Spectroscopic Ellipsometry investigation of broad band optical properties of sputtered AlN films

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Abstract. We report the thickness, roughness, optical constant and band gap of Wurtzite type AlN thin films deposited on Si (100) substrate using DC reactive magnetron sputtering as a function of growth temperature ($T_s$, 35 to 600 °C). Evolution of optical properties with $T_s$ of these films was investigated by Spectroscopic Ellipsometry (SE) technique in the photon energy range of 0.6 to 6.5 eV. The “New Amorphous” dispersion formula was employed to extract optical constants from the experimental SE data. Thickness and roughness of these films were determined from the regression analysis of SE data, which have been corroborated using TEM and AFM technique. The optical parameters $n$ and $k$ strongly depend on $T_s$ as well as crystallite size. Highly a-axis oriented AlN film grown at 400 °C, exhibited high $n$ (2.64) and low $k$ (0.22) at 210 nm (deep-UV region), which can be used in deep UV opto-electronic device applications. All these AlN films exhibit transparent nature from near infrared (NIR) to 336 nm, where optical band gap energies varying between 5.42 to 6.16 eV.

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1. Introduction

In the last two decades, aluminum nitride (AlN) films have been attracted extensively in the semiconductor industry due to their unique outstanding physical and optical properties with great technological advantages. AlN is a wide band gap ($\sim 6.2$ eV) semiconductor in addition to its high thermal conductivity and low thermal co-efficient of expansion \[1, 2\]. It has been used in optoelectronic displays, high temperature devices and short wavelength light source/detector applications due to their high breakdown dielectric strength, high refractive index and low-absorption coefficient \[1, 3\]. AlN films find an important role in deep-ultraviolet light-emitting diodes (deep UV-LED) for sterilization, water purification and environmental protection applications \[4\].
Moreover, AlN has higher solubility for group III elements with better chemical stability and mechanical properties, which is a promising material for electronic packaging application. AlN and Al-rich AlGaN alloy films find a crucial role in UV-LED (covering wavelengths from 200 to 375 nm), where the insulating properties can be used in the fabrication of GaN, GaAs and InP based electronic, radio-frequency UV sensor and optical devices [5, 6].

Mostly, properties of these films depend on the crystal structure, crystal orientation and micro-structure that depend on the deposition conditions. Due to simplicity and reproducibility, reactive magnetron sputtering technique has one of the common methods for growing AlN films under low temperature with a desired crystal structure and orientation [7, 8, 9, 10]. AlN is used in high temperature optoelectronic devices due to its high melting temperature and equitable thermal co-efficient of expansion match to Si and GaAs [11]. So, it is more salient to study and understand the optical properties of these films over a broad range of wavelengths starting from deep UV to NIR. Growth temperature ($T_s$) of thin films has a crucial role on the micro-structure and orientation, that affects the physical properties including optical and mechanical. But, very few reports are available on the optical properties of crystalline AlN thin films with $T_s$ and techniques such as ALD and sputtering [3, 11]. Also, there is no correlation exists between the $T_s$ and optical properties over deep-UV region of the spectrum. Spectroscopic Ellipsometry (SE) measurement is a powerful unique optical characterization technique to determine the optical properties of materials in the wide range of energy, which is a non-invasive and non-contact with a high degree of accuracy [12]. So, in this article, we are primarily concerned with the optical properties of AlN films deposited on Si (100) substrate by reactive sputtering technique at different $T_s$, in the photon energy range of 0.6 to 6.5 eV and reported its properties using SE technique.

2. Experimental

AlN thin films were synthesized by direct-current (DC) reactive magnetron sputtering technique (M/s. MECA 2000, France), using a 4N pure aluminum (Al) target (50 mm diameter) in a mixture of high pure argon (5N) and nitrogen (5N) gases on Si(100) substrate. Before deposition, the sputtering chamber was evacuated to $1 \times 10^{-6}$ mbar. The flow ratio of sputtering (Ar) to reactive gas ($N_2$) was kept constant at 4:1 SCCM for all these films. The target to substrate distance during deposition was maintained at 14 cm and deposition pressure of $5 \times 10^{-3}$ mbar. A thin layer of Al was deposited for few seconds to increase the adhesive strength between substrate and deposited AlN films. These films were grown at different substrate temperatures ($T_s$) such as 35, 200, 400 and 600 °C with a constant power of 200 W.

The SE parameters were measured by a phase modulated spectroscopic ellipsometer (M/s. Horiba Jobin-Yvon, UVISEL2, France) in the photon energy range 0.6 to 6.5 eV with 0.01 eV increment and the angle of incidence is 70° under ambient conditions. SE measures a change in polarization state as the beam of light reflects from the sample
of interest. The polarization change between the parallel (p) and perpendicular (s) components of the reflected light with respect to the plane of incidence is represented as the change in amplitude ($\Psi$) and the phase difference ($\Delta$), which are considered as ellipsometric parameters. So, the ellipsometric parameters $\Psi$ and $\Delta$ are defined by the Eq. (1) below.

$$\rho = \frac{r_p}{r_s} = e^{i\Delta \tan \Psi}$$

where $r_p$ and $r_s$ are the parallel and perpendicular reflection coefficients, respectively [13]. In our experiment, these quantities are measured by two more ellipsometric parameters, namely $I_s$ and $I_c$ and they are defined as shown in Eq. (2) below.

$$I_s = \sin(2\Psi) \sin(\Delta) \quad \text{and} \quad I_c = \sin(2\Psi) \cos(\Delta)$$

A classical non-linear minimization regression analysis was performed by the Levenberg Marquardt algorithm to carry out analysis between experimental data and a model describing the sample to express a goodness of fitting by the root-mean-square error ($\chi^2$), which is defined as

$$\chi^2 = \frac{1}{2N - P - 1} \sum_{i=1}^{N} \left[ \frac{(I_{s,m_i} - I_{s,c_i})}{10^{-2}} \right]^2 + \left[ \frac{(I_{c,m_i} - I_{c,c_i})}{10^{-2}} \right]^2$$

where N is the number of data points, P is the number of parameters to be fitted and indices $m_i$ and $c_i$ are the measured and computed quantity of the $i_{th}$ energy in ellipsometry parameters [14]. The data analysis and fitting were performed using DeltaPsi 2 software to extract the refractive index ($n$) and extinction coefficient($k$).

### 3. Results and Discussion

#### 3.1. Modeling and fitting for the analysis of optical constant

Spectroscopic ellipsometry is a non invasive, non-contact and sensitive characterization technique for thin films and has been used to determine layer thickness, roughness, refractive indices, composition and uniformity. In the current study, we have used “New Amorphous” dispersion formula by considering the nano-crystalline nature of these AlN films to extract refractive index, whereas Bruggeman Effective Medium approximation (BEMA) term was specially introduced for surface roughness. The dispersion formula, derived by Horiba Jobin Yvon on the basis of Forouhi-Bloomer amorphous dispersion relation fits smoothly for broader wavelength ranges i.e. from normal dispersion to anomalous dispersion region [15]. However, this dispersion model was well-grooved to give a Lorentzian shape to the refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$, which is consistent with Kramers-Kronig analysis with five independent parameters as described below.

$$n(\omega) = n_\infty + \sum_{j=1}^{N} \frac{B_j (\omega - \omega_j) + C_j}{(\omega - \omega_j)^2 + \Gamma_j^2}$$

(4)
\[ k(\omega) = \begin{cases} \sum_{j=1}^{N} \frac{f_j(\omega - \omega_j)^2}{(\omega - \omega_j)^2 + \Gamma_j^2} & : \omega > \omega_g \\ 0 & : \omega \leq \omega_g \end{cases} \]

where
\[ B_j = \frac{f_j}{\Gamma_j} \left[ \Gamma_j^2 - (\omega_j - \omega_g)^2 \right] \]
\[ C_j = 2f_j\Gamma_j(\omega_j - \omega_g) \]

where, the term \( n_{\infty} \) is the long wavelength refractive index, \( f_j \) (in eV) is the oscillator strength i.e. amplitude of the extinction coefficient peak, \( \Gamma_j \) (in eV) is the broadening factor of absorption peak, \( \omega_j \) (in eV) is the energy at which the extinction coefficient is maximum and \( \omega_g \) (in eV) is the energy at which the extinction coefficient is minimum, that is energy from which the absorption starts to be non-zero. A systematic approach of inclusion and omission of layers was followed to obtain a reasonably good fit to analyze the data obtained from the experiments. First, we have modeled the data with three phases, namely (Air/AlN/c-Si (substrate)) to evaluate the thickness, \( n \) and \( k \) of these films, by varying the thickness to minimize \( \chi^2 \). However this three phase model did not yield a good fitting. Therefore, in view of this, we have modeled the interface layer as (Al+AlN) on the basis of BEMA and this resulted in a large drop in \( \chi^2 \) with physical significance. Finally, surface roughness was also taken into consideration in this model to improve the quality of the fit. Hence, a five layer model (Air/roughness/AlN/interface(Al+AlN)/c-Si) was employed to fit the model by introducing roughness on the basis of BEMA, where roughness includes AlN and 50% voids mixture, which resulted in good fit.

Typically, ellipsometric parameters measured for AlN films grown at a temperature of 400 °C (\( I_s \) and \( I_c \)) over a spectral range 0.6 to 6.5 eV and corresponding fit are shown in Fig. 1. It is seen that there is an excellent fit throughout full measured spectral range. Here, the surface roughness of AlN films were modeled as a mixture of AlN and void, the ellipsometry parameters were extracted based on BEMA formalism. However, the roughness of these films derived from ellipsometry are found between 8 and 30 nm, which is higher than the root mean square roughness values (3 to 9 nm) using Atomic Force Microscopy (AFM), as discussed in our previous report [16]. Nevertheless, the roughness computed from ellipsometry and AFM both follows a similar trend with substrate temperature. The difference in magnitude of roughness between the two techniques was discussed by Easwarakhanthan et al [17] and Tripura Sundari et al [18]. The surface roughness data by AFM is over an area of 1.5×1.5 \( \mu m^2 \), which is a typical local roughness, whereas in SE, the data are acquired over a larger elliptical area of 2×0.7 \( mm^2 \). So, the difference in magnitude is due to the fact that the data for ellipsometry is from a larger area as compared to AFM. The best fit with thin interface layer (Al+AlN) between AlN film and c-Si substrate is measured which is varying from 2 to 4 nm with an Al volume fraction around 35 to 45%.

The nominal film thickness computed from ellipsometric modeling and the cross sectional transmission electron microscopy (x-TEM) are shown in Fig. 2. A close match has been observed from the five layer model which we have followed. A representative
3.2. Behavior of optical constant with growth temperature

The real ($n$) and imaginary ($k$) parts of complex refractive index of AlN films with different $T_s$ are shown in Figs. 4 (a) and (b), respectively. The $n$ and $k$ exhibit a strong dispersion and increase monotonically with increasing photon energy in normal dispersion region, then it decreases in anomalous dispersion region. It is also interesting to see the significant shift in both parameters as the $T_s$ increases up to 400 °C.

Since, AlN is used as deep-UV light source and LED with emission wavelength
Figure 2. Thickness of AlN films measured by SE and TEM.

Figure 3. Dark field x-TEM and SAED of AlN films grown at 400 °C.

of 210 nm, it is important to know the change in $n$ and $k$ of these films at 210 nm wavelength that are shown in Fig.5 as a function of $T_s$. The $n$ and $k$ values are varying from 2.08 to 2.64 and from 0.22 to 0.27 at 210 nm wavelength (5.9 eV), respectively with $T_s$. With the increase in $T_s$, $n$ value increased up to 400 °C and then it had a fall at 600 °C. However, the $k$ value decreased from 35 to 400 °C and then it has shown an increase at 600 °C. Around photon energy 3.7 eV (336 nm) all these films exhibited transparent nature at $k$ value zero, where the $n$ is varying between 1.91 to 2.16, can be seen in Fig.4. The crystallite size of these films were calculated using Williamson-Hall method is shown Fig.5, as inset. A similar behaviour for $n$ was observed in the crystallite size from 35 to 400 °C and a fall at 600 °C due to dissociation of bonds and
Figure 4. (Color online) A plot of (a) refractive index ($n$) and (b) extinction coefficient ($k$) with respect to incident photon energy for AlN films at substrate temperatures 35 to 600 °C.

strong re-evaporation of ad-atoms at high $T_s$ [16, 9, 10]. AlN grown at 400 °C, a highly a-axis oriented film with large crystallite size ($\sim$ 66 nm) exhibited $n$ as 2.64 at 210 nm (UV region). However, the same is 2.16 in the transparent region (336 nm).

The optical parameters $n$ and $k$ are dependent on the structural disorder like void, lattice defects, oxygen impurity and chemical composition. The parameter $T_s/T_m$ ($T_m$ = melting temperature of growing material) is important for the growth of thin films that defines the film orientation and structure [19]. If the film is deposited using sputtering at room temperature, there is a little surface diffusion due to high melting point of AlN and one would expect voids, nitrogen vacancy and basal oxygen impurity concentration to be much higher than at equilibrium. But, with increase in $T_s$, increases the adatom mobility
Figure 5. The variation of $n$ and $k$ value at 210 nm and the crystallite size (inset) of AlN films with $T_s$.

causes the increase in crystallite size and columnar structure. The higher mobility of adatoms causes formation of dense AlN films and reduces the residual stress, porosity and defects [16]. Increase in growth or annealing temperature reduces the concentration of defects states like nitrogen, oxygen impurity and coordination defects, where refractive index of the film is improved and is proportional to packing density [20, 21]. Hence $n$ value is increasing linearly with $T_s$ upto 400 °C, then a fall at 600 °C due to decrease in crystallite size. Similarly, at 35 °C extinction coefficient $k$ is higher due to more nitrogen vacancy in the film and Al concentration in interface layer, that can additionally contribute to the absorption by creating localized states. But, at 400 °C substrate temperature, ad-atoms has high surface mobility that reduces nitrogen vacancy by the reaction of Al atom with nitrogen in AlN film as well as in interface layer. So, extinction coefficient $k$ reduced to 0.22 at 400 °C. Thus, the optical parameters $n$ and $k$ are strongly depends on $T_s$ as well as crystallite size.

The optical pseudo dielectric function ($\varepsilon(E)$) has been extracted directly from the ellipsometric parameters using the following relation.

$$\varepsilon(E) = N_o^2 \left[\sin^2\phi + \left(\frac{1 - \rho}{1 + \rho}\right)^2 \sin^2\phi \tan^2\phi\right]$$  \hspace{1cm} (6)

where $N_o$ is the refractive index of the ambient, $\rho$ is the ratio of ellipsometric parameters, $\phi$ is the angle and $E$ is the energy of the incident photon [18]. The real $\varepsilon_1$ and imaginary $\varepsilon_2$ parts of the pseudo-dielectric functions $\varepsilon(E)$ are computed for different $T_s$ from 35 to 600 °C. The $\varepsilon_1$ and $\varepsilon_2$ are increasing monotonically with increasing photon
energy in normal dispersion region, then it decreases in anomalous dispersion region as similar to complex refractive index. The $\varepsilon_1$ and $\varepsilon_2$ values of these films are varying from 4.3 to 6.9 and from 1.16 to 1.38 at 210 nm wavelength (5.9 eV), respectively. However, AlN film grown at 400 °C is showing higher dielectric constant, where $\varepsilon_1$ is varying from 4 to 7.4 as increase in photon energy from 0.6 to 6.5 eV.

![Graph showing the relationship between energy and $(E\alpha)^2$ for different substrate temperatures.](image)

**Figure 6.** The $(E\alpha)^2$ is plotted as a function of photon energy $E$ for substrate temperatures 35, 200, 400 and 600 °C. The intersection of straight lines through the abscissa of $(E\alpha)^2$ yields the energy position of optical band edges.

To obtain the optical bandgap of these AlN thin films, we have calculated the absorption coefficient ($\alpha$) over extended energy range (0.6 to 6.5 eV) to cover a larger portion of deep ultra violet to NIR (190 - 2066 nm) using the formalism followed by Looper *et al*, where $\alpha$ is defined as $\alpha = 4\pi k/\lambda$, where $k$ is the extinction coefficient and $\lambda$ is the wavelength of incident light [15]. In Fig.6, $(E\alpha)^2$ is plotted as function of photon energy ($E$) to derive the band gap energy. The linear dependence of $(E\alpha)^2$ curve with $E$, except near the band edge, prevails that these AlN films have a direct energy gap and using a linear extrapolation technique of tangential line to energy axis, optical band gaps are obtained. These results clearly agree with the literature Kar *et al*, where they have reported the bandgap energy of AlN films after annealed as a function of temperature [22]. The optical band gap and crystallite size of AlN films are plotted against the $T_s$, where the band gaps are as 5.42, 5.90, 6.16 and 5.96 eV at 35, 200, 400 and 600 °C, respectively (Fig.7). So band gap increases with $T_s$ up to 400 °C, then it decreased, which strongly depends on the crystallite size. At low temperatures, the band gap is small compared to bulk AlN that is due to the generation of shallow states.
Figure 7. Optical band gap and crystallite size of AlN films against $T_s$.

caused by the formation of lattice distortion by voids, N vacancy and oxygen impurity concentration [20, 22].

The parameters of the “New Amorphous” dispersion were extracted from the fitting are shown in Fig. 8. The oscillator strength i.e amplitude of the extinction coefficient ($f_j$) and the broadening factor of absorption ($\Gamma_j$), both are decreasing with $T_s$. Amplitude of extinction coefficient $f_j$ variation is within 0.16 to 0.8 eV, however broadening factor of absorption $\Gamma_j$ variation is large such as 1.47 (35 °C) to 0.97 eV(600 °C). The broadening parameter $\Gamma_j$ ($= \hbar/\tau_j$, where $\tau_j$ is phonon relaxation time), is the inverse of relaxation time, depends on the phonon contribution and microstructural parameters, such as static impurities, defect density, grain boundary, grain sizes, etc [12] A decrease in $\Gamma_j$ is observed with the increase in $T_s$ implies an increase in phonon relaxation time due to increase in crystallite size. $\omega_j$ defines the energy at which the extinction coefficient is maximum for a material and it is increasing with $T_s$, whereas energy from which the absorption starts to be non-zero ($\omega_g$) is almost constant. So, at 400 °C, AlN film shows high refractive index as well as low extinction coefficient with higher value of $\omega_j$ (6.9 eV) among all due to higher purity, larger crystallite size and also highly a-axis oriented.

4. Conclusion

Optical properties of AlN thin films deposited on Si(100) with different $T_s$ by reactive DC magnetron sputtering have been investigated by SE technique in the photon energy range of 0.6 to 6.5 eV. Thickness, roughness, optical constants and band gaps of these films were obtained by the modeling and fitting procedure to experimental SE data on the basis of “New Amorphous” dispersion formula. The thickness and roughness of
these films were determined from the regression analysis of SE data, which corroborated using TEM and AFM techniques. The optical parameters \( n \) and \( k \) strongly depended on \( T_s \) as well as crystallite size. A highly \( a \)-axis oriented AlN film grown at 400 °C, exhibited high \( n \) and low \( k \) as 2.64 and 0.22, respectively at 210 nm (deep-UV region). With increase in \( T_s \), band gap also increased upto 400 °C, which is closed to bulk AlN.

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