

A STUDY OF THERMAL OXIDATION AND PLASMA-ENHANCED OXIDATION/REDUCTION OF ALD TiN LAYERS

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The applications of TiN films in IC technology (i.e., diffusion barrier, gate material, current conductor, and heater) are based on their high thermodynamic stability, low electrical resistivity, and high mechanical hardness. Sputtered stoichiometric TiN exhibits insignificant oxidation rate at temperatures below 400 °C [1], whereas a non-stoichiometric TiN starts to oxidize even at room temperature [2]. The oxidation behavior of thin TiN layers, realized by ALD technique, is hardly investigated. To further promote the use of ALD TiN in novel electron devices (e.g., 3D low-temperature electronics, TFTs, etc.) and for wafer post-processing, both the stability and evolution of the layer properties at different temperatures, during the device operation or processing in reactive plasmas, must be explored.

In this work, we present new results on thermal oxidation (both dry and wet) of thin (< 10 nm) ALD TiN films (realized at 425 °C using TiCl₄ and NH₃) in the temperature range 300-500 °C. We further investigate plasma enhanced oxidation and reduction (i.e., in oxygen- and hydrogen- containing plasmas, respectively) of the films at room temperature and up to 300 °C. Effects of the surface passivation with silicon oxide and silicon nitride layers (realized by both PECVD at 300 °C and ICPECVD at 150 °C), and with ALD aluminum oxide layers (realized at 325 °C from Al(CH₃)₃ and H₂O), are studied. The TiN layers were characterized (both in-situ and ex-situ) by a Woollam M2000 Spectroscopic Ellipsometer (SE) in the energy range 0.7-5 eV.

For the thermal oxidation carried out in this work, it was observed that, in both dry and wet ambient, the oxidation mechanism followed the linear parabolic law in accordance with the classic Deal-Grove oxidation model. For the linear regime, the formation of first 3-6 nm of TiO_x was limited by the reaction kinetics. From the slope of the Arrhenius plot, we extracted (for the first time to our knowledge) activation energy of the linear reaction rate constant, which revealed values of ~1 eV and ~0.7 eV for the dry and wet oxidation, respectively. For the parabolic regime (i.e., oxidation limited by diffusion of oxidizing species through the oxide layer), the diffusion coefficient revealed the activation energy of about 2 eV and 1.6 eV for dry and wet oxidation, respectively. The latter values were similar to those obtained for sputtered TiN [1]. TiN passivated by a 20-nm thick ICPECVD SiN_y showed no oxidation in wet ambient after 21 hours at 400 °C, and after 3 hours at 500 °C. TiN passivated by ALD alumina (50 nm) exhibited no TiN thickness decrease at 400 °C and a 3% thickness decrease at 500 °C after 3 hours.

The oxidation of ALD TiN in N₂O plasma was carried out at a pressure of 15 mTorr and in the temperature range from room temperature up to 300 °C. The non-passivated samples exhibited very fast oxidation (4-6 nm of TiO_x) in the first minutes (i.e., reaction-limiting regime), followed by a slow parabolic behavior pointing to the diffusion-limiting process. The reduction of both the initial and oxidized TiN layers was further investigated in pure hydrogen plasma at the same conditions.

In this presentation, based on our SE, TEM, EDX, XPS, XRD and resistivity measurements, we will make further considerations regarding kinetics and mechanism of the oxidation and reduction processes.

[1] I. Suni, D. Sigurd, K.T. Ho, and M-A. Nicolet, J. Electrochem. Soc. **130**, 1210 (1983).

[2] S. Logothetidis, E.I. Meletis, G. Stergioudis, and A.A. Adjaottor, Thin Solid Films **338**, 304 (1999).