



Cobalt advanced barrier metallization: A resistivity composition analysis

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ABSTRACT

Cobalt is a high-potential material applicable as liner and seed replacement in BEoL metallization schemes. To enable seedless plating, the resistivity of thin cobalt liners (<5 nm) has to be controlled. In the presented paper, the impacts of impurities, grain boundary scattering, surface scattering and roughness on the resistivity of thin cobalt layers is evaluated and modeled. For analysis, i-PVD TaN_x barrier films are covered by MOCVD cobalt films with thicknesses in the range of 2–90 nm. Film stacks are deposited in a 300 mm AMAT Endura2™ cluster deposition tool without breaking the vacuum. An optional heat treatment at 400 °C is applied to initiate morphology modification. The amounts of precursor induced impurities quantified by *in situ* ARXPS are found to be independent of the deposited film thickness. *Ex situ* characterizations of cobalt films are performed by four point probe measurement, XRR, AFM and TEM revealing resistivity, thickness, roughness and morphology of the cobalt films. A comparison of the measured data with established models for thin film resistivity from Fuchs–Sondheimer, Mayadas–Shatzkes and Namba shows the tremendous impact of the film roughness on resistivity. With implementing a modification on the Namba model to include thickness dependent roughnesses it is possible to reproduce the measured data of the annealed samples very well. Due to the good correlation between measured and calculated resistivity values and the reduced number of fitting parameters, the measurement method can be also used as a simple way to control thin film thicknesses.

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1. Introduction

Barrier layers are necessary to prevent the diffusion of copper atoms into the surrounding interlayer dielectric. Usually, a stack of TaN_x barrier and Ta liner with a combined thickness between 5 and 10 nm is used for VLSI applications. Due to the fact that the feature size reduces with every new technology, the volume available for copper interconnects steadily decreases and barrier film thicknesses are required to scale simultaneously. Thus, the demands on future barrier stacks are tremendous. First, to minimize the occupied cross section area the stack has to be as thin as possible while keeping its barrier and adhesion properties. Second, the direct electrochemical plating onto the liner is desired to eliminate the need of a conventional physical vapor deposited (PVD) Cu seed layer which can lead to trench clogging especially of narrow structures. Third, a low inplane resistivity is essential to keep the overall metallization resistivity at a low value.

Cobalt is regarded as one of the most promising alternatives to conventional Ta liner besides ruthenium [1–3]. However, there is a lack of details regarding the inplane resistivity for thin cobalt films

on the range of 5 nm. Previous studies [4,5] focus on ultra-low (monolayer region) or higher thickness (>28 nm) ranges leaving a gap in the region of interest. The aim of the present work is to find key parameters which mostly affect the resistivity of semiconductor grade deposited cobalt films. Therefore, the measured thickness dependent resistivity data are fitted with one-dimensional classical size effect models.

The intention to decrease liner resistivity is the occurrence of the so called terminal effect [6] during the electroplating. If the barrier conductivity is not sufficient the terminal effect leads to an initial preferred copper deposition near the electrical contacts clamped to the wafer edge. Regions in the wafer center that are not immediately covered by copper are exposed to the acidic plating bath. In consequence the liner corrodes leading to adhesion problems and the formation of voids [6]. Hence, the optimization of the cobalt properties toward low resistivity for films as thin as 5 nm is essential for the seedless electrochemical copper deposition (ECD) on waferscale.

2. Material and methods

The substrates used in our studies are 300 mm Si (100) wafers coated with a CVD ultra-low-k dielectric. All barrier/liner

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depositions and anneal steps are performed in chambers attached to an Endura2™ cluster deposition tool from Applied Materials Inc. After a degas process at 300 °C in argon atmosphere a thin TaN_x barrier is applied by ionized physical vapor deposition (i-PVD) to ensure a stable reference substrate comparable to the conventional TaN/Ta/Cu trilayer. Subsequently the cobalt metal-organic chemical vapor deposition (MOCVD) is done in an alternating mode consisting of a deposition part under H₂ atmosphere and a H₂ plasma step to reduce precursor induced impurities. CCTBA (dicobalt hexacarbonyl *tert*-butylacetylene) is used as Co precursor. For the sample preparation two different process conditions are chosen regarding process pressure P as well as gas flow ratio GR between CCTBA:H₂:Ar. In the following they are referred as sample series A and B where $P_A = 15$ Torr, $GR_A = 1:6:2.5$ and $P_B = 10$ Torr, $GR_B = 1:11:5$ respectively. A substrate temperature of 175 °C is chosen for both cases to ensure a surface reaction limited process. However the other parameters are kept constant. Cobalt thicknesses are varied between 2 nm and 90 nm by adjusting the number of deposition cycles. An optional heat treatment at 400 °C in H₂ atmosphere is used to initiate a morphology modification.

Parallel angle resolved XPS is carried out *in situ* in a Theta 300i from Thermo Fisher Scientific, connected to a standard port of the Endura2™. A high resolution monochromatic Al-K_α X-ray source (1486.86 eV) is used with a spot diameter of 400 μm. The C1s, O1s, Co2p and Ta4f energy envelopes are acquired at a pass energy of 60 eV and a step size of 0.1 eV.

After the *in situ* characterization the sheet resistance is measured by an *ex situ* four point probe resistivity mapping system from KLA Tencor RS100™. For the determination of the average resistance 49 data points are taken. As the film stack consists of two conducting materials the proportions to the total resistivity are separated using a parallel resistor model. The contribution of the underlying TaN layer is below 1% in each case. Texture and film thicknesses are determined by grazing incidence X-ray diffraction (Gi-XRD) and X-ray reflectometry in a Bruker D8 Discover equipped with a Cu-K_α tube. The uncertainty of the thickness measurement is about ±0.25 nm. Finally, the resistivity is obtained by multiplying the measured values of film resistance and thickness. To evaluate the differences of the surface roughness atomic force microscopy (AFM) is carried out using a Veeco 3D AFM. After sampling 1 × 1 μm areas, images are post processed as follows. A defined section of 25 nm is cropped from each side of the image to reduce the impact of tip motion reversal and line correction, plane leveling and image filtering is applied prior to parameter extraction. The morphology and thickness of the films are studied with a FEI Tecnai F20 transmission electron microscope (TEM) with 200 kV acceleration voltage.

Electrochemical deposition (ECD) of copper is conducted on selected samples in a Semitool Raider ECD 300 mm plating tool with a standard additive setup (accelerator, suppressor and leveler) and a low acidic electrolyte. The plating results are evaluated by four point probe resistivity mapping as well as SEM/TEM cross sections.

3. Thin film resistivity models

With thicknesses approaching the intrinsic electron mean free path the resistivity of thin films increases due to growing relative contributions from surface and grain boundary scattering. A common model for the former effect was established by Fuchs [7] and later approximated by Sondheimer [8] (henceforth FS-model). For this well-known size effect two limiting but convenient forms can be obtained [9] for thick $\lambda/d < 1$ (3.1) and thin (3.2) films $\lambda/d > 1$ which differ from the exact calculation by a maximum of 9% for λ/d between 0.05 and 0.5 [9]

$$\rho = \rho_0 + \frac{3}{8} \frac{\lambda \cdot \rho_0}{d} (1 - p) \text{ for } \frac{\lambda}{d} < 1 \quad (3.1)$$

$$\rho = \frac{4\rho_0\lambda(1-p)}{3d(1+p)} \cdot \left[\ln\left(\frac{\lambda}{d}\right) + 0.4228 \right] \text{ for } \frac{\lambda}{d} > 1 \quad (3.2)$$

where ρ is the film resistivity, ρ_0 is the intrinsic bulk resistivity, λ is the mean free path (MFP) of the conducting electrons, d is the film thickness, p represents the specularity of the scattering interface, with $p = 0$ means total diffuse scattering and $p = 1$ entirely specular scattering.

Contrary to ideally defect free, single crystal conductors the contribution due to grain boundary scattering has to be considered. Mayadas and Shatzkes (henceforth MS-model) established a resistivity model based on the assumption of a series of partially reflecting planes perpendicular to the thin film surface causing an additional electron scattering [10]. Assuming an average interplanar spacing between these walls equivalent to the average grain size D a practical formulation can be obtained (3.3) [10]

$$\frac{\rho_0}{\rho} = 1 - \frac{3}{2} \alpha + 3\alpha^2 - 3\alpha^2 \ln\left(1 + \frac{1}{\alpha}\right) \text{ with } \alpha = \frac{R_g}{1 - R_g} \frac{\lambda_G}{D} \quad (3.3)$$

where R_g is the grain boundary reflection coefficient and λ_G is the MFP within a grain. Due to the common geometrical heterogeneous film cross section of thin films Namba proposed an extension to the classical Fuchs size effect to include a one dimensional surface undulation [11]. A practical approximation is given by (3.4) [12]

$$\rho = \rho_0 \left(1 - \left(\frac{H}{d} \right)^2 \right)^{-1/2} + \frac{3}{8} \frac{\lambda \cdot \rho_0}{d} (1 - p) \left(1 - \left(\frac{H}{d} \right)^2 \right)^{-3/2} \quad (3.4)$$

where the additional parameter H represents the roughness amplitude of the surface. It should be noted that in case of $H > d$ the Namba model predicts an infinite resistivity through the interpretation of the film as disconnected islands. Due to the simultaneous presence of the different resistivity contributions and their convolution the resistivity modeling can be very sensitive to these individual parameters. Thus, it is essential to consider some points to improve the quality of the data reproduction. Temperature dependent data are necessary to distinguish between the different scattering mechanisms [13]. Furthermore, the morphology of the thin films must be known in order to estimate realistic parameter ranges of the model [13]. Without accounting all relevant scattering mechanisms, which is commonly very difficult due to a lack of special details about the thin film properties, it is not possible to extract exact material dependent values. However, the comparison of the resistivity models presented in this work is suitable to determine the key thin film properties of cobalt with the largest impact on the resistivity.

4. Results and discussion

4.1. Thin film characterization

The *in situ* XPS characterization directly after the deposition reveals the precursor induced contamination content of the cobalt films which is found to be 4.7 ± 0.3 at.% surface carbon, 2.3 ± 0.4 at.% surface oxygen and 1.5 ± 0.4 at.% cobalt monoxide almost independent of film thickness. After contact with air less than 0.3 at.% carbon is detected. Quadrupole-MS analysis of the UHV composition within the cluster deposition tool shows that oxygen, hydrogen and nitrogen are the main residual gases. The controlled oxidation of a selected sample over several days under these conditions shows the stepwise carbon replacement by oxygen accompanied with a change from C—Co bonds (282.8 eV) to C—H bonds (285.5 eV). Furthermore, a self-passivation of the

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