Microstructural and Optical Properties of $Al_xGa_{1-x}N$/GaN Heterostructure Thin Films Grown on Si(111) Substrate by Plasma Assisted Metalorganic Chemical Vapor Deposition Method

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Abstract

The microstructure and optical properties of $Al_xGa_{1-x}N$/GaN heterostructures thin films grown on Si(111) substrate by Plasma Assisted-Metalorganic Chemical Vapor Deposition (PA-MOCVD) with various of TMAl flow rate from 0.05 to 0.13 sccm have been investigated. The x values of $Al_xGa_{1-x}N$ thin films were determined by NIR-UV visible optical reflectance spectroscope. The crystalline plane orientation and surface morphology of films were determined by X-ray diffractometer (XRD) and scanning electron microscope (SEM), respectively. The films with x = 0.29 and x = 0.36 have single crystalline orientation of $(10\bar{1}0)$ plane while the film with x = 0.12 has two crystalline orientation of $(10\bar{1}0)$ and $(10\bar{1}1)$ planes. The surface morphology of films depend on the x value of film, which is the film with higher of x value showed the smaller grain size and the smoother surface. The patterns of optical reflectance show that the ordered of oscillation depend on smoothness of film surface, on the other hand the number of oscillation related to the thickness of films. These results were confirmed by surface morphology and cross section of films with means of SEM images. Band to band absorption mechanism (≈band gap energy, Eg) were indicated by the end of the peak oscillation position obtained that the Eg of GaN thin films was 3.34 eV and the Eg of $Al_xGa_{1-x}N$ thin films were ranged from 3.34 to 6.20 eV, depend on the x values of films.

Keywords: $Al_xGa_{1-x}N$/GaN, MOCVD, crystalline structure, x value, optical reflectance

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1. Introduction

In recent year, GaN and related III-V nitrides have attracted substantial scientific and industrial interest mainly due to its excellent properties. Specially $Al_xGa_{1-x}N$/GaN heterostructure field-effect transistors (HFETs) are being rapidly developed for high-power, high-temperature operation at microwave frequencies[1–3]. The performances of these devices were governed by the electronic properties of the two-dimensional electron gas (2-DEG) formed in the $Al_xGa_{1-x}N$/GaN quantum well. In addition, there is no doping in $Al_xGa_{1-x}N$ and GaN. The formation of 2-DEG properties was a result of the polarization of $Al_xGa_{1-x}N$ and GaN. Large piezoelectric and spontaneous polarization fields occurring in $Al_xGa_{1-x}N$/GaN heterostructures can generate a triangular well at the interface[4]. The nominally undoped (Al)GaN compounds are mostly n-type, hence electrons from the region of the barrier close to the interface are depleted and the 2-DEG is accumulated in the triangular-shaped potential. In this way, the 2-DEG appears in $Al_xGa_{1-x}N$/GaN heterostructures without doping[5]. However, the exact origin of the electron gas is still unclear and under debate. Some possible candidates have been discussed in the literature and include unintentional dopands, interface states at the $Al_xGa_{1-x}N$/GaN interface, deep-level defects, and surface states at the $Al_xGa_{1-x}N$ surface[6–9]. Moreover, the 2-DEG formation depends on the thickness and the content of the $Al_xGa_{1-x}N$ layer[10]. To better understand the 2-DEG formation, more different experimental investigations are necessary.

Optical reflectance spectroscopy is one of the experimental methods which enable the measurement of thickness layer and band gap energy of each layers material[11-12]. The advantages of this technique were that this method was contactless and non destructive character.

In this paper we reported the preliminary study of microstructure and optical properties investigation of $Al_xGa_{1-x}N$/GaN heterostructure thin films grown on Si(111) substrates by using PA-MOCVD method.

2. Experimental method

The samples were grown on Si(111) substrates in a plasma assisted-metal organic chemical vapor deposition (PA-MOCVD). Trimethylgallium (TMGa), trimethylaluminum (TMAl) and N_2 gas plasma were used as precursors of Ga, Al and N, respectively. The purified H_2 by passing it through a heated palladium cell was used as the carrier gas. A low power downstream plasma cavity supplied the reactive N plasma from N_2 gas and reactive H plasma from H_2 gas. The plasma is generated by 2.45 GHz microwave plasma source of 200 watt.

The silicon (Si) substrates were prepared by cleaving a 2 inch into several 1.0 x 1.5 cm^2 pieces with a diamond scribe. The substrate were sequentially cleaned by acetone and methanol for 10 minutes each, followed by washing in de-ionized water (DI-water) and etched in solution H_2O_2 : H_2SO_4 : DI-water = 1 : 3 : 1 at 70^oC for 5 minutes. Then they were dipped into 2% HF solution for 5 minutes to remove native SiO_2 on the Si substrate. Finally, the substrate were put into running DI-water and then blown with dry nitrogen. The substrate was immediately introduced into the growth reactor and heated up to 650^oC for thermal cleaning in the H_2 ambient to remove native oxide on the surface of Si. *In situ* hydrogen plasma cleaning on substrates was carried out for 10 minutes with the H_2 gas flow rate of 50 sccm. GaN buffer layer was grown with TMGa of 0.19 sccm and N_2 flow of 90 sccm at 500^oC, which produces about 25 nm thick of layer. After the deposition of buffer layer, the substrate temperature was raised to the growth temperature of 680^oC for the growth of GaN films with same parameter as buffer layer and 700^oC for the growth of $Al_xGa_{1-x}N$ films with the flow rate of TMGa and N_2 gas were 0.19 sccm and 90 sccm, respectively. The flow rates of TMAl were varied between 0.05 - 0.13 sccm.

The structural properties of the $Al_xGa_{1-x}N/GaN$ films were measured by X-Ray Difractometer (Cu K_α (λ=1,54056Å), PAN Analytical). The morphological surface and cross-section images of $Al_xGa_{1-x}N/GaN$ films were measured by scanning electron microscope (SEM, JEOL JSM-6360 LA). The optical properties of the films were measured by optical reflectance spectroscopy in the range of wavelength of 200 – 2400 nm (NIR-UV Visible Spectroscope, PC101).

3. Results and discussion

Fig. 1 shows the surface morphology and cross-sectional SEM images of $Al_xGa_{1-x}N/GaN$ thin-films samples which are grown on Si(111) substrates by using PA-MOCVD method. The $Al_xGa_{1-x}N/GaN$ thin-films of sample (A) without buffer layer predominant by hexagonal islands with the rough surface morphology, large grains size, inhomogeneous and nucleation of films seen separately. This matter caused by lattice mismatch and the interface between GaN and substrates have high interface energy. In addition, the large grain size of films indicated that the nucleations of the films are still lower. However, the $Al_xGa_{1-x}N/GaN$ thin-films grown with GaN buffer layer (sample B; C and D) show that the surface morphology of films likes grainy with surface which is progressively refine. The $Al_xGa_{1-x}N/GaN$ thin-films of samples (B), (C) and (D) have smoother and smaller grains size surface morphology and cross-section compared to the sample (A). The surface morphology SEM images of $Al_xGa_{1-x}N/GaN$ heterostructure thin-films seem that the increasingly smooth surface with the increase of the TMAl flow rate. It is due to the ionic radius of Al (0.5 Å) is smaller than the ionic radius of Ga (0.62Å). This ionic radius is a dominant factor on the film grain growth.

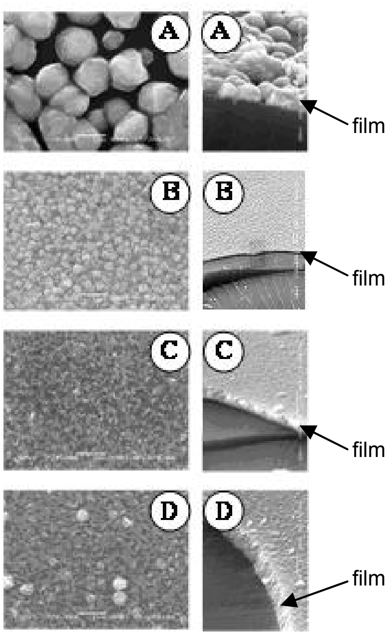

Figure 1. Morphological surface and cross-sectional SEM images of $Al_xGa_{1-x}N/GaN$ thin-films grown on Si(111) substrates by using PA-MOCVD method; (A) without buffer layer; with TMAl flow rate of (B) 0.05; (C) 0.07 and (D) 0.13.

Fig. 2 shows the result of the room temperature reflectance spectra of $Al_xGa_{1-x}N/GaN$ thin-films samples. The $Al_xGa_{1-x}N/GaN$ thin-film sample with rough surface morphology (Fig 1.A.) has disorder oscillation patterns of optical reflectance. This indicated that the excitonic and band-to-band absorption of the material are not perfect due to the inhomogeneous surface of the films which caused the incident beam to the film scattered to any directions. The $Al_xGa_{1-x}N/GaN$ thin-films with smooth and flat surface (Fig. 1.B, C and D) showed that the oscillation patterns of optical reflectance are in order. Oscillation patterns of the optical reflectance related to the quality of the films. The thickness (*d*) of samples is calculated from the interference equation below:[13]

$$d = \frac{N}{2}\left[\frac{\lambda_1\lambda_2}{n_1\lambda_2 - n_2\lambda_1}\right] \qquad (1)$$

where (*N*+1) is the number of maxima from λ_1 to λ_2, n_i is the refractive index at the maximum λ_i. The number of peak of the reflectance oscillation related to the thickness of the film. The thickness value of $Al_xGa_{1-x}N/GaN$ thin-films of sample (B) with 4 oscillation peaks was 261.39 nm; sample (C) with 6 oscillation peaks was 510.91 nm and sample (D) with 6 oscillation peaks was 599.52 nm. The results are similar to the thickness value of the films analyzed by SEM analysis (Fig. 1). The last position of the peak oscillation (shown in dashed line at Fig. 2) related to the band-to-band transitions of the films corresponding to the value of band-gap energy (Eg). The similar results are shown by some researches[14-15].

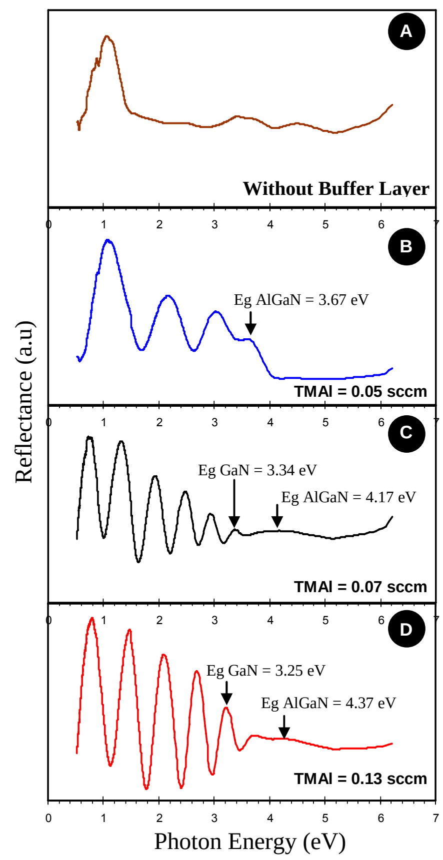

Figure 2. The optical reflectance spectra of $Al_xGa_{1-x}N/GaN$ thin-films samples which are grown on Si(111) substrates by using PA-MOCVD method; (A) without buffer layer; with TMAl flow rate of (B) 0.05; (C) 0.07 and (D) 0.13.

The x value can be obtained by combining the Eg value from optical reflectance and Vegard's law:[16]

$$E_g\,(Al_xGa_{1-x}N) = x.E_g(AlN) + (1-x).E_g(GaN) - b.x.(1-x) \qquad (2)$$

Where x = Al molar fraction of $Al_xGa_{1-x}N$ thin-film; E_g GaN = 3.34 eV; E_g AlN = 6.20 eV and b = bowing parameter.

Based on the previous research has been obtained of the b = -0.012 value, the x value of samples (B), (C) and (D) are 0.12; 0.29 and 0.36, respectively. In other hand the GaN Eg value of samples

(A) and (B) is not clearly observed. The estimated GaN Eg value of sample (C) is 3.34 eV which agree to the reference[16]. While the GaN Eg value of sample (D) is smaller than to that reference. This result shows that the (C sample) is the relaxation film and the sample (D) is the strained film. The strain due to the lattice mismatch between of GaN and $Al_xGa_{1-x}N$ thin-films.

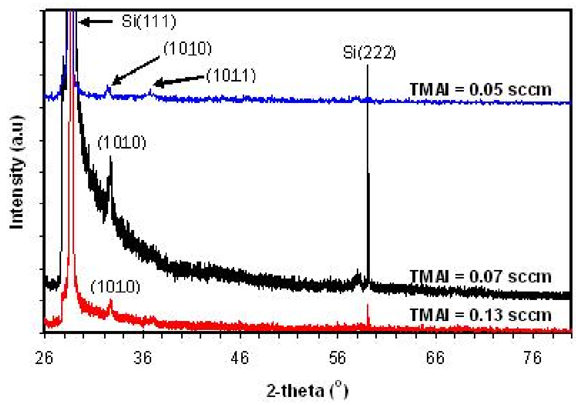

Figure 3. The XRD patterns of $Al_xGa_{1-x}N$/GaN thin-films samples which are grown on Si(111) substrates by using PA-MOCVD method; (A) without buffer layer; with TMAl flow rate of (B) 0.05; (C) 0.07 and (D) 0.13.

Fig. 3 shows the XRD patterns of $Al_xGa_{1-x}N$/GaN thin-films. The X-ray diffraction peaks of sample (B) are observed at 2-theta of 32.46°; and 37.14° which correspond to (10$\underline{1}$0), and (10$\underline{1}$1) planes of the hexagonal, respectively. The X-ray diffraction peaks of sample (C) and sample (D) shows one peak at 2-theta of 32.66° and 32.72° which correspond to (10$\underline{1}$0) planes of the hexagonal, respectively. This result shows that Al incorporation to GaN caused the peak diffraction shift. The crystallinity of films can be identified from the FWHM (*Full Width at Half Maximum*) value. The better crystallinity film associates to smaller FWHM value. The FWHM values of (10$\underline{1}$0) peak are 0.37311°; 0.28587° and 0.37582° for samples (B), (C) and (D), respectively.

4. Conclusions

The $Al_xGa_{1-x}N$/GaN heterostructure thin-films grown on Si(111) by using PA-MOCVD method at various TMAl flow rates have been done. The SEM images of growth films without buffer layer have rough surface morphology compared to the growth films by buffer layer. The surface morphology of films depends on the x value of film. The film with higher of x value showed the smaller grain size and the smoother surface. The optical properties show that the ordered of oscillation depend on smoothness of film surface, on the other hand the number of oscillation related to the thickness of films. Band to band absorption mechanism (≈band gap energy, Eg) were indicated by the end of the peak oscillation position. The films with x = 0.29 and x = 0.36 have single crystalline orientation of (10$\underline{1}$0) plane while the film with x = 0.12 has two crystalline orientation of (10$\underline{1}$0) and (10$\underline{1}$1) planes.

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References

1. W. Knap, C. Skierbiszewski, K. Dybko, J. Lusakowski, M. Siekacz, I. Grzegory, S. Porowski, Journal of Crystal Growth, **281** (2005) 194.
2. W.S. Tan, H.L. Cai, X.S. Wu, S.S. Jiang, W.L. Zheng, Q.J. Jia, Journal of Alloys and Compounds, **397** (2005) 231.
3. J.R. Juang, D.R. Hang, M.G. Lin, T.-Y. Huang, G.H. Kim, C.-T.Liang, Y.F. Chen, W.K. Hung, W.H. Seo, Y. Lee, J.H. Lee, Chin. J. Phys., **42** (2004) 629.
4. O. Ambacher, J. Smart, J.R. Shealy, N.G. Weimann, K. Chu, M.Murphy, W.J. Schaff, L.F. Eastman, J. Appl. Phys., **85**, (1999) 3222.
5. O. Ambacher, J.A.Majewski, C. Miskys, A. Link, M. Hermann, M. Eickhoff, M. Stutzmann, F. Bernardini, V. Fiorentini, V. Tilak, B. Schaff, L.F. Eastman, J. Phys.: Condens. Matter,. **14** (2002) 3399.
6. L. Hsu, W. Walukiewicz, Appl. Phys. Lett., **73** (1998) 339.
7. J.P. Ibbetson, P.T. Fini, K.D. Ness, S.P. Denbaas, J.S. Speck, U.K. Mishra, Appl. Phys. Lett., **77** (2000) 250.
8. H.W. Jang, Ch.M. Jeon, K.H. Kim, J.K. Kim, S.-B. Bae, J.H. Lee, J.W. Choi, J.-L. Lee, Appl. Phys. Lett., **81** (2002) 1249.
9. I.P. Smorchkova, C.R. Elsass, J.P. Ibbetson, R. Vetury, B. Heying, P. Fini, E. Haus, S.P. DenBaars, J.S. Speck, U.K. Mishra, J. Appl. Phys., **86** (1999) 4520.
10. B. Jogai, J. Appl. Phys., **93** (2003) 1631.
11. J. Misiewicz, P. Sitarek, G. Sek, R. Kudrawiec, Mater. Sci.,. **21** (2003) 263.
12. H. Sutanto, A. Subagio, E. Supriyanto, B. Mulyanti, P. Arifin, M. Budiman, Sukirno, M. Barmawi, Proceedings of 3rd Kentingan Physics Forum, ISBN N0: 979-97651-1-0 (2005).
13. R. Palomino-Merino, A. Conde-Gallardo, M. Garcia-Rocha, I. Hernandez-Calderon, V. Castano, R. Rodriquez, Thin Sol. Films, **401** (2001) 116.
14. R. Kudrawiec, M. Syperek, J. Misiewicz, R. Paskiewicz, B. Paskiewicz, M. Tlaczala, Superlattices & Micro., **36** (2004) 633.
15. A.T. Winzer, R. Goldhahn, G. Gobsch, A. Dadgar, H. Witte, A. Krtschil, A. Krost, Superlattices. & Micro., **36** (2004) 693.
16. I. Vurgaftman, J.R. Meyer, Journal of Applied Physics, **89** No. 11 (2001) 5815.