Plasma-enhanced atomic layer deposition of thin vanadium nitride layers as a 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 [1]. In microelectronics TiN and TaN have been extensively investigated for their use as diffusion barriers for copper interconnects [2]. In the same group of materials vanadium nitride (VN) is known as a strongly coupled superconductor with a room-temperature resistivity near 100μΩcm [3]. Thin films of VN are mainly deposited by reactive sputtering, high temperature nitridation of metallic vanadium layers and chemical vapour deposition. The latest reported applications include supercapacitors and diffusion barriers [4,5].

In this work, vanadium nitride layers were grown by plasma-enhanced atomic layer deposition (PE-ALD) using Tetrakis(EthylMethylAmino)Vanadium (TEMAV) as metal-organic precursor and ammonia plasma as reactant. A saturated and linear growth regime was achieved at a deposition temperature of 150°C, resulting in a growth rate of 0.07nm per ALD cycle (Fig. 1). Variation of the plasma power did not have much influence on the growth characteristics. X-ray photoelectron spectroscopy (XPS) confirmed the stoichiometric VN composition (49.6% V and 47.7% N), with only a minor oxygen impurity fraction of approximately 3% (Fig. 2). Moreover, x-ray diffraction (XRD) indicated that the as deposited films were crystalline with a structure closely related to δ-VN (fcc) (Fig. 3). 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. 4), indicating film continuity. Post-ALD annealing to 825°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. It should be noted that the thermal ALD process using the same precursor in combination with exposure to standard NH_3 vapor instead of NH_3 plasma resulted in similar growth rates, but the resistivity of these films was a factor of 50 higher. XPS indicated that in this case an oxygen-rich composition was present, close to V_2NO_2.

A thin PE-ALD VN layer of 5nm proved to be effective as a diffusion barrier for copper (Fig. 5). In-situ XRD was used to monitor the reaction between a sputtered Cu film and the underlying HF-cleaned Si substrate. Without an intermediate barrier, fig. 5a shows the formation of Cu_3Si at 230°C and the melting of this silicide phase at 820°C. A similar experiment was performed on a sample with a 5nm PE-ALD VN barrier in between the sputtered Cu and the HF-cleaned Si substrate. The in-situ XRD graph shows how the VN barrier effectively delays interaction between Cu and Si up to a temperature of 720°C (fig. 5b).

References

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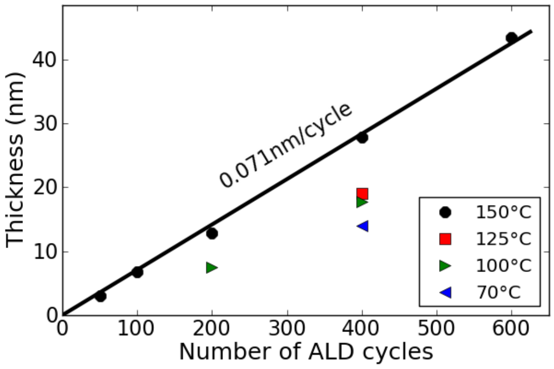

Figure 1: Vanadium nitride film thickness as a function of the number of PE-ALD cycles for various deposition temperatures. A growth rate of 0.07nm per cycle is extracted for a deposition temperature of 150°C.

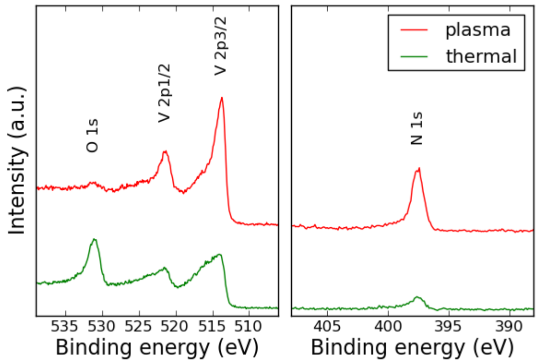

Figure 2: X-ray photoelectron spectroscopy of the plasma-enhanced and thermal ALD processes.

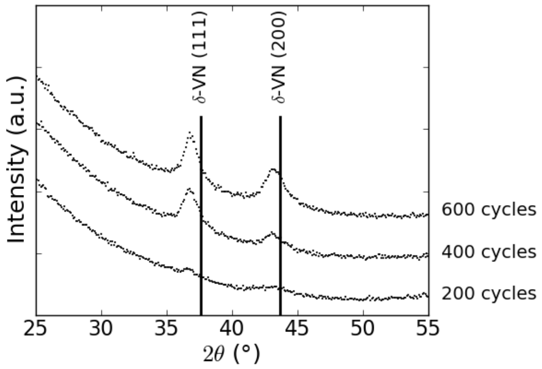

Figure 3: X-ray diffraction of the as deposited PE-ALD VN layers (150°C deposition temperature) reveals a polycrystalline structure, closely related to δ-VN.

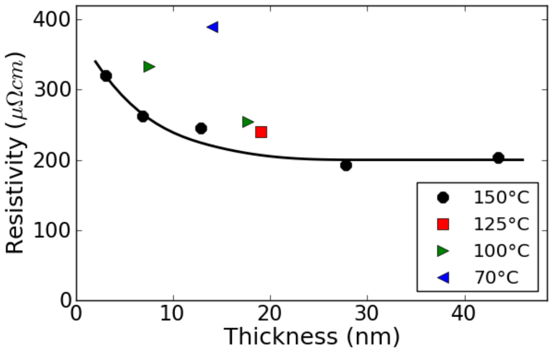

Figure 4: Resistivity of the PE-ALD VN films as a function of film thickness for various deposition temperatures. The black line shows the trend for the 150°C depositions.

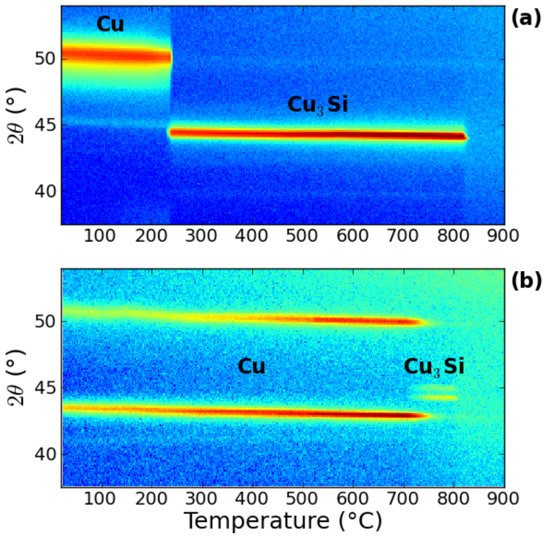

Figure 5: In-situ x-ray diffraction as a function of temperature shows how Cu diffuses into the Si substrate and forms Cu_3Si. (a) 50nm PVD Cu on Si reacts at 230°C, (b) 50nm PVD Cu with a 5nm PE-ALD VN on Si is stable up to 700°C.