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Materials characterization of WN_xC_y, WN_x and WC_x films for advanced barriers

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Abstract

A ternary WN_xC_y system was deposited in a thermal ALD (atomic layer deposition) reactor from ASM at 300 °C in a process sequence using tungsten hexafluoride (WF_6), triethyl borane (TEB) and ammonia (NH_3) as precursors. The WC_x layers were deposited by a novel ALD process at a process temperature of 250 °C. The WN_x layers were deposited at 375 °C using bis(*tert*-butylimido)-bis-(dimethylamido)tungsten $(^t BuN)_2(Me_2N)_2W$ (imido–amido) and NH_3 as precursors. WN_x grows faster on plasma enhanced chemical vapor deposition (PECVD) oxide than WC_x does on chemical oxide. WN_xC_y grows better on PECVD oxide than on thermal oxide, which is opposite of what is seen for WN_x. In the case of the ternary WN_xC_y system, the scalability towards thinner layers and galvanic corrosion behavior are disadvantages for the incorporation of the layer into Cu interconnects. ALD WC_x based barriers have a low resistivity, but galvanic corrosion in a model slurry solution of 15% peroxide (H_2O_2) is a potential problem. Higher resistivity values are determined for the binary WN_x layers. WN_x shows a constant composition and density throughout the layer.

Keywords: Barrier; Atomic layer deposition; ALD; WN_xC_y; WN_x; WC_x

1. Introduction

The deposition of a barrier layer for future technologies in Cu interconnects is inextricably linked to scaling of the barrier thickness. Scaling on the other hand is difficult to maintain with the traditional deposition techniques such as physical vapor deposition (PVD). Traditional PVD cannot fulfill the stringent demands for future barrier layers such as the deposition of a thin (<5 nm), conformal layer with excellent step coverage and minimal overhang. ALD is a possible alternative to the traditional PVD technique since it promises to satisfy these requirements. Pure metal ALD however is difficult, so therefore binary and ternary systems attract a lot of attention, Ref. [1].

In search of a new possible barrier candidate for the 32 nm technology node and beyond three different ALD processes, as developed by ASM Microchemistry, are compared: a ternary WN_xC_y system and two binary (WN_x, WC_x) systems. The processes are compared in terms of growth characteristics, film properties (e.g. homogeneity, crystallinity, roughness, density and sheet resistance) as well as galvanic corrosion behavior in a model solution of 15% H_2O_2 in distilled (DI) water.

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2. Experimental details

The deposition of the ternary system WN_xC_y was performed in a thermal ALD reactor from ASM at 300 °C in a process sequence using WF_6, TEB and NH_3 as precursors. The WC_x layers were deposited by a novel ALD process at a process temperature of 250 °C. Cycle numbers varied between 27 cycles corresponding to nominally 2 nm WC_x and 267 cycles corresponding to nominally 20 nm WC_x on a substrate of 1.1 nm chemical oxide. The WN_x layers were deposited at 375 °C using imido–amido and NH_3 as precursors Refs. [2,3]. The binary layer was deposited on to either 20 nm thermal oxide or 100 nm PECVD oxide with cycle numbers ranging between 30 cycles for 1 nm nominally and 1000 cycles for 20 nm nominally.

The growth characteristics of the different films were analyzed by Rutherford back scattering (RBS). The RBS-measurements were executed on an RBS-400 system, which is installed around a 2 MV tandem-accelerator. The film resistivity was calculated using four point probe sheet resistance measurements and film thickness. X-ray photoelectron spectroscopy (XPS) was deployed to determine the layer composition at the surface and inside the layer on a Thermo VG scientific Theta300. The chemical bonds that are formed between the different elements were also characterized. In order to determine the density of the barrier layers, samples were analyzed with a high-resolution specular X-ray reflectometer (XRR) using a $\Theta/2\Theta$ configuration with a rotating copper anode as the radiation source and a Siemens D5000 two-circle goniometer. X-rays of 1.5418 Å wavelength (Cu Kα) were selected by a graphite secondary monochromator, complemented with electronic discrimination (scintillation counter). The X-ray beam was collimated by a set of adjustable slits with micrometer precision. The reflected intensity was measured as a function of detector angle (Θ) and subsequently plotted versus kz0, the momentum transferred perpendicularly to the sample, which is defined by $(2\pi/\lambda)\sin\Theta$. By means of Auger electron spectroscopy (AES), the surface contamination and film purity were analyzed on a Thermo VG scientific Microlab 350. Surface smoothness of the deposited films was evaluated with atomic force microscopy (AFM) on a Nanoscope IV Dimension 3100. Grazing angle X-ray diffraction (XRD) analysis using Cu Kα radiation ($\lambda = 1.54$ Å) was conducted to determine the crystal structure of the nominally 20 nm thick WN_x sample. The nominally 20 nm thick WC_x layer was analyzed by high temperature XRD with a temperature range between room temperature and 1100 °C. A sequence of XRD spectra were taken at temperatures with an interval of 100 °C and a ramp rate of 50 °C/min. The high temperature X-ray diffraction set-up used is a 3003 TT diffractometer (Seifert, Ahrensburg, Germany) equipped with a parabolic multilayer mirror, which provides a wide parallel incident beam and a furnace in vacuum for heating the sample to the temperature of interest. Cu Kα radiation is used as the X-ray source. Static etch rates of the different barrier layers and of Cu were determined at room temperature in a controlled solution of 15% H_2O_2 in DI water by means of four point probe sheet resistance measurements. In the same medium the open circuit potential (OCP) was measured for the three materials with galvanic series measurements under static conditions. To model the galvanic corrosion behavior in the controlled solution, galvanic currents for the Cu/W-containing barrier couples (area ratio 7:1) were measured.

3. Results

On 100 nm PECVD oxide, WN_x grows well after an incubation period of ±30 cycles but the growth per cycle (Figs. 1 and 2) is even faster on thermal oxide as derived from RBS measurements. On chemical oxide, WC_x has an incubation period of around 20 cycles after which the layer grows in a linear mode (Fig. 3). WN_x grows faster on PECVD oxide than WC_x does on chemical oxide. WN_xC_y grows better on PECVD oxide than on thermal oxide which is opposite of what is seen for WN_x, Ref. [4].

The bulk resistivity among the three materials differs, both WN_xC_y and WC_x have low resistivity of about 300–400 μΩ cm beneficial for barrier application, but the bulk resistivity of WN_x goes up to 4000 μΩ cm.

The layer composition of the different ALD layers was analyzed with in depth XPS. A constant composition throughout a layer is important when scaling down the barrier thickness, because changes in composition imply changes in density and thereby changes in barrier properties. Surface composition of a layer is important because good adhesion to Cu has to be ensured however it falls out of the scope of this paper to investigate the adhesion between the barrier layer and the dielectricum on one hand or the Cu on the other hand.

XPS gives a ratio of W:N:O:C of 60:20:10:10 at.% throughout a very homogeneous layer of nominally 20 nm WN_x layer on 20 nm thermal oxide (Fig. 4). The spectra recorded at half the sputter time, show that the main bonds are W–N bonds together with some minor oxygen

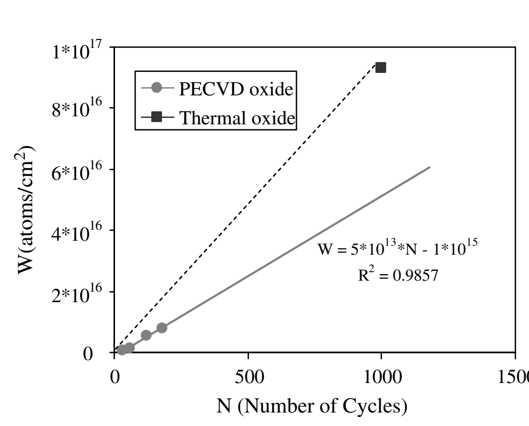

Fig. 1. Growth curve for WN_x on 100 nm PECVD oxide and 20 nm thermal oxide.