Thin Solid Films 524 (2012) 328–333

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Structural and optical properties of *c*-axis oriented aluminum nitride thin films prepared at low temperature by reactive radio-frequency magnetron sputtering

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ARTICLE INFO

Article history:
Received 25 January 2012
Received in revised form 14 August 2012
Accepted 11 October 2012
Available online 16 October 2012

Keywords:
Aluminum nitride
Radio-frequency magnetron sputtering
Transmission electron microscopy
X-ray diffraction
Ellipsometry

ABSTRACT

Spectroscopic ellipsometry, X-ray diffraction and transmission electron microscopy experiments are employed to characterize aluminum nitride (AlN) thin films obtained by radio-frequency magnetron sputtering at low temperature (≈50 °C). To understand the growth mechanism and to get in depth information of such films by using ex situ characterization techniques, the AlN thin film sample series were prepared for different sputtering times, while keeping constant all the other deposition conditions. The diffraction studies reveal a [002] oriented growth of the AlN thin films. The misorientation of this crystallographic axis to the normal to the surface reduces progressively with film growth. A nonmonotonic behavior of the AlN pseudo-refractive index versus deposition time indicates a complex depth profile of the AlN thin films optical properties. The difference in orientation dispersion of the [002] crystallite axis, the variation of defects concentration and each constituent atom density influence the refractive index evolution. Our interpretation validity was verified by producing and characterizing samples obtained at intermediate deposition time. The AlN thin films show also very good pull-out adherence values.

1. Introduction

Among the wide band gap materials, the aluminum nitride (AlN) has the largest piezoelectric coefficient and the higher corrosion resistance, and has attracted a great technological interest due to exceptional properties such as energy band gap (6.2 eV), high breakdown voltage (≈3 MV/cm), high electrical resistivity (≈10^{15} Ω cm), high hardness (11–15 GPa), good thermal stability (≈1000 °C in air), high thermal conductivity (≈170 W/m · K) and high surface acoustic velocity (up to 6000 m/s) [1–6]. Highly *c*-axis oriented AlN thin films are especially attractive for micro-electromechanical (MEMS) and nano-electromechanical (NEMS) devices [7,8]. The MEMS and NEMS resonators are regarded as promising technologies for many hi-tech applications (electrometry, chemical and biological sensing, and scanning probe techniques) [7]. Other applications such as ultraviolet light-emitting diodes and laser diodes, gate dielectrics, high power devices, and insulating layers are also targeted. The acoustic response and piezoelectric coefficients of AlN structures depend mainly on their crystallinity, crystal orientation, reduced surface roughness and polarity distribution [9–12]. However, extensive research is still necessary to find out the influence of the crystallographic structure and of the crystallinity degree of AlN films on their functionality as MEMS/NEMS devices.

In order to develop better opto- and micro-electronical devices, a wide range of deposition methods have been employed with the aim to grow high quality oriented AlN thin films, as chemical vapor deposition [13], molecular beam epitaxy [14], metal organic chemical vapor deposition [15–18], hybrid vapor phase epitaxy [19], pulsed laser deposition [20,21] and direct current (DC) and radio-frequency (RF) magnetron sputtering [22–26]. The compatibility with the current microelectronic processes requires a low temperature deposition process. However, the synthesis of AlN films with a definite crystalline structure at low temperature is still challenging. Reactive RF magnetron sputtering (RF-MS) presents the advantage of low deposition temperatures (usually below 200 °C), allowing the synthesis of AlN films with the preferred crystal orientations and reduced surface roughness at low pressure [24,27]. Moreover, RF-MS possesses many other advantages such as reproducibility, efficiency, versatility and the ability to grow high quality adherent thin films [28].

In this work AlN layers of different thicknesses were grown onto (100) silicon substrates in identical experimental conditions [29] by reactive RF-MS. We investigated the films growth architecture, their structural and optical qualities versus thickness and their behavior during prolonged exposure to ambient media. The presented results could be important for the further development of self-sustainable opto- and micro-electronical devices designs. The study attempts to offer a comprehensive and insightful view of such *c*-axis oriented AlN layers grown on

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0040-6090/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2012.10.015

(100) silicon wafers, the dependence of the film structure on its thickness being specifically addressed. Results obtained by X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and pull-out adherence measurements are presented. Also a special focus is put on films optical properties, extensive results of spectroscopic ellipsometry studies of the effect of deposition time on the growth of RF-MS AlN films and on their optical characteristics being presented and discussed.

2. Experimental methods

2.1. Thin films preparation

The AlN thin films were synthesized using a 1.78 MHz UVN-75R1 sputtering deposition system having planar water-cooled magnetron cathodes with a plasma ring of ≈55 mm diameter. An aluminum disc (Angstrom Sciences, 99.9999% purity, 1.5 mm thick) was used as a cathode target and high resistivity silicon wafers (100) were used as substrates. Before their introduction into the stainless steel deposition chamber, the substrates were successively cleaned ultrasonically in acetone and ethanol for 10 min and then dried in nitrogen flow. The target-to-substrate distance was set at 35 mm. Prior to deposition, the sputtering chamber was evacuated down to a base pressure of $\approx 10^{-4}$ Pa. In the next step, the substrates were out-gassed in situ in vacuum with a quartz-halogen heater lamp at a temperature of ≈500 °C. Further on, high purity argon (99.99%) was introduced and the gas flow was maintained at a value of 40 sccm. The Al target was sputter-cleaned at a working pressure of 0.3 Pa for 15 min to remove surface contaminants. During cleaning, the substrates were masked with a stainless steel shield in order to avoid undesired deposits onto their surface. Subsequently, the substrates were etched in situ for 10 min, at a 0.4 kV DC bias voltage in argon plasma (gas pressure 0.3 Pa) produced by a Wolfram plasmatron at a power of ≈200 W, in order to remove contaminants which might persist after the ultrasonic cleaning. This substrate plasma treatment increases film adhesion and reduces the possibility of delamination [30].

For the deposition of AlN layers, a radio-frequency generator was used and maintained at a constant and low RF power of 100 W in order to avoid overheating of the target surface which can produce an undesirable radiative heating of the deposition substrates. The film deposition was carried out at a 0.2 Pa Ar–N_2 gas mixture with a nitrogen concentration of 25%, for 5, 15, 30 and 60 min, further on referred as T5, T15, T30 and T60, respectively. The gas flows were controlled with Teledyne Hasting electronic mass flow meters and the gas pressure was monitored by an Alcatel capacitance vacuum gauge. The substrate temperature was only dependent on plasma self-heating. During deposition, the substrates had a temperature closing 50 °C, as monitored with a built-in Chromel–Alumel thermocouple system.

2.2. Characterization techniques

X-ray diffraction measurements were performed using a BrukerAXS D8 Advance diffractometer in parallel beam setting, equipped with Cu target X-ray tube with linear focus. The goniometer setting includes a two bounce Ge (022) monochromator, assuring a monochromatized Cu–$K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å). Diffraction data were collected in symmetric (θ–θ) geometry and through rocking curves.

Cross section samples for electron microscopy have been prepared in the conventional way by sawing the specimens, gluing the pieces film to film, mechanical thinning with the tripod, followed by ion milling using the PIPS Gatan machine. TEM investigations have been performed with a JEOL 200CX instrument operating at 200 kV, equipped with a Keen View CCD camera for image recording. The SAED patterns were recorded using the same apparatus.

Optical measurements are done with a Woollam Variable Angle Spectroscopic Ellipsometer system, equipped with a high pressure Xenon discharge lamp incorporated in an HS-190 monochromator. Measurements are performed in the IR-Vis–UV region of the spectrum at photon energies between 0.7 and 6.2 eV, step of 0.01 eV, at 45, 60 and 75° angles of incidence.

The pull-out measurements were carried out using an adhesion tester — DFD Instruments PAT MICRO adhesion tester AT101 (maximum pull force = 1 kN) equipped with $\Phi = 2.8$ mm stainless steel test elements. The test elements were glued to the film surface with a cyanoacrylate one-component Epoxy adhesive, E1100S. The stub surface was polished, then ultrasonically degreased in acetone and ethanol and dried in a nitrogen flow. After gluing, the samples were placed in an oven for thermal curing (130 °C/1 h). Each test element was pulled-out vertically with a calibrated hydraulic pump until detachment. The experimental procedure was conducted in accordance with the ASTM D4541 and ISO 4624 standards. The adhesion strength was determined from the recorded failure value divided by the quantified detached surface area. Mean values and standard deviations were computed. The statistical significance was determined using an unpaired Student's t-test. The differences were considered significant when $p<0.05$.

3. Results and discussion

3.1. XRD results

X-ray diffraction patterns of the magnetron sputtering grown layers of AlN show a gradual alignment of the *c*-axis of the crystallites perpendicular to the sample surface with the deposition time and with film thickness increase correspondingly. In the symmetric diffraction patterns all samples showed only the 002 and 004 AlN diffraction peaks. The full width at half maximum (FWHM) of 002 line decreases gradually from 0.52° down to 0.22° by increasing the film thickness, pointing to the increase of the *c*-axis crystallite size (Fig. 1a). At the same time, the orientation of the crystallites *c*-axis gradually approaches the sample normal, which can be observed (Fig. 2a) from the decrease of the rocking curves FWHM from 16° (T5) down to 3.5° (T60). These results suggest that with the progressive growth of the thin film, a better alignment of the *c*-axis crystallites is obtained toward the film surface. The increase of the AlN line intensity (area below the curve) is obviously related to the growing film thickness with increasing deposition time. The line breadth is affected both by the small crystallite size and the local disorder inside the AlN crystallites, and it is given by the overall film structure (the penetration depth of the X-ray beam at $2\theta = 36°$ exceeds the highest film thickness). We imagined an unusual procedure to deconstruct the film structure in depth: one can assume that the film is gradually structured with thickness and that the intensity is the sum of the signal originating from different depths. Thus, if one subtracts the intensities given by films with successive thicknesses, the resulting line intensity and profile would be such as that given by the upper part of the minuend thickness. Fig. 1b depicts the line profiles obtained by subtracting consecutive raw data: T15–T5, T30–T15 and T60–T30. The resulting profiles correspond to the upper parts of the films in samples T15, T30, and T60, and they are narrower than those given by the full thickness films, shown in Fig. 1a. This suggests that AlN is gradually ordering and/or has larger crystallites at the upper part of the films, therefore as the growth progresses on each sample. Furthermore, this imagined subtracting procedure also applies to the rocking curves, as seen in Fig. 2b. In this case the resulted decrease of FWHM states the better c axis ordering toward the film surface.

3.2. TEM and SAED analyses

In Fig. 3a is shown a cross section TEM image at low magnification on T60 sample, showing the columnar morphology of the AlN thin