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Combined assessment of $Al_{1-x}Sc_xN$ thin films by RBS, XRD, FTIR and BAW frequency response measurements

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***Abstract*— $Al_{0.7}Sc_{0.3}N$ films were reactively sputtered from Al-Sc segmented targets by ac powered dual-cathode S-gun magnetron. Films with homogeneous Sc concentration within 30 ± 0.5 at. % were grown at ambient temperature directly on 200-mm (100) silicon wafers and on 100-mm silicon substrates covered with SiO_2/Mo-based acoustic reflectors terminated by highly (110) textured Mo electrodes. The piezoelectric assessment derived from the frequency response of bulk acoustic resonators yields values of the electromechanical coupling factor k^2 up to 12.8%. Infrared absorption and X-ray diffraction measurements reveal that tiny structural changes may lead to deviation in the value of k^2 across the wafer, which can be reduced by performing a post-processing heat treatment at around 600ºC.**

***Keywords*— AlScN films; Sc-doped AlN; reactive magnetron sputtering; 200-mm silicon substrates; variation of Sc content.**

I. Introduction

$Al_{1-x}Sc_xN$ piezoelectric thin films are being considered as possible candidates for the new 5G family of filters based on bulk acoustic wave (BAW) resonators since they offer the possibility of extending the bandwidth towards the targeted 200 MHz, owing to the enlargement of the electromechanical coupling factor k^2 with the increasing Sc content [1]. In addition, the drop of the acoustic velocity accompanying the reduction of the material stiffness as the scandium content increases [2] makes $Al_{1-x}Sc_xN$ suitable as high-k^2/low-velocity films capable of guiding surface acoustic waves (SAW) when sandwiched between two high speed materials, with applications in temperature sensors for harsh environments [3].

Since Akiyama first reported in 2009 that doping AlN films with scandium leaded to a significant increase of the piezoelectric activity [4], manufacturers and researchers have been seeking to develop reliable physical vapor deposition tools and processes enabling to bring the new material to current AlN production technology. Depending on the foreseen scandium concentration several approaches have been envisaged, which includes the use of compound alloys targets for low Sc contents [5], and sputtering from two independent Al and Sc targets [6] or engineered Al/Sc targets [7] when the desired amount of scandium exceeds 15%, although in these two last cases, composition and morphological homogeneity over large substrates areas is hardly achieved. Despite the considerable effort invested by the scientific community during the last decade, the viability of $Al_{1-x}Sc_xN$ films for the mentioned applications and possibility of their mass production has not been fully proven yet. Indeed, the growth of films with uniform composition and piezoelectric activity across large area substrates remains a challenge [7]. Moreover, there is still not unanimous agreement on the preferred composition of the films, since a tradeoff between k^2 and Q has to be reached depending on the foreseen application [1].

This work is an extension of our previous investigation on the characterization of AlScN films with different contents of Sc grown by the sputtering technique in an Endeavor-MX PVD cluster tool from OEM Group LLC. In this work the percentage of scandium in the metal has been extended to 30% with the hope of achieving highly-doped films with uniform composition over 200-mm silicon substrates. The films have been assessed at UPM by different characterization techniques and their properties compared with previous results obtained in films with Sc contents of 8% and 15%. The assessment reveals that although films with excellent composition uniformity along large area substrates can be achieved, inhomogeneity in the piezoelectric activity is observed, which is mainly attributed to variations in the radial morphology of the films.

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II. Production of $Al_{0.7}Sc_{0.3}N$ films

A. Sputter Technique for the growth of $Al_{0.7}Sc_{0.3}N$ Films

$Al_{0.7}Sc_{0.3}N$ films were grown in an Endeavor-MX PVD cluster tool equipped with an S-gun magnetron containing two coaxial ring-shaped magnetron targets adapted for the deposition of highly Sc-doped films. The targets were engineered to alternate Al and Sc segments, which is a low-cost solution to achieve films of different compositions by varying the quantity and/or width of Al and Sc segments. Prior to the deposition of the films the targets were preconditioned, first in the metallic mode (Ar atmosphere) and then in the poison mode to prevent the films from being contaminated with Al_3Sc precipitations. A highly-oriented AlN seed layer was used to improve crystallinity of the films. More details on the sputter process can be found in [8]. The substrates were not intentionally heated during the deposition of the $Al_{0.7}Sc_{0.3}N$ films. However, some samples were subjected to post-deposition heat treatments under vacuum (10^{-6} Torr) in a temperature-controlled quartz tube furnace at temperatures of 600ºC for 1 hour to investigate possible structural changes in the films and their effects on the piezoelectric activity.

B. Substrates

Two kind of substrates were used. To determine the composition and morphology uniformity of the $Al_{1-x}Sc_xN$ films we used 200-mm silicon wafers that were cut along the diameter into pieces of 2 cm × 2 cm. In addition, to carry out the assessment of the electroacoustic properties of the films, 100-mm silicon wafers substrates with Bragg mirrors were prepared at UPM facilities. They were covered with a seven-layer stack of alternated SiO_2 and Mo films acting as acoustic reflectors for longitudinal bulk acoustic wave resonators tuned at 2.5 GHz. These substrates were eventually completed at OEM facilities by depositing the piezoelectric capacitor composed of the $Al_{1-x}Sc_xN$ film under study sandwiched between two (110) highly-oriented Mo electrodes.

III. Characterization of $Al_{1-x}Sc_xN$ films

A. Composition of the films

The atomic composition of the $Al_{1-x}Sc_xN$ films grown on 200-mm Si wafers was assessed by Rutherford backscattering spectrometry (RBS). The RBS spectra were measured using $4He^+$ ions accelerated at 2 MeV impinging normally on the samples at a dose of 5 µC. The ions backscattered at 170º were measured with a solid state surface barrier detector with a solid angle of 3.9 msr and a resolution of 20 keV. The RBS spectra were fitted with the SIMNRA code to obtain the composition and thickness of the $Al_{1-x}Sc_xN$ film along the radius of the wafer. The results are shown in table I, which reveals that the Sc concentration is close to 30% with a slight increase as we move towards the edge of the wafer, in agreement with energy dispersive X-ray spectroscopy (EDX) measurements performed at University of Florida [8].

TABLE I. Composition and thickness of the $Al_{1-x}Sc_xN$ films

distance from center (cm)	% Sc	% Al	% N	thickness $10^{15}\cdot cm^2$	% Sc metallic
0-2 cm	14.3	36	49.7	5208	28.4
2-4 cm	14.5	35.8	49.7	5197	28.8
4-6 cm	14.2	35.2	50.3	5225	28.7
6-8 cm	14.8	33.5	51.6	5186	30.6
8-10 cm	15.2	34.5	50.2	5112	30.6

B. Structural analysis of the films

The AlScN films deposited on Si substrates were characterized by Fourier transform infrared absorption spectroscopy (FTIR) in the transmission mode and by X-ray diffraction measurements to explore their preferred orientation (theta-2theta measurements) and the degree of alignment of the microcrystals along the 00·2 direction (rocking curve around the wurtzite c-axis).

Fig. 1 shows the XRD patterns of two samples of $Al_{0.7}Sc_{0.3}N$ located at the center and the edge of the silicon wafer, respectively. The diffractograms are shown in logarithmic scale in order to highlight the presence of orientations others than the 00·2.

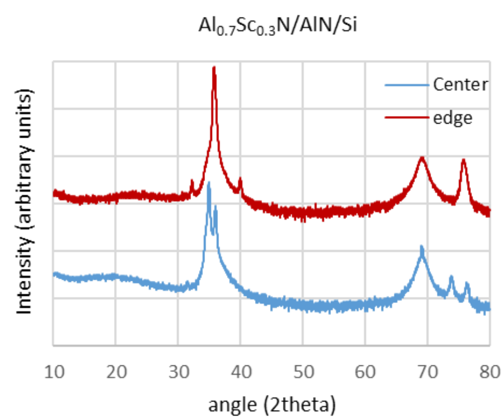

Fig. 1. XRD diffractogram of $Al_{0.7}Sc_{0.3}N$ films at the center and at the edge of a 200-mm Si wafer. Note that the signal of the sample at the edge has been displaced for clarity.

The figure shows that the films are purely c-axis oriented, since the typical 1·01, 1·02 and 1·03 reflections revealing the presence of tilted grains are not visible. The 00·2 and 00·4 reflections corresponding to the AlN film and $Al_{0.7}Sc_{0.3}N$ are clearly resolved in the film located at the center of the wafer but superimposed in the film located at the edge, due to a shift of the 00·2 $Al_{0.7}Sc_{0.3}N$ towards higher angles. This cannot be related with the tiny variations in the composition of the films, but must be associated to changes in the crystal microstructure, probably owing to inhomogeneity in the deposition process. The high degree of orientation is confirmed by the values of the FWHM of the rocking curves around the 00·2 peaks close to 1.5º.

FTIR measurements performed on the films confirm the microstructural radial deviation along the diameter of the silicon wafer. Fig. 2 shows a typical FTIR spectra of a sample and the decomposition of the main feature into the different vibrational modes.

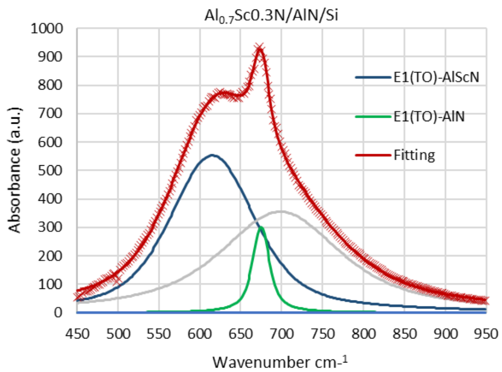

Fig. 2. FTIR spectrum of a representative $Al_{0.7}Sc_{0.3}N$/AlN/Si sample and the decomposition of the main features into E1(TO) peaks corersponding to the AlN seed layer (green) and to the AlScN layer.

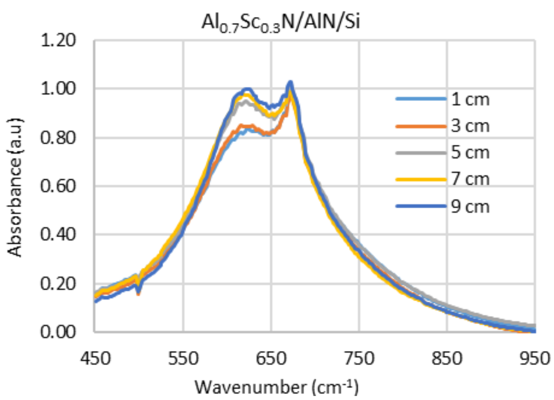

Fig. 3. FTIR spectra of five $Al_{0.7}Sc_{0.3}N$/AlN/Si samples distributed from the center to the edge of the Si wafers.

Fig. 3 shows the variation in the FTIR absorption spectra of the samples as a function of their position in the wafer relative to the center. The main absorption mode is associated to a combination of the E1(TO) vibrational modes corresponding to the well oriented AlN seed layer (at around 674 cm^{-1}) and the $Al_{0.7}Sc_{0.3}N$ layer (at around 616 cm^{-1}), the position of which remain constant regardless of the location of the sample. Previous FTIR measurements performed in 8% and 15% Sc doped films revealed that the TO modes in $Al_{1-x}Sc_xN$ films shift towards lower wavenumbers as the Sc content increases, which was confirmed by other researchers [9]. According to this, the lower mode at 616 cm^{-1} is attributed to the E1(TO) mode of the $Al_{1-x}Sc_xN$ layer, and not to the A1(TO) mode that appears typically at 612 cm^{-1} in poorly oriented AlN films. Fig. 3 also highlights that the intensity of the E1(TO) mode corresponding to the $Al_{1-x}Sc_xN$ layer increases significantly as we move toward the edge of the wafer, revealing again morphological variations in the films that cannot be attributed to thickness changes. Post-processing heat treatments induce a narrowing of all peaks, indicating a better crystal quality.

C. Frequency response measurements

Solidly mounted resonators of different size and shape were manufactured on top of the Mo top electrodes. Their S_{11} parameter was measured with a network analyzer as a function of frequency, from which the electrical impedance spectrum was derived. The fitting of the electrical impedance using Mason's model allowed deriving the longitudinal acoustic velocity, the dielectric constant and the electromechanical coupling factor (k^2) of the AlScN films. The latter is characteristic of the material and almost independent of the geometry of the resonators. We analyzed the radial homogeneity in the piezoelectric activity of 100-mm silicon substrates. Fig. 4 shows the frequency response of the best resonator achieved in the four samples located at the edge of one of the wafers displaying a k^2 of 12.8%.

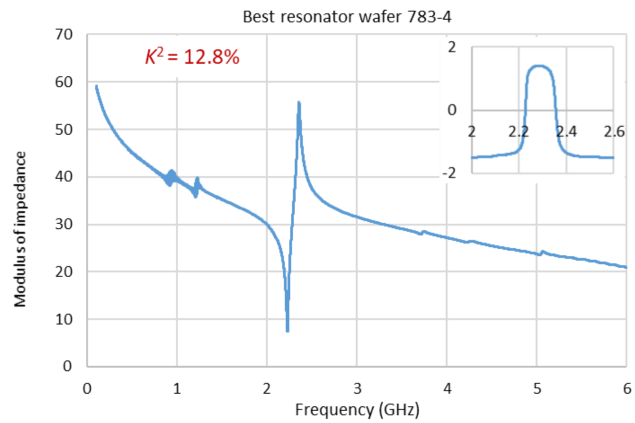

Fig. 4. Modulus of the impedance and phase of the best resonator measured at the edge of the wafer.

The analysis of the frequency response of more than 200 resonators revealed that the values of k^2 were systematically larger at the edge of the wafer than at the center. A significant variation in k^2 was observed that could not be attributed to the slight change of the radial composition, but rather to the microstructural changes revealed by XRD and FTIR measurements.

Fig. 5 shows the radial variation of k^2 in the best sample, before and after a heat treatment at 600ºC under vacuum. It is surprising that the heat treatment tends to homogenize the value of k^2, increasing it in the resonators located closer to the center of the wafer, but reducing the higher values achieved in the resonators located at the edges. This trend is observed in all the samples analyzed, and it is worth noting that the best k^2 achievable after the heat treatment is close to 11%, similar to that achieved previously in $Al_{1-x}Sc_xN$ films with 15% scandium content.

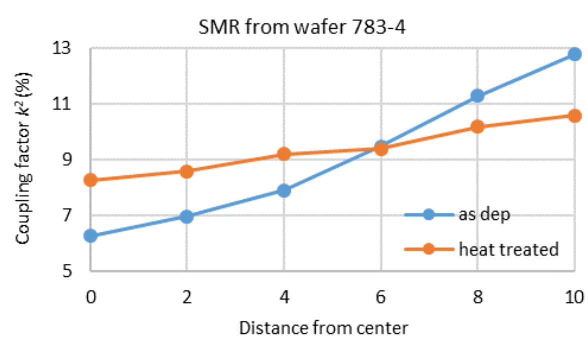

Fig. 5. Wafer radial variation of k^2 in as deposited and heat treated samples.

CONCLUSIONS

AlScN films were deposited by an original PVD system employing an ac-powered dual-cathode magnetron containing an engineered target alternating Al and Sc segments. After optimizing the sputter conditions to improve composition uniformity, films with homogeneous thickness and Sc concentration within 30 ± 0.5 at. % were deposited on 200-mm silicon substrates and on molybdenum electrodes grown on top of Bragg reflectors. The properties of the films appear to be excellent from a structural point of view as they are highly c-axis oriented, as XRD reveals. Indeed, solidly mounted resonators with k^2 up to 12.8% were measured in the areas close to the periphery of the wafers. However, despite the high degree of orientation, microstructural deviations revealed by XRD and FTIR induce inhomogeneity in their piezoelectric activity, observing variations of k^2 from 6% to 12.8% across the 200-mm wafer. Post-processing heat treatments tend to homogenize the piezoelectric activity at expenses of a reduction of the electromechanical coupling factor, which tend to saturate at a maximum value of about 11%.

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REFERENCES

[1] Azadeh Anzari, "Single crystalline scandium aluminum nitride: an emerging material for 5G acoustic filters", Proc. of the 2019 IEEE MTT-S International Wireless Symposium (IWS). DOI: 10.1109/IEEE-IWS.2019.8804148

[2] F. Bartoli, T. Aubert, M. Moutaouekkil, J. Streque, P. Pigeat, S. Hage-Ali, P. Boulet, H. M'Jahed, S. Zhgoon, O. Bou Matar, A. Talbi and O. Elmazria, "Theoretical and experimental study of ScAlN/Sapphire structure based SAW sensor" in Proc. IEEE Sensors 2017. DOI: 10.1109/ICSENS.2017.8233938

[3] M. Moreira, J. Bjurström, I. Katardjev, V. Yantchev, Aluminum scandium nitride thin-film bulk acoustic resonators for wide band applications, Vacuum. 86 (2011) 23–26. DOI::10.1016/j.vacuum.2011.03.026.

[4] M. Akiyama, K. Kano, and A. Teshigahara, "Influence of growth temperature and scandium concentration on piezoelectric response of scandium aluminum nitride alloy thin films" Appl. Phys. Lett. 95, 162107 (2009).

[5] R. Matlou, A. Artieda, C. Sandu, E. Milyutin, and P. Muralt, "Electromechanical properties of Al0.9Sc0.1N thin films evaluated at 2.5 GHz film bulk acoustic resonators", Appl. Phys. Lett. 092903 (2011).

[6] G. Wingqvist, F. Tasnádi, A. Zukauskaite, J. Birch, H. Arwin, and L.Hultman, "Increased electromechanical coupling in w−$Sc_xA_{(1-x)}N$", Appl. Phys. Lett. 112902 (2010).

[7] V. Felmetsger, M. Mikhov, M. Demiguel-Ramos, M. Clement, J. Olivares, T. Mirea, E. Iborra, Sputtered Al1-xScxN thin films with high areal uniformity for mass production, 2015 Jt. Conf. IEEE Int. Freq. Control Symp. Eur. Freq. Time Forum, FCS 2015 - Proc. 2015. 117–120. DOI: 10.1109/FCS.2015.7138803.

[8] V. Felmetsger, M. Mikhov, M.Ramezani, R. Tabrizian, "Sputter Process Optimization for $Al_{0.7}Sc_{0.3}N$ Piezoelectric Films", unpublished.

[9] P. M. Mayrhofer, C. Eisenmenger-Sittner, H. Euchner, A. Bittner, and U. Schmid, " Influence of c-axis orientation and scandium concentration on infrared active modes of magnetron sputtered $Sc_xAl_{1-x}N$ thin films, Appl. Phys. Lett. 103, 251903 (2013); doi: 10.1063/1.4850735