

Structural and Optical Properties of Chromium Doped Aluminum Nitride Thin Films Prepared by Stacking of Cr Layer on AlN Thin Film

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Abstract— Chromium stacked aluminum nitride (Cr-AlN) thin film was deposited on glass substrates by elemental stack method using rf sputtering. Annealing treatment was carried for about 1 hour at 100°C, 300°C, and 500°C in nitrogen atmosphere for doping. Variations of the structural and optical properties of the films were studied using XRD, AFM, FESEM and UV-Vis spectroscopic technique. Structural analysis showed the presence of only (111) planes with very low intensity. From AFM and FESEM images, reduced grain size and smoothed surface morphology was achieved as the annealing temperature increases. Improved optical transmittance of Cr-AlN may be due to the diffusion of Cr into AlN as the annealing temperature increases. Decreased film thickness was also noticed for Cr-AlN thin film with annealing temperatures.

Keywords— AlN, Structural analysis, Optical Properties.

I. INTRODUCTION

Aluminum nitride (AlN) is a direct band gap material which is a promising III-Nitride material due to good properties in terms of high thermal conductivity, thermal and chemical stability, wide energy band gap (6.2eV), and high acoustic wave velocity with fairly good piezoelectricity [1-6]. In addition, good mechanical and thermal matching with substrate material make AlN is a suitable material in the fabrication of optical, ultraviolet optoelectronic, high frequency electroacoustic devices, and sensor [7, 8]. On the other hand, AlN based UV light source becomes more attractive in laser industry due to good material for polymer, epoxies, and resins curing application [9].

Several methods can be applied for the growth of AlN thin films on various substrates at room temperatures by radiofrequency (RF) magnetron sputtering, reactive evaporation, pulsed laser deposition (PLD), molecular beam epitaxy (MBE), metal organic chemical vapour depositions (MOCVD), and ion implantation [1-5]. Among the physical deposition method, stacking elemental layer for doping is a suitable method to control the material composition with good properties and can be avoided from the target contaminant. This technique gives large-area deposition, uniform, and inexpensive technique among others technique [4-5].

Transition metal doped AlN have already been reported by several researchers for different application in semiconductor

technology [10]. In this study, chromium was chosen as dopant since it is responsible for optical characteristics of AlN thin film [10]. The Cr doped AlN film were grown on Al₂O₃ (001) and observed wurtzite-type hexagonal with an epitaxial relation of the (100) direction of the films on the (001) direction of Al₂O₃ substrates [11]. Among the published work, electronic and magnetic properties of Cr doped AlN thin films have been addressed by several researchers than the structural and optical properties [12, 13].

The aim of this study is to deposit Cr doped AlN thin film on Glass substrates by post annealing of Cr stacked AlN thin film and investigate the optical properties and structural properties of Cr-AlN thin films on glass substrates. Few researchers have been successfully reported about the effect of ion implantation on structural and optical properties of Cr doped AlN thin film prepared by RF sputtering [10]. The structural and optical properties of Cr-AlN thin films were examined by X-ray diffraction (XRD) technique and UV-Vis spectrophotometer. The surface properties of annealed samples were analyzed by Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM) respectively were used to analyze the surface morphology of Cr doped AlN thin films.

II. EXPERIMENTAL METHOD

Cr-AlN thin films stacked were deposited on glass by RF magnetron sputtering using a Cr target with purity (99.9%) and AlN target with purity (99.9%). The glass was then cleaned by rinsing in ultrasonic bath of acetone and then loaded in the central region of the substrate holder. The sputtering chamber was initially evacuated to the base pressure of about 4.18×10^{-5} mbar. The vacuum pressure for film deposition was maintained at 1.91×10^{-2} mbar with gas ratio of Ar:N₂ (18:2) for AlN thin film. RF power of 150W for 45 min and 100 W for 15 min was used to get the desired film thickness of AlN and Cr respectively. Prior to the film deposition, pre-sputtering was carried out for 5 min to remove any other contaminants on the surface of the material source target. The stacked layers (AlN/Cr/AlN/Cr) were allowed to isochronal annealing from 100°C-500°C for about 1 hr in N₂ ambient in a separate furnace.

In order to characterize, the structural properties of Cr-AlN thin films grown on glass substrates at different annealing

temperatures (100°C, 300°C, and 500°C) were analysed by XRD using phase angle technique. The morphology of the Cr-AlN thin films was observed by FESEM, and AFM. Beside that, optical transmittance measurement was carried out using a UV-VIS-NIR with in the wavelength range of 200nm - 1000nm for Cr-AlN thin films on glass substrates which were annealed at 100°C, 300°C, and 500°C.

III. RESULT AND DISCUSSION

A. Optical

Figure 1 shows the transmission spectrum as a function of the wavelength for Cr-AlN sample deposited on glass at various annealing temperature (100°C, 300°C, and 500°C) and it is evident from the figure that the films are not transmit well for the wavelength at far UV range and transmission starts to increase (40%-86%) at the near UV spectrum and reaches a maximum value in the visible range of wavelength and near to IR region. The influence of annealing temperature on the optical characteristics of the Cr-AlN thin films can be seen through their optical transmission measurement. From the figure 1, the optical absorption edge of Cr-AlN is blue shifted for the films treated at high annealing temperatures. In addition, the transmission percentage increases as the annealing temperature increases. This may be due to structural rearrangement or the diffusion of atomic nitrogen favouring the development of a less disordered AlN matrix as a result of annealing [10].

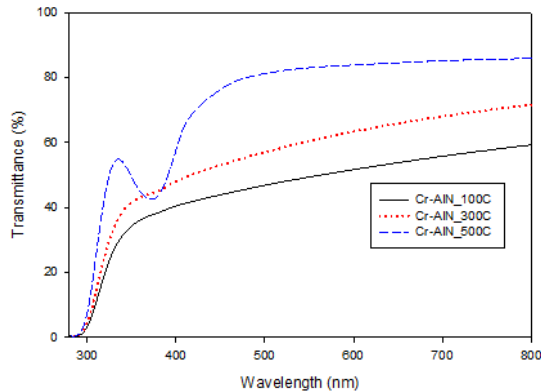


Fig. 1 The transmittance spectra as a function of the wavelength for Cr-AlN samples deposited on glass at various temperatures (100°C, 300°C, and 500°C)

In order to measure the band gap, the derivative method has recently been used and the position of the peak with maximum intensity is the indication of band gap energy [14]. On consequence, the same method is applied in this study to measure the band gap energy and the calculated derivative curve is observed as given in the figure 2. The optical band gap (E_g) of the films can be obtained by plotting $dT/d\lambda$ against transmission wavelength (λ). The energy band gap was evaluated by using the following relation:

$$E_g = hc/\lambda_{max} \quad (1)$$

Where h is Planck constant, c is the light velocity and λ_{max} is the maximum wavelength observed from the derivative curve. The calculated band gap energy of Cr-AlN thin films is summarized in table-1. The variation in energy band gap may be associated to the presence of defects in Cr-AlN.

TABLE I
ENERGY BAND GAP OF Cr-AlN AT DIFFERENCE ANNEALING TEMPERATURES (100°C, 300°C, AND 500°C) FOR 1HR.

Cr-AlN_Annealed (°C)	Wavelength (nm)	Band gap (eV)
100	324	3.83
300	316	3.92
500	317	3.91

Since, reported values shows high band gap value for high quality bulk AlN which 6.03 eV [16]. Thus, add the dopant to any material cause the band gap to shrink [15]. As evident, Cr doped AlN shows decreasing in band gap of AlN film. This is due to the fact that the wave functions of the electron bound to the impurity of the atoms start to overlap as the density of the impurities increases [16].

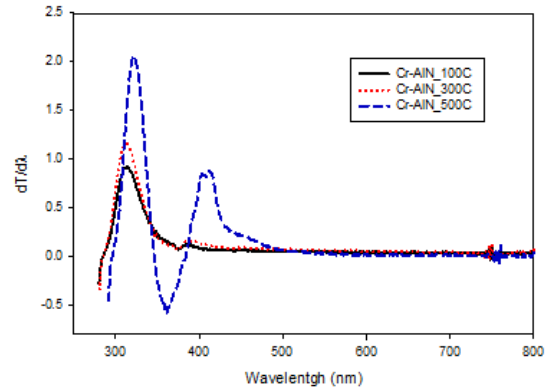


Fig. 2 The band gap of Cr-AlN samples deposited on glass at various temperatures (100°C, 300°C, and 500°C)

B. Surface Analysis

The x-ray diffraction spectra of annealed Cr-AlN thin film was recorded and the structural properties of Cr-AlN thin film were observed from the spectra as summarized in table 2. Since the intensity of observed peaks is very low, the spectra are not presented here for discussion. The indexed peaks are search matched and the results are driven. From the Table – 2, it is noticed that all annealed films exhibit only the AlN (111) peak indicating that the films have cubic structure. Overall, the lattice constant and d -space of Cr-AlN thin film increases with annealing temperature increases.

TABLE III
STRUCTURAL PROPERTIES OF Cr-AIN AT VARIOUS ANNEALING TEMPERATURE (100°C, 300°C, AND 500°C) FOR 1HR IN N₂.

Cr-AIN	Lattice Constant, a (Å)	d _{hkl} (Å)	Angle 2θ (°)	R _{rms} (nm)
100°C	4.34	2.57	35.79	5.39
300°C	4.32	2.49	35.99	3.96
500°C	4.37	2.52	35.59	3.88

In order to study the effect of Cr doping into AlN thin film, the surface morphology of Cr-AlN thin film was recorded using AFM as shown in fig. 3. The surface image was captured by tapping mode. The surface morphology of the Cr-AlN thin films on glass substrates was significantly rough. The high resolution AFM image reveals the formation of ring shape particle on the surface of Cr -AlN on glass substrates. Using image processing software, the recorded image was processed and the surface roughness of the prepared film were measured of about 5.39 nm, 3.96 nm, and 3.88 nm for 100°C, 300°C, and 500°C respectively. It clearly shows that the surface roughness decreases with annealing temperature increases. Hence, it is attributed to the diffusion of Cr atom in to AlN thin film as a result of thermal annealing. [17]. For detailed analysis, FESEM images are also captured for the prepared film annealed at different temperatures as shown in Figure 5 It is shown that the sample surface become smoother as annealing temperature increases. These results are correlated with the AFM results as the roughness decreases with annealing temperature increases. This may be due to the influence of Cr on the surface morphology of AlN. There may be a chance to decrease or increase the film thickness when the doping process carried out using the stack annealing process [18]. To verify this statement, the thickness of the Cr doped AlN thin films were also evaluated by recording the cross sectional FESEM image (figure 6) and observed that the thickness is decreasing as with annealing temperature increases. This may be due to the reaction of Cr with AlN at given temperature during annealing process.

IV. CONCLUSIONS

The surface and optical properties of RF sputtered Cr-AlN thin films have been investigated. Using the transmission spectra, the band gap energy was obtained by plotted dT/dλ against transmission wavelength. In this case, the band gap value increases as the annealing temperature increases. The surface roughness of the Cr-AlN film was found to be decreases as the annealing temperature increase. The decreasing in surface roughness of the sample has correlated results with FESEM surface analysis.

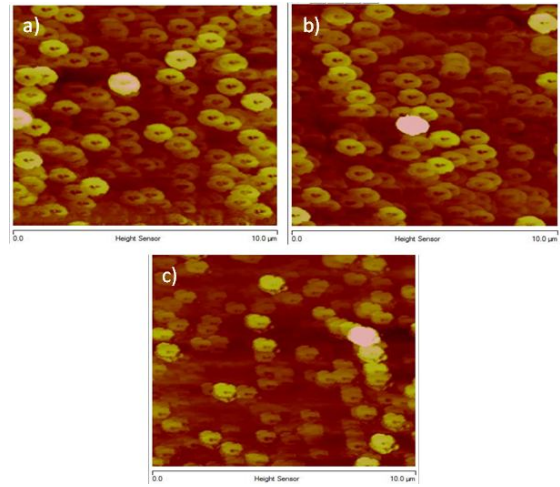


Fig. 3 The AFM images of Cr-AlN samples deposited on glass at various temperatures (100°C, 300°C, and 500°C)

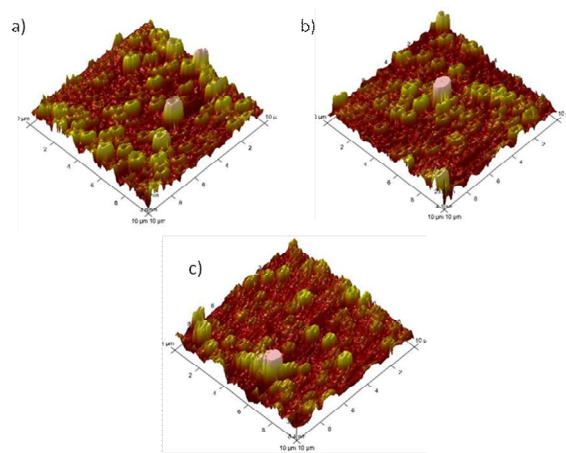


Fig. 4 The 3D AFM images of Cr-AlN samples deposited on glass at various temperatures (100°C, 300°C, and 500)

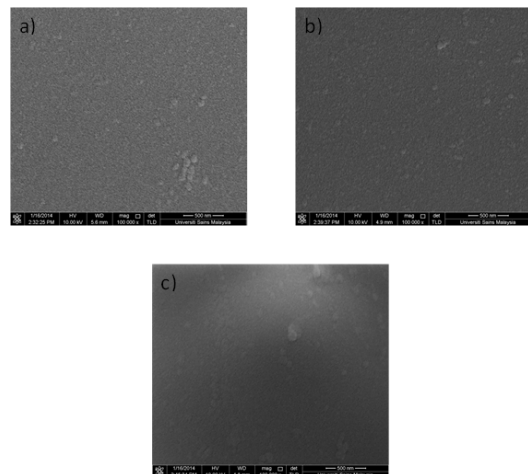


Fig. 5 The FESEM images of Cr-AlN samples deposited on glass at various temperatures (100°C, 300°C, and 500°C)

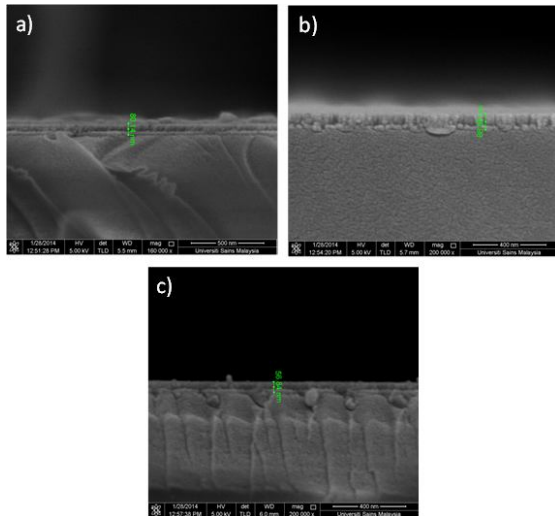


Fig. 6 The cross section of Cr-AlN samples deposited on glass at various temperatures (as-grown, 100°C, and 300°C)

REFERENCES

[1] J. Y. Han, and K. J. Hyeong, "Spectrophotometric Analysis of Aluminum Nitride Thin Films," *Journal of Vacuum Science Technology*, vol. 3, pp. 862-870, 1999.

[2] H. K. Lee, and D. K. Kim, "Effect of second phase after heat treatment on the thermal conductivity of AlN ceramics," *Key Engineer Materials*, vol. 403, pp.61-63, 2009.

[3] K. Jagannadham, A. K. Sharma, Q. Wei, R. Alyanraman, and J. Narayan, "Structural characteristics of AlN films deposited by pulsed laser deposition and reactive magnetron sputtering: A comparative study," *Journal of Vacuum Science Technology*, vol. 16, pp.2804-2815, 1998.

[4] M. H. Park, and S. H. Kim, "Thermal conductivity of AlN thin films deposited by RF magnetron sputtering," *Material science in Semiconductor Processing*, vol. 15, pp. 6-10, 2012.

[5] S. Shanmugan, P. Anithambigai, and D. Mutharasu, "An effect of synthesis parameters on structural properties of AlN thin films deposited on metal substrates," *IJASCSE*, vol. 1, pp. 1-10, 2012.

[6] Y. Xu, D. D. L. Chung, and C. Mroz, "Thermally conducting aluminium nitride polymer-matrix composites," *Composite Part A: Applied Science and Manufacturing*, vol. 32, pp. 1749-1757, 2001.

[7] K. A. Aissa, N. Semmar, D. D. S. Meneses, L. L. Brizoual, M. Gaillard, A. Petit, P. Y. Jouan, C. B. Leborgne, and M. A. Djouadi, "Thermal conductivity measurement of AlN films by fast photothermal method," *Journal of Physics*, pp. 1-8, 2012.

[8] A. T. Wieg, Y. kodaera, Z. Wang, T. Imai, C. Dames, and J. E. Garay, "Visible photoluminescence in polycrystalline terbium doped aluminium nitride (Tb:AlN) ceramics with high thermal conductivity," *Applied Physics Letters*, pp. 1-5, 2012.

[9] M. Okamoto, Y. K. Yap, M. Yoshimura, Y. Mori, and T. Sasaki, "Fabrication of conductive AlN films by pulsed laser deposition," *Proc. International Workshop on Nitride Semiconductors*, pp. 198-201, 2000.

[10] L. C. Cossolino, and A. R. Zanatta, "Influence of chromium concentration on the optical-electronic properties of ruby microstructure," *Journal Physics D: Applied Physics*, pp. 1-8, 2010.

[11] Z. Jun, H. L. Sy, and J. S. david, "Epitaxial growth and magnetic properties of Cr-doped AlN thin films," *Journal of Physics: Condensed Matter*, vol. 17, pp.3137-3142, 2005.

[12] H. Cheng, F. Jun, and K. Hong, "Electronic structure and magnetic properties of Cr-Doped AlN," *Communications in Theoretical Physics*, vol. 48, pp. 749, 2007.

[13] E. Yasushi, S. Takanobu, K. Kawamura, and Y. Masahiko, "crystal structure and magnetic properties of Cr-doped AlN films with various Cr concentration," *Material Transaction*, vol. 28, pp. 465-470, 2007.

[14] M. K. M. Ali, K. Ibrahim, E. M. Mkawi, and A. Salhin, "Characterization of phosphoric acid doped N-type silicon thin films printed on ITO coated PET substrate," *International Journal Electrochemical Science*, vol. 8, pp. 535-547, 2013.

[15] L. Vina, and M. Cardona, "Effect of heavy doping on the optical properties and band structure of silicon," *Physical Review B*, vol. 29, pp. 6739-6751, June 1984.

[16] (1996) Doping dependence of the energy band gap website. [Online]. Available: <http://ecee.colorado.edu/~bart/book/eband6.htm>

[17] S. Shanmugan, S. Balaji, and K. Ramanathan, "synthesis of ZnTe thin films using stacked elemental layer method: structural studies," *Optoelectronics and Advanced Materials-rapid communications*, vol. 3, pp. 468-471, 2009.

[18] E. Silveira, J. A. Freitas, S. B. Schujman, and L. J. Schwalter, "AlN band gap temperature dependence from its optical properties," *Journal of Crystal Growth*, vol. 310, pp. 4007-4010, 2008.