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Metal-Semiconductor Transition in Ultra-Thin Titanium Oxynitride Films Deposited by ALD

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Abstract : Titanium nitride (TiN) films have been widely used in variety of fields, due to its unique electrical, chemical, physical and mechanical properties, including low electrical resistivity, chemical stability, and high thermal conductivity. In microelectronic devices, thin continuous TiN films are commonly used as diffusion barrier and metal gate material. However, as the film thickness decreases below a few nanometers, electrical properties of the film alter considerably. In this study, the physical and electrical characteristics of 1.5nm to 22nm thin films deposited by Plasma-Enhanced Atomic Layer Deposition (PE-ALD) using Tetrakis(dimethylamino)titanium(IV), (TDMAT) chemistry and Ar/N2 plasma on 80nm SiO2 capped in-situ by 2nm Al2O3 are investigated. ALD technique allows uniformly-thick films at monolayer level in a highly controlled manner. The chemistry incorporates low level of oxygen into the TiN films forming titanium oxynitride (TiON). Thickness of the films is characterized by Transmission Electron Microscopy (TEM) which confirms the uniformity of the films. Surface morphology of the films is investigated by Atomic Force Microscopy (AFM) indicating sub-nanometer surface roughness. Hall measurements are performed to determine the parameters such as carrier mobility, type and concentration, as well as resistivity. The >5nm-thick films exhibit metallic behavior; however, we have observed that thin film resistivity is modulated significantly by film thickness such that there are more than 5 orders of magnitude increment in the sheet resistance at room temperature when comparing 5nm and 1.5nm films. Scattering effects at interfaces and grain boundaries could play a role in thickness-dependent resistivity in addition to quantum confinement effect that could occur at ultra-thin films: based on our measurements the carrier concentration is decreased from 1.5E22 1/cm3 to 5.5E17 1/cm3, while the mobility is increased from < 0.1 cm2/V.s to ~4 cm2/V.s for the 5nm and 1.5nm films, respectively. Also, measurements at different temperatures indicate that the resistivity is relatively constant for the 5nm film, while for the 1.5nm film more than 2 orders of magnitude reduction has been observed over the range of 220K to 400K. The activation energy of the 2.5nm and 1.5nm films is 30meV and 125meV, respectively, indicating that the TiON ultra-thin films are exhibiting semiconducting behaviour attributing this effect to a metal-semiconductor transition. By the same token, the contact is no longer Ohmic for the thinnest film (i.e., 1.5nm-thick film); hence, a modified lift-off process was developed to selectively deposit thicker films allowing us to perform electrical measurements with low contact resistance on the raised contact regions. Our atomic scale simulations based on molecular dynamic-generated amorphous TiON structures with low oxygen content confirm our experimental observations indicating highly n-type thin films.

Keywords : activation energy, ALD, metal-semiconductor transition, resistivity, titanium oxynitride, ultra-thin film
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