Low temperature plasma-enhanced ALD of Vanadium Nitride as copper diffusion barrier

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Transition metal nitrides are well known for their superior characteristics such as high temperature stability, hardness, corrosion resistance and metallic resistivity. In microelectronics TiN and TaN_x have been extensively investigated for their use as diffusion barriers for copper interconnects. In the same group of materials vanadium nitride (VN) is less studied, but during the last decade several publications highlighted some potential applications, such as VN nanocrystalline supercapacitors and diffusion barriers.

In this work, vanadium nitride layers were grown by plasma-enhanced ALD using Tetrakis(EthylMethylAmino)Vanadium (TEMAV) as metal-organic precursor and NH_3 plasma as reactant in the low temperature range from 150°C down to 70°C. A saturated and linear growth regime was achieved, resulting in a growth rate of 0.7Å per ALD cycle at 150°C (fig. 1). X-ray photoelectron spectroscopy (XPS, fig. 2) confirmed the stoichiometric VN composition (50% V and 48% N), with only a minor oxygen impurity fraction (<3%). Moreover, x-ray diffraction (XRD) indicated that the as deposited films were crystalline with a structure closely related to δ-VN (fcc). At optimized conditions the resistivity was as low as 200µΩcm for films thicker than 20nm, while for a 3nm thick film the resistivity only increased to 320µΩcm (fig. 3). Post-ALD annealing to 820°C lead to further reduction of the resistivity, from 200µΩcm to approximately 145µΩcm in N_2 ambient and 95µΩcm in a mixture of H_2 and N_2. Decreasing the deposition temperature lead to a reduced growth rate and a slightly higher resistivity.

At 70°C deposition on polymer foil (PET) resulted in a semi-transparent conductive coating, proving the ability to use this process for depositions on flexible and temperature-sensitive substrates. In addition, the effectiveness of a PE-ALD VN layer as a copper diffusion barrier was tested. Whereas Cu reacts with Si at temperatures near 230°C, a 5nm VN layer in between the Cu and HF cleaned Si substrate prevented Cu diffusion into the Si up to a temperature of 720°C, as monitored by in-situ x-ray diffraction (fig. 4).

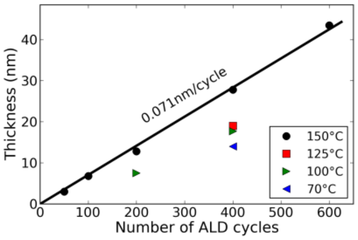

Figure 1: Linearity of the PE-ALD process at 150°C. Depositions at lower temperatures are also indicated.

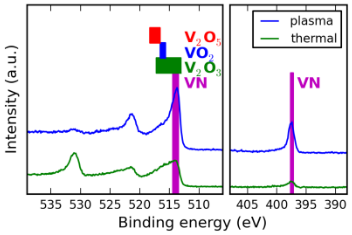

Figure 2: XPS for plasma-enhanced and thermal ALD films.

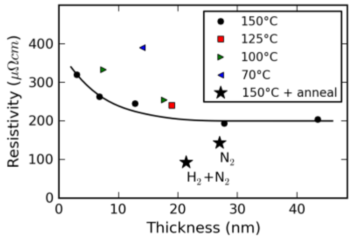

Figure 3: Resistivity as a function of thickness, temperature and post-ALD annealing process.

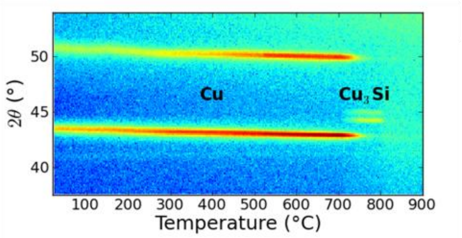

Figure 4: In-situ XRD shows the stability of Cu on Si by the insertion of a 5nm PE-ALD VN layer as diffusion barrier.