Microsyst Technol (2016) 22:1613–1617
DOI 10.1007/s00542-015-2787-x

TECHNICAL PAPER

Magnetron sputtering of piezoelectric AlN and AlScN thin films and their use in energy harvesting applications

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Received: 30 September 2015 / Accepted: 18 December 2015 / Published online: 9 January 2016

Abstract This paper reports on the deposition of AlN and $Al_XSc_{1-X}N$ films by pulse magnetron sputtering. The first part will focus on the $Al_XSc_{1-X}N$ deposition process in comparison to the already established AlN process. The effect of doping AlN with Sc regarding piezoelectric and mechanical properties is presented. The films show the expected increase of piezoelectric properties as well as the softening of the material with higher Sc concentrations. Above a threshold concentration of around 40 % Sc in the $Al_XSc_{1-X}N$ films, there exists a separation into two phases, an Al-rich and a Sc-rich wurtzite phase, which is shown by XRD. At Sc concentrations higher than 50 %, the films are not piezoelectric, as the films are composed primarily of the cubic ScN phase. The second main part of this paper evaluates the films for application in energy harvesting. Especially the Sc doping allows a significant increase in the energy generated in our test setup. Directly measuring the AC voltage at resonance depending on load resistance with base excitation of ±2.5 µm, 350 µW power have been generated under optimum conditions compared to 70 µW for pure AlN. For a more application oriented measuring setup, a standard and a SSHI-based ("Synchronised Switch Harvesting on Inductor") AC/DC converter circuit have been tested. The SSHI interface showed a significant improvement to 180 % compared to the standard interface.

1 Introduction

Aluminum nitride is a piezoelectric but not ferroelectric material with a hexagonal wurtzite crystal structure. Unlike widely used ferroelectric materials such as lead zirconate titanate (PZT), AlN cannot be electrically polarized. Therefore, piezoelectric activity can only be observed in single crystals or in a polycrystalline structure with a strong texture. To achieve a thickness vibration of a device, a crystalline orientation in the (001) direction is necessary (i.e., the c-axis of the AlN crystalline structure is oriented perpendicular to the substrate surface). It is a piezoelectric material often used as thin film in SAW/BAW devices. Furthermore, there is an increasing interest in its use as basis for energy harvesting applications. While it has relative low piezoelectric coefficients compared to PZT, it is a suitable choice for energy harvesting applications due to its low dielectric constant and good mechanical properties, such as Young's modulus. By doping the AlN films with scandium, the piezoelectric properties can be improved significantly (Akiyama et al. 2009a, b). This is mainly attributed to a softening of the C_{33} elastic constant as well as increase of piezoelectric constant e_{33} (Tasnádi et al. 2010). The increase of piezoelectric coefficient d_{33} compared to pure AlN was calculated to be 400 %.

The aim of this work is to examine the influence of Sc-doping on piezoelectric, mechanical and energy harvesting properties for AlScN films deposited by reactive pulse magnetron sputtering.

2 Experimental

2.1 Coating equipment

All depositions were done at a cluster tool by reactive pulse magnetron sputtering using the Double Ring Magnetron DRM 400 sputter source developed by Fraunhofer FEP (Frach et al. 1997). This type of magnetron combines two

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concentric discharge targets to deposit uniform films on substrates with a diameter of up to 200 mm. Figure 1 shows a schematic diagram of the deposition set up. In the case of AlN depositions, pure Al targets (5N) were used. $Al_XSc_{1-X}N$ was deposited by reactive co-sputtering of an Al outer and Sc inner target (3N5). Argon and nitrogen (5N) were used as the inert gas and reactive gas, respectively. The Argon gas flow (30…60 sccm) was used to adjust the pressure in the range of 0.3…0.7 Pa. For reactive AlN depositions, a closed loop reactive gas control was applied to stabilize the process in the transition mode (Frach et al. 1997). The resulting nitrogen flow rates were between 25 sccm and 40 sccm. There was no additional substrate heating or cooling. The deposition process of AlN is described in (Bartzsch et al. 2011; Barth et al. 2014).

2.2 Characterization

Determinations of piezoelectric properties were done using a PM300 piezometer (Piezotest Ltd., London, UK) on a simple ultrasound transducer layout. It is a three-layer structure, consisting of a circular AlN layer with a diameter of 13 mm, sandwiched between two aluminum electrodes with 10 mm diameter with contact pads.

The scandium content was determined by energy dispersive spectrometry of X-rays (Apollo XV, EDAX) using a silicon drift detector with an energy resolution of 125 eV. For the analysis, an acceleration voltage of 10 keV was used, which allows a good excitation of Aluminum and Scandium K_α-lines. The relative measurement uncertainty is in the range of ±5 %. The occurring phases were analyzed by X-ray diffraction using Cu–K_α radiation in Bragg–Brentano geometry (Seifert ID 3003T/T, GE Sensing & Inspection Tech.). Hardness and Young's modulus are determined by nanoindentation technique (MTS, Nano-Indenter XP) using continuous stiffness measurement and Oliver and Pharr theory for evaluation (Oliver and Pharr 1992).

Energy harvesting measurements were done using an electromechanical shaker system (Bruel and Kjær, Denmark) for the excitation of defined vibrations for cantilevers clamped to a base at one side. A laservibrometer (Polytec GmbH, Germany) was used for determination of displacement of the free end of the samples. By measuring the displacement depending on excitation frequency, the resonance frequencies of the samples were identified. The generated power was determined by measuring the AC voltage as function of electric load at resonance. Si cantilevers with thickness of 600 µm and area of approximately 8 × 80 mm^2 were used. The electrodes were Al films with a thickness of 100 nm and an area similar to the cantilever. The piezoelectric films with a thickness of 10 µm were sandwiched between these electrodes.

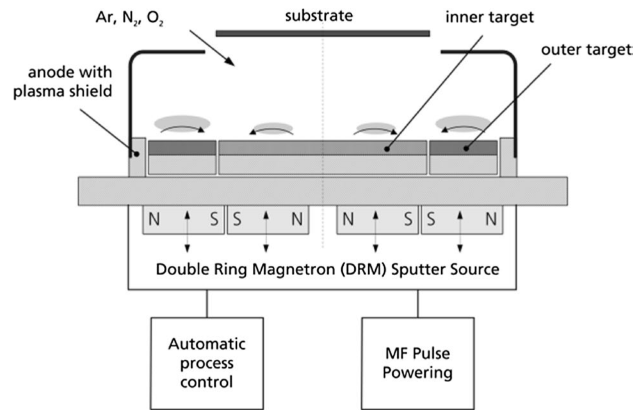

Fig. 1 Deposition setup for sputter deposition by DRM400 as shown in (Bartzsch et al. 2011)

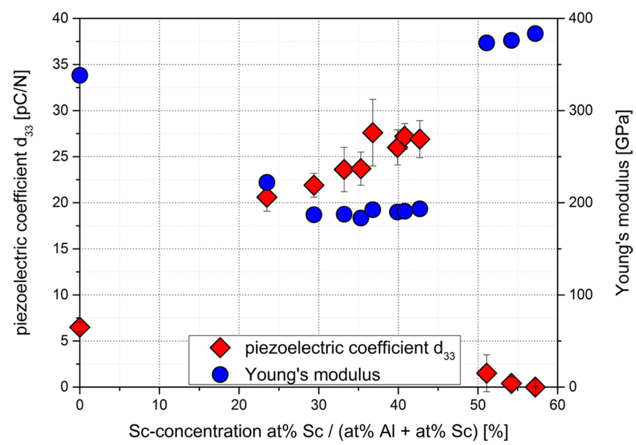

Fig. 2 Piezoelectric coefficient d_{33} and Young's modulus depending on Sc concentration in $Al_XSc_{1-X}N$

3 Results and discussion

3.1 Piezoelectric and XRD characterization of AlN and $Al_XSc_{1-X}N$ films

The dependency of piezoelectric properties and Young's modulus on Sc concentrations is shown in Fig. 2. The piezoelectric coefficient d_{33} is increasing with higher Sc concentration up to $Al_{0.57}Sc_{0.43}N$. At the same time, the Young's modulus decreased from 340 GPa of pure AlN to 190 GPa for $Al_XSc_{1-X}N$ with 30 % Sc and then remains constant at that value up to 43 % Sc. Above 50 % Sc, the films exhibit no piezoelectric properties and a much higher Young's modulus of about 380 GPa. These films consist primarily of the cubic ScN with non-polar rock salt structure. The lowering of Young's modulus is congruent with the expectations from the literature, although the decrease was reported to be gradually from 340 GPa of AlN to 230 GPa at 41…43 % Sc

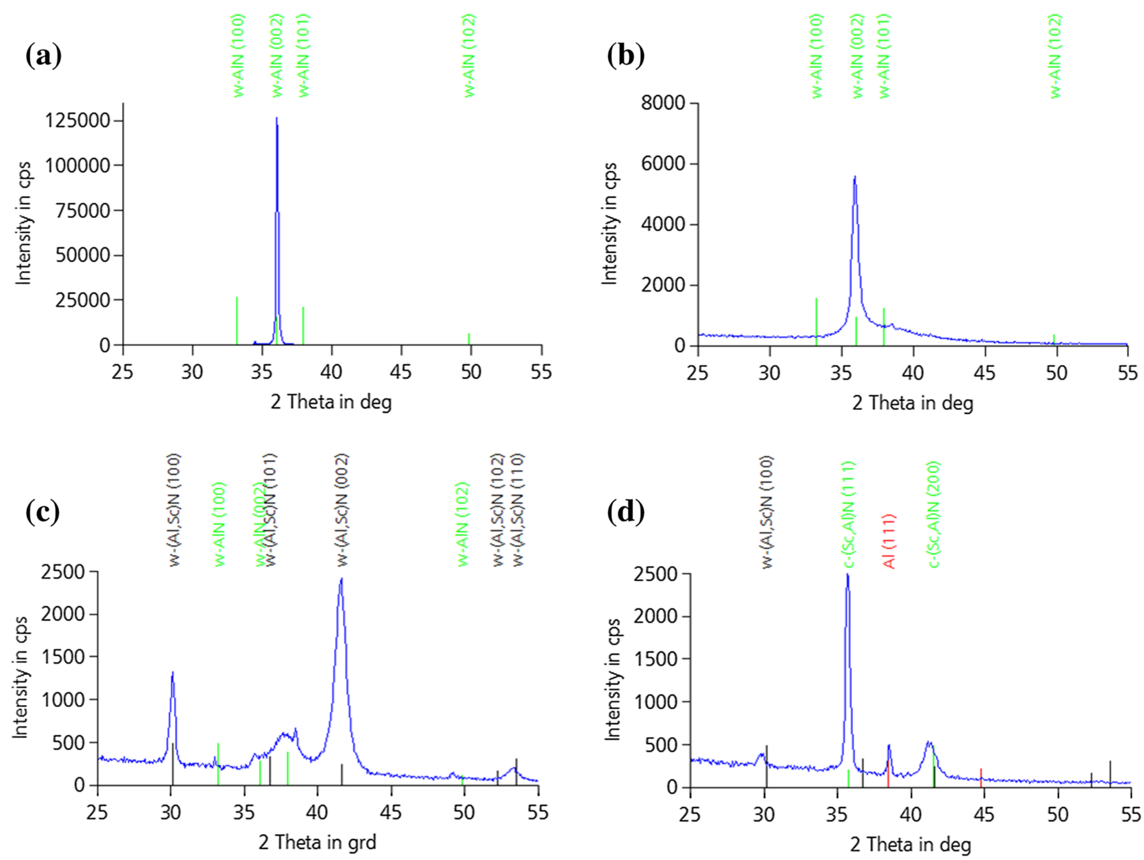

Fig. 3 XRD of **a** AlN, **b** $Al_{0.632}Sc_{0.368}N$, **c** $Al_{0.573}Sc_{0.427}N$ and **d** $Al_{0.489}Sc_{0.511}N$, showing the separation in an Al-rich and a Sc-rich wurtzite phase at higher Sc concentrations and the predominant cubic rock salt phase above 50 % Sc

(Teshigahara et al. 2012), with calculations being as low as 175 GPa at 41 % Sc (Akiyama et al. 2013).

In Fig. 3, the XRD measurements of $Al_XSc_{1-X}N$ at four different Sc concentrations are shown. For pure AlN (Fig. 3a), only the (002) peak is visible. The film with composition $Al_{0.632}Sc_{0.368}N$ (Fig. 3b) also has mainly the (002) peak, although the intensity is only a fraction of that of pure AlN and the FWHM of the peak is much higher. Interestingly, above a threshold concentration of around 40 % Sc, the $Al_XSc_{1-X}N$ films exhibit a separation in two phases, an Al-rich and a Sc-rich wurtzite phase. This can be seen in Fig. 3c with the peaks at 30.1°, 41.5° and 53.4°. Despite this, the films still exhibit very good piezoelectric properties (as seen in Fig. 2). The XRD of $Al_{0.489}Sc_{0.511}N$ in Fig. 3d confirm the dominance of non-piezoelectric cubic rock salt phase expected from Fig. 2 and literature.

3.2 Energy harvesting

To demonstrate the relevance of Sc-doping of AlN, the AlN and $Al_XSc_{1-X}N$ films were characterized regarding their effectiveness in energy harvesting (see Table 1). The resonance frequencies of the cantilevers were determined to be around 650 Hz for AlN coating and 1.1 kHz for AlScN coating due to shorter free length of the cantilever. The generated power at resonance of an $Al_XSc_{1-X}N$ film with approx. 40 % Sc is shown in Fig. 4 for a base displacement of 5 µm peak-to-peak. As can be seen, the power reached 350 µW at 10 kΩ load. A cantilever with AlN film and similar design showed generated powers of around 70 µW at optimal load. Due to the differences in resonance frequencies, these numbers are not directly comparable but show a good view of the trend. Additionally, a higher film thickness of AlN increased the generated power to 141 µW.

The measurement shown in Fig. 4 was done using the simple measurement of the AC voltage dependent on the

Table 1 Examples of generated AC power for AlN and $Al_XSc_{1-X}N$ films

Material	Film thickness (µm)	Free length of cantilever (cm)	d_{33} (pC/N)	P_{RMS} ([µW)
AlN	10	8	7	70
	50	8	7	141
$Al_{0.601}Sc_{0.399}N$	10	6	25	350

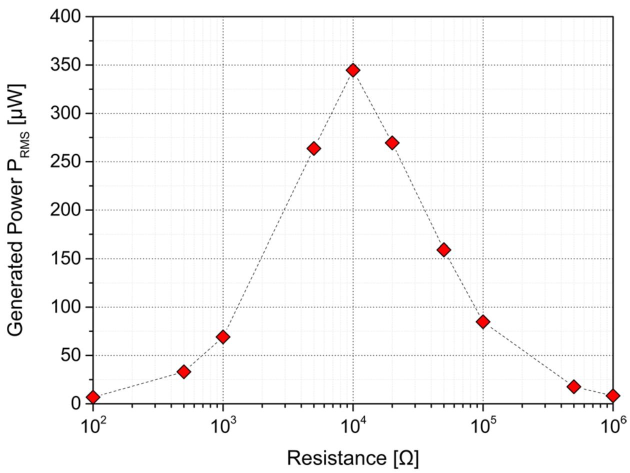

Fig. 4 Generated Power depending on electrical load for $Al_{0.601}Sc_{0.399}N$ ($f_r = 1.14$ kHz; base displacement $d_{pk\text{-}pk} = 5$ µm)

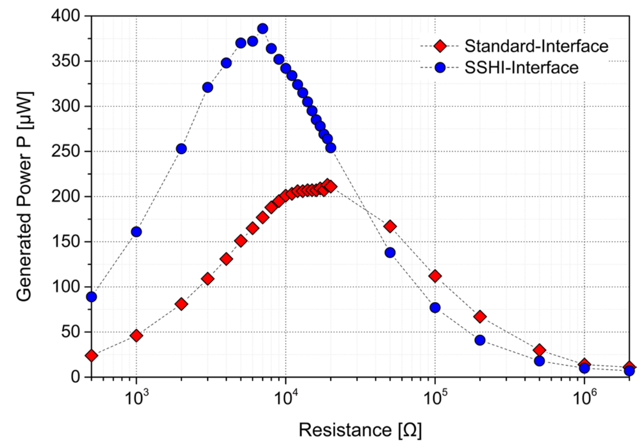

Fig. 5 Generated Power depending on electrical load for $Al_{0.601}Sc_{0.399}N$ with two different AC/DC converter circuits ($f_r = 1.17$ kHz; base displacement $d_{pk\text{-}pk} = 5$ µm)

resistive load described in the experimental section of this paper. However, for use as a means to charge a battery or capacitor, a DC output is necessary (Ottman et al. 2002). Hence, there is a need for an AC/DC converter. In a first step, a standard interface using a diode rectifier bridge and filter capacitor was tested. Following that, an improved circuit was designed based on SSHI-principle ("Synchronised Switch Harvesting on Inductor"), which uses non-linear processing of the voltage of the piezoelectric element (Guyomar et al. 2005; Lefeuvre et al. 2006). For this, an inductor and an electronic switch are connected in series with the piezoelectric element and the rectifier input ("Series-SSHI"). The switch is triggered at maximum value of displacement of the sample. In that moment, the switch closes and a part of the energy stored in the capacitor of the piezoelement is transferred to the filter capacitor. A voltage inversion is occurring. This setup can significantly improve the energy conversion efficiency, thereby increasing the harvested power.

The generated power as a function of the resistive load for both circuits is shown in Fig. 5. The $Al_{0.601}Sc_{0.399}N$ sample from Fig. 4 was measured under the same excitation conditions. Due to the manual fixation of the sample in the base, the free length of the cantilever was not absolutely the same. The resonance frequency of the cantilever was 1.17 kHz instead of 1.14 kHz. The measurement with standard circuit resulted in a generated power of 208 µW at an optimal load of 17–18 kΩ. The SSHI circuit achieved a maximum output of 380 µW at an optimal load of 7 kΩ.

4 Summary

This paper reports on the influence of Sc concentration on film properties in $Al_XSc_{1-X}N$ films. The $Al_XSc_{1-X}N$ films show the expected raise in piezoelectric properties as well as a softening of the material with increasing Sc concentrations. The measured d_{33} reaches up to 30 pC/N, whereas the values of Young's modulus and Hardness drop to about 50 % of those of pure AlN. Interestingly, above a threshold concentration of around 40 % Sc in the $Al_XSc_{1-X}N$ films, there exists a separation into two phases, an Al-rich and a Sc-rich wurtzite phase. Above 50 % Sc, the non-piezoelectric, cubic ScN phase was detected.

Additionally, Energy harvesting measurements were done using an electromechanical shaker system for the excitation of defined vibrations and a laservibrometer for determination of displacement of the samples. The generated power was determined by measuring the AC voltage as function of electric load at resonance. The $Al_{0.601}Sc_{0.399}N$ films showed an increase in generated power per volume of several times compared to pure AlN. Furthermore, two AC/DC converter circuits were tested to better simulate the use of the energy harvester for charging a battery or capacitor. The SSHI interface resulted in much higher output powers compared to the standard interface using a normal diode rectifier bridge and filter capacitor.

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