Growth and Properties of Subnanometer Thin Titanium Nitride Films

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This research brings new insights into the relation between properties of ultra-thin conductive metal nitrides made by atomic layer deposition (ALD) and their possible industrial applications. The advantage of conductive nitrides over pure metals is (i) better established ALD processes allowing depositing high-quality films and (ii) the presence of nitrogen as an extra tool to manipulate the electron transport properties. In this work, we study titanium nitride (TiN) films with the aim to investigate the growth mechanism in combination with physical and electrical properties as a function of the layer thickness. In microelectronic devices, thin continuous TiN films are commonly used as diffusion barriers and metal gate material. Scaling electronic devices to nanometer dimensions requires a close look at electrical material properties as ultra-thin conductive materials encounter an insulating regime due to the depletion of carriers.

Real-time growth of ALD TiN on thermal SiO_2. We used in-situ spectroscopic ellipsometry (SE) to observe the real-time growth of ALD TiN at 350 ^oC, at low process pressures of $2\text{-}3\times10^{-2}$ mbar and employed atomic force microscopy (AFM) and electrical test structures to characterize the films. The entire growth was divided into 3 stages: (i) 2D growth of a continuous wetting layer; (ii) 2D-3D transition at a thickness of about 0.69 nm followed by the formation and coalescence of 3D islands; (iii) constant-rate ALD growth. The results remarkably indicated that TiN films down to sub-nanometer in thickness on SiO_2 were continuous.

Resistivity and Temperature Coefficient of Resistance (TCR). We determined resistivity of TiN films down to 0.65 nm by both SE and electrical test structures. The results showed that for films thicker than 4 nm, the resistivity decreased slowly and flattened out with increasing film thickness. Below 4 nm, the resistivity increased steeply with decreasing thickness. Regarding the TCR, for films thicker than 2.5 nm, the electrical resistance increased linearly with temperature. At a thickness of about 2.5 nm, the resistance was nearly temperature-independent. Below 2.5 nm, the resistance decreased linearly with increasing temperature exhibiting a negative TCR. We ascribed this effect to the metal-semimetal transition occurring at about 2.5 nm of thickness. This was further confirmed by the results on the electric field effect.

Electric field effect. The field effect was observed in both metallic (i.e. TiN thicker than 2.5 nm) and semi-metallic (i.e. TiN thinner than 2.2 nm) states. In the metallic state, the effect was small (i.e. 0.069 % for a 2.5 nm TiN film). In the semi-metallic state, a large field effect was observed. It increased drastically with decreasing film thickness and reached a value up to 11% for a 0.65-nm-thick TiN.

Concluding, the experimental results indicated the remarkable changes of TiN electrical properties in the thickness range between 2 and 3 nm, attributed to the metal-semimetal transition at about 2.5 nm of the thickness. Accordingly, the conduction in the TiN films thinner than 2.5 nm could be contributed by both electrons and holes.

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