considered come from the As- $E_g$  mode.<sup>18</sup> From Fig. 2(b) one can also see that the peak at 245 cm<sup>-1</sup> is broadening with increasing  $P_{N_2}$ , which may be due to the increased content of GaN in GaAs matrix or the more complex interleaving of (GaAs)<sub>m</sub>(GaN)<sub>n</sub> clusters.

The second scattering band at 845 cm<sup>-1</sup> becomes obvious at high  $P_{N_2}$  and the peak position almost does not change with increasing  $P_{N_2}$ . The Gaussian fitting gives two peaks and situates at 750 and 845 cm<sup>-1</sup>, respectively [there is only one peak at 750 cm<sup>-1</sup> for the  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> film with 8%  $P_{N_2}$ , as shown in the left inset in Fig. 2(b)]. A very broad weak feature at about 750 cm<sup>-1</sup> has also been observed by Bandet *et al.* in amorphous GaAs<sub>0.7</sub>N<sub>0.3</sub>.<sup>19</sup> A Raman scattering study of GaAs<sub>1-x</sub>N<sub>x</sub> layers with  $x=0-0.05$  demonstrated the presence of diagonal components for both the GaAs- and GaN-type optical phonons.<sup>20</sup> Further study is needed to clarify the exact mechanism of the peak at 845 cm<sup>-1</sup>, which might result from the distortion of GaAs<sub>1-x</sub>N<sub>x</sub> or the (GaAs)<sub>m</sub>(GaN)<sub>n</sub> clusters as its intensity increases with increasing  $P_{N_2}$ . The broaden of the Raman peak at 750 cm<sup>-1</sup> might be also due to (GaAs)<sub>m</sub>(GaN)<sub>n</sub> clusters. These results suggest the formation of GaN clusters in GaAs<sub>1-x</sub>N<sub>x</sub> matrix.

Figure 3(a) shows the optical absorption spectra of the  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films. One can see that the optical absorption

edge moves to the short wavelength region with the increase of  $P_{N_2}$ . The absorption coefficient  $\alpha$  is connected with the band-gap energy  $E_g$  by the equation<sup>21</sup>

$$\alpha^n \propto (h\nu - E_g),$$

where  $E_g$  is the band gap and  $n$  is an index that characterizes the optical absorption process and is theoretically equal to 1/2 and 2 for indirect allowed and direct allowed transitions, respectively. The better plot that covers the widest range of data is obtained for the  $(h\nu\alpha)^2-h\nu$  dependence, as shown in Fig. 3(b), indicating the direct transition domination in  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> thin films. The same results were also reported in the literatures.<sup>22,23</sup> Therefore, we believe that the band-gap behavior of  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> will be similar to that of the crystalline system, as is generally the case.<sup>1</sup> The exact positions of the optical band gap of  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> with different  $x$  values are not known, because of the very much blurring of the band gap due to the existence of many quantum mechanical energy levels outside the actual conduction and valence bands for amorphous material. Nevertheless, as a reference, it is evident in Fig. 3(b) that the optical band gap shifts from 1.43 eV [close to the band gap of  $a$ -GaAs: 1.12–1.6 eV (Refs. 24 and 25)] to 2.72 eV [close to the band gap of  $a$ -GaN: 2.80–3.30 eV (Ref. 26)] with increasing  $P_{N_2}$ , which is thought closely related to the atomic composition imposed by various  $P_{N_2}$  during deposition. The optical band gap for the  $a$ -GaAs film is about 1.43 eV, which is slightly larger than crystalline GaAs film (1.424 eV), which, on the other hand, might suggest that the deposited film has relatively high quality. When N atoms are inserted in the GaAs at the expense of As,<sup>19,27</sup> large numbers of N are assumed to decrease the energy of the top of the valence band, leading to the increase of the optical band gap, as pointed out by Zanatta *et al.* for Er-doped  $a$ -GaAsN alloys.<sup>28,29</sup> Because the optical band gap of  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films has moved from 1.43 to 2.72 eV, it is proved that As atoms have been readily replaced by N atoms with the formation of Ga–N bonds.<sup>30</sup>

The ellipsometric data were acquired and displayed as  $Is/Ic$  values. The advantage of these variables over  $\Psi$  and  $\Delta$  is that they stay within the same range and have a similar and constant error over the full wavelength. These values are the effective raw data for the phase-modulated systems, and the interband absorption dispersion Tauc-Lorentz (TL) formula was applied to describe the dispersion of these samples. The refractive indices and the extinction coefficients can be extracted from the fitting procedures. The refractive indices and the extinction coefficients of the  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films were simulated and the simulating results are shown in Fig. 4. From Fig. 4(a) one can see that the  $a$ -GaAs film has a larger index of refraction than  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films ( $x > 0$ ) in the wavelength range longer than 500 nm. For  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films the refractive index firstly increases and then decreases with the wavelength after reaching the maximum value regardless  $P_{N_2}$ . The maximum refractive index slightly moves to short wavelength with increasing  $P_{N_2}$ . The refractive index of  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films decreases with the increase of  $P_{N_2}$ , which might be due to the formation of the GaN clusters in

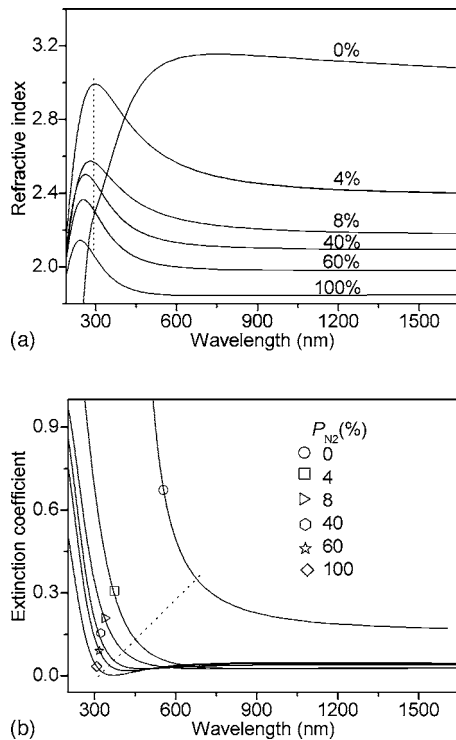


FIG. 4. (a) Refractive index and (b) extinction coefficient of  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films with different N<sub>2</sub> partial pressures.

the GaAs matrix. The extinction coefficient of  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films also decreases with increasing  $P_{N_2}$  in the wavelength shorter than 600 nm and has a near zero value in the wavelength longer than 600 nm. This result indicates that the  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films are transparent in red and near infrared wavelength regions. The formation of GaN clusters or N atoms absorbed on the substrate and/or the film surface during sputtering is considered responsible for the decrease of the refractive index and the extinction coefficient with increasing  $P_{N_2}$ . Our results indicate that the refractive index of  $a$ -GaAs<sub>1-x</sub>N<sub>x</sub> films can be adjusted by various  $P_{N_2}$  in a large range. The obtained data of optical constants can provide the technical reference for a precise optical device design.

#### IV. CONCLUSIONS

In summary, amorphous GaAs<sub>1-x</sub>N<sub>x</sub> films have been fabricated by rf magnetron sputtering technique with different N<sub>2</sub> partial pressures. A decreased surface roughness and a blueshifted optical absorption edge have been observed with increasing N<sub>2</sub> partial pressure. In the Raman spectra of amorphous GaAs<sub>1-x</sub>N<sub>x</sub> films, the peaks at 245–250 cm<sup>-1</sup> of “GaAslike” assigned to disorder mode have a slightly redshift, and the appearance of a shoulder at about 750 cm<sup>-1</sup>

related to GaN indicates the formation of GaN cluster in amorphous GaAs<sub>1-x</sub>N<sub>x</sub> films. The refractive index and the extinction coefficient of amorphous GaAs<sub>1-x</sub>N<sub>x</sub> films all decrease with increasing N<sub>2</sub> partial pressure.

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