

Amorphous GaN films deposited by DC sputtering

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The films are deposited by direct current (DC) planar magnetron sputtering at different argon concentration in the sputtering gas (defined as Ar%). X-ray diffraction (XRD), Fourier Transform Infrared spectra (FTIR) and Raman spectra indicate that the films are amorphous. The main absorption of the FTIR is due to Ga-N bond stretching vibration. Spectroscopic Ellipsometry (SE) and UV-VIS spectra show that the refractive index of the a-GaN is very similar to that of crystalline GaN (c-GaN). When increasing Ar concentration from 10 % to 40 %, the thicknesses of the films change from 565.6 nm to 1526.1 nm linearly, which implies that Ar promotes the deposition rate. The Tauc band gap of the film deposited at lower Ar (~ 0%) is 3.9 eV, which is much larger than that of c-GaN, due to the structural disorder. While the films deposited at higher Ar%, the band gaps become much smaller (3.3 eV–2.8 eV), probably because of more excess Ga in the films. The band tails extending to lower energies are modeled, and the parameters indicate that a-GaN films have a wider absorption tail than that of c-GaN film.

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1. Introduction

Wide band gap semiconductor GaN and related materials have attracted more and more attention for their potential electronic and optoelectronic device applications, such as blue-ultraviolet light-emitting diodes, and laser diodes [1, 2]. In the past, many researches focused on how to grow perfect crystalline GaN (c-GaN) for conventional semiconductor device applications. But up to now, GaN layers prepared by epitaxial methods contain lots of defects. Theoretical studies [3, 4] predicted that a-GaN is a promising wide band gap semiconductor with few defect levels in the mid gap. Since amorphous GaN (a-GaN) has some similar properties to that of c-GaN, it may replace c-GaN in certain fields. Comparing with c-GaN, many parameters of a-GaN are still not well known. For example, the fundamental band gap energy and band tail characteristics are key properties of materials. The knowledge of the band characteristics of a-GaN film is very limited, to our understanding. Experimental studies of a-GaN grown by different mechanisms have been reported, such as reactively sputtered a-GaN [5-9], molecular beam epitaxy (MBE) of a-GaN [10], ion-assisted deposition (IAD) of a-GaN [11], hydrogenated a-GaN [12], etc. Comparing to the others, sputtering method can produce large-area and uniform films at relatively low cost.

In this paper, a-GaN films deposited by direct current (DC) planar magnetron sputtering method are reported. The structural characteristics and optical properties of the films affected by argon composition of the sputtering gas have been studied. The existence of different band gaps in a-GaN is presented experimentally. The band tail of the material is modeled.

2. Experiment

The sputter target was Ga metal (99.999% pure) in a 5-inch diameter steel dish. The target-to-substrate distance was kept at 5cm. The base pressure was 3×10^{-3} Pa before the plasma was turned on. The reacting gas and sputtering gas were N₂ (99.999%) and Ar (99.999%), respectively. The total flux of the gases was constant 30 sccm. The sputtering pressure and the sputtering power were 4 Pa and 40 W. The sputtering time was 1 hour. The films were deposited on both silicon and glass substrates. The Si (111) substrates were first degreased in organic solvents of acetone and ethanol. Then the substrates were dipped in a diluted HF solution (H₂O: HF (49%) = 10:1) for 30 s at room temperature. The HF dipping treatment can etch off the natural oxide layer on the silicon substrate and produce a hydrogen termination to passivate the surface from re-oxidation [13-16]. The glass substrates were only degreased using the same organic solvents. All the substrates were not intentionally heated during the deposition. We define the composition of argon flux in the total flux of gas mixtures as Ar%. The color of the films is light yellow.

All the measurement results were obtained at room temperature. The film structures were studied by X-ray diffraction technique (XRD) (Philips X'Pert) using Cu K α ($\lambda=0.154056$ nm) source. Fourier transform infrared (FTIR) absorption spectra were recorded by Nicolet NEXUS 670 spectrometer. Raman spectra were collected by Jobin-Yvon LabRAM HR80 micro-area spectrometer, and it was excited by 532 nm line of Torus 50 mW diode-pumped solid-state laser. The Spectroscopic Ellipsometry (SE) spectra were obtained by Jobin-Yvon MM-16 Spectroscopic Ellipsometry System, and the UV-VIS spectra were recorded by TU-1901 spectrometer.

3. Results and discussion

Fig.1 shows the typical XRD pattern of our a-GaN film ($Ar\%=10\%$) on Si substrate. The scanning model is θ - 2θ . The diffraction large peak centered at $2\theta = 34^\circ$ is associated with (0002) plane in wurtzite GaN, but no sharp lines can be found in XRD spectra. This indicates that the film has a typical amorphous structure [17]. The peak at $2\theta=28.44^\circ$ is referred to Si (111) plane from substrate.

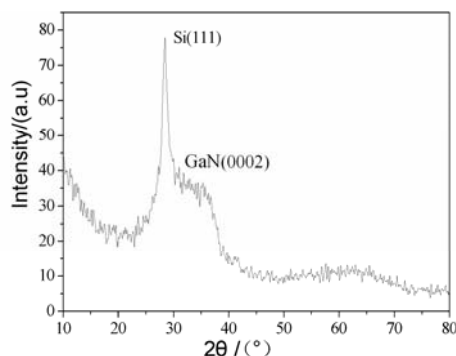


Fig.1. Typical XRD spectra of the a-GaN film deposited on Si substrate ($Ar\%=10\%$), using medium angle X-ray scattering mode.

Fig. 2 is the typical FTIR spectra of the a-GaN film ($Ar\%=10\%$) on Si substrate. The absorption peak of 560.6 cm^{-1} is derived from Ga-N bond stretching vibration [18]. The peak of 605.5 cm^{-1} corresponds to the vibration mode of carbon (C) atom substituting crystal Si atom. It is possible that C is from contaminant in the substrate [19]. The 1107 cm^{-1} absorption peak is assigned to Si-O bond vibration, due to the natural oxidization of Si exposed in atmosphere [20]. The $3000\text{--}3500\text{ cm}^{-1}$ absorption packet is attributed to O-H vibration of H_2O in air. No absorptions of Ga-O vibration were found.

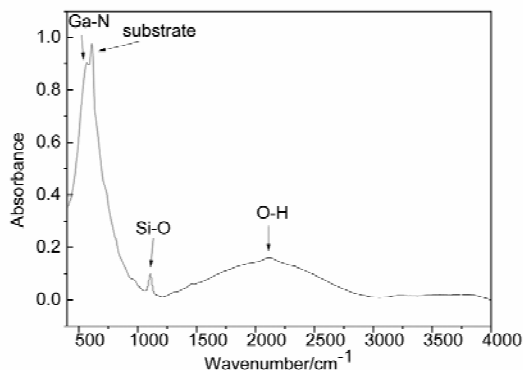


Fig. 2. Typical FTIR spectra of the a-GaN film deposited on Si substrate ($Ar\%=10\%$).

Fig. 3 shows the Raman spectra of the a-GaN films on

Si substrates, deposited at different $Ar\%$. The curves between 470 cm^{-1} and 570 cm^{-1} are omitted, because of a very strong peak at 520 cm^{-1} that stems from Si substrates. The peak at 307 cm^{-1} comes, also, from the Raman scattering of Si substrates. In the spectra, three peaks centered at 440 cm^{-1} (A1, E2), 620 cm^{-1} (LO(X)) and 670 cm^{-1} (LO(L)) are observed. The pattern is different from that of c-GaN, which displays a series of narrow lines in Raman spectra [19]. This indicates that the films are amorphous, which is consistent with the XRD result. The wave-vector selection rule, which is restricted in crystalline materials, is relaxed in the amorphous solid. This result is similar to that of a-Si and a-Ge [11].

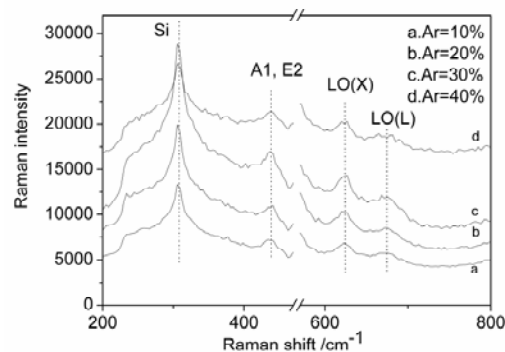


Fig. 3 Raman spectra of the a-GaN films deposited on Si substrates. The region near the first order Si signal at 520 cm^{-1} has been removed for clarity. (a. $Ar\%=10\%$; b. $Ar\%=20\%$; c. $Ar\%=30\%$; d. $Ar\%=40\%$)

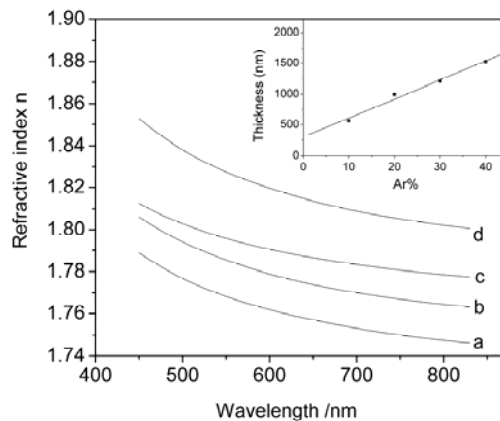


Fig. 4. Refractive index of a-GaN films obtained by SE measurement (a. $Ar\%=10\%$; b. $Ar\%=20\%$; c. $Ar\%=30\%$; d. $Ar\%=40\%$) ; inset is the final film thicknesses increasing proportionally to the $Ar\%$.

SE measurement shows the refractive index (n) of a-GaN films deposited on Si substrates at different $Ar\%$

(Fig.4). It is obvious that n is getting higher as the Ar% increases. This is likely due to more non-bonding Ga in the films as the Ar% increases. The final thicknesses of the films on glass were also obtained by SE measurement (the inset of Fig.4). When Ar% increases from 10% to 40%, the film thicknesses increase from 565.6 nm to 1526.1 nm linearly. This implies that the film deposition rates increase proportionally to the Ar%. It is consistent with the reported result that the deposition rates of nitrides increase with increasing argon partial pressure at certain extent [21].

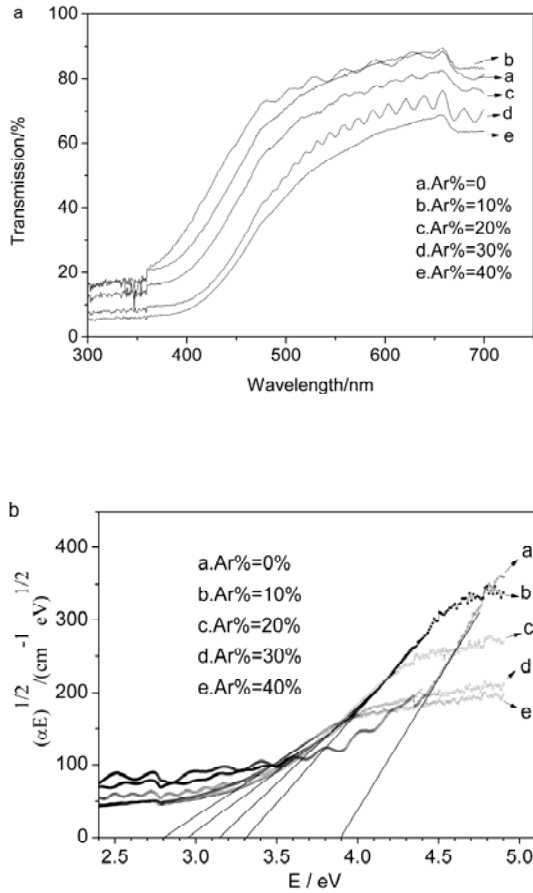


Fig. 5(a). UV-VIS spectra of the a-GaN films deposited on glass. (b) $(\hbar\omega\alpha)^{1/2}$ vs. $(\hbar\omega)$ curves. In these curves, a linear fit was superimposed, and the fit was extrapolated to yield Tauc band gaps of $E_g = 2.8\text{--}3.9$ eV, with a tail of localized states extending into the gap. (a. Ar%=0; b. Ar%=10%; c. Ar%=20%; d. Ar%=30%; e. Ar%=40%)

Fig. 5(a) shows the transmission spectra of the a-GaN films on glass deposited at different Ar%. The average transmission ratio of the samples exceeds 60% at visible

zone, and it is getting smaller with higher Ar%. The curves display relatively low transmission ratios below 400nm, because of the band-to-band absorptions. The interference patterns can be seen in the sample a, c and d. This is probably because the surfaces of these samples are smoother than the others. The increasing film thickness can reduce the transmission ratio.

The optical band gap E_g can be obtained by Tauc formula [22]:

$$(\hbar\omega\alpha)^n \propto (\hbar\omega - E_g)$$

where $\hbar\omega$ (shown as E in the figures) is the energy of the incident photons, α is absorption coefficient, $n=2$ is for indirect transitions and $n=1/2$ is for direct transitions. The E_g value can be calculated by extrapolating the linear portion to the photon energy axis in the figure. Fig. 5(b) shows $(\hbar\omega\alpha)^2$ vs. $(\hbar\omega)$ curves of the a-GaN films, obtained from transmission and reflectance spectra (not shown here). The Tauc band gaps calculated are 2.80 ~ 3.90 eV. Absorptions above these energies are due to band-to-band transitions and absorptions over lower energy regions are due to the transitions between the states in the gap. When Ar% is 0%, the band gap is 3.9 eV, which is much larger than that of c-GaN (~3.4 eV). This is because in amorphous films, the absence of long-range translational periodicity makes the extended localized states in the conduction and valence bands increase, which leads to the blueshift of absorption edge [23]. Shown in Table 1, the band gap E_g decreases with increasing Ar%. The possible reason is that at lower Ar%, there are more N atoms to react with Ga atoms. While at higher Ar%, the N atoms are not enough to react with excess Ga atoms. The gap drops below 3.9 eV when the amorphous network incorporates homopolar (Ga-Ga) bonds, which have metallic behaviors.

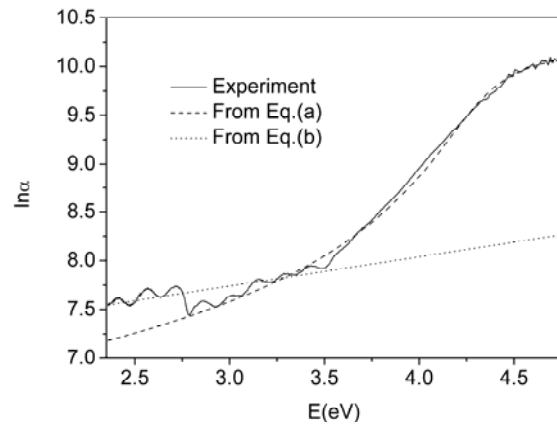


Fig. 6 Typical spectra of $\ln \alpha$ of a-GaN film on glass (Ar%=0%), and the fitting curves around the band gap by Eq. (a) and Urbach tail by Eq. (b).

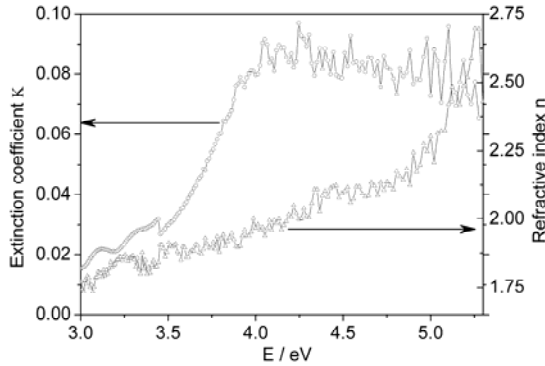


Fig.7. Extinction coefficient and refractive index of a-GaN film on glass (Ar%=10%) obtained from UV-VIS spectra.

Around the fundamental band gap, these tails extend towards wavelengths longer than those corresponding to E_g . Localized states in band tails constitute a fundamental feature of amorphous materials, and it is likely that structural disorder is the most important reason for these states. The band tails were modeled by the following equations [24]:

$$\alpha(E) \propto \left[1 - \frac{2}{\pi} \tan^{-1} \left[\frac{E_g - E}{\Sigma} \right] \right] \quad (1)$$

$$\alpha(E) \propto \exp \left[\frac{E - E_0}{\Delta E} \right] \quad (2)$$

Eq. (1) is based on an approximation of the quantum-mechanical transitions between initial and final states according to time-dependent perturbation theory, where the parameter Σ represents the energy spread (broadening) of the electronic transitions. Illustrated in Fig.6, the experiment curve is fitted quite well by Eq. (1) at higher energies around the band gap. The parameter Σ describing the width of the transition at $E > 3.3$ eV is 0.257~0.338 eV (shown in Table 1), this value is much bigger than that of the c-GaN obtained by Jacobson et al, indicating that the broadening of the electronic transitions is much wider than the crystalline structure. This broadening is believed to be attributed to the intrinsic electric field due to impurities, structural defects and strains caused by mismatch between the film and the substrate [25]. The Urbach tail over low energy region was modeled by the Eq. (2) [26, 27], where E_0 is a constant characteristic of the material and ΔE so called Urbach energy represents the width or slope of the exponential tail. This region is attributed to the transition from localized valence band states to extended conduction band states. Fig. 6 also illustrates fits for the absorption at $E < 3.3$ eV by

Eq. (2). Clearly the Urbach tail is approximately exponential. In Table 1, parameter ΔE is 1.44~1.89 eV. The width of the exponential tail is larger than that of c-GaN films reported by Nakanishi et al [28], indicating that amorphous films have a wider Urbach tail, while the crystalline films display a narrower one, and this is to be expected probably since band tail states arise from structural disorder. ΔE increases when Ar% increases. This is believed to be partly attributed to the increasing film thickness [29].

Table 1. The Tauc band gap E_g and two parameters (Σ and ΔE) describing the width of the transitions.

Sample	Ar%	Tauc E_g (eV)	Σ (eV)	ΔE (eV)
a	0	3.90	0.281	1.44
b	10	3.30	0.263	1.55
c	20	3.15	0.257	1.72
d	30	2.95	0.296	1.77
e	40	2.80	0.338	1.89

Below the band gap (Fig. 5b), the curves are smooth and without any obvious lines. And $(\alpha E)^{\frac{1}{2}}$ increases slowly for the incident photons from lower energy side, while for the higher energy photons, $(\alpha E)^{\frac{1}{2}}$ increases rapidly. It is easy to understand that α follows the same trend. Supposing that α is determined by initial state n_i and final state n_f :

$$\alpha \propto \sum p_{if} n_i n_f \quad (3)$$

where p_{if} is the transition matrix. The small α value over the low energy regions indicates that the a-GaN has a very low density of states in the midgap. This result is consistent with the theoretical studies [3, 4].

Fig. 7 shows the typical extinction coefficient K and refractive index n of the a-GaN film on glass substrate (Ar%=10%) as a function of photon energy. This is obtained by:

$$\alpha(E) = 4\pi K(E) / \lambda \quad (4)$$

It seems that K and n of a-GaN film was very close to that of c-GaN [30].

4. Conclusions

The GaN thin films have been prepared by DC sputtering deposition. XRD results and Raman spectra show the films are amorphous and FTIR spectra indicate the main absorbance is from Ga-N bond stretching vibration. From SE and UV-VIS result, the refractive index of a-GaN is very similar to that of c-GaN. While

Ar% increases from 10% to 40%, the thickness of the films increases from 565.6 nm to 1526.1 nm linearly, which implies that Ar% influences the film deposition rates. The Tauc band gap of the film deposited at low Ar% (~0%) is 3.9 eV. This is much larger than that of c-GaN, due to the absence of long-range translational periodicity in the amorphous structure. While the films are deposited at higher Ar% (10% ~ 40%), the band gaps become smaller (3.3 eV ~ 2.8 eV), probably due to more excess non-bonding Ga in the films, which have metallic behavior. Two parameters Σ and ΔE describing the width of transitions of absorption are 0.281 ~ 0.338 eV and 1.44 ~ 1.89 eV, respectively, indicate that amorphous films have a wider absorption tail than that of c-GaN films. The small α value over the low energy regions indicates that the a-GaN has a very low density of states in the midgap.

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