

Silver Precipitation in Energy Scavenging Aluminum Nitride Resonators

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ABSTRACT

Structural and compositional modifications of hexagonal AlN grown on silicon substrates implanted with 100 keV Ag²⁺ ions at room temperature and annealed under different conditions are investigated. Compositional analysis was performed by XRD and structural analysis by RBS and cross-sectional TEM, aided by TRIM and TRIDYN modeling. The peak Ag concentration occurred at ~ 65nm below the implantation surface, with some Ag nanoprecipitates detected in the as-implanted samples. Annealing caused variations in composition due to Ag diffusion into the surrounding AlN and coarsening of the precipitate distribution. As annealing temperature increased from 500 to 1050°C, the concentration of Ag in the projected range of the implantation zone decreased by a factor of two. TEM images revealed 50-70 nanometers sized Ag particles in the AlN matrix that recrystallized during annealing.

Keywords: ion implantation, ceramics, aluminum nitride, MEMS, interface

1 INTRODUCTION

Energy scavenging, one of the most attractive sources of green energy, can be achieved through conversion of mechanical force to electrical current with piezoelectrics [1]. However, despite more than a decade of experience in manufacturing of nanoelectromechanical systems (NEMS) incorporating piezoelectric elements, modern devices are still plagued by delamination at the electrode/ piezoelectric interface [2]. Consequently the electric field essential to generate and sustain the piezoelectric response of such devices is lost, resulting in device failure.

Ion implantation, a technological tool commonly employed during semiconductor device manufacturing, introduces dopants but also causes damaged-induced structural changes. It causes modified surface, electrical and mechanical properties of such piezoelectric materials [3-5]. Earlier work has shown that implantation of heavy ions into piezoelectrics reduces damage to the crystal structure

and circumvents amorphization [6], [7]. Previous work in our group has also demonstrated the formation of heavy metal nanoprecipitates in ceramic materials at high implantation doses [8]. The goal of this investigation is to explore the use of heavy ion implantation to develop a buried conducting layer in aluminum nitride that might be employed during device applications.

We have designed our experiments to exceed the local solid solubility of Ag in the AlN host matrix, forcing the precipitation of Ag with highest concentration at the projected range of the implanted metallic ions, in an attempt to generate a continuous sub-surface conducting layer. We seek to understand the phase transformation behavior during Ag precipitation with the intent to ultimately control the electrical operation of AlN piezoelectric resonators in energy scavenging and other potential applications.

2 METHODOLOGY

Multiple source reactive ion sputtering was employed to deposit $\approx 1.8 \mu\text{m}$ of AlN on a $525 \mu\text{m}$ thick Si substrate. Samples were then implanted with 100 keV ¹⁰⁸Ag²⁺ ions at room temperature over the dose range 1×10^{16} ions/cm² to 2.68×10^{16} ions/cm² using a 200 keV Metal Vapor Vacuum Arc (MEEVA) implanter. All substrates were implanted at an angle 7° normal to the substrate to prevent channeling.

Samples were subsequently thermal annealed under different experimental conditions: 550°C for 8 hours, 800°C for 5 hours and 1050°C for 3 hours. The different annealing conditions were selected based on the material with the lowest melting temperature (T_m) and conditions necessary to promote re-crystallization of AlN and allow morphological equilibration of Ag precipitates in experimentally accessible times.

Silver concentration with respect to depth was simulated using Transport of Ions in Matter (TRIM) and TRIDYN and confirmed by Rutherford Backscattering Spectrometry (RBS). RBS was conducted using a 3 MeV alpha particle beam generated by a 5SDH Pelletron tandem accelerator (National Electrostatics Corporation (NEC)) with a terminal voltage of 1.7MV. The Silicon surface barrier

detector was positioned at 168° with respect to the incident beam. Measurements were carried out on untreated samples to evaluate any structural modifications as a result of thermal annealing. X-ray Diffraction (XRD) was employed using a Siemens D5000 X-ray Diffractometer to obtain crystalline structure information. Cross-sectional transmission electron microscopy samples were then prepared and analyzed using a JEOL 2011 with a lanthanum hexaboride filament operated at 200 keV. Structural information was obtained via imaging and selected area diffraction (SAD).

3 RESULTS

Figure 1 shows the simulated and experimental data for Ag implantation in aluminum nitride conducted at 100 keV. The experimental data represents Ag implanted AlN with no post-treatment

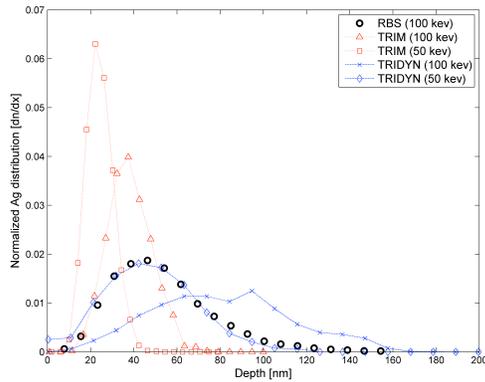


Figure 1. Computer simulation models (TRIM and TRIDYN) and experimental data comparison for Ag implanted in AlN. Peak concentration attained

annealing process. As seen in most of the literature, TRIM is the preferred method for computer simulation [6], [9], [10]. Here we evaluate the reliability of models to predict the behavior of high-energy implantation in a multi-component system. Figure 2 illustrates the Ag concentration profile after different annealing conditions. It is apparent that the silver concentration decreases by half as the temperature increases from 500 to 800°C. At 1050°C, there is a slight increase in the Ag concentration, which could be attributed to chemical modifications in the structure as a result of an accelerated oxidation rate at temperatures exceeding 1000°C [11,12].

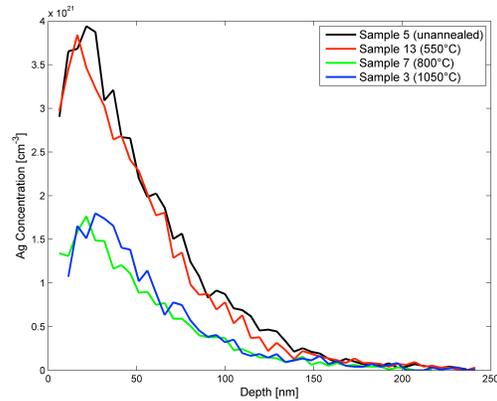


Figure 2. RBS data for unannealed and annealed samples at temperature ranges from 550°C and 1050°C. The Ag concentration decreases with increasing temperature.

Figure 3 represents the x-ray diffraction pattern for unannealed and annealed samples. Our results are consistent with previously reported data for AlN (36°), Ag (62°) and Si (69°) peak positions. Additional peaks are visible at 2θ values of 22° and 77° but with low intensities.

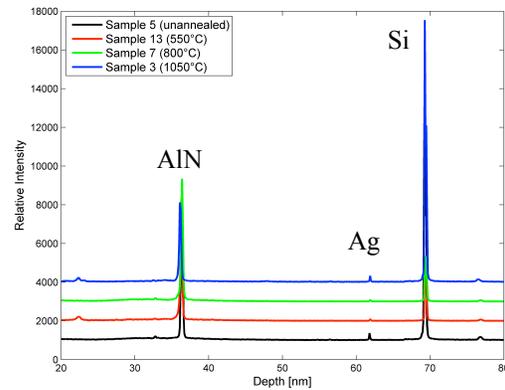


Figure 3. XRD data for unannealed and annealed samples.

Figure 4 shows cross-sectional TEM images of unannealed and annealed samples at 550°C. It is seen in Figure 4 that an amorphous layer develops as a result of ion implantation but a columnar morphology is revealed in the annealed sample. The average columnar grain diameters were determined to be approximately 50 nanometers. This observation

supports the fact that thermal annealing can relieve induced damage as a result of ion implantation.

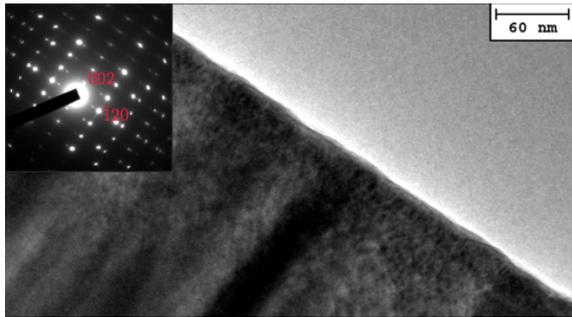


Figure 4. Transmission electron micrograph of AlN columnar grain morphology after Ag ion implantation and a post-annealing treatment at 550°C. Inset diffraction pattern confirms high crystalline quality and dominant [210] zone axis orientation of the columnar grains.

Figure 5 represents a Ag nanoprecipitate and defects developed during ion implantation. The average Ag nanoparticle size is confirmed to be 70 nanometers. Precipitate size increases at higher annealing temperatures consistent with higher growth rates and coarsening. These observations explain the RBS results in Figure 4, showing a decreased matrix concentration of Ag because of the coarser precipitate distribution.

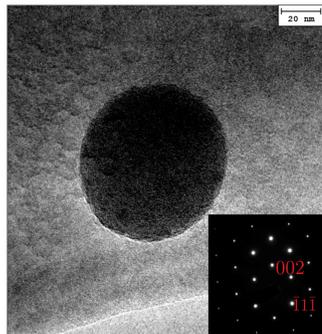


Figure 5. Nanoparticle of Ag near the sample surface. Diffraction pattern (inset) confirms FCC crystal structure with a dominant zone axis orientation of [110].

4 DISCUSSION

Results presented in this work confirm that simulation models provide a reasonable estimate of the depth profile of heavy metal ion implantation in a multi-component system. In Figure 1, we show that at 100 keV the maximum peak position obtained using

TRIM, ~ 46 nanometers, matches the RBS data with a concentration twice that of the experimental values. The concentration profile calculated using TRIDYN deviates significantly from the experimental data, shifted by +25nm with respect to the peak position in RBS and reduced in concentration by approximately one-third of the experimental value. This deviation is attributed to the proportion of beam energies corresponding to single-charged, double-charge and triple-charged ions.

The data in Figure 2 confirms that the Ag concentration is dependent on annealing conditions, decreasing at higher temperature. This decrease can be caused by one of several factors: (1) the evaporation of Ag into the furnace, (2) the coalescence of Ag precipitates to form larger particle sizes, and (3) chemical reaction with other constituents to form a compound structure. Additional data (not shown here) confirmed that there were no compounds formed at 500°C but a thin oxide formed at 800°C. This oxide increased in size for samples annealed at 1050°C due to the accelerated oxidation rate observed at temperatures above 1000°C. It is therefore concluded that the decrease in Ag concentration in the matrix is a result of nanoparticle coalescence.

In Figures 3-5, imaging and diffraction analyses confirm a columnar morphology of AlN in its post-annealed state and the formation of Ag nanoprecipitates. The electron microscopy images shown above reveal that the sputtered AlN film grew epitaxially, and recrystallized to its original morphology during annealing. During ion implantation, Ag nanoprecipitates were generated and they subsequently coarsened during annealing.

Figure 5 shows Ag nanoprecipitates near the surface in the AlN matrix post-annealing (550°C). The diffraction pattern (inset) confirms an FCC crystal structure with a dominant zone axis orientation of [110]. The average nanoprecipitate size is approximately 70 nanometers. Nanoprecipitates in the surrounding region are similar in size, with the highest concentration found near the surface. In addition to nanoprecipitate formation and coarsening, there was also evidence of defect formation (not shown).

5 CONCLUSIONS

In conclusion, the formation of silver nanoprecipitates in an aluminum nitride matrix and its depth profile has been studied via RBS, XRD and TEM. The main results of this work are:

- (a) Thermal annealing treatments alter the profile of Ag nanoprecipitates induced by Ag²⁺ ion implantation of AlN.
- (b) At temperatures higher than 550°C, these nanoprecipitates coarsen, coalesce and exhibit

the potential to form a sub-surface conducting layer.

- (c) Thermal annealing at temperatures above 1000°C accelerates oxidation, retarding the coalescence process and limiting control of Ag nanoprecipitate morphology.

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