Effect of substrate–target distance and sputtering pressure in the synthesis of AlN thin films

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Abstract In this work, we analyze the influence of the processing pressure and the substrate–target distance on the synthesis by reactive sputtering of c-axis oriented polycrystalline aluminum nitride thin films deposited on Si(100) wafers. The crystalline quality of AlN has been characterized by high-resolution X-ray diffraction (HR-XRD). The films exhibited a very high degree of c-axis orientation especially when a low process pressure was used. After growth, residual stress measurements obtained indirectly from radius of curvature measurements of the wafer prior and after deposition are also provided. Two different techniques are used to determine the curvature—an optically levered laser beam and a method based on X-ray diffraction. There is a transition from compressive to tensile stress at a processing pressure around 2 mTorr. The transition occurs at different pressures for thin films of different thickness. The degree of c-axis orientation was not affected by the target–substrate distance as it was varied in between 30 and 70 mm.

1 Introduction

Reactive sputtering is a commonly used process to fabricate compound thin film coatings on a wide variety of substrates. The industrial applications request high rate deposition processes. In reactive sputtering synthesis, target "poisoning", i.e. the formation of compound at the target surface, may reduce that sputter erosion rate substantially and thereby represents a major limitation to achieve high deposition rates. It is known that during reactive sputtering the reactive gas contributes to the formation of compound by both implantation of reactive gas ion into the subsurface layer as well as by chemisorption of reactive gas molecules on the surface of the target. Both chemisorption and ion implantation of energetic reactive ions are the two main mechanisms for the formation of the poisoned layer. Thus, there exist optimum processing conditions where both high rate and stoichiometric film composition can be obtained. Further, extensive studies (Chen et al. 2008; Dubois and Muralt 2001; Felmetsger and Laptev 2008; Felmetsger et al. 2009) of the intrinsic stress and microstructure of thin films deposited by magnetron sputtering at relatively low substrate temperatures have established the existence of a universal transition behavior where the stress evolves from compressive to tensile (or vice versa) depending on the specific process parameters. Moreover, under certain conditions, there is a similar transition behavior regarding the degree of c-axis orientation as the processing pressured is varied, with films showing a high orientation at low pressure and a poor orientation at high pressure. All these studies indicate that this transition behavior is highly dependent on the kinetic energy delivered to the growing film during deposition through various mechanisms.

The crystallographic properties of layered film structures consisting of a piezoelectric material layer, aluminum nitride (AlN), and a silicon substrate have been examined. X-ray diffraction (XRD) analysis indicate that the deposited AlN films were c-axis oriented with a full width at half maximum (FWHM) of the rocking curve of the AlN-(0002) peak below 2.0° at low pressure. Aluminum nitride films were deposited by reactive DC magnetron sputtering using an aluminum target in an N_2/Ar gas mixture. Effects of the mean free path of Al atoms correlated with the processing pressure and target–substrate distance on the preferentially orientated growth of AlN thin films were investigated in detail. The relationships between deposition conditions and crystallographic orientation of the films are discussed in terms of surface energy minimization and ion bombardment effects. Aluminum nitride (AlN) is an interesting III–V compound with many remarkable characteristics such as a wide bandgap (6.2 eV) or a high thermal conductivity of 140–180 W/m K (AlShaikhi and Srivastava 2009). AlN also has satisfactory electro-acoustic properties such as moderate coupling coefficient, known stiffness as well as piezoelectric and dielectric tensors, compatibility with IC planar processing, chemical stability etc. Further, AlN is also a potential candidate in the fabrication of blue light emitting diodes, short wavelength lasers, and ultraviolet light detectors. The high phase velocity of acoustic waves in AlN makes possible to fabricate SAW devices for high frequency applications (Fujii et al. 2007; Kirsch et al. 2007). The demand for small size GHz-range surface acoustic wave (SAW) devices with low insertion loss and good out of band rejection has risen in the last decade, especially for mobile communication. For SAW device applications, it is important to control the crystallographic orientation of the AlN films. Moreover, low substrate temperature is required to deposit AlN in order to minimize grain size as well as to decrease the thermal budget of the manufacture procedure. The aim of this work is to study the effect of the process pressure during reactive sputter deposition of c-axis oriented polycrystalline AlN thin films as well as to find optimal conditions for the synthesis of low stress AlN thin films grown on Si(100) substrates. The residual stress as well as the degree of c-axis orientation often observed in polycrystalline A1N thin films is responsible for both electro-acoustic device performance deterioration as well as reduced lifetime. Substrate deformation and distortion necessarily arise from stresses in the overlying films. In integrated circuit technology, even a slight bowing of silicon wafers may result in significant problems with regard to maintaining precise tolerances in pattern delineation. The majority of the commonly used substrates have a large lattice mismatch with A1N, with the exception of SiC (Chung and Hong 2009). The lattice mismatch between AlN and Si(100) is 23%. In addition to high defect density, residual stress and/or a poor c-axis orientation might also arise from the large difference in lattice parameters. There exist a number of methods to measure thin film stresses. Many of them, e.g. X-ray diffraction (Iancu et al. 1990), neutron diffraction (Wang et al. 1994) and Raman spectroscopy (Benrakkad et al. 1995) measure directly the lattice parameters and hence effectively the strain resulting from lattice deformation. In this report, both a X-ray diffraction and an optical analysis method were employed to measure the radius of curvature of both the uncoated and coated substrates.

2 Experimental

A standard two-step RCA process was used to clean the Si(100) wafers, seethed in a 5:1:1 solution of H_2O:NH_3:H_2O_2 and subsequently in a 6:1:1 solution of H_2O:HCl:H_2O_2. Thereafter, the wafers were etched in 2% HF–H_2O for 45 s prior to loading them into the load lock to remove oxide impurities originated during the RCA2 cleaning procedure. The films were deposited on 75 mm p-doped Si(100) wafers with a thickness of 325 ± 15 μm and a resistivity of 7E-16 Ohm-mm. AlN thin films were sputter deposited in an N_2/Ar reactive atmosphere by pulsed DC sputtering (Barshilia et al. 2008). The sputtering system consisted of a balanced magnetron powered by an ENI 500RPG asymmetric bipolar-pulsed DC power supply. The aluminum target used was 100 mm in diameter with a purity of 99.9995% and bonded to a Cu-backing plate (155 mm diameter, 6 mm thick). Unless otherwise specified, the following synthesis parameters were used. The distance between target and substrate was of 55 mm. The pulsed DC power supply at the target was operated at a frequency of 250 kHz with a 500 ns duty cycle. The sputtering system was pumped down to a base pressure lower than 5E-7 Torr before admitting the gas mixture. As the process pressure was varied, the partial pressure of N_2 as well as Ar was kept constant with the flow values of 20/45 (sccm) for Ar/N_2 respectively, the power at the target was 900 W and the substrate at ambient temperature (no substrate heating was used). This parameters are summarized in Table 1. Prior to each run, the target was operated first in pure Ar for 15 min (pre-sputtering) followed by a 5 min sputtering in a the N_2/Ar atmosphere. During the target cleaning procedure, the substrates were shielded with a shutter. Film thickness measurements were performed using a Stylus Dektak 200-Si Veeco[1] profilometer. The deposition rate is approximately 30 nm/min although it varied considerably as the target was being eroded. Of course, the variation of processing parameters such as the processing pressure also influences the deposition rate, but in all cases the deposition time was adjusted to obtain films of constant thickness of 2 μm for the proper comparison of the stress and crystallographic properties between the different films. In the case of the pressure dependence of the stress, a complementary curve for films 1 μm thick was also taken to illustrate the importance of comparing films of equal thickness since the measured stress values are highly dependent on the latter due to the stress gradient in

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[1] Veeco Metrology Inc., Santa Barbara, CA, USA.

Table 1 Parameters used during the AlN synthesis unless otherwise specified

Parameters	Values
Base pressure	<5E−7 Torr
Ar-flow	20 sccm
N_2-flow	45 sccm
Discharge power	900 W, pulsed DC
Substrate temperature	<70°C
Frequency	250 kHz
Duty cycle	13%
Incidence angle	0°
Film thickness	1,000–1,200 nm
Target–substrate distance	55 mm

the film. The stress was evaluated from the change in the radius of substrate curvature before and after deposition. The FSM 500 TC apparatus[2] for stress measurements use a laser optical lever to measure the curvature induced in a wafer. The important parameter to use when calculating the stress from the strain is the quotient $Es/(1-\nu s)$, referred to as the biaxial Young's modulus of the substrate (180.5 GPa for 100 oriented silicon wafers) (Windischmann 1989). When measuring the curvature radius of a bent wafer, it is important to realize what kind of curl the wafer has. If the curl is cylindrical then the plate modulus rather than the biaxial modulus (spherical shape) should be used (Szilard 1974). The wafers measured in this work all showed a spherical kind of curl, which was determined by measuring the curvature radius in paths perpendicular to each other, and hence the biaxial rather than the plate modulus was considered. Chaudhuri et al. (1995) calculated the biaxial modulus for AlN in different planes and directions. The elastic modulus and the Poisson's ratio used in this calculations are $E_{AlN} = 308$ GPa, $\nu_{AlN} = 0.18$, for the AlN thin film (Gerlich et al. 1986) and $E_{Si} = 125$ GPa, $\nu_{Si} = 0.28$ for the Si(100) substrate. A Phillips X-Pert Pro MRD diffractometer[3] with a two-bounce hybrid monocromator (25 arcsec) and an open detector was used to measure the curvature radius and the crystallographic properties of the synthesized thin films. The principle of this method is to evaluate how the incident angle of the X-ray beam must be varied to maintain the scattering condition of maximum intensity (Fewster 2000). These measurements are carried out at different regions of the wafer, which is curled into a spherical shape because of the stress in the AlN film. Maximum intensity occurs when the incident angle ω equals the Bragg angle θ, that is, when the orientation of the crystallographic planes is totally horizontal to the surface plane (ignoring refractive index corrections). This method relies on defining the surface plane very precisely and relating this to the crystallographic planes. The surface normal plane, i.e. the Si(100) plane was used. The Si substrates were measured before the AlN film deposition and the data was compared to measurements taken on the same wafer after film deposition.

3 Result

The pressure dependence of the universal transition region has been studied by a some authors (Fardeheb-Mammeri et al. 2008; Kamohara et al. 2006; Vashaei et al. 2009). Figure 1 shows the FWHM evolution of the rocking curve of the (0002) reflection in AlN films as a function of the process pressure for the four pressures studied, 2, 4, 6 and 8 mTorr. The deposition rates were 30, 27, 22 and 20 nm/min, respectively. Rocking curve X-ray diffraction analysis is one of the most widely used techniques in crystallography. In a rocking curve measurement, the sample is rotated (rocked) through an angular range, bringing the plane in and out of the Bragg condition. The width of the measured peak, normally measured in terms of the FWHM value contains information of the amount by which the measured plane is off the surface normal, sometimes referred to as the "degree of orientation" of the specimen. It seems that the ad-atom mobility is favored at low pressures due to lower amount of energy loss of the AlN molecules in the gas phase. But also, as shown in Fig. 2, the voltage at the target as well as at the substrate surface tends to slightly increase at low pressures (around 2 mTorr), which may result in a "self-bias" voltage enhancing the energy of the ad-atoms arriving at the substrate surface and hence improving their energetic conditions to grow in a preferred (0002) orientation.

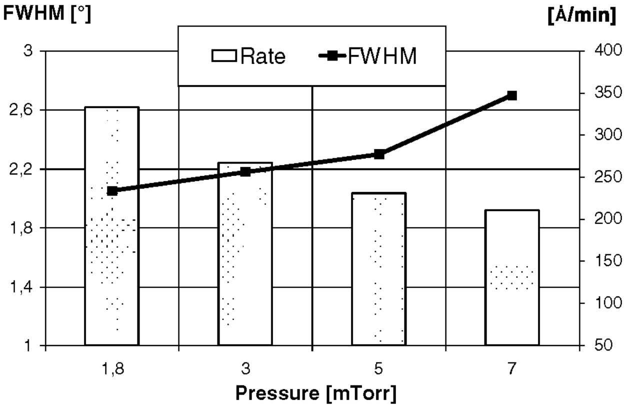

Fig. 1 FWHM and deposition rate of AlN films deposited at room temperature as a function of the process pressure

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[2] Frontier Semiconductor Measurements, San Jose, CA, USA.

[3] PANalytical B.V., Almelo, The Netherlands.

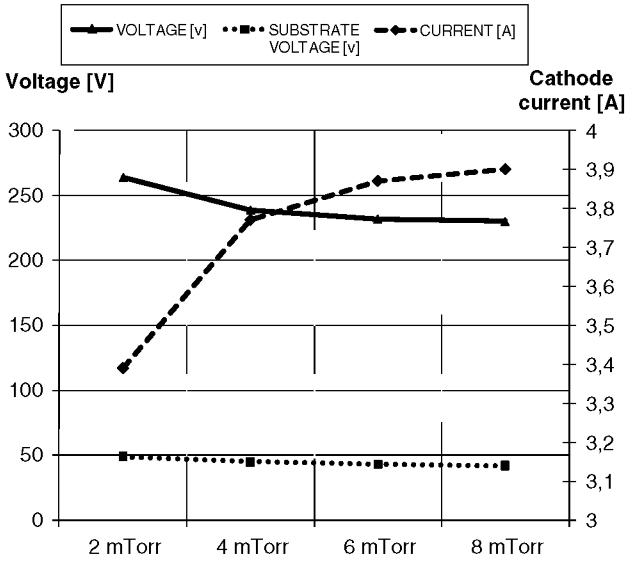

Fig. 2 Pressure dependence of discharge voltage, substrate voltage and current sheath of highly oriented AlN films deposited by reactive sputtering in an Ar/N_2 atmosphere

The major mechanisms to transfer kinetic energy to the growing film are atomic peening (Hoffman and Thornton 1977; Windischmann 1992), bias deposition or atom assisted deposition (Iriarte et al. 2002) (which may be considered a sort of "substrate temperature" since it is related to the ad-atom mobility at the substrate surface). In the first instance, the growing film is bombarded by either energetic particles (which are in fact energetic ions reflected off the target and simultaneously neutralized) or negative ions, which are accelerated away from the target by the cathode dark space. The reflection mechanism requires that the mass of the sputtering gas is smaller than that of the target, while the negative ion bombardment mechanism requires that the yield for negative ions is sufficiently large. A fraction of the ions bombarding the Al target are positively charged N_2^+ ions, which are dissociated upon impact against the target surface resulting in an effective energy of the N atoms of half the target voltage. It is noted also that the reflection coefficient increases with decreasing energy of the bombarding ions. All this creates conditions for a significant reflection of energetic N atoms off the target resulting in additional bombardment of the growing film with energetic N neutrals. The second mechanism at work here is bias deposition. The ion assisted deposition mechanism is only observed when a negative bias is applied to the substrate that results in energetic ion bombardment of the growing film. It is more or less independent of process parameters and the materials involved. This effect is not considered in this work. The third major mechanism relies on energy delivered to the growing film by the condensing species (Iriarte et al. 2002) (either by heating up the substrate or by enhancing their energy by other means such as decreasing the pressure). It is well known (Settaouti and Settaouti 2009) that the energy distribution of the sputtered atoms exhibits a maximum at around half the surface binding energy of the material being sputtered with a high energy tail. According to the kinetic theory of molecular gases, the mean free path of a gas molecule at constant temperature has a value that is inversely proportional to the pressure. Thus, the kinetic energy transfer from the plasma to the growing film surface is enhanced as the sputtering pressure decreases. At low sputtering pressures, the mean free paths of the chemical species increases owing to the decrease of the particle scattering, and the particles in the plasma can easily transfer their kinetic energy to the ad-atoms at the growing film surface. The basal plane in the hexagonal structure has the lowest surface energy and the maximum atomic density. The c-axis orientation, therefore, is increased due to the increase of kinetic energy transfer at the film surface as the sputtering pressure decreases. At low process pressures, the AlN layer surface may show a non-uniform grain growth, which may be due to stress-induced in the AlN thin film. On the other hand, when the sputtering pressure is increased, the surface exhibits a wave-like stripe texture, which may be due to the coexistence of some types of crystals. Further increase of the sputtering pressure, may give a surface showing small grain aggregates with a closely packed texture. The atomic "peening" or atom assisted mechanisms depend both on the species involved and the process pressure. The net effect of the first and third mechanisms is to deliver energetic particles (both Al and N) at the film surface resulting in enhanced surface diffusion (film densification) as well as lattice damage (both interstitials and vacancies). This gives rise to films showing compressive stress. Both mechanisms require a sufficiently low process pressure so that the energetic particles do not lose much of their energy through gas phase collisions.

Figure 3 illustrates the characteristic transition from compressive to tensile stress with increasing process pressure. It also illustrates the fact that the stress depends on the thickness of the thin film under study and hence the transition occurs at different pressures for thin films of different thickness. Figure 3 also shows the sign of the stress gradient in the film changing from tensile at small thickness towards compressive at larger film thickness. This observation is readily explained by the large lattice mismatch between AlN and Si(100) giving rise to strained AlN films and which strain is gradually relieved with thickness. In addition, it may also indicate that the initial growth is nucleation limited resulting in void formation and hence tensile stress, which again is relieved with thickness through grain coalescence (Saravanan et al. 2005). The evolution of the stress in this case is primarily

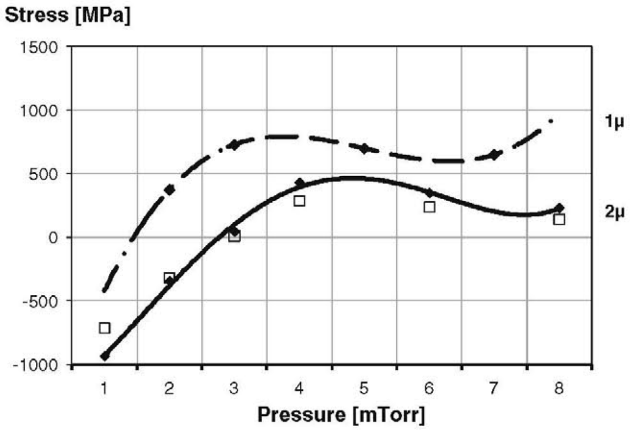

Fig. 3 Residual stress as a function of the process pressure as measured with the laser beam method. Two different AlN film thickness are analyzed; 1 and 2 μm

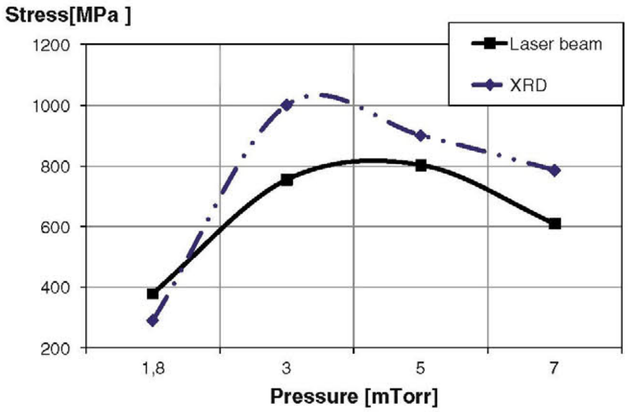

Fig. 4 Residual stress as a function of the process pressure as measured with two different techniques; an optically levered laser beam and an X-ray diffraction method

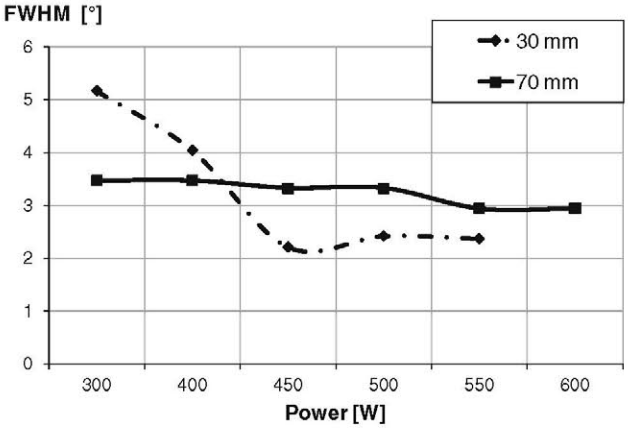

Fig. 5 Rocking curve FWHM values of highly oriented AlN thin films deposited at two different target–substrate distances

due to the atom assisted and atomic peening mechanisms. Thus, as the pressure is decreased the mean free path of the sputtered atoms becomes comparable with the target to substrate distance and hence they experience less gas phase collisions. This result in that the sputtered Al atoms arrive at the surface of the growing film with most of their original energy (of the order of several electronvolts) retained, providing substantial deposition energy at the surface of the growing film. It should also be mentioned that the sputtering pressure, at which a stress reversal from compressive to tensile happens, increases with the atomic mass of the metal being sputtered. In our case the substrate to target distance is 55 mm while the mean free path at 2 mTorr is 33 mm. In fact, the energy delivered to the growing film by the condensing Al atoms is sufficiently high so that (0002) oriented AlN films with FWHM of the rocking curve as low as 2.0° are readily obtained at room temperature. The magnitude of compressive stress increases drastically with decreasing sputtering pressure (see Fig. 4). This can be understood in terms of internal stress accumulation by relatively high momentum transfer at the film surface at low sputtering pressures. Atomic bombardment at the film surface results in compressive stress in the film and film densification by decreasing the voided regions in the microstructure, since atoms with sufficient kinetic energy at film surface may rearrange themselves under thermal equilibrium conditions. Figure 5 shows the rocking curve FWHM values of the (0002)-peak of AlN thin films deposited using two different target–substrate distances, namely 30 and 70 mm. At low discharge power, a slight improvement is obtained by increasing the target–substrate distance to 70 mm. However, better results are obtained at shorter distances using higher target powers. Although not shown here, it should be noted that other target-substrate distances such as 45 mm have also been examined, obtaining similar FWHM rocking curve values. These results, as well as the high amount of data available in the literature, showing highly textured AlN thin films at a multitude of target–substrate distance values (Chen et al. 2005; Kar et al. 2008; You and Kim 2007) lead us to the conclusion that this parameter by itself does not play a significant role. In other words, highly oriented AlN thin films can be obtained in a wide range of target–substrates distances going from 30 to 70 mm.

4 Conclusions

The (FWHM) of the rocking curve of the AlN-(0002) peak shows values as low as 2.0°, which indicates that the films are highly oriented in the c-axis. This is rather remarkable particularly taking into account that the films were grown at room temperature. Further, the high orientation of the AlN thin films is not due to a good matching of the lattice constants film-substrate. No other additional crystal growth promoting factors such as substrate bias were used during the synthesis. The films exhibited a very high degree of c-axis orientation especially when the process pressure was lowered. This is considered very relevant for electro acoustic devices such as SAW resonators and filters. The average energy of the sputtered atoms is of the order of several eV,[4] which is a sufficiently high energy to promote surface diffusion and film densification, as well as a certain amount of damage. Thus, this mechanism is very sensitive on the process pressure and the target to substrate distance. At high pressures the atoms are thermalized before they reach the surface of the film and hence this mechanism is suppressed. Compressive stress is usually attributed to an 'atomic peening' mechanism in which reflected neutral atoms bombard the growing film at low sputtering pressures. An increase in sputtering pressure increases the frequency of gas phase collisions, reducing the kinetic energy of sputtered neutral atoms and reflected neutrals bombarding the growing film. This reduction in 'atomic peening' reduces compressive stress. The degree of c-axis orientation was not affected by the target–substrate distance when it was changed from 30 to 70 mm.

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[4] electronvolts.