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Structural and Dielectric Investigation of Spin Coated AlN Thin Films by Sol-Gel Route

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ABSTRACT

In this study we have AlN thin films synthesized using sol gel technique with sols of different molarity. The molarity of the sol concentration is varied as 0.1mM, 0.3mM and 0.5mM.AlN thin films are deposited by spin coating. Owning to its good physical and mechanical properties like high thermal conductivity, high electrical resistivity, good mechanical strength, low coefficient of thermal expansion and high chemical stability. AlN is extensively used in optoelectronics, SAW devices, piezoelectric sensors and in the fabrication of micro electro-mechanical systems. Structural properties are investigated using X-ray diffractometer. Dielectric properties are studied by Impedance Analyzer. All the samples show amorphous behavior, but the sample prepared with 0.5mM molarity shows prominent peaks between 30° to 80°(2-theta). These peaks are corresponding to hexagonal phase of h-AlN according to Joint Committee on Powder Diffraction Standards (JCPDS) card no. 25-1133.Transmission spectrum shows the high value of transmission ~90% for 0.1mM sample. The band gap for 0.5mM sample is highest (4.0eV) which is due to the good crystal quality as confirm by the XRD results. Room temperature dielectric measurements show that dielectric constant and tangent loss decreases with increases in frequency suggesting potential application of AlN thin films in high frequency applications.

1. INTRODUCTION

Aluminum nitride has high breakdown voltage (15 kV/mm), very hard mechanically shows hardness of 20GPa, wide band gap of about 6.2 eV, piezoelectric constants comparatively quit high, and very low values of electron affinity (0.25 eV). It is shows resistance to corrosive attack demonstrate stability at high temperatures. AlN thin films shows high thermal conductivity high thermal conductivity~ 280W/mK at 300 K, high sound velocity propagation(~ 9 km/s),high electrical resistivity (109 _~ 1011_m), stable on high temperature, and possess stronger piezoelectric constants. AlN thin films have variety of applications from fusion reactor, RF filters, sensors, actuators, semiconductor packaging in high frequency, high power devices and optoelectronic devices (Kim et al. 1998). AlN thin films can have solution to overheating of the IC's, as compared to SiO_2 as thermal conductivity of AlN is much higher with insulating properties can reduce the effect of self-heating effect and which is widely influence the performance of microelectronic field. AlN has been used for LEDs in visible range (2-4 eV); the energy transfer processes have been studied extensively (Kim et al. 1998;

Jones et al. 2000; Ambacher 1998; Shiosaki and Kawabata 1892). Luminescence in visible range correlated to the oxygen related defects in the matrix (Shiosaki and Kawabata 1892; Chubachi et al. 1984). Recently AlN based UV-LED has been fabricated by using MOVPE technique with emission wavelength 210nm (Saxler et al. 1994). AlN shows ferromagnetic behavior when doped with transitions elements such as (Fe, Co, Ni, Mn, Cr, V, Cu) and also rare earth elements. Magnetic Semiconductors which shows Curie temperature above room temperature is current topic of research specifically spintronic devices.

Varity of methods has been adopted for AlN thin film deposition, most frequently used in PVD are Pulsed Laser Deposition, Molecular beam epitaxy, Sputtering, Filtered arc deposition, Ion beam enhanced deposition, In CVD are metal organic CVD, reactive ion beam deposition (RIBD), etc. All these techniques require high or ultrahigh vacuum systems that increase the production cost of material and hence devices. Another chemical based techniques, there are expensive and toxic chemicals which reduces applications on large scale. Among these chemical routes sol gel provide us advantage of formation all type of nanostructures, thin films, control over different parameters by using low cost, low cost and nontoxic precursors (Riaz et al. 2011).

In this research work, sol gel technique was adopted for synthesize of aluminum nitride thin films with 0.1mM, 0.3mM and 0.5mM, sol concentration, and study effect on the structural, dielectric, magnetic and optical properties.

2. EXPERIMENTAL DETAILS

AlN thin films were synthesized by sol gel routes. For preparation of sol, $Al(NO_3)_3$ 9H2O, 0.6 g (99.8% pure) used as precursor was dissolved in DI water (de-ionized). As-synthesized sol was stable and transparent without any kind of cloudiness of precipitation. Sol was stirred ultrasonically for 1 hour at ambient temperature. AlN thin films were spun coated on to copper and glass substrates at 3000rpm for 30sec. Thin films were dried for 24h in ambient temperature. To study structural properties Thin films characterized with X-Ray diffractometer (XRD) Rigaku D/MAX-IIA with Cuk_{α} (λ=1.5405Å) radiations (nickel filtered) was used for structural characterization. Copper target was operated at 25mA current and 35kV potential with step width of 0.05.JA Wollam variable angle spectroscopic Ellipsometer used for optical properties. In order to check response of the material to external electric field, the dielectric analysis was carried out. Dielectric analysis was performed using Wayne Kerr Precision Impedance Analyzer 6500B. For this purpose, the thin films were deposited on copper substrates of area 10 mm by 10 mm and thickness in the range of 700nm. All measurements were taken at room temperature in the frequency range of 20 Hz to 20 M Hz. The sample holder was made of two copper electrodes and the samples were sandwiched in between these electrodes.

2. Results and Discussion

Fig. 1 reveals XRD patterns of aluminum nitride samples XRD patterns. AlN thin films are synthesized by sol gel method with molarities 0.1mM-0.5mM with 0.2mM

interval. All the sample shows amorphous behavior, but the sample prepared with 0.5mM molarity shows prominent peaks between 30° to 80° (2-theta). These peaks are corresponding to hexagonal phase of h-AlN according to Joint Committee on Powder Diffraction Standards (JCPDS) card no. 25-1133.AlN thin films with molarities 0.1mM and 0.3mM are considered amorphous.

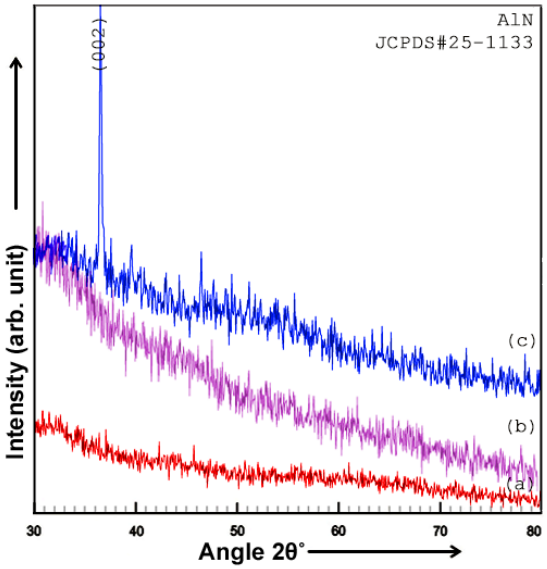

Fig. 1.XRD patterns of the AlN thin films synthesized by sol gel method with molarities (a) 0.1mM, (b) 0.3mM, (c) 0.5mM

Fig. 2 shows that transmission increases sharply at a particular range of 292-299nm, which shows the absorption edge. AlN thin films have transparent behavior more than 90% transparency in visible region which is an important requirement for optical uses. From the graph it is clear that transmission decreases with the increase in molarities of the samples and that decrease are due to the increase in number of particles or molecules, more number of particles will offer more hindrance and more blockage of light. And so there will be more absorption and less transmission. Maximum transmission is observed for 0.1mM sample.

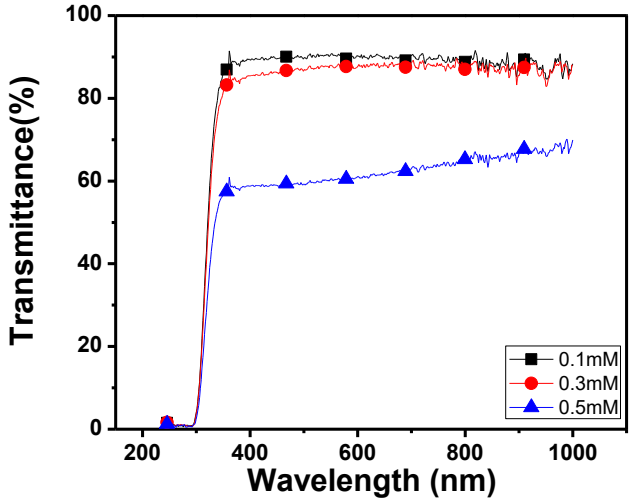

Fig. 2. Transmission curves of AlN thin films synthesized by sol gel method with molarities 0.1mM, 0.3mM and 0.5mM

The absorption coefficient (α) is important parameter for the band gap calculations by using following equation 1.

$$\alpha = \frac{1}{t}\ln\left[\frac{2\mathrm{Ref}^2\mathrm{Trans}}{-(1-\mathrm{Ref})^2+\sqrt{(1-\mathrm{Ref})^4+4\mathrm{Ref}^2\mathrm{Trans}^2}}\right] \quad (1)$$

Here, 'Ref' is the reflection, 'Trans' is the transmission, and 't' is the thickness of the film. To calculate the band-gap, we extrapolate the curve obtained by plotting (α^2) against E (eV), where value of α should be zero as depicted in Fig. 3.

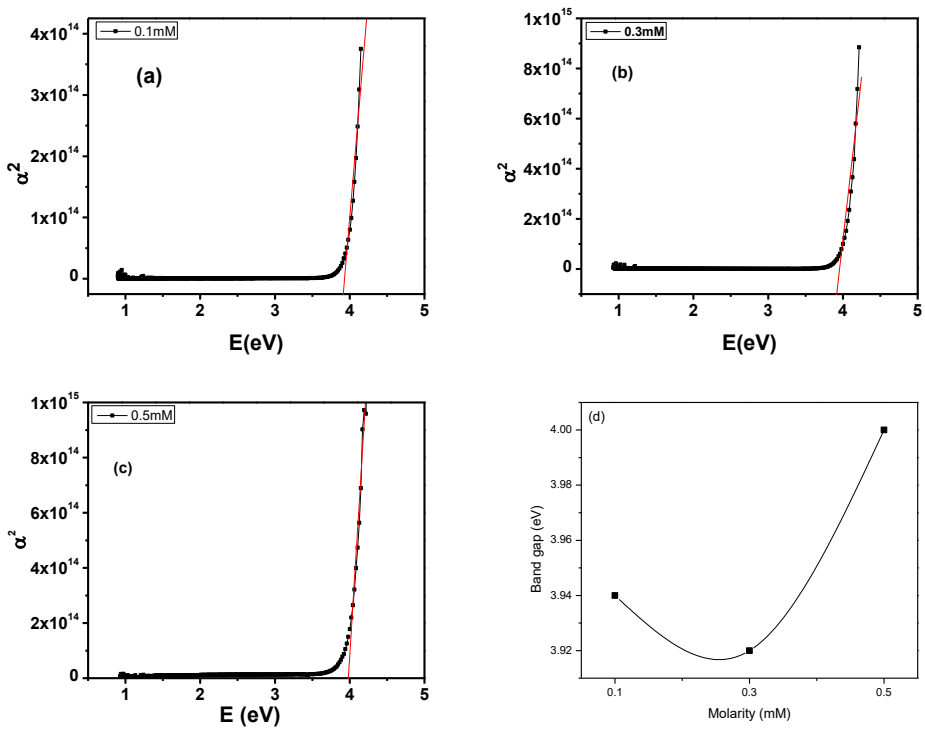

Fig. 3. α^2 versus E (eV) curves for aluminum nitride thin films; inset shows bandgap versus sol concentration, AlN thin films synthesized by sol gel method with molarities (a) 0.1mM (b) 0.3mM and (c) 0.5mM (d) Band gap vs. molarities.

From all graphs of Fig. 3 it is clear that band gap energies lies in the range of 3.92- 4.0 eV as shown in table below.

Table 1: Aluminum nitride thin films Bandgap versus sol concentration, AlN thin films synthesized by sol gel method with molarities 0.1mM, 0.3mM and 0.5mM

Sample no.	Molarities (mM)	Eg(eV)
1	0.1	3.94
2	0.3	3.92
3	0.5	4.0

In literature we found the band gap values of single crystal of AlN are in the range of 6.02-5.6 eV. But our values for band gap are less than the expected values which may be due to the reason that our films are amorphous. Inset Fig 3 molarities are plotted Vs band gap. Above graph shows that by increasing molarity band gap slightly decreases. The band gap for 0.5mM sample is highest (4.0eV) which is due to the good crystal quality as confirmed by the XRD results. The very small decrease in band gap by increasing molarity from 0.1mM to 0.3mM is due to the presence of surface states;

absorption may arise from the surface states of the Al-N material. These surface states increase with increase in molarity, and will decrease the band gap.

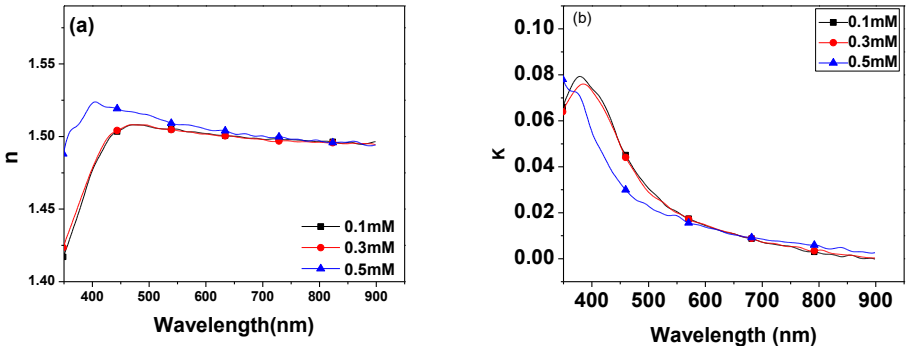

Fig.4. (a) Refractive index (n) and (b) extinction coefficient (k) for AlN thin films synthesized by sol gel method with molarities 0.1mM, 0.3mM and 0.5mM.

To calculate refractive index and extinction coefficient we have used ellipsometer, experimental data was fitted by using two layers Cauchy model as given by the following equations 2 and 3 respectively.

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \ , \tag{2}$$

$$\kappa\,(\lambda) = ae^{b(\frac{1240}{\lambda} - E_g)}, \tag{3}$$

Where A, B and C are constants for fitting parameters the n and k are plotted according to the wavelength 300 – 900 nm. The value of n index and k decreased as the wavelength was increased and shows normal dispersion at the long-wavelength region. Fig. 4 (a) and (b) show the plot of n and 'κ' as the function of wavelength. Plot shows that 'n' increases with the increase in wavelength and 'κ' decreases with the increase in wavelength which is according to the normal dispersion behavior. And with increase in molarities 'n' and 'κ' increases. Increase in 'n' and 'κ' with increasing molarity can be explained on the basis of absorption, as by increasing molarity absorption of light increase so 'n' and 'κ' increase.
The dielectric constant and dielectric loss were calculated based on the following equations. 4 and 5, and the measurements were performed by 6500B precision impedance analyzer,

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \ , \tag{4}$$

$$\tan\delta = \frac{1}{2\pi f \varepsilon_0 \varepsilon' \rho} \ , \tag{5}$$

Where C is the capacitance, d is the thickness, A is the area of the device, ρ is the resistivity $\mathcal{E}_0$ is the permittivity of free space. The dielectric constant and tangent loss are plotted as functions of sol concentration in Fig. 5(a) and (b).

Dielectric constant has shown values comparatively high at low frequency for all samples. And these values become constant at low frequencies. It can be explained on the basis of relaxation time of dipole alignment according to external electric field. The alignment is easy at low frequencies but flipping is difficult at high frequencies and dielectric constant decreases and remains constant after that. The polarization almost ceases due to which at very high frequency, dielectric constant becomes independent of frequency. The Maxwell-Wagner theory explains the decrease in dielectric constant. Where samples were heterogeneous, it contains grains and grain boundries, due to which dipolar and interfacial polarization occurs in these materials at low frequency while at high frequency only electronic polarization occurs due to which dielectric constant decreases at high frequency. This is the point where dielectric constant decreases while dielectric loss becomes prominent. In Fig. 5 (a) variations of molarities with dielectric constant is shown. Graph shows that the dielectric constant decrease with increasing molarity, which may be due to the reason that by increasing molarity density of defects sites also increase. So the polarization effect in the material reduces with the increase in molarity, hence the dielectric constant decrease. When alternating voltage is applied across a dielectric material then energy is stored in dielectric material but some energy is dissipated in the form of heat called loss factor. Voltage inside the material lags behind applied voltage due to which some energy lost is called tangent loss. Trend of tan loss for AlN thin films is shown in the following Fig 5(b). Voltage always leads by $\frac{\pi}{2}$when a.c. Voltage is applied across dielectric material due to which energy is absorbed and is dissipated in the form of heat. In Fig. 5(b) variations of tan loss vs. molarities is shown. Above graph indicates that tan loss increase with increase in molarity which is again due to the increase in defect density. And due to increase in the defect density polarization is less and so the tan loss is high. Perfect dielectric materials consist of neutral atoms and do not contain free electrons which cause the conduction mechanism in materials but there is some leakage current in dielectric materials.

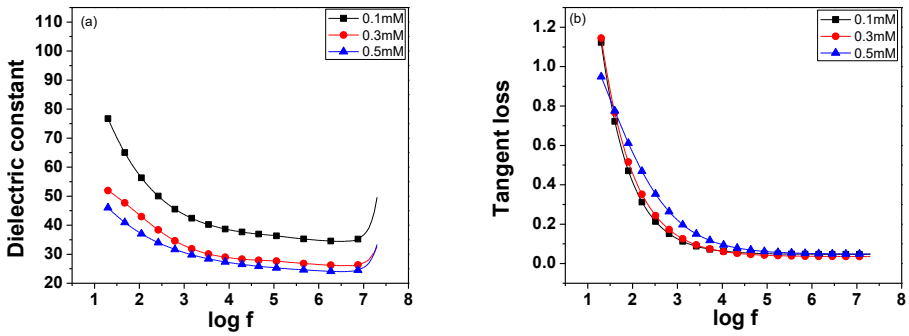

Fig. 5. (a) Dielectric constant and (b) tangent loss for AlN thin films synthesized by sol gel method with molarities 0.1mM, 0.3mM and 0.5mM

Conductivity can be calculated by using following formula

$$\sigma_{a.c} = \mathcal{E}'\mathcal{E}_0\omega \tan\delta \quad (6)$$

Where ε' is dielectric constant, ε_0 is permittivity of free space, ω is angular frequency and $\tan\delta$ is tangent loss Conductivity can be explained by Maxwell-Wagner theory.

Fig. 6 shows that at low frequency the value of conductivity is low. The trend is increasing as frequency is increased after log (f) = 6 or more, value of conductivity is increased. It is well known that the grain boundaries have shown high resistance at low frequency while at high frequency, conductivity is increased due to the grains effect. As impedance is decreased at high frequency it means conductivity increased at high frequency as shown in Fig. 6 show that a. c. conductivity slightly increase with the increase in molarity.

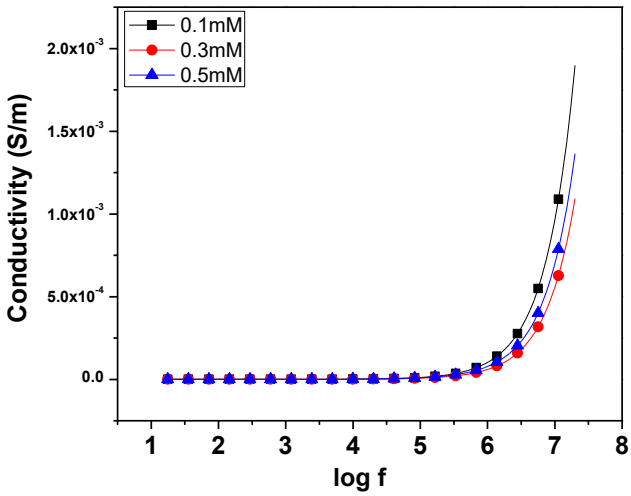

Fig. 6.Frequency dependent ac conductivity Vs Log (f) for AlN thin films synthesized by sol gel method with molarities 0.1mM, 0.3mM and 0.5mM

The increase in a. c. conductivity is due to the increase in density of defect site. As the defect sites increase hopping of charge carriers between the pairs of localized states takes place which increase the a. c. conductivity. So a shift in a. c. conductivity is observed.

4. CONCLUSIONS

Aluminum nitride thin films have been successfully synthesized by low cost sol-gel route. The simple procedure includes the synthesis of sols with variation in molarities 0.1mM, 0.3mM and 0.5mM.These sols were obtained after thirty hours stirring at 50˚C. Thin films showed very interesting optical and dielectric results. Optical measurements revealed that AlN thin films exhibit high transparency in visible region which is an important requirement for optical applications especially in solar cells as window layer. Refractive index and extinction coefficient were normal range, refractive index lies in the range 1.26-1.57 and extinction coefficient in the range 0.001-0.1. Results also confirmed the direct and wide band-gap of AlN thin films in the range of 3.92-4.0eV.

Dielectric measurements revealed that dielectric constant and tangent loss decreases with increase in frequency while ac conductivity increases with increase in frequency. This implies that we can use AlN thin films for high frequency applications. Highest dielectric constant ~40 (at log f =4.0) along with low tangent loss has been observed at 0.1mM.

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