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Piezoelectric and structural properties of c-axis textured aluminium scandium nitride thin films up to high scandium content

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ABSTRACT

Partial substitution of aluminium by scandium in the wurtzite structure of aluminium nitride (AlN) leads to a large increase of the piezoelectric response by more than a factor of 2. Therefore, aluminium scandium nitride (ASN) thin films attracted much attention to improve piezoelectric MEMS devices such as RF filters, sensors, micro actuators and energy harvesting devices. In this work, process-microstructure-property relationships of ASN thin films containing up to 42% Sc were investigated. Like AlN thin films, ASN films are sputter deposited at 300–350°C with pulsed DC powered magnetrons. The influence of the process parameters on the film structure, the intrinsic stress and the piezoelectric response was investigated in order to achieve optimal piezoelectric coefficients up to high Sc concentrations. X-Ray diffraction (XRD) and transmission electron microscopy (TEM) were used to analyse the quality of c-axis texture. The films showed exclusively (002) texture with rocking-curve widths in the range of 1.3–2° (FHWM). The films were further analysed by scanning electron microscopy (SEM). The Sc content was determined by energy-dispersive X-ray spectroscopy (EDX). A good compositional homogeneity in the range of 0.5–1 at.% was achieved between border and centre of 200-mm wafers. So far, we obtained ASN films with transversal piezoelectric coefficients of up to $e_{31,f} = -2.77$ C/m^2, which is a factor 2.6 higher than in pure AlN thin films.

1. Introduction

Aluminium nitride (AlN) is widely used as piezoelectric thin-film material in RF-MEMS (Micro Electro Mechanical Systems) in thin film bulk acoustic wave resonators [1,2]. In recent years, also vibration energy harvesters [3,4], microphones [5], and fingerprint detectors [6] were investigated and developed. The material is also particularly attractive for monolithic integration (see, e.g. Dubois et al. [7]), as it is completely semiconductor compatible. Recently it was discovered that partial substitution of aluminium by scandium leads to a large increase of the piezoelectric response [8]. Scandium has always a valence of 3, like aluminium. However, it is somewhat larger, and more suited for a higher coordination than the tetrahedral one, as realised in the wurtzite structure. The compositional parameter describing the Sc concentration on the metal site is denoted by $x = [\mathrm{Sc}]/([\mathrm{Al}] + [\mathrm{Sc}])$. It is observed that the wurtzite structure is lost above about $x = 0.45$ [9], and goes finally over to the non-piezoelectric cubic structure of ScN at $x = 1$. The larger Sc ions lead to an increase of the a lattice constant [10], as well as to a change of the bond angles, leading to a softening of the overall structure [11]. The decrease of the stiffness was indeed predicted by ab-initio simulations [12].

The substantial increase of the piezoelectric properties attracted much attention and makes $Al_{1-x}Sc_xN$ (ASN) a promising upcoming piezoelectric material for use in the next generation of radio-frequency (RF) filters [13], sensors, micro actuators and energy harvesting devices [13,14]. Piezoelectric microphones, speakers and ultrasonic transducers are also expected to be soon produced in large quantities [5,15]. The upper limit for Sc concentration in high-performing films will not only be a question of phase stability, but also a question of performance requirements. The bandgap of ASN steadily decreases with increasing Sc content [16], and reaches about 2.5 eV for pure ScN [17]. It is thus expected that dielectric losses will be larger at higher Sc concentration.

The increase of piezoelectricity was predicted by Alsaad et al. [18] for isostructural GaN—ScN systems based on density functional theory (DFT). First relatively precise DFT studies are now also available for the

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AlN—ScN system [19]. As these methods are not without errors – and not able to predict the dielectric constant – the evaluation of the functional film properties of optimised thin films is an inevitable task. There are two ways to deposit ASN by magnetron sputtering, either by conventional reactive sputtering from a single Al-Sc alloy target [13], or reactively co-sputtered from pure metal Al and Sc targets [8,20]. The latter is of advantage in material research as the Sc concentration can be tuned by adjusting the two powers of the sputtering targets. For industrial high-volume production, however, single-target sputtering is the preferred method as it provides a higher deposition rate. In addition, it is of advantage that Sc content is constant across large substrates, as intrinsically defined from the alloy target content. Furthermore, tight control of film stress and thickness uniformity over target lifetime can be managed by leveraging existing long-term experience in piezoelectric AlN thin films as used in large volumes for RF-MEMS devices. The preferred wafer size in the MEMS industry is 200 mm. However, up to now, alloy targets with high Sc content ($>$ 20% Sc) are not yet available for targets size larger than 200 mm diameter. For this reason, alternative solutions are applied for the time being, i.e. single or dual target configurations with rotating substrates. We thus studied three possible configurations for coating 200-mm wafers:

1. Single-target sputtering on stationary substrates using 304-mm alloy targets in case of low Sc content (Sc = 6 at.% and 9.5 at.%), represented as blue circles in the graphs;
2. Single-target sputtering on rotating substrates using 100-mm alloy targets (for Sc = 15 at.% and 28 at.%), represented as black diamonds in the graphs;
3. Co-sputtering on rotating substrates using 100-mm pure metal Al and Sc targets, represented as green triangles in the graphs.

In this work, we focus on the transversal piezoelectric coefficient $e_{31,f}$ as functional property. This coefficient dominates applications with flexural structures used in all applications mentioned above with the exception of RF filters. The use of $e_{31,f}$ rather than the standard transverse coefficients such as e_{31}, or d_{31} is imposed by the fact that the piezoelectric effect couples through strain with the substrate in the direct effect $D_3 = e_{31,f} \times (S_1 + S_2)$. As no forces are applied in the out-of-plane direction (direction 3), and the film is free to deform perpendicular to the film plane, one cannot use e_{31} directly. In the converse mode, flexural structures are bent by the piezoelectric stress $e_{31,f} \times E_3$. This coefficient can directly be measured and does not need the knowledge of elastic constants [21,22]. This coefficient also has the advantage that a good value is only obtained when the microstructure of the film is dense. Porosity, voided grain boundaries, etc. lead to a reduction of this coefficient, because mechanical forces are not well transmitted between the grains in such cases.

Furthermore, some process-microstructure-property relationships of piezoelectric active ASN films were evaluated. The applied processing parameters were essentially the same as for pure AlN films. The process variations concerned target issues, pressure and power. The investigated parameters address microstructure, film stress, Sc homogeneity across 200-mm wafers, and $e_{31,f}$ values as a function of Sc content, and the correlation of film stress with $e_{31,f}$ for a specific Sc concentration. The obtained results are very promising towards industrial application and large-volume production.

2. Experimental

The ASN films were reactively sputter deposited at 300–350°C substrate temperature with pulsed DC powered magnetrons (150 kHz), closely matching processes for pure AlN [23,24]. The pulsed DC process exhibits a higher deposition rate than RF sputtering, and is thus preferred for industrial processes. Both, single-target sputtering as well as co-sputtering configurations were carried out on a CLUSTERLINE® 200 II from *Evatec*. The magnetrons were driven at various powers (0.2–1 kW on 100-mm targets (up to 12.7 W/cm^2), up to 7.5 kW (up to 10.6 W/cm^2) on 304-mm targets). The deposition rate for the single source was in the order of 1 nm/s, whereas for the co-sputtering around 0.2 nm/s. The obtained 1σ thickness uniformity was better than 0.5% and 2% for the single-source sputtered and co-sputtered films, respectively. The 200-mm diameter, (100)-oriented silicon wafers were covered with 200 nm thermal oxide, and coated with 111-oriented platinum (Pt) or 110-oriented molybdenum (Mo) electrodes. The base pressure of the deposition chambers was in the lower range of 10^{-7} mbar. The process gases Ar and N_2 were applied with a ratio of 1:2. The total gas flow was varied between 22.5 SCCM and 45 SCCM.

The film crystal structure was assessed by dark-field imaging and electron diffraction in a FEI Talos transmission electron microscope (TEM) at 200 kV acceleration voltage, as well as by X-ray diffraction (XRD) on a Bruker D8 Discover at 8047.7 eV (monochromic Cu Kα_1). The chemical composition of the films was determined on a Zeiss Merlin scanning electron microscope (6 kV accelerative voltage, 1 nA beam current) by energy-dispersive X-ray spectroscopy (EDX), which allowed to measure the Sc concentration across the large 200-mm substrates. For functional characterisation, TE/ASN/BE/SiO_2/Si(100) multilayer stacks were fabricated, whereby the bottom electrode (BE) was either a polycrystalline, (111)-textured Pt film, or a (110)-textured Mo thin film. For the top electrode (TE), we applied either Pt films or Au films on Cr adhesion layers. The transversal piezoelectric coefficient $e_{31,f}$ of the ASN films was determined with an aixACCT four-point bending setup [25] using Si(100) cantilevers along the [110] direction having a Poisson ratio ν_s of 0.064 [26]. Due to the in-plane strain S_1 a charge difference (ΔQ) is produced between top and bottom electrode (ΔA, surface of plate capacitor). The cantilever displacement (which is directly linked to S_1) is measured with a laser interferometer. Since the out-of-plane stress is zero, the simple relation for the dielectric displacement

$$D_3 = \frac{e_{31,f} S_1}{1 - \nu_s}$$

holds, and the $e_{31,f}$ value can be derived from measured charge and displacement with $D_3 = \Delta Q/\Delta A$. The film stress was assessed with a *Frontier Semiconductor* (FSM) 128L film stress measurement system. A laser beam is moved above the sample in one direction. The reflected beam strikes a position-sensitive photo diode. The curvature radius of the wafer along the axis is measured by a line scan before and after the film deposition and hence allows the determination of the curvature change due to the deposition. The film stress is then calculated by means of Stoney's equation.

3. Results and discussions

3.1. Structural characterisation

The influence of the Sc content on the thin-film microstructure and piezoelectric properties of aluminium scandium nitrite (ASN) was investigated. Fig. 1 (a)–(c) shows TEM dark-field images for films with 10, 31 and 42% Sc content, grown on Pt. The columnar growth, similar to the columnar microstructure of pure AlN, is clearly visible. The size of columns with the same in-plane orientation can be estimated to approx. 45–50 nm at a height of 400 nm. The corresponding TEM selective area electron diffraction (SAED) patterns reveal out-of-plane c-axis orientation for all films up to 42% Sc. The c/a ratio of the two lattice parameters estimated from the SEAD patterns is decreasing with increasing Sc content in the films as formerly described by Matloub et al. [10]. The SEM plane views of the same films are illustrated in Fig. 1 (d)–(f). From the SEM images the average grain size can be estimated to approx. 30 nm for 10 and 31% Sc content, and to approx. 50 nm for 42% Sc.

The discrepancy between the grain size from TEM cross sections and from SEM plane views at lower Sc concentration can be explained by a