Influence of sputtering pressure on optical constants of a-$GaAs_{1-x}N_x$ thin films*

Jia Baoshan(贾宝山), Wang Yunhua(王云华), Zhou Lu(周路), Bai Duanyuan(白端元),
Qiao Zhongliang(乔忠良), Gao Xin(高欣),
and Bo Baoxue(薄报学)†

State Key Laboratory on High Power Semiconductor Lasers, Changchun University of Science and Technology,
Changchun 130022, China

Abstract: Amorphous $GaAs_{1-x}N_x$ (a-$GaAs_{1-x}N_x$) thin films have been deposited at room temperature by a reactive magnetron sputtering technique on glass substrates with different sputtering pressures. The thickness, nitrogen content, carrier concentration and transmittance of the as-deposited films were determined experimentally. The influence of sputtering pressure on the optical band gap, refractive index and dispersion parameters (E_o, E_d) has been investigated. An analysis of the absorption coefficient revealed a direct optical transition characterizing the as-deposited films. The refractive index dispersions of the as-deposited a-$GaAs_{1-x}N_x$ films fitted well to the Cauchy dispersion relation and the Wemple model.

Key words: a-$GaAs_{1-x}N_x$ thin films; sputtering deposition; optical constants
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1. Introduction

Amorphous $GaAs_{1-x}N_x$ (a-$GaAs_{1-x}N_x$) has received much attention in recent years[1] because of its special material properties such as lattice matching with Si[2, 3] and very few phase separations at an appreciable nitrogen content[4]. In addition, a-$GaAs_{1-x}N_x$ is expected to have varying characteristics according to the N content, from a GaAs-like film to a GaN-like film[5, 6]. Therefore, studies on optical, electrical and structural properties of a-$GaAs_{1-x}N_x$ are of essential importance. Knowledge of optical constants such as the absorption coefficient, optical band gap and refractive index of the semiconductor is indispensable for the design and analysis of various optical and optoelectronic devices[7, 8]. The experimental data of transmittance can be analyzed to obtain material optical constants[9]; less work, however, has been devoted previously to an a-$GaAs_{1-x}N_x$ alloy system[1, 6].

On the other hand, the direct-current magnetron sputtering technique is particularly attractive because of its overwhelming advantages in comparison with other deposition methods. It is low cost, easy-to-use, safe and very suitable for the fabrication of amorphous thin film[10, 11].

In the present work, a-$GaAs_{1-x}N_x$ thin films were sputtering-deposited on glass substrates by different sputtering pressures at room temperature. The thickness, nitrogen content, carrier concentration and transmittance of the as-deposited films were measured. A systematic investigation of the optical constants of a-$GaAs_{1-x}N_x$ thin films depending on sputtering pressure has been carried out.

2. Experiment

a-$GaAs_{1-x}N_x$ films were prepared on Corning 7059 glass substrates by the radio frequency (RF, 13.56 Hz) reactive magnetron sputtering technique using a conventional sputtering setup (JCP-350, Beijing Technol Science Co. Ltd). Glass substrates were ultrasonically cleaned in acetone, rinsed in alcohol, and subsequently dried in flowing nitrogen gas. The substrate temperatures were maintained at about 20 ℃ by cooling water in order to obtain the amorphous phase of the $GaAs_{1-x}N_x$ films. Two non-doped GaAs crystal wafers with a diameter of 50 mm were used as the sputtering targets with a high deposition rate. A mixture of N_2 and Ar gas was used as the working gas. The target-substrate distance was 110 mm. Before film deposition, the targets were sputtering-etched in Ar plasma for 30 min to maintain a clean target surface. The sputtering chamber was evacuated with a background pressure well below 1×10^{-4} Pa by a turbo-molecular pump coupled with a rotary pump. High purity (99.999%) N_2 and Ar gases were let into the chamber through the individual mass flow controller. Flow rates of N_2 and Ar gas were fixed at 3 and 30 sccm respectively. The sputtering time was 60 min and the RF power of every target was kept at 50 W for every run. The total chamber pressure was varied from 0.5 to 3 Pa for different samples using a throttle valve. Substrate holder rotated with a speed of 10–15 round/min by a step motor during the deposition in order to obtain a uniform film.

The film thickness d was determined by a surface profiler (Tencor Alpha-Step 200 Instrument). For the atomic concentration of elements in the films, the energy-dispersive spectroscopy (EDS) measurement was done in a Noran Instrument EDS System. The carrier concentration was determined by the hall measurement using the Van Der Pauw method. The optical transmittance spectra were measured by a spectrophotometer (UV-3100, Shimadzu) over the wavelength range of 300–2600 nm.

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† Corresponding author. Email: bbx@cust.edu.cn

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Table 1. Thickness, N content and carrier concentration of a-GaAs$_{1-x}$N$_x$ thin films deposited at different sputtering pressures.

Sputtering pressure (Pa)	Thickness (nm)	x value (%)	Carrier concentration (10^{17}cm^{-2})
0.5	934	11.3	1.52
1	905	11.5	3.07
2	718	14.8	4.09
3	522	32.3	6.89

3. Results and discussion

The thicknesses of the deposited films, determined by a surface profiler were listed in Table 1. A reduction in thickness indicates that the deposition rates decrease with the increase of sputtering pressure. At low pressure, the ion energy distribution in the plasma is sharper and the average energy is larger than that at high pressure. Therefore the effect of ion bombardment is more significant. On the other hand, a low sputtering pressure leads to a long mean free path of Ar$^+$ with high kinetic energy, and consequently the atoms sputtered from the target have higher kinetic energies[12]. It is believed that there is an increased probability of a sputtered atom being returned to the target by gas collision at a high pressure, thereby reducing the deposition rate.

The nitrogen incorporation of the as-deposited films was controlled by the variation of sputtering pressure. Using the EDS analysis, x values of as-deposited a-GaAs$_{1-x}$N$_x$ films were obtained as shown in Table 1. It is found that the films with high N content were deposited by high sputtering pressures. The fact can be explained in terms of the impurity incorporation model[13] which states that the fraction of a gas trapped during film deposition is inversely proportional to the deposition rate. It has been experimentally and theoretically verified that the deposition rate decreases with increased sputtering pressure. So the N content increases as the sputtering pressures increase in the present cases.

The n-type-carrier concentrations determined by the Hall measurement, for each sputtering pressure of a-GaAs$_{1-x}$N$_x$ thin films were summarized in Table 1. The free carrier concentration is increased as the sputtering pressure increases. Some of the incorporated N atoms are inserted in the a-GaAs matrix at the expense of As produced a-GaAs$_{1-x}$N$_x$. Other N atoms generate point defects as vacancies and interstitials which lead to N-related doping levels[2,14]. Consequently, we now suggest that the high concentrations of N in a-GaAs$_{1-x}$N$_x$ thin films under a high sputtering pressure are responsible for the high carrier concentrations.

The absorption spectrum is a simple method for analyzing the band structure of semiconductors. Figure 1 shows the transmittance of as-deposited a-GaAs$_{1-x}$N$_x$ thin films at different sputtering pressures. Interference maxima and minima due to multiple reflections on the film surface can be observed. The well oscillating spectra indicate that the as-deposited films have a high uniformity in thickness and composition and have little scattering loss on the surface of films. Furthermore, it is found that the absorption edge has a blue shift (towards the energy band with a shorter wavelength) and the transmittance increases with increasing sputtering pressure. This agrees with the theory that the change of carrier concentration is induced by the N content.

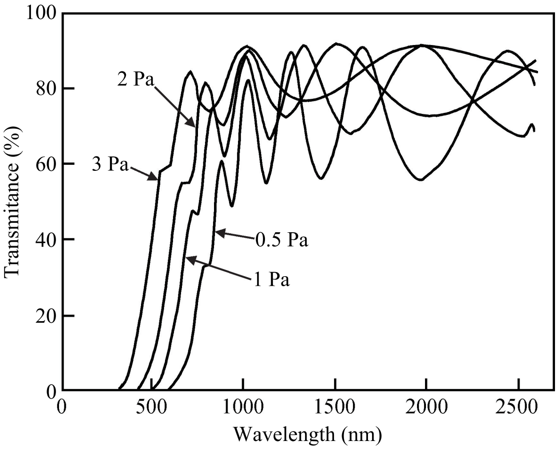

Fig. 1. Transmittance spectra of the as-deposited a-GaAs$_{1-x}$N$_x$ thin films.

In order to determine the optical band gap, the absorption coefficient α was estimated as a function of transmittance using the well-known relation:

$$\alpha = \frac{1}{d} \ln \frac{1}{T}, \tag{1}$$

where d and T are the film thickness and transmittance, respectively. The obtained value of α for an a-GaAs$_{1-x}$N$_x$ thin film in the region of strong absorption is in the order of 10^4 cm^{-1}. This strong absorption is attributed to the interband transitions. The optical absorption edge is analyzed by the following equation according to Tauc[15]

$$\alpha h\nu = A(h\nu - E_g)^p, \tag{2}$$

where A is a constant, which is almost independent of the chemical composition of investigated materials. E_g is the optical band gap and p is a number related to transition process. In amorphous semiconductors, the exponent p takes values of 1/2 and 2 for the direct and indirect transitions respectively. The curves of $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ were plotted using the E_g value to determine the value of p, and it was found about 1/2 from the slope of these curves. Therefore, the as-deposited films appear to have a direct band gap. Plots of $(\alpha h\nu)^2$ as functions of $h\nu$ yield good linear relations over a wide range of photon energy (Fig. 2), indicating the presence of direct transitions. The extrapolations of these lines on the energy axis can give the optical band gaps of the prepared films as shown in Table 2. Similar results have also been obtained by Zantta[8]. The experimental results of E_g are inconsistent with the values of the optical band gaps of GaAs$_{1-x}$N$_x$ alloys following the dielectric theory of Van Vechen[16]. It can be seen from Table 2 that the optical band gap widens (blueshift) with increasing sputtering pressures. The noticeable blueshift can be explained on the basis of the Burstein effect[17], which attributed the blueshift of E_g to the increase of carrier concentration as shown in Table 1. This result is very important because it reveals that the optical band gap of a-GaAs$_{1-x}$N$_x$ can be controlled by varying the sputtering pressure.

The refractive index n of as-deposited a-GaAs$_{1-x}$N$_x$ thin films at different sputtering pressures are obtained using

Table 2. Optical band-gap (E_g), Cauchy dispersion constant (a), Wemple–DiDomenico parameters (E_d, E_o) and refractive index (n_∞) for the as-deposited a-GaAs$_{1-x}$N$_x$ thin films.

Sputtering pressure (Pa)	E_g (eV)	a	b (10^4)	E_d (eV)	E_o (eV)	n_∞	$E_g = E_o/1.77$ (eV)
0.5	1.95	2.59	16.68	20.03	3.49	2.60	1.97
1	2.25	2.15	9.29	14.63	4.02	2.15	2.27
2	2.47	2.08	7.84	14.18	4.26	2.08	2.40
3	2.83	1.88	6.81	11.83	4.6	1.89	2.59

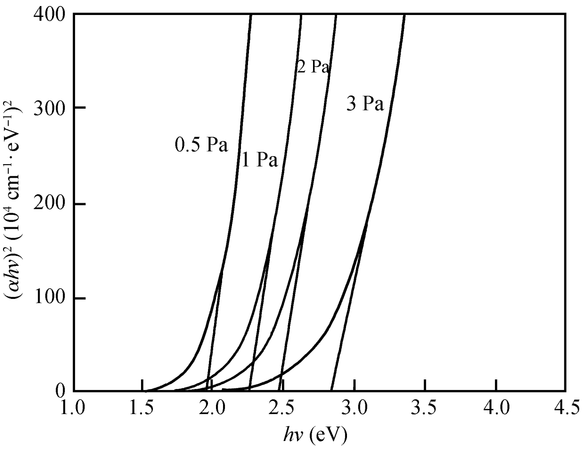

Fig. 2. Plots of ($\alpha h\nu$) as a function of $h\nu$ for the as-deposited a-GaAs$_{1-x}$N$_x$ films.

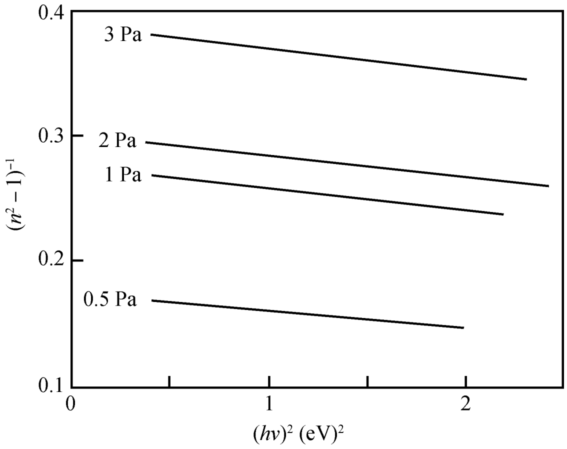

Fig. 4. Plots of $(n^2 - 1)^{-1}$ for the as-deposited a-GaAs$_{1-x}$N$_x$ films versus $(h\nu)^2$.

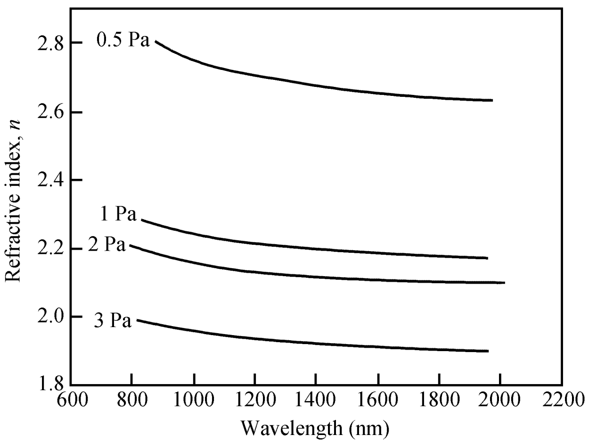

Fig. 3. Spectral distributions of refractive index for the as-deposited a-GaAs$_{1-x}$N$_x$ films.

the well-known envelope technique[18, 19] with transmittance spectra measurements as shown in Fig. 3. The value of n can be fitted to a reasonable function such as the two-term Cauchy dispersion relation[20]:

$$n(\lambda) = a + \frac{b}{\lambda^2}, \tag{3}$$

where a and b are Cauchy parameters and λ is the wavelength of incident light. For $\lambda \to \infty$, the significance of the parameter a appears immediately as n_∞. Equation (3) can be used for extrapolating the refractive index at a short wavelength[21]. The obtained values of a and b from Eq. (3) are also given in Table 2. It is observed from Fig. 3 that the refractive index tends to decrease with increasing wavelength exhibiting normal dispersion. Additionally, the change in the n value is strongly related to the change in N content induced by different sputtering pressures, i.e. the refractive index decreases with increasing N concentration. This result can be explained on the basis of the Kramers-Kronig relation which states that the change of the refractive index is the inverse of the variation of carrier concentration[22].

The refractive index dispersion is extremely relevant to communication and spectral analysis device design. Wemple and DiDomenico[23] have developed a refractive index dispersion model below the optical band gap (in the optical transparent region) using the single oscillator approximation. The model plays an important role in analyzing the behavior of the film refractive index. Defining two parameters, the oscillator energy E_o denoting the average excitation energy for electronic transitions and the dispersion energy E_d which represents the strength of interband optical transitions, this model concludes that:

$$n^2 = 1 + \frac{E_o E_d}{E_o^2 - (h\nu)^2}. \tag{4}$$

A plot $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ is shown in Fig. 4. Both Wemple parameters of E_o and E_d can be obtained from the slope $(E_o E_d)^{-1}$ and intercept (E_o/E_d) respectively. The values of E_o, E_d and the refractive index (n_∞) at long wavelengths are summarized in Table 2. Comparison of n_∞ between the third and seventh column in the table shows a good agreement of the two optical models. As can be seen, E_d decreases with increasing sputtering pressure which corresponds to the optical band gap widening in the deposited samples. Moreover, it has been verified that E_o was an average energy gap which was related to the value of the optical band gap by an empirical formula: $E_o = 1.77 E_g$[24, 25]. The values of E_g derived from E_o

are reasonably consistent with those obtained from the Tauc relation as tabulated in Table 2.

4. Conclusion

The optical constants and optical band gaps of the amorphous $GaAs_{1-x}N_x$ films prepared by a reactive sputtering method on glass substrates at different sputtering pressures have been investigated by the optical characterization method. It has been found that as the film deposition rate decreases, N and carrier concentrations in the deposited films increase as the sputtering pressure increases. The blueshift of E_g, dependent on the sputtering pressure, can be interpreted as the Burstein effect. The refractive index n of as-deposited a-$GaAs_{1-x}N_x$ thin films can be fitted well to the two-term Cauchy dispersion relation; the refractive index decreases monotonously with increasing wavelength and increases with decreasing sputtering pressure. The refractive index dispersion curves of the prepared films fit well to a single-oscillator model. The experimental data of the optical constants and optical band gaps of a-$GaAs_{1-x}N_x$ thin films can provide a reference for the application of a-$GaAs_{1-x}N_x$ materials in the future.

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