ALD Growth of High Quality Nitrides

Introduction

It has often been noted that while the growth of oxides remains quite accessible via ALD, the growth of high quality nitrides has sometimes been elusive. Nevertheless, the metal nitrides represent an important class of materials that are relevant for a wide range of semiconductor, superconductor, photonic, and tribological applications. In this newsletter we will examine some of the important factors that influence the quality of nitrides. Specifically, we will feature the work done on the growth of TiN by staff at Tower Semiconductor in collaboration with Technion- Israel Institute of Technology. The work demonstrates how excellent nitrides can be produced using the plasma enhanced ALD capabilities of the Fiji ALD system.

Factors Affecting TiN Growth

Recently an excellent series of studies on the growth of nitrides has been conducted and published by Krylov and Korchnoy[1,2]. The experiments provides excellent insight into ways in which low resistivity ALD nitrides can be deposited by systematically examining various factors that affect the film quality

Experimental Details:
The key experiment involves the growth of TiN on a range of substrate materials. Si substrates with a 100nm of thermal oxide were coated with the following interface layer materials via PEALD - Al2O3, TiO2, Ta2O5, MoO3, WO3 (in the case of the oxides,O2 plasma was used as the co-reactant). Following the interface layer growth, the samples were simultaneously coated with 30nm of TiN – grown using tetrakis dimethylamido titanium (TDMAT), and three different plasma compositions – NH3, N2-H2, and N2. The plasma source was a quartz tube inductively coupled remote plasma (ICP) (13.5MHz). Plasma power was 300W. The process temperature for the films was 300˚C.

TiN Resistivity as a function of Substrate Material and Plasma Type:
The results clearly indicate that the TiN resistivity is affected by the substrate material, as well as the co-reactant composition.

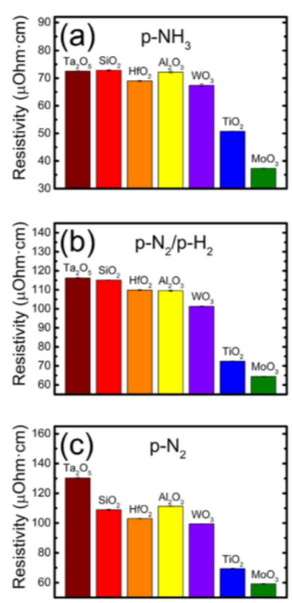

FIG. 1. Resistivity of 30 nm thick TiN films deposited on various ~10 nm thick interfacial layers using (a) NH_3, (b) N_2/H_2, and (c) N_2 plasma gases.

While the TiN resistivity for most of the interface materials is similar, in all cases the TiN grown on TiO2 and MoO3 surfaces show a marked reduction in resistivity compared to the other oxide interfaces, and this is further enhanced by using an NH3 plasma, where one sees resistivities on the order of 40$\mu\Omega$-cm. The authors also used XPS in the study to measure Oxygen and Carbon content in the TiN and noted that they were < 2% and <1% respectively.

Electron Mean Free Path and Resistivity:
In large part, the reduction in resistivity of TiN grown on TiO2, and MoO3 compared to TiN grown on SiO2 can be attributed to the relationship between the electron mean free path (λ) of TiN compared to other relevant length scales, such as the film thickness (t_F), and the thickness of the interface layer (t_{IL}). To test these dependencies Krylov and Korchnoy compared the growth of TiN on SiO2, and TiN on TiO2 and MoO3 by varying the thickness of the TiN as well as the interface layers (TiO2, and MoO3).
What they observed were the following three effects:

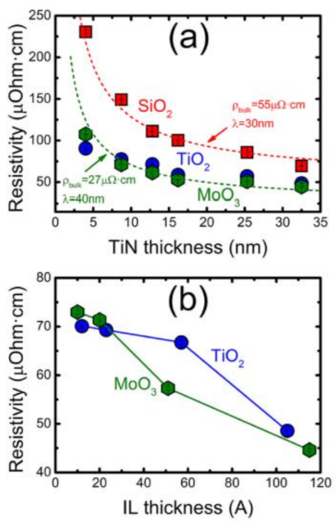

FIG. 2. (a) Resistivity of TiN films with various thicknesses simultaneously deposited on SiO_2 (100 nm)/Si substrates with or without either TiO_2 (10 nm) or MoO_3 (11 nm) interfacial layer. The experimental data fitting using the Fuchs–Sondheimer model is also presented (dashed lines). (b) Resistivity of 33 nm thick TiN films simultaneously deposited on TiO_2/SiO_2 (100 nm)/Si and MoO_3/SiO_2/Si substrates with various interfacial layer thicknesses.

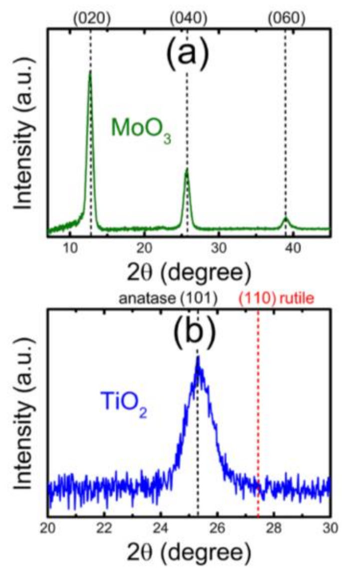

FIG. 3. Glancing angle XRD spectra measured for (a) MoO_3 (11 nm)/SiO_2/Si and (b) TiO_2 (10 nm)/SiO_2/Si samples.

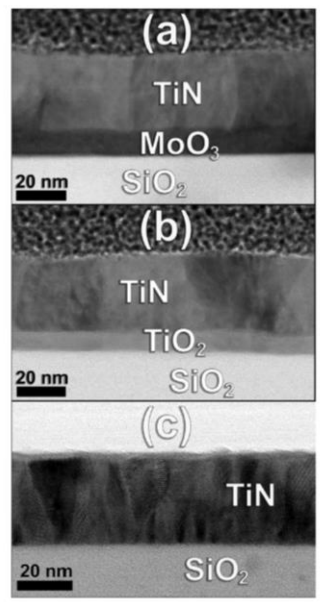

FIG. 4. Bright-field STEM micrographs acquired for (a) TiN(30 nm)/MoO_3(11 nm)/SiO_2/Si, (b) TiN(30 nm)/TiO_2(10 nm)/SiO_2/Si, and (c) TiN (30 nm)/SiO_2/Si samples.

1. They noted (Figure 2a), that when the TiN thickness is equal to or less than the electron mean free path (λ), the resistivity increased as a result of increased scattering at the surfaces – a phenomena observed also by Chawla and co-workers[3]. The data in Figure 2a was fitted using the Fuchs-Sondheim model, which output theoretical values of the resistivity (55$\mu\Omega$-cm) and λ (30nm) for the TiN grown on SiO2, and a resistivity of 27$\mu\Omega$-cm) and λ (40nm) for the TiN grown on MoO3. Furthermore, they saw that when the interface layer (TiO2,MoO3) thickness was varied for a fixed TiN thickness (33nm), the resistivity of the TiN could also be altered (Figure 2b).

2. By performing XRD measurements they noted that all of the interface layers and the SiO2 layer on which the TiN was grown were amorphous - with the exception of the TiO2, and MoO3 interfaces, which were crystalline (Figure 3). The crystalline interface layers in turn act as a template for large TiN grain growth. Therefore, when the interface layer thickness is reduced the crystallinity also decreases, resulting in smaller grain sizes leading to increased resistivity in the TiN as seen in Figure 2

3. Finally, Bright Field STEM was employed to determine whether TiN grain sizes were bigger or smaller when grown on crystalline surfaces or amorphous surfaces. Figure 4, clearly shows that when TiN is grown on crystalline surfaces, large square grains are observed, compared to small V-shaped grains when TiN is grown on amorphous material such as SiO2. Again, when grain sizes are small compared to the electron mean free path, the resistivity will increase compared to large size grain growth (compared to λ) which results in lower grain boundary densities, lower levels of electron scattering and lower resistivity.

The Role of Substrate Crystallinity on TiN Resistivity:
Having determined that the substrate crystallinity affects the TiN resistivity, the final experiment carried out by Krylov and Korchnoy was to examine the growth of TiN on single crystal substrates. They deposited TiN films on substrates having hexagonal symmetry [sapphire (0001)], and cubic symmetry [SrTiO3 (001) and MgO (001))]. As before, the properties of the TiN films grown on single crystalline substrates were compared to those of films deposited on a 100 nm thick amorphous SiO2 layer. A 57nm TiN film were deposited simultaneously on all substrates.
The experiment yielded the following:

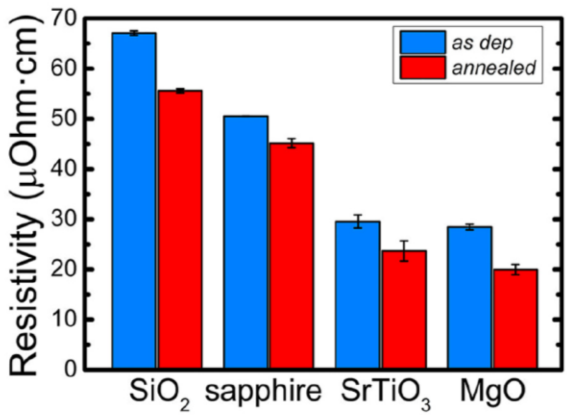

FIG. 5 Resistivity of TiN films (57 nm) grown on various substrates: sapphire (0001), $SrTiO_3$ (001), MgO (001), and SiO_2/Si before and after postdeposition annealing (650 °C/vacuum/1 h).

Figure 5 shows that the resistivity of TiN films deposited on the single crystalline substrates is less than that of the films deposited on the amorphous SiO2 layer. Compared to the TiN films grown on single crystalline structures, the films grown on amorphous SiO2 had a significantly smaller grain size, as shown in Fig. 4(c). The oxygen contamination estimated by XPS depth profiling grown on single crystalline substrates was observed to be <1%. Among the TiN films on single crystalline substrates, the lowest film resistivity of 20–30 μΩ cm was obtained for TiN films grown on cubic symmetry substrates, namely, on SrTiO3 and MgO. <u>The resistivity of the TiN films grown on these substrates is comparable to the resistivity of bulk TiN (13 μΩ cm)[3], and appears to be the lowest value reported for ALD TiN films</u>. TiN grown on single crystal substrates also exhibits resistivity which is lower than that of TiN films grown on the polycrystalline substrates (e.g., MoO3), indicating larger lateral grain size.

<u>Quality of Nitrides and Plasma Sources</u>
While PEALD oxides are relatively common, a question that sometimes arises when users are interested in growing nitrides is whether the use of high power (kW sources) plasma sources, or more exotic sources such as microwave ECR, or Hollow Cathodes would be preferable in producing high quality nitrides. This best is answered by examining the extensive studies by Krylov and Korchnoy which have shown that high quality nitrides can be grown using PEALD. Furthermore, as evidenced by the near-bulk value of the PEALD TiN resistivity of 20μΩ-cm - excellent film quality with low O2 levels can be achieved using a quartz tube ICP source at modest power levels, obviating the need for complex and expensive plasma hardware.

References

1. Krylov et al., *Effect of the substrate on structure and properties of titanium nitride films grown by plasma enhanced atomic layer deposition*, J. Vac. Sci. Technol. A 37(6), Nov/Dec 2019, https://doi.org/10.1116/1.5109717

2. Krylov et al., *Electrical and structural properties of conductive nitride films grown by plasma enhanced atomic layer deposition with significant ion bombardment effect.* J. Appl. Phys. **128**, 065301 (2020); https://doi.org/10.1063/5.0015961

3. Chawla et al., Effective electron mean free path in TiN, J. Appl. Phys. **113**, 063704 (2013); http://dx.doi.org/10.1063/1.4790136