Effects of post-deposition vacuum annealing on the piezoelectric properties of AlScN thin films sputtered on 200 mm production wafers

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Abstract— **Sc-doped AlN polycrystalline films are attractive active layers for high frequency (GHz range) acoustic resonators owing to the significant rise in the material piezoelectric activity with the increasing Sc content. AlScN films are sputtered on 200 mm Si wafers using configurable cathode containing a variable number of embedded Sc pellets which allows controlling both the Sc content in the films and the composition homogeneity across the wafer. The method is implemented in an Endeavor-AT™ cluster tool from OEM Group adapted for sputtering on 200 mm wafers. The piezoelectric activity of the as-deposited AlScN films appears to improve after a 15-minute post-deposition annealing at 600°C, leading to a 20% increase in the electromechanical coupling factor.**

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

I. Introduction

Electronic systems for the 5G wireless communication technologies require filters and resonators with increasingly wider bandwidths and higher communication speeds. Part of the bands will be allocated below 6 GHz where electroacoustic filters based on piezoelectric thin films can still play an important role [1]. However, widening the bandwidth requires significant amount of work in the filter side in order to fulfill the demanding specifications of the 5G systems. In particular, the piezoelectric activity of the active layers needs improving to increase the electromechanical coupling factor, main responsible of bandwidth limitations in filters. To tackle the lower frequency bands, resonators based on Sc-doped AlN films are being increasingly considered owing to the significant enhancement of their piezoelectric response, which can be doubled compared to that achievable with pure AlN mature technology. Besides prospective communication systems, other applications in the field of micro-electromechanical devices will benefit from the synthesis of piezoelectric materials of high piezoelectric activity [2], especially if piezoelectric activity can be tuned for the foreseen application.

Since Akiyama first synthesized Sc-doped AlN thin films in 2009 [3], significant efforts have been devoted to the in-depth understanding of the material properties. Presently, manufacturers are seeking to develop reliable deposition processes to bring the new material to production and incorporate it into current AlN technology. Co-sputtering from two independent Al and Sc targets is a possible alternative, although homogeneity over large substrates areas is hardly achieved, which restricts co-sputtering to low scale production over small substrates. So far, reactive sputtering of alloyed Al-Sc targets is still the best choice to achieve good quality AlScN films of controlled composition. However, it is known that the fabrication of AlSc targets with high Sc contents presents some difficulties [4], being the available targets of moderate Sc contents. The possibility of varying the Sc content to modulate the piezoelectric response in films for small volume production of micro-electromechanical devices is desirable. However, the use of alloyed targets of different compositions, is not economically viable. Finally, reactively sputtered ternary films, such as AlScN, tend to grow with microscopic homogeneities and defects. Post deposition annealing of thin films can be performed to improve film properties, relieve strain, reduce surface roughness, or favor the formation of specific structural phases [5,6].

In this work we investigate the effect of post deposition annealing of sputtered AlScN films with Sc contents ranging from 7 at. % to 10 at. %. The films are deposited using a special target arrangement consisting of two concentric ac-powered aluminum targets containing a variable and easily removable number of embedded Sc pellets. The method allows obtaining films with homogeneous and controllable composition across 200 mm silicon production wafers. We investigate the effects of in-situ and external in-vacuum annealing processes in the piezoelectric activity of the AlScN films through the frequency response of bulk acoustic wave test resonators and the assessment of their electromechanical coupling factor. In addition, the structure and composition of the films are assessed by X-ray diffraction and Rutherford backscattering spectrometry.

II. Experimental

A. *Sputter deposition method*

The deposition system used in this work was an Endeavor-AT sputter tool of OEM Group LLC. The tool contains a load-lock module, a transfer module equipped with a vacuum high-speed robot, a pre-cleaning process module equipped with a planarized rf plasma source (PRF) plasma source for substrate pre-conditioning, and up to four sputter modules equipped with S-gun magnetrons.

A special characteristic of the S-Gun magnetron is its dual concentric target arrangement [7] composed of two independently controlled ring-shaped sputtering targets of 7" and 11" in diameter, as shown in figure 1. Reactive sputtering of oxides or nitrides is routinely achieved by powering the cathode with a 40 kHz ac power supply with a floating output directly connected to the inner (7") and outer (11") targets. This cathode arrangement provides stable and arcing-free operation along with the ability to control intrinsic stress in the sputtered films, regardless of other film properties, by controlling the ionic bombardment of the substrate. This S-gun has demonstrated its capability to deposit high-quality c-axis oriented AlN films (even of very low thickness) by reactive co-sputtering from two concentric Al targets without heating or biasing the substrates [8].

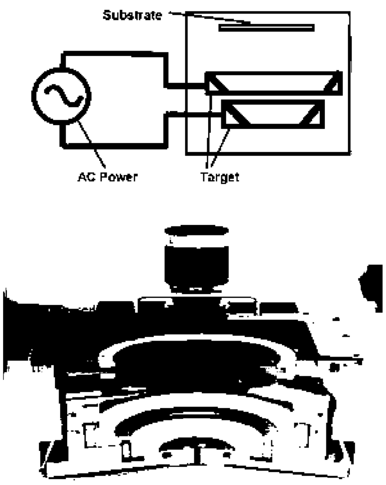

Fig. 1. The dual-target S-gun magnetron: (a) ac-powering schematic diagram and (b) process module arrangement.

Our first attempt to grow AlScN films was to take advantage of the dual-cathode S-gun arrangement by using two single-element concentric targets of Al and Sc. However, this method failed in achieving radial homogeneity in the composition of the films. A better procedure to improve composition homogeneity along the substrate consisted in embedding Sc pellets in two concentric Al targets, as shown in figure 2. The number of pellets allows setting the Sc concentration in the films to up to 14% at., although higher Sc concentration can be achieved by using denser pellet distribution. Additionally, the Sc pellets can be substituted by Al ones to reduce the Sc content to zero. Their spatial distribution within the inner and outer targets enables adjusting homogeneity in the radial composition. It is worth noting that many authors refer the Sc content as the fraction of Sc in the AlSc metallic part (x in $Al_{(1-x)}Sc_xN_1$), taking for granted that the atomic percentage of nitrogen is always 50%. We prefer specifying the concentration of Sc as the molar fraction y in the compound $Al_xSc_yN_z$, since the N concentration in the films is not necessarily 50%, as RBS measurements reveal.

Given that the structural properties of sputtered AlScN films significantly depend on the nature and conditions of the substrates, most of the samples were deposited on 200 mm silicon wafers covered with acoustic reflectors terminated with Mo top electrodes, intended for the production of solidly mounted bulk acoustic wave resonators (SMRs). The Mo layer, which acts as the bottom electrode, was ionically cleaned in the same vacuum cycle prior to the AlScN deposition.

We attempted to grow films with two different Sc concentrations. In the two cases, we placed 14 Sc pellets in the outer target. However, to vary the final concentration in the films we used either 10 or 20 pellets (out of 20) in the inner target for the two families of films, respectively. Before the deposition of the films, the substrates were etched in PRF module (capacitively-coupled Ar plasma at rf power) and then pre-heated to about 350°C in the sputter module. In addition, the wafers were intentionally heated during the first stage of the deposition process (from 50 nm to 600 nm) to improve the structure of the growing films.

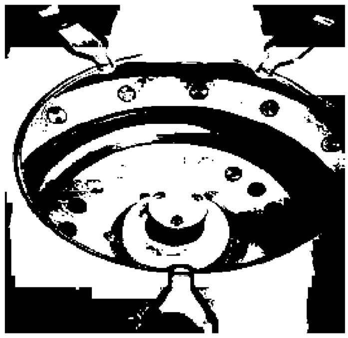

Fig. 2. S-gun magnetron housing two Al concentric targets containing the inserted Sc pellets.

After deposition, some wafers were in-situ annealed in the deposition chamber with an infrared heater (we will refer to them as "in-situ annealed samples") at a pressure below 10^{-7} Torr and an estimated temperature of around 500°C. Other wafers were cut into smaller pieces, processed to produce the BAW devices and finally annealed in vacuum (10^{-6} Torr) in a well temperature-controlled quartz tube furnace at temperatures ranging between 400°C and 800°C.

B. *Material characterization*

The 200 mm wafers were cut into 1×1 cm^2 pieces along a radius in order to analyze their homogeneity. The atomic composition of the samples was assessed by Rutherford backscattering spectrometry (RBS) using a 5 MeV tandem accelerator. The RBS spectra were measured using 4He+ ions accelerated at 2.3 MeV impinging normally on the samples at a dose of 5 μC. The ions backscattered at 170° were measured with a solid state surface barrier detector with a solid angle of 3.9 msr and a resolution of 20 keV.

The AlScN films were characterized by Fourier transform infrared absorption measurements (in the reflectance 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) [9].

Finally, to carry out the electroacoustic characterization of the films we manufactured test bulk acoustic wave (BAW) resonators over two types of acoustic reflectors; the first one composed of five alternated Al and Mo layers (providing sufficient acoustic isolation) and the second one composed of five alternated SiO_2 and Mo layers, which provided better acoustic isolation and improved high-temperature stamina. In the electrical tests, the reflection scattering parameter S_{11} was measured by 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 [10] allowed deriving the longitudinal sound 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.

III. RESULTS

A. As-deposited samples

XRD measurements revealed that all the analyzed films had a wurtzite structure and were highly c-axis oriented. The plane spacing of the AlScN films, obtained from the (00•2) diffraction angle, was around 5.00 Å ±0.005 Å, a value 5% larger than that of pure AlN. This indicates an increase in the piezoelectric activity, which we associate to the deformation of the wurtzite structure that takes place as the Al atoms are substituted by Sc atoms. Narrow peaks with full width at half maximum (FWHM) of the (00•2) reflections in the θ/2θ diffractograms of around 0.15° point out to relatively large microcrystals and suggest that the Sc atoms are uniformly distributed in the crystal network. The FWHM of the rocking curve around the (00•2) reflection in all the analyzed samples varies from 1.6° to 3°, indicating a very good crystal quality. As expected, the samples with highest Sc contents exhibited the poorer crystal quality. Some AlScN films deposited over considerably rough Al/Mo-based acoustic reflectors also displayed wider rocking curves, very likely due to the effect of the substrates.

A typical RBS spectrum is shown in figure 3, where the number of counts has been depicted in log scale in order to highlight the signals corresponding to the lees abundant elements. The fitting of the RBS spectra with the SIMNRA code [11] allowed performing the compositional analysis of the samples. This yielded an average Sc content of 7 at. %, (ranging from 6.5 at. % to 7.5 at. % from wafer to wafer) for the low concentration family of films and of 10 at. % (with lower dispersion) for the higher concentration.

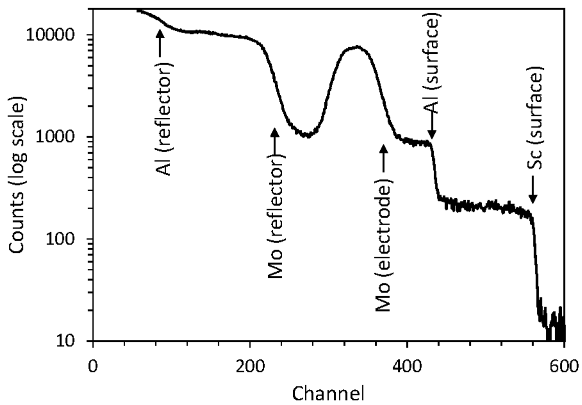

Fig. 3. RBS spectrum of a representative sample of a wafer with 6.5 at.% of Sc. The origin of the different features are marked in the graph. Al and Sc arrows point out to the signals corresponding to the surface of the AlScN film. The signal corresponding to the Mo bottom electrode is superimposed to the Al signal. The signal corresponding to the first Mo and Al layers of the reflector appears at lower backscattered energies

This corresponds to a Sc content of the metallic part of around 14% and 20% for the two types of samples, although it is worth noting that the N content in the samples departs from 50%. The homogeneity across the 200 mm diameter of the wafer was always below the 10% of the mean value, being the Sc content always slightly higher at the edges of the wafer. To avoid this, a restructuration of the Sc pellets into the targets described above should be undertaken.

The analysis of the frequency response of the BAW resonators located along a radius of the wafer revealed that the values of k^2 were larger at the edge of the wafer than in the center. This is not clearly related with the radial variation of the Sc content, nor to the variation of any other accessible parameter of the sputtering system. We attribute this variation to an inhomogeneous ionic bombardment of the surface of the wafer caused by the independent control of stress and other film parameters [7] carried out during the deposition process. Ionic bombardment may have some detrimental effects, such as the growth of misaligned grains that lower the piezoelectric response [8,9]. Regarding the sound velocity of the longitudinal mode in the AlScN films, this appeared to be slightly lower than that of AlN films, with values ranging from 9500 m/s to 10400 m/s, as estimated from the fittings of the resonator response. Similarly, the dielectric constant of the AlScN films was larger than that AlN films (85 pF/m), reaching values of 90 pF/m, depending on the composition.

B. Effects of vacuum annealing on samples

After the external annealing process, most of the resonators implemented on the less efficient Al/Mo-based reflectors suffered from a dramatic decrease in their quality factors (down to 10 in some cases), owing to a significant increase in the roughness of the Al layers, which made it impossible to obtain reliable values of the coupling factor k^2 of the AlScN films. Therefore, most of the annealing studies were carried out on samples grown on SiO2/Mo-based acoustic reflectors.

XRD measurements revealed that "in-situ" thermally annealed samples did not experience significant structural changes as compared with those without thermal treatment. Likewise, externally annealed samples did not show any variation in the crystal structure. This implies that the annealing processes did not produce recrystallization or structural rearrangement of the microcrystals. However, some differences were found in the infrared reflectance spectra, indicating a microscopic restructuration of the Sc atoms [12] that could account for the observed variations in the piezoelectric behavior.

In-situ annealing always resulted in an improvement of the piezoelectric activity, even though the samples initially exhibited different piezoelectric activity, owing to a variation in the growth procedure. For example, after an in-situ annealing at 500°C for 15 min the k^2 of Sc 7 at. % samples deposited on Mo electrodes in the same vacuum cycle increased from 6.5% to 8.5 %, whereas in films of similar composition grown on Mo electrodes exposed to air k^2 rose from 7% to 8.5%. Figure 4 shows the effect of the in-situ annealing in the radial distribution of k^2 in a typical 7 at. % Sc sample.

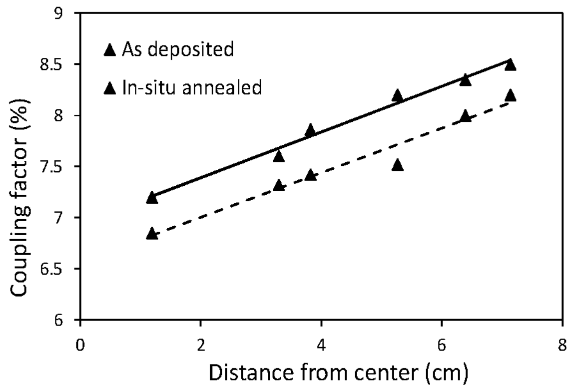

Fig. 4. In wafer radial variation of k^2 of two samples with 7 at. % of Sc, as-deposited and after an in-situ annealing as described in the text.

Post-deposition annealing in vacuum leaded to similar results. Heat treatments at temperatures ranging from 400ºC to 800ºC for times from 5 min to 60 min were investigated. The greater improvements in the piezoelectric response were achieved after annealing at temperatures between 500ºC and 600ºC for 15 min to 30 min.

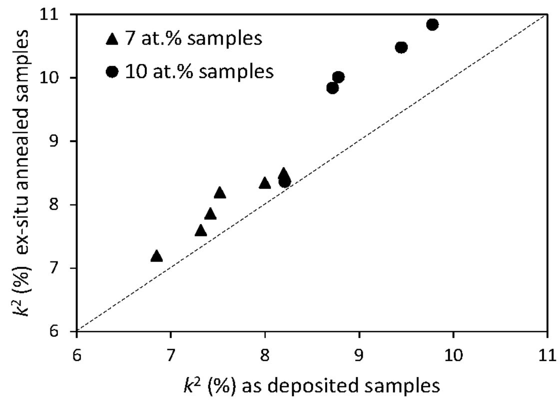

Fig. 5. Graph comparing the values of k^2 of particular devices before and after external annealing processes. Samples with 7 at. % and 10 at. % are shown.

These results show that post-deposition annealing enables achieving remarkably higher k^2 values than those reported for AlScN films of similar compositions [13,14] as well as those predicted from ab-initio calculations [15].

CONCLUSIONS

AlScN films were deposited by an original PVD employing an ac-powered dual-cathode magnetron containing pure Al targets with a variable number of pure Sc pellets embedded in the Al matrix. The number and distribution of pellets in the cathodes allowed controlling the film Sc content and the composition uniformity in 200 mm production wafers. As an example, 7 at. % Sc films were deposited under different deposition conditions, yielding reasonably good uniform distribution of Sc in each wafer (within 10% of variation) and a slight variation from 6 at. % to 7.5 at. % of Sc from wafer to wafer. Properties of the films are excellent under a structural point of view and can be further improved by making more uniform the ionic bombardment in order to reduce the slight radial variations in their piezoelectric response. Post-deposition wafer annealing in vacuum for 15-30 min at temperatures of 500-600ºC enables remarkably increasing electromechanical coupling in low-doped AlScN films (up to 20% compared to as-deposited films).

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