Piezoelectric Al$_{1-x}$Sc$_x$N thin films: A semiconductor compatible solution for mechanical energy harvesting and sensors


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The transverse piezoelectric coefficient $e_{31,f}$ of Al$_{1-x}$Sc$_x$N thin films was investigated as a function of composition. It increased nearly 50% from $x = 0$ to $x = 0.17$. As the increase of the dielectric constant was only moderate, these films are very suitable for energy harvesting, giving a 60% higher transformation yield ($x = 0.17$) as compared to pure AlN. A higher doping might even lead to a 100% augmentation. The thickness strain response ($d_{33,f}$) was found to increase proportionally to the ionic part of the dielectric constant. The $e$-type coefficients (stress response), however, did not augment so much as the structure becomes softer. As a result, the transverse voltage/strain response ($h_{31,f}$-coefficient) was raised only slightly with Sc doping. The low dielectric loss obtained at all compositions suggests also the use of Al$_{1-x}$Sc$_x$N thin films in sensors.

AlN is one of the standard piezoelectric thin film materials for vibration energy harvesters in miniaturized MEMS (Micro Electro Mechanical Systems) versions. In comparisons for vibration energy harvesters in miniaturized MEMS with its flexural structures, is not characterized yet. The relevant piezoelectric coefficient in this case is $e_{31,f}$, describing the situation of a film clamped to an elastic layer in the 1 and 2 directions and free to move perpendicular to the layer plane, i.e., in the 3rd-direction. The $e$-coefficients are products of $d$-coefficients with the stiffness, i.e., $e_{ijk} = d_{ilm}c_{mjk}$. It was shown by ab-initio calculations that the $e_{33}$ coefficient is increasing in spite of the softening of $c_{33}$. The question is whether the $e_{31,f}$-Coefficient increases as well, and how much voltage and power yield are expected to be raised by Sc doping. The goal of this work was thus to measure the transverse piezoelectric coefficient as a function of Sc concentration.

We prepared polycrystalline (001)-textured AlN, Al$_{0.88}$Sc$_{0.12}$N, and Al$_{0.80}$Sc$_{0.17}$N thin films by reactive, pulsed, direct current magnetron sputtering. 200 mm either exhibiting a 4 mm thick plate of an Al, Al$_{0.9}$Sc$_{0.1}$, or Al$_{0.825}$Sc$_{0.175}$ alloy of at least 99.9% purity has been used. The system was pumped down to a base pressure smaller than $1 \times 10^{-7}$ millibars before admitting nitrogen and argon in. The cathode power was 1500 W, and an RF bias was applied to the substrate to enhance the ion bombardment of the growing film. The films were grown on 100 nm thick Pt (111) bottom electrodes on a 10 nm thick Ti layer, both sputter deposited onto 100 mm silicon wafers coated with a 200 nm thick thermal oxide. We analyzed the composition of the Al$_{1-x}$Sc$_x$N films using Energy Dispersive Analysis of X-ray...
emission in the transmission electron microscopy (TEM), obtaining x = (12 ± 1) at. % with the Al$_{0.9}$Sc$_{0.1}$ target and (17 ± 1) at. % with the Al$_{0.825}$Sc$_{0.175}$ target. As the mechanical stress in AlN based films was very much depending on the sputter process, we tuned the processes to keep the stress level low. They were evaluated by means of a stress analyzer (Tencor FLX-2900) as 110, 115, and 270 MPa for 0, (12 ± 1)%, and (17 ± 1)% atomic Sc concentration on the Al site.

X-ray diffraction (XRD) pattern and transmission electron microscopy (TEM) revealed a pure c-axis orientation with columnar microstructure with no traces of other orientations or phases for doped AlN films, similar as observed for un-doped AlN thin films. Selected area electron diffraction—calibrated with the XRD (002) peak—yielded a and c lattice parameters of 3.11 and 4.98 for pure AlN, 3.177 and 4.996 for x = (12 ± 1)%, and 3.196 and 5.01 for x = (17 ± 1)%. The c/a ratio decreased from 1.601 of pure AlN to 1.572 to 1.568 by increasing Sc concentration. The lattice constant a increased about 5 times stronger than lattice constant c with increasing Sc addition (Fig. 1). This was reported for (Ga,Sc)N system before. The decrease of the c/a ratio was also predicted from density functional theory. To evaluate basic dielectric and piezoelectric properties, parallel plate capacitor structures of 0.6 mm diameter as well as specific electrodes for $e_{31,f}$ measurements on $1.5 \times 15 \text{ mm}$ cantilevers were formed by sputtering Au/Cr through a shadow mask to form top electrodes. Finally, samples were diced into $15 \times 1.5 \times 0.38 \text{ mm}$ beams for $e_{31,f}$ measurements in the charge/deflection mode whereby the beam was deflected with a modulation frequency of 110 Hz by a strain gauge controlled PZT actuator, as described in Ref. 13. Capacitances were measured using an HP 4194A-Impedance/Gain-Phase Analyzer (Agilent) as a function of frequency in the range of 1-100 KHz. The major error source for the dielectric constant was the film thickness. Estimating the error of the latter as ±50 nm, we obtained the following values $e_{33,f} = 13.1 \pm 0.7$ and $e_{33,f} = 13.6 \pm 0.55$ for x = 0.12 and 0.17, respectively. The dielectric loss did not increase above the 0.2% value of pure AlN. In addition, we assessed the longitudinal, clamped piezoelectric coefficient $d_{33,f}$ by double-side beam interferometry (DBI), a method that measures the thickness change of the piezoelectric film. The thickness modulation upon application of an ac (alternating current) electric field at 5 kHz frequency was measured. Figure 2 shows $d_{33,f}$, $e_{31,f}$, and dielectric constants of our AlScN thin films as a function of composition. All three properties augmented with increasing Sc content. The dielectric values compare well with the measurements published by Moreira et al. The absolute value of $e_{31,f}$ piezoelectric coefficient increased from 1.0 (C/m$^2$) for pure AlN thin film to 1.36 (C/m$^2$) for Al$_{0.88}$Sc$_{0.12}$N and to 1.46 (C/m$^2$) for Al$_{0.83}$Sc$_{0.17}$N.

The Sc doping has led essentially to an increase in unit cell volume and as a consequence to softening. The larger displacement amplitudes upon application of an ac electric field should give an equal relative increase for the ionic part $e_{33,f} - \epsilon_0$ of the relative dielectric constant. The proportionality requires that the line starts at (0/0).
charge separation as for the piezoelectric strain, meaning that the relative ionic contribution to the dielectric constant should increase as much as the relative piezoelectric coefficient $d_{33}$, which thus should closely correlate with the ionic part of the dielectric constant $e_{33} - e_{ir}$ (electronic part of dielectric constant), the latter being the dielectric constant at optical or infrared frequencies (often abbr. $e_{ir}$). This was indeed the case, as shown in Fig. 3, i.e., $d_{33} = const \cdot (e_{33} - e_{ir})$. $e_{ir}$ amounts to 4.68 according to Refs. 15 and 16.

Figure 4 shows the relative change of $d_{33}$ ($e_{06}e_{33}$) and $e_{31}$ ($e_{06}e_{33}$). It shows that there is an additional increase of almost 50% in the thickness strain response ($d_{33}$ ($e_{06}e_{33}$)) is equal to $g_{33}$ and 10% in the in-plane stress (corresponding to the $h_{31}$ coefficient) at $x = 17%$. The smaller increase of the $e_{31}$ coefficient could be explained by the softening of the in-plane elastic constants with increasing $x$ content.

As figure of merit (FOM) for energy harvesting, one generally could take the product of the piezoelectric coefficients for charge and voltage response, i.e., $e_{31} \cdot h_{31} = e_{31}^2 / (e_{06}e_{33})$. The FOM of voltage is the coefficient $h_{31} = e_{31} / (e_{06}e_{33})$. Both are depicted in Figure 5. We observed a 60% increase of the electrical energy content to be harvested. As we can see, the energy harvesting FOM of 18.0 (GJ/m$^3$) for Al$_{0.83}$Sc$_{0.17}$N is comparable with good PZT thin films like the ones having a $e_{31}$ of 16 C/m$^2$ and a dielectric constant of 1600 (close to what was published in Ref. 17). However, thanks to the much lower dielectric constant of Al$_{1-x}$Sc$_x$N thin films, the output voltage is over a factor of 10 larger.

For sensor applications, similar arguments hold as for energy harvesting. The charge/strain response increased with $e_{31}$. However, the dielectric noise determines the signal to noise ratio as well. The latter did not increase with $Sc$ doping and remained at 0.2% for all concentrations. The figure of merit for the signal to noise ratio is given as $\frac{\delta}{N} = e_{31} / \sqrt{e_{06}e_{33}} \tan \delta$. This value increased from $2.2 \times 10^6$ ($\sqrt{J/m^3}$) to $2.9 \times 10^6$ ($\sqrt{J/m^3}$) to $3.0 \times 10^6$ ($\sqrt{J/m^3}$) for Al$_{1-x}$Sc$_x$N, for $x = 0, 0.12$, and 0.17, respectively.

In conclusion, piezoelectric AlScN alloys look very interesting for harvesting as well as for sensor applications. We showed here that the harvesting efficiency is potentially increased by more than 60% as compared to pure AlN. Going to even higher $Sc$ concentrations, a doubling of the harvested power is conceivable. The voltage increase is small, but in this respect, AlN thin films are anyhow much superior to PZT thin films. The dielectric loss did not increase with $Sc$ doping. For this reason, AlScN thin films can also improve the performance of AlN films in sensors.

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