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ALUMINUM NITRIDE LAYERS PREPARED BY DC/RF MAGNETRON SPUTTERING

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Thin films of AlN are deposited by DC/RF reactive magnetron sputtering in Ar-N_2 gas mixture. The properties of the layers are investigated by AES, SEM, LAXRD, and microindentation (hardness measurement). The optical constants (n, k, R, Tr) are measured with a Carry-5E spectrophotometer. A strong stoichiometry and monodispersity of the films is found. LAXRD has shown a hexagonal {0002} predominant orientation when the layers were deposited on silicon (100) substrates at $t_s \geq 200\ ^oC$. The refractive index (n) is 2.08-2.04 for the wavelengths from 400 to 900 nm. The microhardness (Knoop) for a film thickness ≥ 2000 nm is 6-7 GPa. The AlN layers are employed as protective films for the production of reference Al mirrors for spectrophotometers.

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1. Introduction

Aluminum nitride (AlN) layers are among the most attractive materials investigated over the past several years [1,2,3] due to their peculiar features, such as high electrical resistivity (10^{11}-10^{13} ohm.cm), high thermal conductivity [4], high hardness (11-15 GPa), wide band gap 6.0-6.2 eV [5], high velocity of acoustic waves. These exceptional properties make AlN a very promising candidate for a variety of technological applications: surface passivation of thin films, barrier layers [6,7] in microelectronics [8], various surface acoustic wave (SAW) devices [9,10], protection of optical elements. There are different methods for obtaining AlN layers: chemical vapor deposition (CVD) [11], plasma enhanced CVD (PECVD) [12], pulsed laser deposition [13], ion implantation [14], reactive sputtering [15,16,17], and molecular beam epitaxy [18]. Due to its low cost, versatility and low-temperature deposition, the reactive sputtering is a preferable technique widely used for AlN layer deposition.

In the present work, the properties (stoichiometry, homogeneity, morphology, structure, microhardness) and optical characteristics (transmittance, reflectance, refractive index and extinction coefficient) of AlN layers obtained by DC/RF magnetron sputtering of an Al target in Ar-N_2 gas mixture are described.

2. Experimental

The AlN layers are obtained in an industrial high vacuum deposition system Z700P - Leybold Heraeus. It consists of a stainless-steel vacuum chamber (300 l volume), turbo molecular pump P < 2×10^{-6} Torr, measured with Penningvac PM 411S2 (1×10^{-2} – 1×10^{-7} Torr). The Penning cathode with an Al (4N) target (488 mm × 88 mm) is mounted parallel to the vertical axis of the

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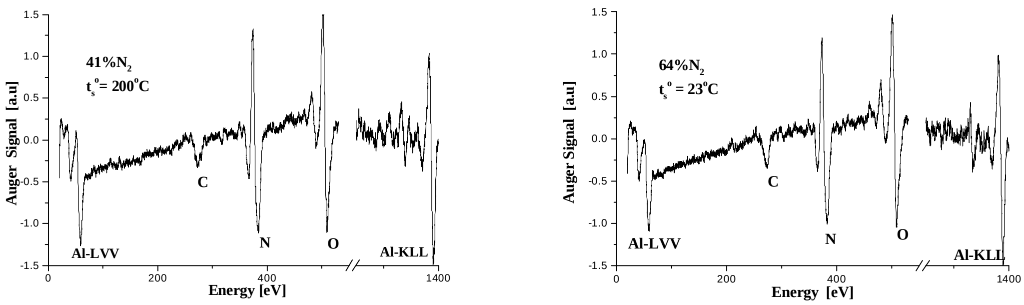
vacuum chamber. The cleaned substrates (SLW-glass, Si) are mounted on stainless-steel substrate carriers at 45 mm from the target and can rotate around the chamber axis with a desired velocity. Thus, the AlN layers can be deposited on static or rotating substrates. The substrates can be heated to 250 °C. The cathode is connected to a DC generator (7.5 KW) for DC magnetron sputtering, as well as to an RE generator (2.5 KW) for RF magnetron sputtering. The gas flow (Ar-N_2) is controlled with precise flow rate meters and the partial pressures in the vacuum chamber during deposition were measured with Ionivac IM 110D. The layers of AlN (40 nm – 5000 nm) were investigated with respect to their basic (morphology, structure) and microhardness properties by AES, SEM, LAXRD, and microindentation.

The total transmittance T_{tot} and the absolute specular reflectances $R_{f,tot}$, $R_{b,tot}$ and R_m of the samples were measured by a high-precision spectrophotometer (*Cary 5E*) at normal light incidence in the spectral range of 400 - 1200 nm with an accuracy of 0.1% and 0.5%, respectively. The subscripts "*f*" and "*b*" denote reflectance measurements from the front (film) and back (substrate) side of the samples on glass substrates. R_m is the reflectance of the films deposited onto Si substrates. The transmittance T and the reflectance R_f of the films utilized in the calculation of the optical constants and thickness were evaluated from T_{tot}, $R_{f,tot}$ and $R_{b,tot}$ after applying a correction [19]. The model used for T and R_f after this correction is applicable for uniform layers on a semi-infinite substrate. The refractive index n, extinction coefficient k and the thickness d of the films are determined simultaneously by a previously developed three-step algorithm [20]. It includes the application of the algebraic inversion method (Tr_fR_m) [21], followed by double (Tr_f) and (Tr_m) [22] and single $T(k = 0)$ [23] methods, and finally a selection of the most accurate solutions of all applied methods. The (Tr_fR_m) method is based on three spectrophotometric measurements (T, R_f and R_m) for the simultaneous determination of n, k and d at each wavelength. The most accurate solution for d is used as a parameter in the double and single methods. The combination of these methods makes possible the evaluation of n and k with high accuracy: $\Delta n/n$ and $\Delta k/k$ are about 1-2% and 4-5%, respectively. The calculated thicknesses are in good agreement with those obtained by profilometry or cross-section SEM.

3. Results and discussion

The deposition rate of the layers obtained by RF magnetron sputtering in all experiments is 30-50 nm/min. The best results are found at N_2 concentrations in the gas mixture between 41-64% at a total sputtering pressure $P_s = 8.10^{-3}$ torr. After a given time period, the deposition with DC magnetron sputtering leads to a "poisoning" (nitrification) of the Al target (generating an insulating AlN film) and the cathode current grows rapidly. For this reason, our experiments are carried out predominantly with RF magnetron sputtering.

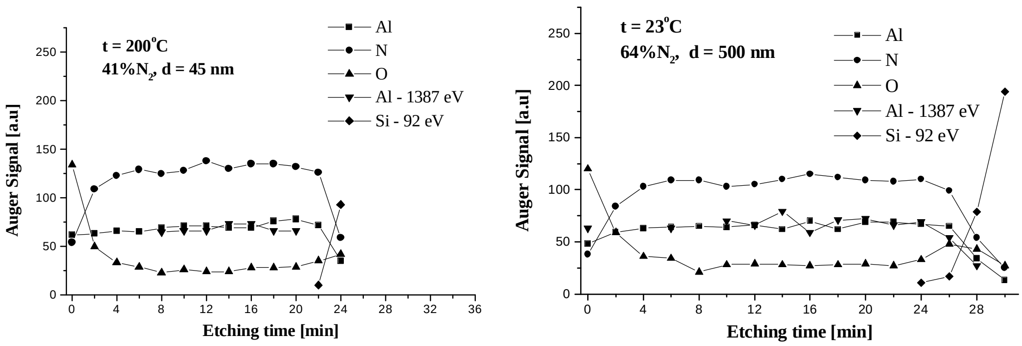
Initially, a series of experiments were carried out in order to establish the reproducibility of the obtained results, regarding the stoichiometry and homogeneity of the layers. AES was employed for establishing the stoichiometry and, in combination with ion etching (Ar^+, 3 KeV), for checking the homogeneity in depth of the AlN layers. In addition to the nitrogen peak (381 eV), the peaks of aluminum (low energetic LVV and high energetic KLL) which shift (by 8 eV and 6 eV, respectively) towards lower energies were followed, since these shifts unambiguously point out the formation of a nitride bond of Al. The peaks of oxygen and carbon (strong active pollutants) were also examined. The latter can be found only on the surface of the layers and disappear quickly after the first step of etching. No other elements were found on the surface.



a) b)

Fig. 1. AES spectra of the AlN layers (surface) deposited on: a) heated (200 °C) and b) cool (23 °C) substrates at different N_2 concentrations in the gas mixture. No visible differences in the spectra can be observed.

The homogeneity of the layers is investigated on 40-60 nm thick layers. From etching experiments on 500 nm thick layers, the reliability of the results is confirmed (Fig. 2). The AES profiles show perfect homogeneity in depth of the layers. They also show some quantity of oxygen uniformly built in the layers. After adjustment of suitable deposition conditions (prolonged pre-evacuation of the vacuum chamber to 1.10^{-6} torr, pre-sputtering of the Al target), the oxygen concentration drops down to 1.5-2.8 at%, as defined by electron probe microanalysis. The oxygen concentration is independent of the Ar-N_2 gas mixture and slightly decreases when the deposition is carried out on heated substrates.



a) b)

Fig. 2. AES profiles of the same layers as in Fig. 1 (a,b). The homogeneity in depth of the layers is clearly seen.

The stoichiometry of the AlN layers defined by electron probe microanalysis (EPMA) and AES show a high stability; the maximum deviation of the aluminum content in the layers does not exceed 8.3%. Under the described deposition conditions, the maximum deviation is 0.3% from sample to sample.

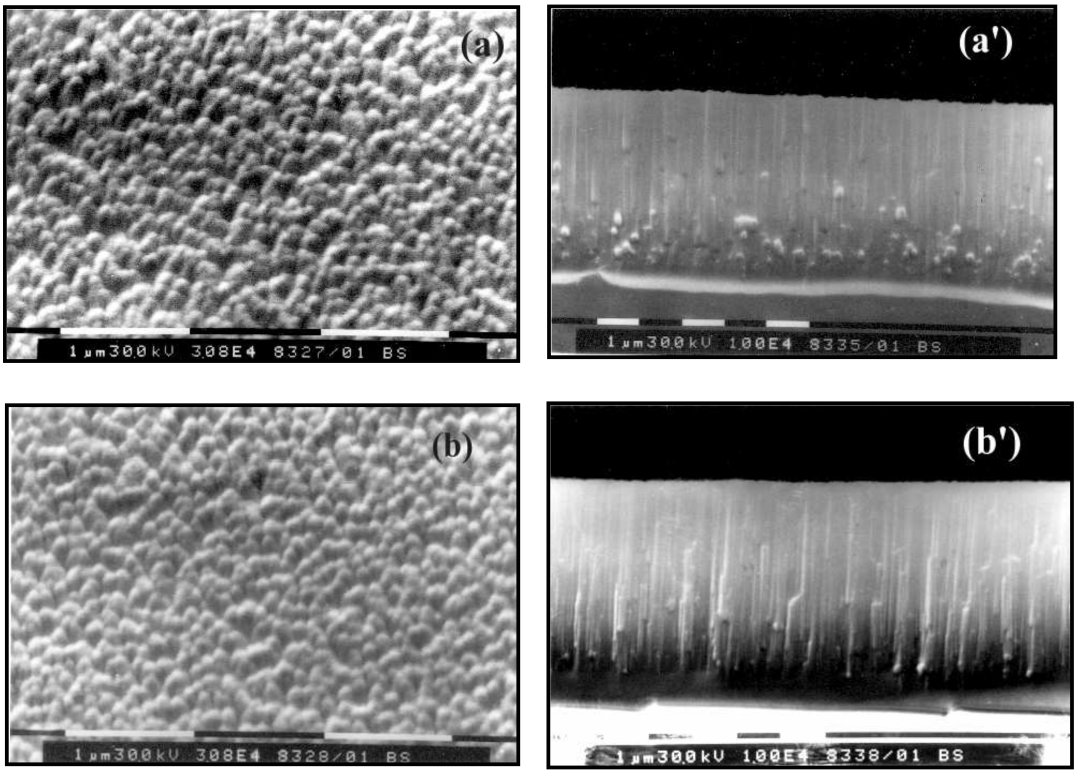
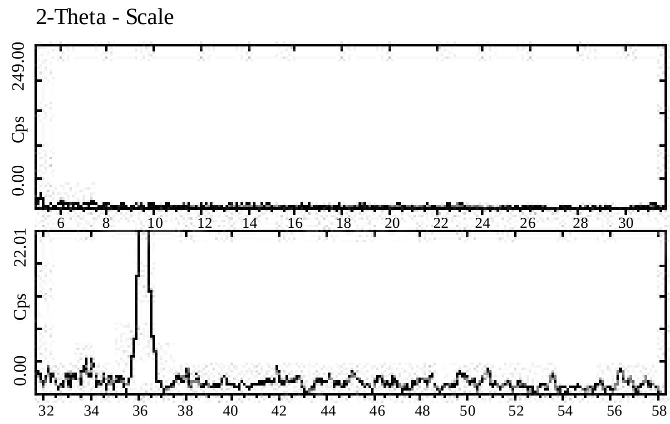


Fig. 3. SEM pictures of AlN layers: (a) → (a') surface and cross-section of the layers with thickness 4.5 μm deposited on heated (200 °C) substrates and (b) → (b') with thickness 4.9 μm deposited at 23 °C.

The morphology and crystallographic structure of the AlN layers are investigated with SEM (Fig. 3) and LAXRD (Fig. 4). The layers are deposited by RF magnetron sputtering (P_{RF} = 2400 W, U_{DC} = 250 V) at 64% N_2 in the Ar-N_2 mixture on static glass substrates (SLW) adjusted in front of the aluminum target. The minimal rotation velocity of the substrates is not sufficient to obtain layers thicker than 1 μm at the applied maximum RF power (2400 W), so in this case the experiments are carried out on static substrates. This way of deposition leads to the formation of a less dense and homogeneous structure.

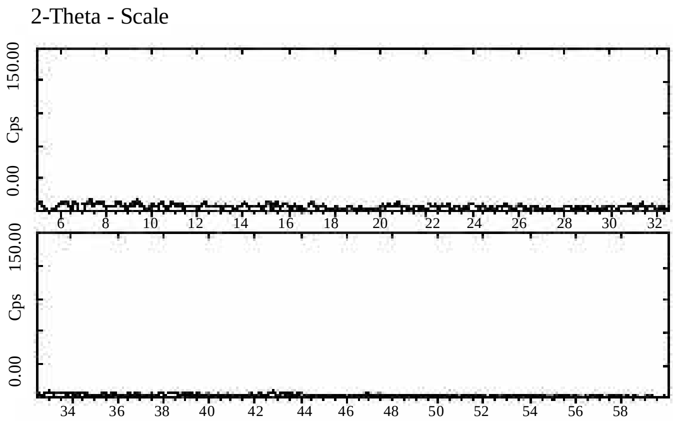
The microstructure of the layers is not strictly homogeneous. It consists of equiaxed small grains near the substrate surface, causing the growth of columns with the rise of the layer thickness. The mean grain size is 0.12-0.15 μm on the heated substrates, while on the cool substrates it is 0.9-1.0 μm. This can be explained by the theory of phase formation and crystal growth. The columnar structure is clearly visible in all cases. The homogeneity of the grains on cool substrates is better.

The crystallographic orientation of the AlN layers is established with low-angle X-ray diffraction (LAXRD). The layers were obtained by RF and DC magnetron sputtering on Si wafers (100) rotating in front of the aluminum target at 64% N_2 in the Ar-N_2 gas mixture at a deposition rate of 30 nm/min.



a

N_2 = 64%, t_s = 200 ^{o}C, d = 60 nm



b

N_2 = 64%, t_s = 23 ^{o}C, d = 56 nm

Fig. 4. LAXRD of AlN layers deposited on Si substrates, N_2 concentration in the gas mixture Ar-N_2 64%: a) RF sputtering, t_s = 200 ^{o}C, layers with strongly preferred orientation along the {0002} axis (2θ = 36^o); b) RF or DC sputtering, t_s = 23 ^{o}C, layers are polycrystalline without preferred orientation.

Due to the higher mobility of the atoms (molecules) on heated substrates, they can coalesce and grow in one direction. It is difficult to say when and where the AlN compound is generated: in the plasma medium, on the substrate or in both cases. With our experiments, this question cannot be answered. It is assumed that the knowledge of this mechanism can elucidate better the act of preferred orientation of the AlN layers.

Table 1 shows microhardness values (Knoop) of the AlN layers deposited on glass substrates at t_s = 200 ^{o}C and 23 ^{o}C and at different concentrations of N_2 in the gas mixture. The deposition conditions of the layers are the same as shown in Fig. 3 (condensation on static substrate, lower densification of the grains). There is no substantial difference in the microhardness values.

%N_2 in gas mixture	Sputtering RF power = 6.25 W/cm^2	Substrate temperature (^{o}C)	Thickness of the layers (μm)	μH (Knoop) (GPa)
64	RF	200	2,4	7.15
64	RF	23	5,0	7.05
41	RF	200	4,5	6.72
41	RF	23	4,9	5.45

A tendency to decreasing microhardness with decreasing N_2 concentration is observed, especially at the low substrate temperature. The microhardness is lower than that reported in [3].

The optical constants are determined for AlN layers deposited on glass and Si substrates (Fig. 5).

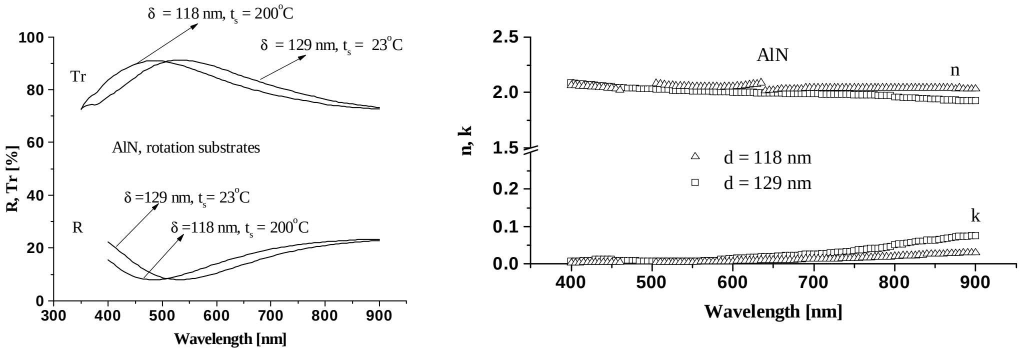


Fig. 5. Optical characteristics of the AlN layers in the visible spectral range.

The layers are deposited on heated (200 °C) and cool (23 °C) rotating substrates. The transmittance (Tr) and reflectance (R) are measured on layers deposited on glass (SLW) substrates. The maximum transmittance (91%) is observed at 463-495 nm (heated substrates) and 506-555 nm (cool substrates). The minimum of the reflectance (7-8%) is in the same range. The refraction coefficient (n) in the range 400-900 nm decreases slightly (2.08-2.04) for layers on heated substrates and drops down to 1.93 for cool substrates. The extinction coefficient (k) increases from 400 nm to 900 nm, reaching values of 0.029 (cool) and 0.077 (heated substrates), respectively. The results are in good agreement with those reported in [13,16].

4. Conclusions

AlN layers deposited by reactive DC/RF magnetron sputtering in an industrial high vacuum deposition system in Ar-N_2 gas mixture are obtained. By adjusting the deposition parameters, layers with desired properties can be formed. It is found that 41-64% N_2 in the Ar-N_2 gas mixture is the optimal concentration for the achievement of good homogeneity and stoichiometry. The change of the substrate temperature strongly affects the crystallographic orientation of the layers. At $t_s \geq 200\,^{\circ}C$, a preferred orientation along the {0002} axis ($2\theta = 36^{\circ}$) is found. The morphology of the layers (0.1-0.12 μm mean grain size) and the microhardness are not influenced substantially by the substrate temperature. The maximum transparency of the layers (91%) is observed at 463-495 nm (heated substrates) and 506-555 nm (cool substrates). The minimum of the reflectance (7-8%) is in the same range. The refractive index is 2.08-2.04 and the extinction coefficient increases from 400 nm (0.002) to 900 nm, reaching values of 0.029 (cool substrates) and 0.077 (heated substrates).

The AlN layers obtained under these conditions are successfully employed as protective layers for reference Al mirrors [24].

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References

[1] F. Randreiamora, J. C. Bruyere, A. Deneuville, Mater. Sci. Eng. **B50**, 272-276 (1997).
[2] T. P. Drusedau, J. Blasing, Thin Solid Films **377-378**, 27-31 (2000).
[3] X. H. Ji, S. P. Lau, G. Q. Yu, W. H. Zhong, B. K. Tay, J. Phys. D: Appl. Phys. **37**, 1472-1477 (2004).
[4] S. Stritc, H. Morkoe, J. Vac. Sci. Technol. **B 10**, 1237 (1992).
[5] E. I. Bienk, H. Jensen, G. N. Pedersen, S. Sorensen, Thin Solid films **230**, 121 (1993).
[6] D. Zanghi, A. Traverse, F. Petroff, et al., J. Appl. Phys**. 89,** 6329 (2001).
[7] S. Manish, H. N. Janice, C. A. Thomas, X. W. Shan, Appl. Phys. Lett. **77**, 2219 (2002).
[8] M. Park, J-P. Maria, J. J. Cuomo et al., Appl. Phys. Lett. **81**, 1797 (2002).
[9] F. Engelmark, G. Fucntes, I. V. Katadgiev, A. Harsla, U. Smith, S. Berg, L., Vac. Sci. Technol. **18**, 1609 (2000).
[10] M. Penza, M. F. De Ricardis, L. Mirenghi, M. A. Tagliente, E. Verona, Thin Solid Films, **259,** 154 (1994).
[11] P. Kung, A. Zaxler, X. Zhang, D. Walker, T. C. Wang, I. Ferguson, M. Razeghi, Appl. Phys. Lett. **66**, 2958 (1995).
[12] Y. J. Young, J. Y. Lee, J. Vac. Sci. Technol. **A 15**, 390 (1997).
[13] R. Bathe, R. D. Vispute, D. Habersat, R. P. Shurma, T. Venkatesan et al., Thin Solid Films **398-399**, 575-580 (2001).
[14] C. T. M. Ribeiro, F. Alvarez, A. R. Zanatta, Apl. Phys. Lett **81**, 1005 (2002).
[15] J. C. Loretz, B. Despax, P. Marti, A. Mazel, Thin Solid Films **15**, 265 (1995).
[16] X. S. Miao, Y. C. Chan, Z. Y. Lee, J. Electronic Materials **26**(1), 21-24 (1997).
[17] T. P. Drusedau, Th. Neubert, A. N. Panckow, Surface and Coatings Technology **163-164**, 164-168 (2003).
[18] C. Henlein, J. K. Grepstad, S. Einfeldt, D. Hommel, T. Berge, A. P. Grande, J. Appl. Phys. **83**, 2990 (1998).
[19] H. Liddell, Computer-Aided Techniques for Design of Multilayer Filters, Bristol, Adam Hilger, p. 19 (1981).
[20] Tz. Babeva, S. Kitova, I. Konstantinov, Appl. Opt. **40**, 2682-2686 (2001).
[21] V. Panayotov, I. Konstantinov, Proc. SPIE **2253**, 1070-1079 (1994).
[22] I. Konstantinov, Tz. Babeva, S. Kitova, Appl. Opt. **37**, 4260-4267 (1998).
[23] V. Panayotov, I. Konstantinov, Appl. Opt. **30,** 2795-2800 (1991).
[24] Tz. Babeva, S. Kitova, B. Mednikarov, I. Konstantinov, Appl. Opt. **41**, 3840-3846 (2002).