Piezoelectric Al1−xScxN thin films: A semiconductor compatible solution for mechanical energy harvesting and sensors

R. Matloub, M. Hadad, A. Mazzalai, N. Chidambaram, G. Moulard et al.

Additional information on Appl. Phys. Lett.

Piezoelectric Al₁₋ₓScₓN thin films: A semiconductor compatible solution for mechanical energy harvesting and sensors

R. Matloub,[1] M. Hadad,[1] A. Mazzalai,[1] N. Chidambaram,[1] G. Moulard,[2] C. S. Sandu,[1] Th . Metzger,[2] and P. Muralt[1]

[1]*Ceramics Laboratory, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland*
[2]*EPCOS AG, Munich, Germany*

The transverse piezoelectric coefficient $e_{31,f}$ of Al₁₋ₓScₓN 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 Al₁₋ₓScₓN thin films in sensors. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4800231]

AlN is one of the standard piezoelectric thin film materials for vibration energy harvesters in miniaturized MEMS (Micro Electro Mechanical Systems) versions.[1,2] In comparison to Pb(Zr,Ti)O₃ (PZT) thin films, higher output voltages are much more easily reached applying the simple parallel plate geometry, because the ratio of the transverse piezoelectric coefficient $e_{31f} = d_{31}/(s_{11}^E + s_{12}^E)$ to the dielectric constant $\varepsilon_{33,f}$ is about 10 times higher in AlN than in PZT thin films. A further advantage of AlN is its semiconductor compatibility, the lower processing temperature, and thus the easy integration into silicon devices. A drawback of AlN devices is the lower piezoelectric coupling at identical geometries, resulting in smaller electrical energy content in AlN for a given elastic energy in the device. This fact might not be so important when dealing with resonant harvesting devices that are based on the acceleration of an inertial mass, as the quality factor of the resonance amplifies the power yield.[3,4] This quality factor can be raised by vacuum packaging[5] thus circumventing the lower piezoelectric coupling of AlN. If, however, the coupling to the mechanical force is performed by a direct deflection input as in the pull-and-release case, the piezoelectric coupling is directly giving the amount of energy that can be exploited in one event. For this reason—and when applied in low-*Q* resonating devices—it is of paramount interest to raise the piezoelectric coefficient $e_{31,f}$ of AlN.

In recent works, it was shown that the longitudinal piezoelectric coefficient $d_{33f} = e_{33}/c_{33}^E$ of AlN increased when Al is partially substituted by Sc. Akiyama *et al.* demonstrated a four times increase in the longitudinal piezoelectric coefficient d_{33} measured by the "piezotest" method for ScₓAl₁₋ₓN alloys with x = 43%.[6] This increase was reproduced by other groups for x < 20%, using different measurement methods, i.e., by double beam interferometry[7] and bulk acoustic wave resonator characterization.[8] This increase was predicted earlier for the (Ga,Sc)N system based on first principle calculations.[9] Recently, it was shown by density functional theory that substitution of Al by Sc leads indeed to a softening of the wurtzite phase, interpreted as a competition of Al³⁺ and Sc³⁺

ions about the coordination of nitrogen (Al³⁺ preferring 4-fold and Sc³⁺ preferring 6 fold coordination) that results in a frustrated system.[10] With increasing Sc concentration in the wurtzite phase, the potential wells of the ions become shallower, and thus the ionic displacements in an electric field become larger, leading to larger dielectric and piezoelectric responses. It was found that the e_{33} increased while the stiffness simultaneously decreased.[10]

Whereas the longitudinal piezoelectric effect in AlScN thin films is well characterized, the transverse piezoelectric effect, which is the most interesting one for piezoelectric 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.[11] The *e*-coefficients are products of *d*-coefficients with the stiffness, i.e., $e_{ijk} = d_{ilm}c_{lmjk}$. It was shown by *ab-initio* calculations that the e_{33} coefficient is increasing in spite of the softening of c_{33}.[10] 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, Al₀.₈₈Sc₀.₁₂N, and Al₀.₈₃Sc₀.₁₇N thin films by reactive, pulsed, direct current magnetron sputtering. 200 mm either exhibiting a 4 mm thick plate of an Al, Al₀.₉Sc₀.₁, or Al₀.₈₂₅Sc₀.₁₇₅ alloy of at least 99.9% purity has been used. The system was pumped down to a base pressure smaller than 1×10^{-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 Al₁₋ₓScₓN 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.[12] The decrease of the *c/a* ratio was also predicted from density functional theory.[10]

To evaluate basic dielectric and piezoelectric properties, parallel plate capacitor structures of 0.6 mm diameter as well as specific electrodes for e_{31f} measurements on 1.5 × 15 mm cantilevers were formed by sputtering Au/Cr through a shadow mask to form top electrodes. Finally, samples were diced into 15 × 1.5 × 0.38 mm beams for e_{31f} 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 ε_{33f} = 13.1 ± 0.7 and ε_{33f} = 13.6 ± 0.55 for x = 0.12 and 0.17, respectively. The dielectric loss did not increase above the
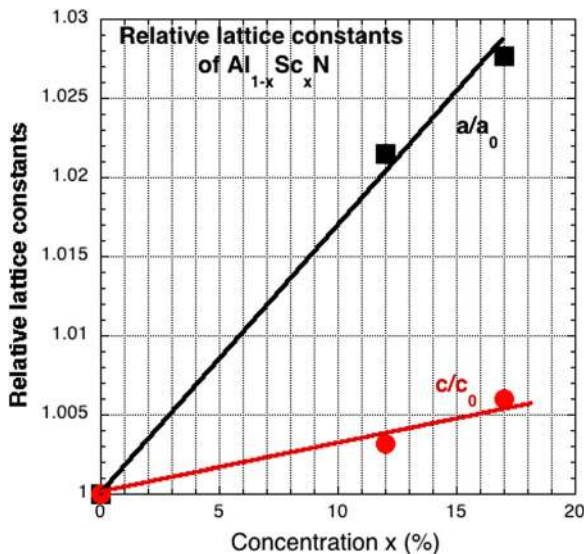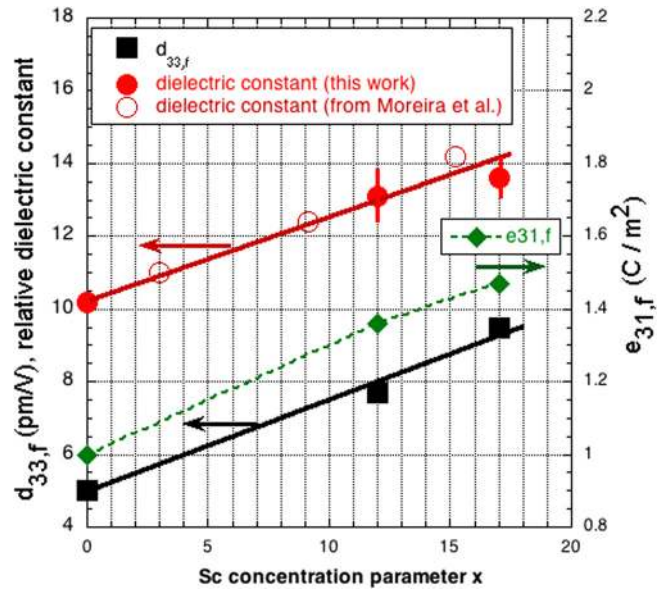

FIG. 2. Dielectric constant, $d_{33,f}$ and $e_{31,f}$ as a function of Sc content.

0.2% value of pure AlN. In addition, we assessed the longitudinal, clamped piezoelectric coefficient d_{33f} by double-side beam interferometry (DBI), a method that measures the thickness change of the piezoelectric film.[14] 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.*[8] The absolute value of e_{31f} piezoelectric coefficient increased from 1.0 (C/m²) for pure AlN thin film to 1.36 (C/m²) for $Al_{0.88}Sc_{0.12}N$ and to 1.46 (C/m²) 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
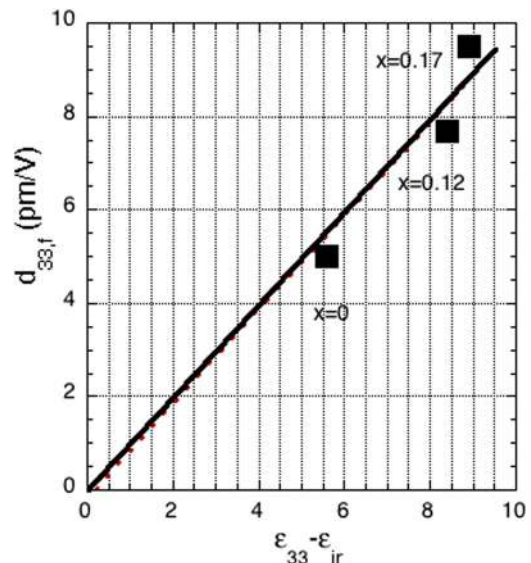

FIG. 1. Relative change of a and c unit cell dimensions.

FIG. 3. The longitudinal piezoelectric thin film response as a function of the ionic part $\varepsilon_{33f} - \varepsilon_{ir}$ of the relative dielectric constant. The proportionality requires that the line starts at (0/0).
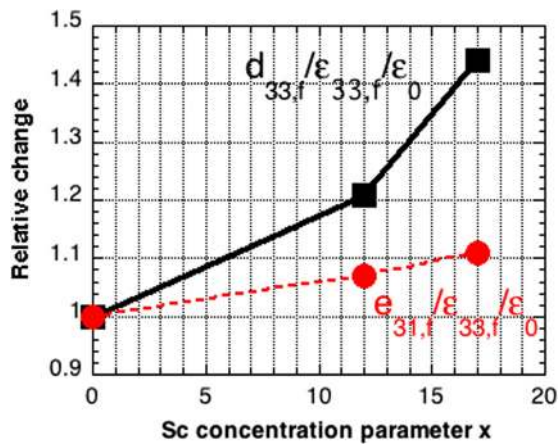
FIG. 4. $d_{33,f}/(\varepsilon_0\varepsilon_{33,f})$ and $e_{31,f}/(\varepsilon_0\varepsilon_{33,f})$ as a function of Sc content.

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 $d_{33,f}$, which thus should closely correlate with the ionic part of the dielectric constant $\varepsilon_{33,f} - \varepsilon_{ir}$ (ε_{ir} electronic part of dielectric constant), the latter being the dielectric constant at optical or infrared frequencies (often abbr. ε_∞). This was indeed the case, as shown in Fig. 3, i.e., $d_{33,f} = const \cdot (\varepsilon_{33,f} - \varepsilon_{ir})$. ε_{ir} amounts to 4.68 according to Refs. 15 and 16.

Figure 4 shows the relative change of $d_{33,f}/(\varepsilon_0\varepsilon_{33,f})$ and $e_{31,f}/(\varepsilon_0\varepsilon_{33,f})$. It shows that there is an additional increase of almost 50% in the thickness strain response ($d_{33,f}/(\varepsilon_0\varepsilon_{33,f})$ is equal to $g_{33,f}$) and 10% in the in-plane stress (corresponding to the $h_{31,f}$ coefficient) at x = 17%. The smaller increase of the $e_{31,f}$ coefficient could be explained by the softening of the In-plane elastic constants with increasing Sc 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., $e_{31,f} \cdot h_{31,f} = e_{31,f}^2/(\varepsilon_0\varepsilon_{33,f})$. The FOM of voltage is the coefficient $h_{31,f} = e_{31,f}/(\varepsilon_0\varepsilon_{33,f})$. 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 $e_{31,f}$ 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 $e_{31,f}$. 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 $\frac{S}{N} = e_{31,f}/\sqrt{\varepsilon_0\varepsilon_{33,f}\tan\delta}$. This value increased from 2.2×10^6 ($\sqrt{\text{J/m}^3}$) to 2.9×10^6 ($\sqrt{\text{J/m}^3}$) to 3.0×10^6 ($\sqrt{\text{J/m}^3}$) 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
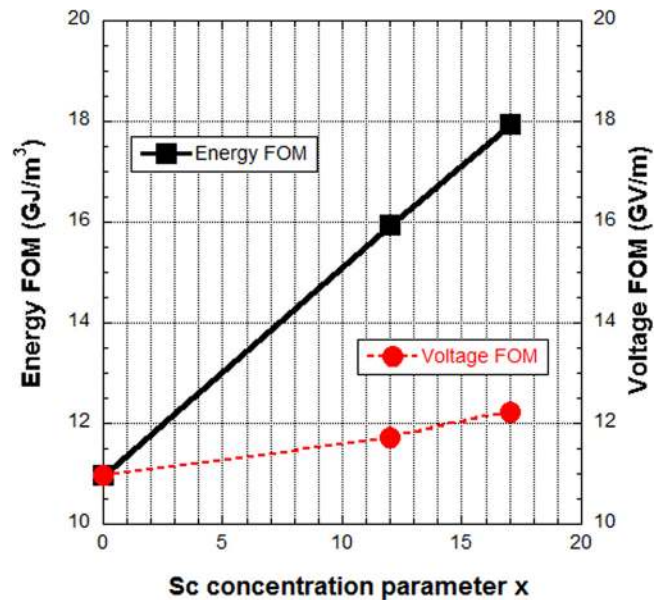

FIG. 5. The FOMs for energy transformation and voltage response with the transverse piezoelectric effect as a function of Sc concentration.

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.

[1]R. Elfrink, T. M. Kamel, M. Goedbloed, S. Matova, D. Hohlfeld, Y. van Andel, and R. van Schaijk, J. Micromech. Microeng. **19**, 094005 (2009).
[2]M. Marzencki, S. Basrour, B. Belgacem, P. Muralt, and M. Colin, in *Proceedings Nanotech., May 20-24, 2007, Santa Clara, U.S.A.* (2007), Vol. 3, pp. 21–24.
[3]S. Roundy, P. K. Wright, and J. Rabaey, Comput. Commun. **26**, 1131–1144 (2003).
[4]P. D. Mitcheson, E. M. Yeatman, G. K. Rao, A. S. Holmes, and T. C. Green, Proc. IEEE **96**, 1457–1486 (2008).
[5]R. Elfrink, M. Renaud, T. M. Kamel, C. de Nooijer, M. Jambunathan, M. Goedbloed, D. Hohlfeld, S. Matova, V. Pop, L. Caballero, and R. van Schaijk, J. Micromech. Microeng. **20**, 104001 (2010).
[6]M. Akiyama, T. Kamohara, K. Kano, A. Teshigahara, and N. Kawahara, Appl. Phys. Lett. **93**, 021903 (2008).
[7]R. Matloub, A. Artieda, C. Sandu, E. Milyutin, and P. Muralt, Appl. Phys. Lett. **99**, 092903 (2011).
[8]M. Moreira, J. Bjurstrom, I. Katardjiev, and V. Yantchev, Vacuum **86**, 23–26 (2011).
[9]A. Alsaad and A. Ahmad, Eur. Phys. J. B **54**, 151–156 (2006).
[10]F. Tasnádi, B. Alling, C. Höglund, G. Wingqvist, J. Birch, L. Hultman, and I. A. Abrikosov, Phys. Rev. Lett. **104**, 137601 (2010).
[11]P. Muralt, Integr. Ferroelectr. **17**, 297–307 (1997).
[12]C. Constantin, H. Al-Brithen, M. B. Haider, D. Ingram, and A. R. Smith, Phys. Rev. B **70**, 193309 (2004).
[13]M.-A. Dubois and P. Muralt, Sens. Actuators A **77**, 106–112 (1999).
[14]A. L. Kholkin, C. Wütchrich, D. V. Taylor, and N. Setter, Rev. Sci. Instrum. **67**, 1935–1941 (1996).
[15]M. F. MacMillan, R. P. Devaty, and W. J. Choyke, Appl. Phys. Lett. **62**, 750–752 (1993).
[16]I. Akasaki and M. Hashimoto, Solid State Commun. **5**, 851–853 (1967).
[17]F. Calame and P. Muralt, Appl. Phys. Lett. **90**, 062907 (2007).