Title: Effect of NH_3 flow on electrical and mechanical properties of ALD TiN thin films

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Abstract

As the generations of memory devices evolve, the successful fabrication of high aspect ratio features becomes more and more challenging. Apart from the traditional patterning and etch-related issues, the conformal film deposition onto these structures becomes a critical parameter in determining the overall device yields. It is now well established that ALD [1, 2] offers a pathway to highest conformality and step-coverage, compared to the conventional deposition techniques such as CVD [3] and PVD [4]. In recent nano-scale device applications, especially in DRAM capacitor electrodes, ALD TiN films have been used due to the excellent physical and electrical properties. However, it is necessary to improve mechanical properties such as hardness and modulus, especially under 30 nm film thickness, because ALD TiN films can be easily bent and/or broken during the following integration steps. From the perspective of the intrinsic ALD TiN film property improvement, many studies have been conducted on the ALD TiN thin-film physical and electrical properties [5], however, there are not many reports focused on mechanical properties such as hardness and modulus. In this paper, we report on the strong relationship between ALD TiN thin-film mechanical and electrical properties and NH_3 flow rate, especially on thinner films from 25 nm to 150 nm.

Four TiN samples of approximately 26 nm thickness were fabricated by varying the NH_3 flow from 500 to 4,000 sccm at a constant 140 sccm $TiCl_4$ flow for a $NH_3/TiCl_4$ flow ratio of 3.5 to 28.5. GIXRD confirmed that the TiN films were poly-crystalline, as shown in Fig. 1a. Increasing the NH_3 flow enhanced the TiN(111) peak intensity and significantly reduced the TiN(200) peak intensity, however the TiN(220) peak did not change. The maximum peak intensity ratio of TiN(111)/TiN(200) increased from 0.4 to 1.4. This means that the TiN preferred crystal orientation was changed from TiN(200) to TiN(111) by increasing the NH_3 flow. TEM and nano-beam diffraction (NBD) method were used to confirm the TiN crystal grain size and orientation using the TiN sample grown with NH_3 4,000 sccm flow. Columnar TiN crystal growth with average grain size 8.2 nm and poly-crystalline electron diffraction pattern are shown in Fig. 1b and c, respectively.

Resistivity values decreased approximately 20% by increasing the NH_3 flow from 500 to 4,000 sccm, even though the TiN growth rate decreased at the same time, as shown in Fig. 2a. This indicates that the volume of TiN film grown with higher NH_3 flow rate decreased by enhancing TiN(111) crystal orientation and reducing the Cl impurity (Not shown here). To check the TiN hardness and modulus, three 150 nm films, at 500, 2,000 and 4,000 sccm NH_3 flow, were measured by nanoindentation. The TiN hardness and modulus increased 75% and 40% by increasing NH_3 from 500 to 4,000 sccm, respectively, as shown in Fig. 2b. It indicates that the close-packed TiN(111) crystal structure can improve the mechanical properties of ALD TiN thin-film. Therefore, it was confirmed that higher NH_3 flows make improvement on the TiN electrical and mechanical properties in this study.

Reference

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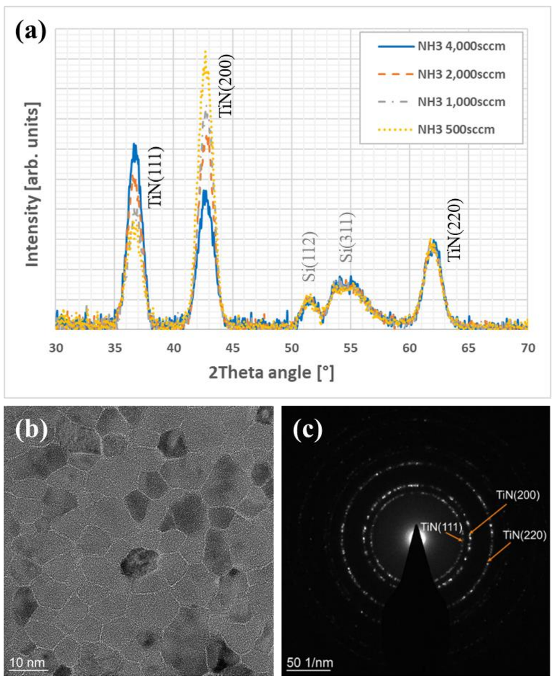

Fig. 1. Analysis of TiN samples grown using NH_3 flow rates from 500 to 4,000sccm: (a) GIXRD profiles, (b) TEM plan-view image and (c) NBD pattern.

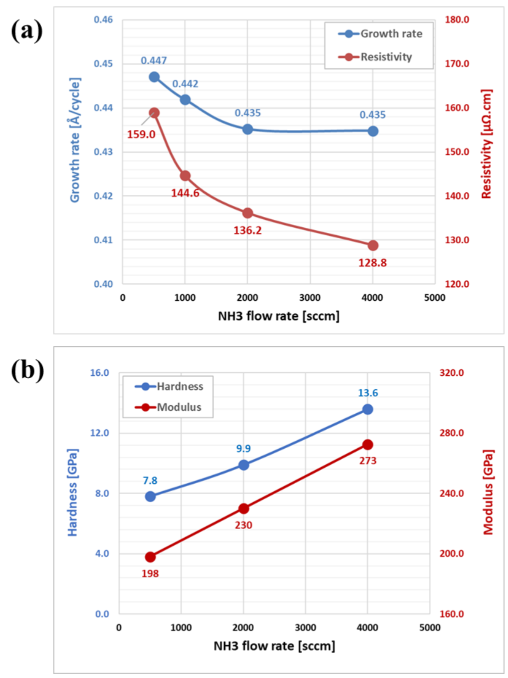

Fig. 2. (a) TiN resistivity/growth rate and (b) TiN hardness/modulus by changing NH_3 flow