Deposition of High Thermal Conductivity AlN Heat Spreader Films

Scott T. Ueda, Aaron McLeod, Michelle Chen*, Chris Perez*, Eric Pop*, Dan Alvarez**, Andrew C. Kummel

University of California, San Diego, USA
* Stanford University, USA
**RASIRC, USA
E-mail: sueda@eng.ucsd.edu

Abstract

The low-temperature (<400 °C) deposition of polycrystalline AlN films is demonstrated by atomic layer annealing using either trimethyl aluminum (TMA) and anhydrous hydrazine (N_2H_4) or tris(dimethylamido) aluminum (TDMAA) and anhydrous N_2H_4 with an argon plasma treatment where the ion energy is precisely controlled. High-quality AlN films are deposited with large grain size and low oxygen/carbon contamination and can be used as a templating layer for further high speed AlN film growth.

I. Introduction

As transistor size continues to decrease, it becomes a significant challenge to remove the heat generated during the operation of microelectronic circuits. The use of conductive heat spreaders complicates 3D integration in VLSI CMOS or stack memory devices and induces parasitic losses in RF MMICs. Crystalline AlN has a thermal conductivity close to that of Cu and is a good insulator and, therefore, an ideal heat spreader material.

Using trimethyl aluminum (TMA) and the highly reactive nitrogen-containing precursor hydrazine (N_2H_4), aluminum nitride can be deposited at 200 °C [1]; however, these films are amorphous and would have low thermal conductivity due to phonon scattering. Using tris(dimethylamido) aluminum (TDMAA) or tris(diethylamido) aluminum (TDEAA) in conjunction with N_2H_4 or NH_3 at temperatures $\geq$350 °C, polycrystalline films can be deposited via a purely thermal process; however, the reported grain sizes are small (<5 nm) or there is a mixture of polycrystalline and amorphous phases [2-3]. Atomic layer annealing (ALA) is an ALD process in which a pulse of ions is employed in each cycle to enhance crystallinity. ALA has been used to deposit crystalline films such as AlN [4-5] and GaN [6] at low temperature, but the ion energy was not controlled, a nitrogen-containing plasma was used, and the thermal transport of the films was not characterized.

In this work, the deposition of high quality, stress controlled AlN films deposited by ALA are successfully used as templates for thicker heat spreading layers deposited via high speed sputtering and polycrystalline sputtered AlN films with near-record thermal conductivities of ~70 $Wm^{-1}K^{-1}$ were obtained for sub-0.5 micron thick films.

II. Results

Adapting optimized TDMAA and N_2H_4 thermal ALD conditions to atomic layer annealing experiments produces films with similar purity, but enhanced crystallinity. Representative XPS data, shown in **Figure 1a**, demonstrates low oxygen and carbon contamination, of 2% and 3% respectively. GI-XRD data, shown in **Figure 1b**, reveals preferential (200) grain orientation, with small amounts of (002) and (220) orientations also present.

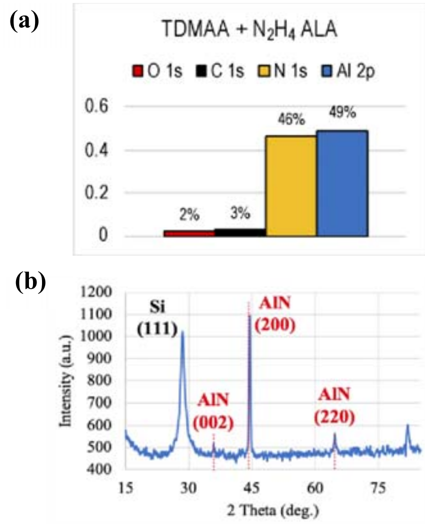

Figure 1. XPS elemental composition and GI-XRD crystallographic information for 250 cycles of TDMAA + N_2H_4 ALA at 400 °C. (a) Using a 150 ms pulse of TDMAA, a 100 ms pulse of N_2H_4 with 4s and 8s purges and a 20s Ar plasma treatment using a bias voltage of -25V at 400 °C, a 48 nm thick sample with very low oxygen and carbon is deposited. **(b)** GI-XRD data for a 48 nm thick film grown using TDMAA and N_2H_4 ALA, with preferential (200) grain orientation, with a FWHM of 0.36° corresponding to a grain size of 25 nm.

TMA and N_2H_4 were used in an ALA experiment to grow a 33 nm thick film. Composition information for this sample is shown in **Figure 2a**, also demonstrating low oxygen and carbon contamination. The diffraction data, shown in **Figure 2b**, demonstrates preferential (002) grain orientation with a 17 nm crystallite size.

Films grown by reactive sputtering of Al with low pressure (~2.8 mTorr) 100% nitrogen plasma contain very little oxygen and demonstrate preferential (002) and (220) grain orientations, such as the 290 nm film shown in **Figure 3**. A 25 nm layer of amorphous AlN serves as a strain relief layer, as films sputtered with pure N_2 contain large amounts of compressive strain. Diffraction data, **Figure 3b**, reveals (002)

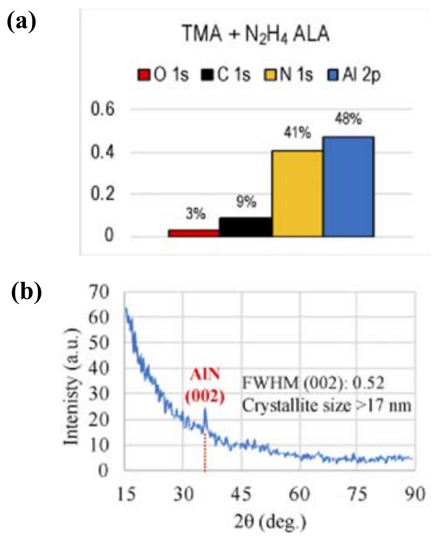

Figure 2. XPS elemental composition and GI-XRD crystallographic information for 250 cycles of TMA + N_2H_4 ALA at 225 ºC. (a) XPS elemental composition for 250 cycles of TMA + N_2H_4 ALA at 225 ºC. Using a 400 ms pulse of TMA, a 100 ms pulse of N_2H_4, 15s pump times, and a 20s Ar plasma treatment with a bias voltage of -25V at 225 ºC, a 33 nm thick sample with low oxygen (3 at. %) is deposited. **(b)** GI-XRD data for a 33 nm thick film grown using TMA and N_2H_4 ALA. Preferential grain orientation of (002), with 0.52° peak FWHM corresponds to ~17 nm grains.

and (220) texture, with corresponding crystallite sizes of 6 nm and 8 nm, respectively. This film was measured to have a thermal conductivity of 70 W m^{-1} K^{-1} by time domain thermoreflectance (TDTR), which is a record for films sub-0.5 micron thick.

A 24 nm thick template was grown using TDMAA and N_2H_4 ALA, with conditions similar to those described previously. Composition information for the template layer is shown in **Figure 4a**. Following this deposition, 290 nm of crystalline AlN were sputtered in-situ. Diffraction data shown in **Figure 4b** demonstrates the ability of the technique to retain the large crystallite size of the ALA template (~20-25 nm) throughout the sputtered material and have a crystalline interface to the substrate which is advantageous for thermal conduction.

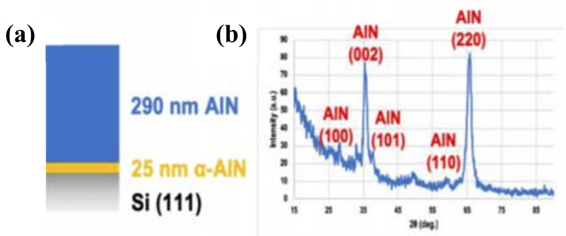

Figure 3. Characterization of in situ sputtered buffer layers (a) Schematic diagram and **(b)** corresponding X-ray diffractogram for sputtered crystalline films with a 25 nm amorphous buffer layer. Film is primarily (002)/(220) textured with a 1.1°/1.7° FWHM (crystallite sizes ~6-8 nm).

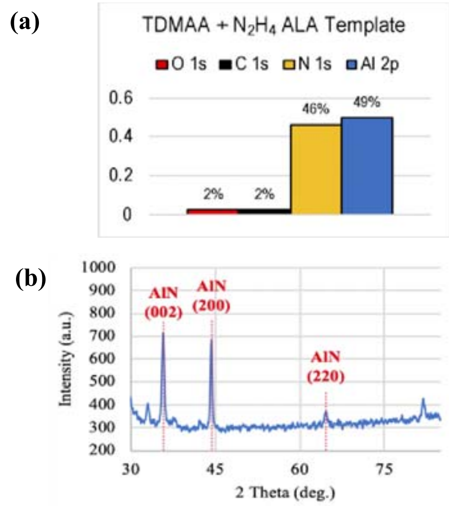

Figure 4. Composition information by XPS and crystallographic information by GI-XRD for a film structure with 25 nm ALA template created using TDMAA and N_2H_4 ALA followed by 290 nm of polycrystalline sputtered AlN. (a) XPS elemental composition for a 24 nm thick TDMAA + N_2H_4 ALA template grown at 400 ºC using a 150 ms pulse of TDMAA, a 100 ms pulse of N_2H_4, 4s and 8s purges, and a 20s Ar plasma treatment at -25 V bias. **(b)** GI-XRD data for a sample grown using 24 nm thick TDMAA and N_2H_4 ALA template followed by 290 nm of sputtered AlN. Preferential (002) and (200) grain orientations with 0.45° and 0.35° peak FWHM, corresponding to 20 nm and 25 nm grain sizes.

III. Conclusion

The ALA of AlN using TMA or TDMAA and N_2H_4 demonstrate the growth of high-quality, crystalline films with large grain size and the ability to template further high speed polycrystalline AlN growth via sputtering. By minimizing the oxygen content, the high deposition rate sputtered layers of 200-300 nm demonstrate thermal conductivities of ~70 $Wm^{-1}K^{-1}$ and it is expected that further optimization in combination with the ALA and increase in crystalline layer thickness will yield results in excess of 100 $Wm^{-1}K^{-1}$.

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