SAND99-0994J

Effect of substrate composition on the piezoelectric response of reactively sputtered AlN thin films

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Abstract

Deposition parameters were found to have a marked effect on piezoelectric response of reactive radio frequency (RF) sputtered AlN thin films. We observed piezoelectric response values ranging from -3.5 to + 4.2 pm/V for 1 μm thick AlN films deposited onto Ti//Ru electrode stacks. An investigation of the effects of deposition parameters, in particular the nature of the Ru//AlN interface, was conducted. The lag time between deposition of adjacent thin film layers appeared to have the greatest affect on the value of the piezoelectric response. This suggests that chemical reaction occurring on the Ru thin film surface is responsible for changing an important thin film property such as dipole orientation within the overlying AlN thin film.

Introduction

AlN is an excellent material for use in flexural plate and surface acoustic wave

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devices for a variety of reasons. First it offers good piezoelectric response, with a piezoelectric coefficient of 5.4 pm/V, coupling coefficient of 0.1 and Q factor of 5,000 at 10 MHz. AlN also offers excellent flexural strength (5,000 kg/cm^3), high electrical resistivity ($10^{11} - 10^{14}$ Ω cm), low thermal expansion (4.5 ppm/°C) and low toxicity. The use of AlN thin films in SAW devices is well-established [1-8]. In addition, the effects of sputter deposition parameters on the crystalline and microstructural properties of the AlN thin film and the resultant piezoelectric response also have been reported [4-11]. To our knowledge, this work represents the first investigation into the effect of the electrode//AlN interface on the dipole orientation and resultant value and sign of the piezoelectric response.

We observed that many of our preliminary sputtered AlN samples exhibited near-zero piezoelectric responses, while some exhibited positive values and others exhibited negative values. A change in magnitude might be indicative of a difference in crystalline orientation, grain size, or concentration of defects. However, a change in sign of piezoelectric response indicates not a change in film quality, but a complete reversal of some property. The likely property in the case of the AlN thin films is the net dipole orientation. A change in the net dipole orientation could explain a number of phenomena that we observed in our early experiments including that piezoelectric response (1) could exhibit a positive, negative, or zero value, (2) could vary markedly for AlN thin films exhibiting the same crystallographic orientation per x-ray diffraction results, and (3) could be strongly dependent on conditions at the thin film interfaces and subsequently subtle differences in the thin film deposition process. Ishii et al. have reported on the sign of the piezoelectric response as a function of crystalline orientation within single crystals of AlN [12].

Experiment

Several multilayered samples were sputter deposited and tested in order to determine the effect of presputter target conditioning on the resultant piezoelectric response. Silicon wafers with a 400 nm thick thermal oxide layer were used as substrates. Each substrate was sputter coated with 30 nm Ti, 100 nm Ru, and then 1 or 2 micron thick films of AlN that served as the adhesion, electrode, and piezoelectric layers, respectively. All depositions were performed in a Unifilm PVD-300 Multisource Sputter Deposition Chamber (base pressure = 2×10^{-7} torr) using the deposition parameters listed in Table I.

The length of time between deposition of two sequential films was varied in order to determine the effect of contamination on the newly deposited underlying film on the properties of the overlying film. In addition, the length of time between presputtering a target and depositing a thin film from it was varied in order to determine the effect of target contamination on the properties of the film. Presputtering the targets prior to deposition is routinely performed in order to remove surface contaminants and atmospheric reaction products. Presputter/deposition sequences for the constituent thin films in several samples are shown in Table II. For Samples 1-5, the sequence was presputter Ti/deposit Ti/presputter Ru/deposit Ru/presputter AlN/deposit AlN (denoted $P_{Ti}/D_{Ti}/P_{Ru}/D_{Ru}/P_{AlN}/D_{AlN}$). This led to a lag time between deposition of any two adjacent thin film layers, allowing the underlying film to react with residual gases in the chamber. Sample 6 was identical, except the sequence was presputter Ti/presputter Ru/presputter AlN/deposit Ti/deposit Ru/deposit AlN (denoted $P_{Ti}/P_{Ru}/P_{AlN}/D_{Ti}/D_{Ru}/D_{AlN}$). This led to a lag time between presputtering (cleaning) the targets and using them for the actual deposition. It is possible for the targets to react with residual gases in the chamber to form oxide and/or nitride compounds on the target surface

during that time. As a result, the first few monolayers of the subsequently deposited thin films may consist of a compound instead of the pure target material. Finally, Sample 7 was identical except additional target power supplies were used to enable presputtering of all three targets immediately prior to their depositions with no lag time between deposition of adjacent thin films (denoted $D_{Ti}/D_{Ru}/D_{AlN}$). This deposition technique was used to promote compositionally pure and sharp interfaces between thin film layers and resulted in the largest negative piezoelectric response value.

The resultant samples were characterized using a variety of techniques. Piezoelectric response was measured by sectioning the samples into cantilever beams of known area and measuring deflection as a function of applied voltage at 100 Hz. Crystallographic phase, orientation and average diameter perpendicular to the plane of the substrate were determined using standard θ-2θ x-ray diffraction (XRD) on a Siemens D-500 XRD. Thin film topography was imaged using a Digital Instruments Nanoscope II Atomic Force Microscope. Compositional depth profiling was also performed on samples using a Cameca Secondary Ion Mass Spectroscopy (SIMS) system in order to determine the composition of the thin films as a function of depth. Two samples were fabricated specifically for SIMS analysis using the parameters shown in Table III. The total time between Ru and AlN depositions was varied in order to determine the effect of the lag time on the interface composition and ultimately the piezoelectric response.

In order to determine the relative dipole orientation within the AlN thin films, etch rate experiments also were performed. Previous researchers [13] have performed etching experiments on LiNbO3 crystals and determined that etch rate was highly dependent upon dipole orientation. Because piezoelectric response in dependent upon dipole orientation in a

material such as AlN, we used a similar approach to assess the dipole orientation in our samples. Sections of the AlN//Ru//Ti//SiO2//Si wafer samples were etched for times ranging from 5 to 120 minutes in a 50% nitric acid solution held at 80° C. The etched samples then were blown dry using N_2 and imaged using atomic force microscopy. The Nanoscope II contains software that calculates the root mean square (rms) surface roughness of a sample. This roughness value, combined with the detailed topological map of the sample surface, is extremely useful in determining how the surface evolves as it is etched away and the likely role of the dipole orientation. An additional sample of Ti//Ru was deposited in order to verify that the nitric acid etch had no effect on the Ru surface or underlying Ti film. In addition, a single film of AlN was deposited directly onto an oxidized silicon wafer in order to measure the etch rate as a function of time. That the AlN was deposited onto a substrate (oxidized Si) other than that used for the samples (Ru) may have affected its crystalline and dipole orientation and consequently the resultant etch rate. Nevertheless, the measurements yielded an effective AlN etch rate that corresponded to the time required to reach the underlying insoluble Ru layer as indicated by no further change in the AFM image or calculated rms surface roughness.

Results and Discussion

The piezoelectric response for each of the Ti//Ru//AlN samples is shown in Table II and is graphed in Figure 1 as a function of lag time between deposition of the Ru and AlN thin film layers. For samples in which there was a relatively long lag time ($\geq$ 0.5 hours), the piezoelectric response tended to positive values (e.g. Samples 1, 2 and 3). Given our typical base pressure of 2×10^{-7} torr, a monolayer of residual gas contaminants is deposited on a pristine surface every five seconds. Exposure of the pristine Ru thin film surface to residual

gases in the vacuum chamber likely resulted in oxidation of the Ru surface. Although the resultant RuO_2 layer was probably limited to the first several monolayers of the surface, it appears to have been sufficiently thick to affect crystalline and dipole orientation of the subsequently deposited AlN. For samples in which there was a minimal lag time (< 20 minutes) between deposition of the Ru and AlN thin film layers, the piezoelectric response tended to negative values (Samples 4 - 7). This suggests that the composition of the Ru surface affects the dipole orientation of the subsequently deposited AlN thin film which determines the sign of the piezoelectric response.

Compositional depth profiling using SIMS was performed on Samples 8 and 9 (lag times between Ru and AlN depositions = 18 and 0.05 hours respectively) in order to determine the composition of the thin films as a function of depth. In Figure 2, Sample 8 exhibits a high oxygen-to-aluminum concentration ratio at the Ru//AlN interface (sputter time $\approx$ 1,200 seconds), suggesting the presence of an RuO_2 layer at that interface. Crystalline and dipole orientations of subsequently deposited thin film layers can be dramatically affected by this change in composition at the interface as a result of the substrate (Ru)/thin film atomic interactions. Subsequent deposition of the AlN on the oxidized Ru surface resulted in preferential dipole orientation of the AlN in the positive sense. Figure 2 shows a high oxygen-to-aluminum concentration ratio (sputter time $\approx$ 1,800 seconds) for both Samples 8 and 9 that corresponds to the thermal oxide layer on the silicon substrate.

The dependence of piezoelectric response on the composition of the Ru surface can be explained in terms of sputtering kinetics and chemical bonding between the thin film materials. During the reactive sputter deposition of the AlN thin film, the plasma contains Al^{+3} and N^{-3} ions. The sticking coefficient of these ions to the Ru thin film is dependent

upon their relative charges. A pristine Ru surface which is exposed to residual oxygen gas will develop an RuO_2 "skin" with oxygen atoms at the outermost surface. When this surface is bombarded with Al^{+3} and N^{-3} ions during the sputtering process, the Al^{+3} ions will preferentially bond to the O^{-2} ions at the surface. Therefore, the first monolayer of atoms is likely to consist almost entirely of Al. Nitrogen is highly reactive with Al and so the second monolayer of atoms is likely to consist mostly of nitrogen atoms. In this way, the thin film is deposited, effectively one atomic monolayer at a time, such that the dipoles of the resultant AlN molecules are all oriented in the same direction (away from the RuO_2 surface). This is apparently a very effective orientation technique as the piezoelectric response (4.2 pm/V) for an AlN film deposited in this manner (Sample 1) approaches the bulk value (5.4 pm/V). On the other hand, a pristine Ru surface will preferentially bond with the N^{-3} ions in the plasma, resulting in a first monolayer consisting mostly of nitrogen. The second monolayer will consist of Al^{+3} and so on. The dipole orientations of the resultant AlN molecules will be reversed compared to those for the oxidized Ru surface. The negative piezoelectric response values for samples with a pristine Ru//AlN interface support this explanation. In addition, the fact that the largest negative piezoelectric response value (3.5 pm/V) that we achieved is substantially lower than the bulk value (5.4 pm/V) suggests that there may be some mixing of dipole orientations. A small amount of oxygen contamination at the Ru//AlN interface could account for this mixture of orientations. In addition, progressive contamination at the interface would explain the gradual shift from negative to positive values of the piezoelectric response as the lag time between Ru and AlN depositions was increased as shown in Figure 1.

Etch rate experiments were conducted in conjunction with these samples in order to determine the dipole orientation as a function of deposition conditions. Previous researchers have reported the ability to determine the dipole orientation within crystalline $LiNbO_3$ by the relative etch rates of the opposite surfaces [13]. Due to the different bonding conditions for the opposite dipole orientations, one dipole configuration exhibits a higher etch rate than the other. We observed a similar behavior in reactively sputtered AlN thin films as shown in Figure 3. A highly oriented, crystalline AlN sample shows a relatively rough surface (rms surface roughness = 5.85 nm) as-deposited when imaged using atomic force microscopy as shown in Figure 3a. The surface of the sample becomes progressively smoother when it is etched for 5 and 10 minutes (rms = 4.15 nm and 1.18 nm, as shown in Figures 3b and 3c respectively), but then becomes rougher when etched for 15 minutes (rms = 2.93 nm) as shown in Figure 3d. A possible explanation for this is that one of the two dipole orientations has a relatively faster growth and etch rate than the other. Its faster growth rate results in an uneven, rough surface as shown schematically for the as-deposited sample in Figure 3a. As the sample is etched, the relatively tall peaks are preferentially etched away until the sample is very smooth, as shown in Figures 3b and 3c. With continued preferential etching of those grains, their surfaces subside below those of the surrounding, more chemically resistant grains. As a result, the surface begins to roughen again, as shown in Figure 3d.

Ultimately, as the AlN film is etched away completely, the rms roughness of the sample approaches that of the as-deposited underlying Ru thin film (2.2 nm). Etching experiments performed on a Ti//Ru stack showed that the overall appearance and roughness of the electrode stack did not change appreciably for etch times of up to 180 minutes. This indicates that the changes in the appearance of Ti//Ru//AlN samples with etching can be

attributed to etching of the AlN film only. In addition, a single thin film of AlN deposited on a silicon substrate was determined to have an average etch rate of 32 nm/min. That means that a 1 micron thick AlN thin film should be completely etched away in approximately 31 minutes. The AFM images for typical AlN samples showed little change for etch times beyond 40-50 minutes, suggesting that the AlN thin film had been etched away by that time and the chemically resistant Ru electrode layer was exposed at the surface. That the AlN thin film etches unevenly as shown in Figure 3 suggests preferential etching of a particular crystallographic or dipole orientation. X-ray diffraction of these samples showed strong preferential orientation of the AlN (0002) hexagonal net of atoms parallel to the plane of the substrate. Given the highly oriented crystallographic nature of this sample, it is likely that the increased roughness resulted from preferential etching of one of the two dipole orientations commensurate with that crystallographic orientation.

Conclusions

The piezoelectric effect of AlN thin films deposited using reactive RF sputtering was found to have a strong dependence upon the composition of the underlying electrode (Ru) layer. Deposition of AlN onto a pristine Ru surface resulted in a piezoelectric response in the negative sense while deposition onto a heavily oxidized Ru surface resulted in a piezoelectric response in the positive sense. Deposition of AlN onto a partially oxidized Ru surface (exposed to residual chamber gases for approximately 20 minutes) resulted in very low piezoelectric responses (~ 0 pm/V). Given that the AlN crystallites were oriented in the (0002) direction with respect to the substrates, the near-zero piezoelectric response in these films suggests a nearly equal mixture of the two dipole orientations. Therefore, it may be

possible to optimize piezoelectric response (magnitude and sign) of AlN thin films by controlling the composition of the interface.

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Figure Captions

Figure 1 Piezoelectric response as a function of lag time between deposition of Ru and AlN thin films.

Figure 2 SIMS data for two Ti//Ru//AlN samples showing regions of high oxygen-to-aluminum concentration ratios for samples with and without a break between Ru and AlN depositions.

Figure 3 AFM images of Sample 4 a) as deposited and for etch times of b) 5 minutes, c) 10 minutes and d) 15 minutes.

	Ti	Ru	AlN
Thickness (nm)	30	100	1,000 or 2,000
Substrate temperature (°C)	300	300	500
Ar pressure (mTorr)	2.5	2.5	2
N2 pressure (mTorr)	0	0	0.2 – 0.5
Power	53 W DC	23 W DC	147 W RF
Deposition rate (nm/min)	7.9	5.9	7.9

Table I Deposition parameters for Ti//Ru//AlN thin film samples.

Sample	Sample	Presputter/Deposition sequence	Total time between Ru and AlN dep. (hours)	AlN thickness (μm)	Piezoelectric response (pm/V)
1	24e	$P_{Ti}/D_{Ti}/P_{Ru}/D_{Ru}/P_{AlN}/D_{AlN}$	2.2	1	4.2
2	24f	$P_{Ti}/D_{Ti}/P_{Ru}/D_{Ru}/P_{AlN}/D_{AlN}$	1.0	1	2.35
3	61A	$P_{Ti}/D_{Ti}/P_{Ru}/D_{Ru}/P_{AlN}/D_{AlN}$	0.3	1	0.5
4	24c	$P_{Ti}/D_{Ti}/P_{Ru}/D_{Ru}/P_{AlN}/D_{AlN}$	0.2	1	-1.29
5	24d	$P_{Ti}/D_{Ti}/P_{Ru}/D_{Ru}/P_{AlN}/D_{AlN}$	0.2	1	-1.92
6	62a	$P_{Ti}/P_{Ru}/P_{AlN}/D_{Ti}/D_{Ru}/D_{AlN}$ *	0*	1	-2.5
7	60a	$D_{Ti}/D_{Ru}/D_{AlN}$ †	0	1	-3.5

Table II Presputter/deposition sequence, lag times between Ru and AlN depositions, and piezoelectric responses for AlN//Ru//Ti thin film stacks on oxidized Si. * All targets were presputtered prior to deposition of Ti layer resulting in lag time between presputtering and deposition of all 3 materials.

† No lag time between presputter and deposition of thin films.

Sample	Sample	Presputter/deposition sequence	Total time between Ru and AlN dep. (hours)	Piezoelectric response (pm/V)	AlN thickness (μm)
8	ALN24	$P_{Ti}/D_{Ti}/P_{Ru}/D_{Ru}/P_{AlN}/D_{AlN}$	18	3.3	2
9	ALN26	$P_{Ti}/D_{Ti}/P_{Ru}/D_{Ru}/P_{AlN}/D_{AlN}$	0.05	0.1	2

Table III Total time between Ru and AlN depositions and piezoelectric response for Ti//Ru//AlN samples for SIMS analysis.

Figure 1

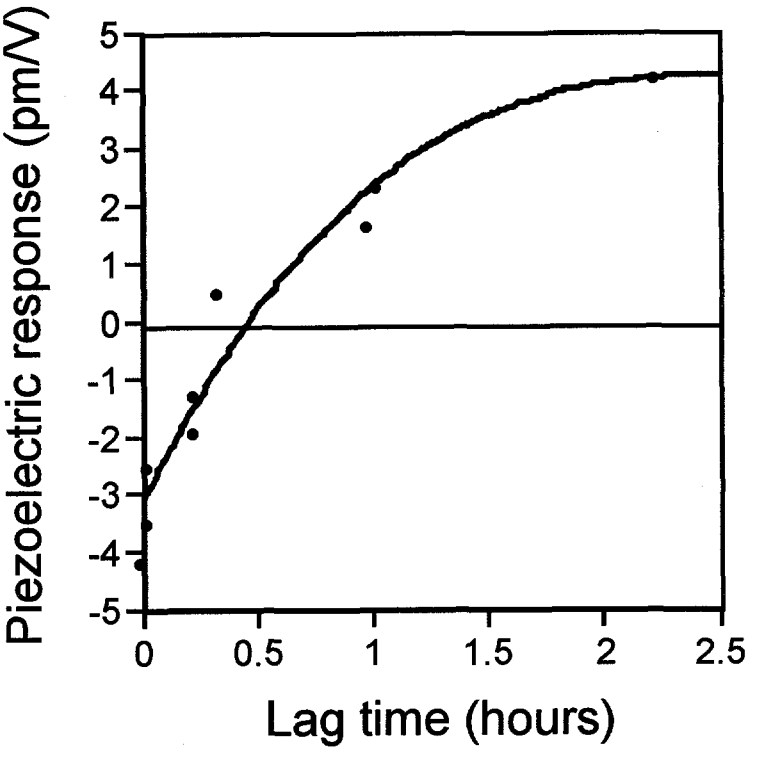

Piezoelectric response (pm/V)
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
0.5
1
1.5
2
2.5
Lag time (hours)

Figure 2

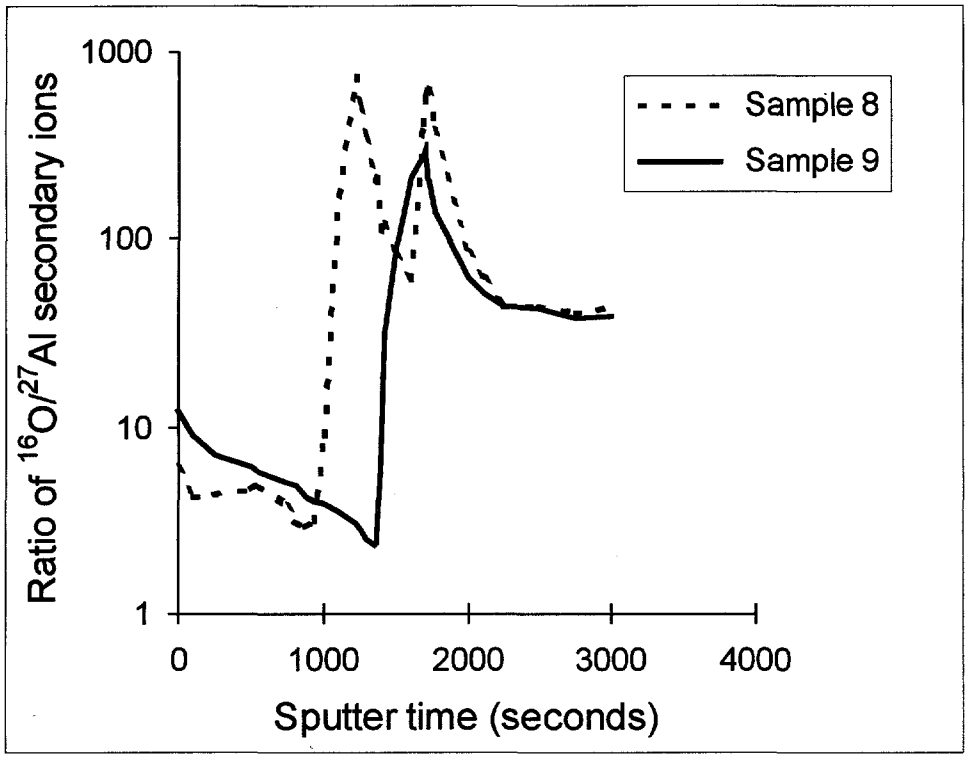
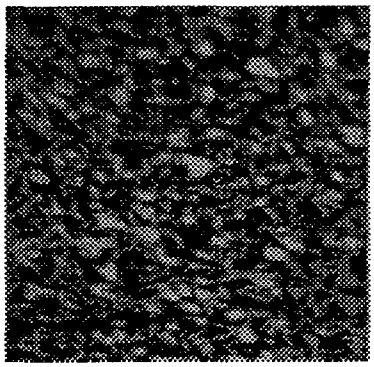
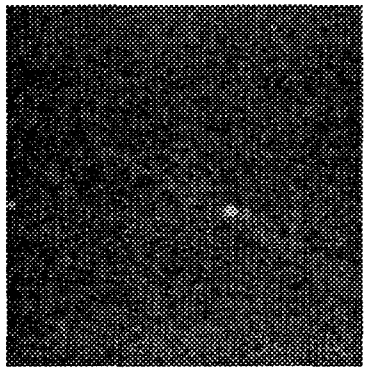

1000
100
10
1
Ratio of $^{16}O/^{27}Al$ secondary ions
0
1000
2000
3000
4000
Sputter time (seconds)
Sample 8
Sample 9

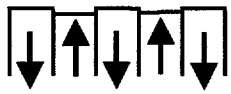
Figure 3

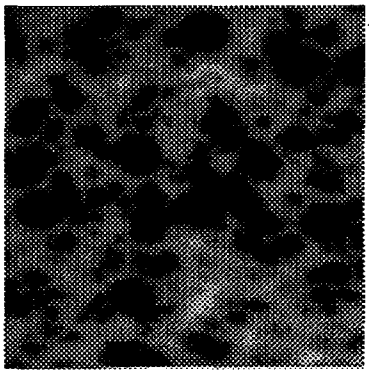


a) as deposited
rms = 5.85 nm

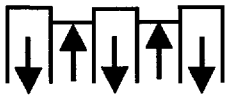


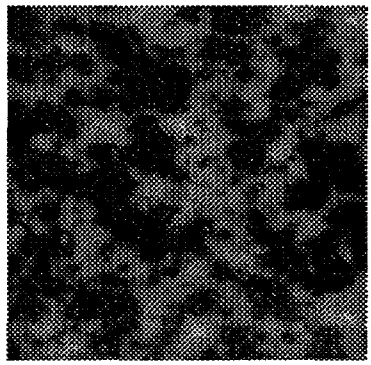
c) 10 minute etch
rms = 1.18 nm





b) 5 minute etch
rms = 4.15 nm





d) 15 minute etch
rms = 2.93 nm