



Investigation of organic impurities adsorbed on and incorporated into electroplated copper layers

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Abstract

At room temperature electroplated copper layers exhibit changes in resistivity, residual stress, and microstructure. This process, known as self-annealing, is intimately linked to the release of organic impurities, which stem from the incorporation of organic additives into the Cu layer in the course of the electroplating process. The behavior of these impurities during self-annealing, represented by the carbon content, could be detected by analytical radio frequency glow discharge optical emission spectrometry (GD-OES) and carrier gas hot extraction (CGHE). The precondition of a quantitative determination is a surface cleaning procedure to remove adsorbed organics from the copper surface. It was observed that at first almost all impurities have to leave the Cu metallization before an accelerated abnormal grain growth can start. The small amount of remaining organic species after self-annealing could be quantified by both examination techniques, GD-OES and CGHE.

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1. Introduction

The electrochemical deposition of copper is widely used as a method for the preparation of metallization layers and to fill vias and trenches with high aspect ratio in the damascene process. Commonly, electrochemical deposition is made from sulphuric acid-based copper electrolytes containing a small amount of organic and inorganic substances, the so-called additives. Additives are necessary to achieve uniform

and homogeneous plating, fine grains, and sufficient trench filling. Furthermore, additives support an abnormal grain growth immediately after deposition, which leads to the observation of self-annealing, a process of a significant microstructure evolution at room temperature. During this period lasting up to a few days or even months, film properties like residual stress, resistivity, grain growth and texture are changed. During electroplating, organic and inorganic impurities are incorporated into the growing copper layer, mainly into the free volume between the grains, up to an amount of 1 wt.% [1]. Incorporation of the organics leads to their partial or full bond cleavage. It

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was shown that organic impurities, which are present in the copper layer presumably as fragments of hydrocarbon chains and heterofunctional groups, migrate along significant diffusion paths to the copper layer surface and desorb as CO, C₂H₂, and CO₂ [2].

2. Experimental

For this study we used thermally oxidized 3-in. Si (1 0 0) wafers. First, a 50 nm Ta layer, which acts as a diffusion barrier for highly diffusive Cu atoms, and a 50 nm Cu seed layer were deposited by magnetron-sputtering (PVD, physical vapor deposition) without vacuum break. The electrochemical deposition was performed using a FIBROplate™ IKo™ plating station (ECSI FIBROtools Company). The electrolyte solution contained 0.24 M CuSO₄·5H₂O, 1.8 M H₂SO₄ and 1.41 mM Cl⁻ in the form of KCl (all chemicals p.A., Merck, Germany). A prescribed amount of two commercially available additives, SC MD and SC LO 70/30 (Enthone Inc., Germany), was admixed. A dc-current density of 15 mA/cm² was applied to generate electroplated Cu films with an average thickness of 1 μm.

Immediately after deposition, the stress was investigated using a Flexus stress measuring system from Tencor Instruments. Simultaneously, the behavior of resistivity could be monitored by an in-house fabricated four-point probe resistivity measurement. Focused ion beam (FIB) analysis was carried out on an FIB200 (FEI Company) to examine the grain growth evolution. To prove the incorporation of impurities in copper and their influence on the self-annealing process, the carbon content was determined by CGHE (RC-412, LECO) and GD-OES (SDP-750, LECO) experiments.

3. Results and discussion

To investigate incorporated impurities in electroplated Cu films, a perfect surface cleaning is mandatory. Some of the organic compounds in the plating bath have a strong tenside character and adhere to the wafer surface, which leads to incorrect results of the amount of incorporated carbon. Several cleaning procedures with thermally pre-cleaned Si samples

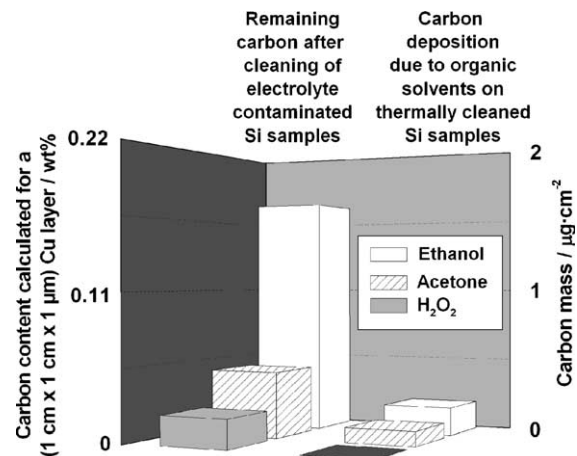


Fig. 1. Cleaning effect of ethanol, acetone, and hydrogen peroxide regarding to surface contamination.

(2 min at 600 °C in an oxidizing atmosphere) were tested using ultrasonic treatments in ethanol, acetone, and hydrogen peroxide (H₂O₂) solution. In Fig. 1, the success of cleaning samples reproducibly contaminated with electrolyte is represented by the results of CGHE carbon quantification. The H₂O₂ conditioning yields the best cleaning effect, whereas treatments with ethanol or acetone are less effective. Furthermore, persistent traces of the organic solvents lead to additional carbon contamination on the wafer surface, as shown in Fig. 1. After cleaning with H₂O₂, FIB analysis of copper films only shows a thin copper oxide layer of 30 nm thickness. According to these cleaning results, all samples were pre-treated with H₂O₂ in ultrasonic for 3 min before carbon determination.

To follow the self-annealing process, residual stress and resistivity were continuously measured over 40 h after deposition (Fig. 2). During the first 10 h no significant changes in resistivity were found. In the following 30 h a microstructure evolution started and the initial grains of less than 100 nm grew into larger grains several micrometers in diameter. In this period, resistivity decreased by about 20% as a result of lower electron grain boundary scattering in accordance with the Mayadas-Shatzkes model [3].

The role of incorporated organic impurities was revealed by qualitative and quantitative GD-OES examinations over the whole self-annealing period in 1-h time intervals. Fig. 3 confirms the hypothesis of

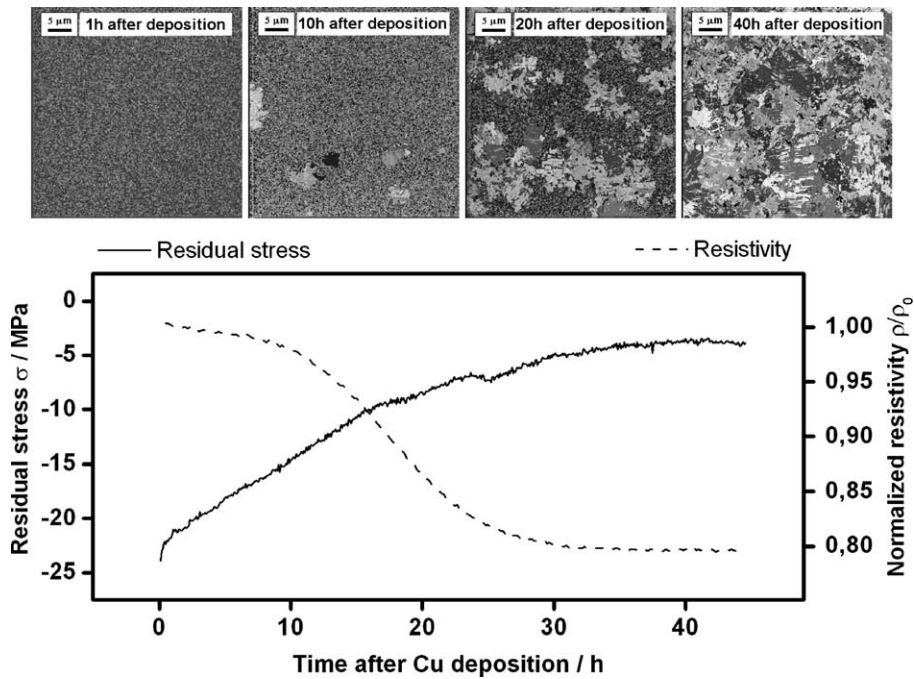


Fig. 2. Microstructure evolution, residual stress, and resistivity during self-annealing process.

impurity diffusion in the first 10 h after electrochemical Cu deposition by a strong diffusion of carbon towards the copper surface. The microstructure evolution starts as soon as the majority of carbon is released by the layer. After self-annealing, GD-OES quantification gave a constant carbon level of 17 ppm

(w/w) in the copper layer. Sixty percent of these impurities were situated in the first 200 nm presumably because of a lack of energy to leave the Cu layer. After thermal treatment at 450 °C for 0.5 h in a (5% H₂/95% Ar)-atmosphere further 54% of impurities left the metallization layer.

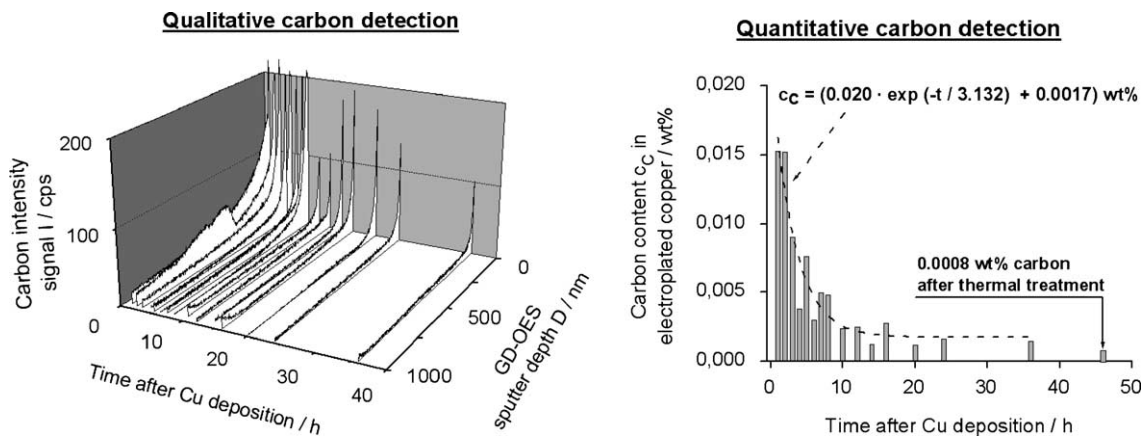


Fig. 3. GD-OES carbon depth profiles and quantitative carbon contents of a 1000 nm Cu layer over a time period of 50 h.

4. Conclusion

An experimental study of the behavior of additives in electroplated Cu during a self-annealing process was performed. Surface contamination could be effectively removed by H₂O₂ treatment at ultrasonic as a precondition for carbon quantification by GD-OES and CGHE. According to resistivity and stress measurements the duration of self-annealing was found to proceed for 40 h after deposition. In agreement with CGHE investigations, GD-OES depth profiles showed that the majority of organic impurities have to leave the Cu before an accelerated abnormal grain growth can start. Subsequent to the microstructure evolution process, only a small amount of impurities measured as 17 ppm (w/w) of carbon remains near the surface of the Cu metallization.

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