

Original Paper

Segregation of organic impurities in thin electroplated Cu metallizations

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Abstract. This article presents investigations regarding the incorporation of organic impurities in thin electroplated Cu metallizations. RF-GD-OES (radio frequency glow discharge optical emission spectrometry) was used for detection of C and H as indicators for incorporated hydrocarbon molecules. The presented results indicate a fragmentation of incorporated hydrocarbons and their constrict segregation near the Cu surface. The bilateral relationship between incorporated organic impurities and intrinsic stress behavior is associated with the Gorky effect.

Key words: Electrochemical deposition; copper; impurities; segregation; GD-OES.

The electrochemical deposition of Cu is widely applied for manufacturing of conducting lines and vias of semiconductor devices. This technique is very cost-effective by offering a high deposition rate, low temperature processing, system simplicity, and good process controllability. Particularly, Cu electroplating is favored for damascene process, which requires a good trench filling with high aspect ratio [1, 2]. To achieve void free trench filling the application of additives in the plating bath is an essential requirement. However, these additives or fragments of them incorporate into the deposit and influence the self-induced microstructure evolution at room temperature [3, 4], called self-annealing.

Cu self-annealing represents an abnormal grain growth in analogy to the Ostwald ripening [5]. It was well studied in the past by investigating changes in grain growth, texture, reflectivity, residual stress and resistivity as function of time after deposition [6–12]. Stangl et al. [13] also identified a strong influence of incorporated impurities on Cu self-annealing. They conclude from their results, that only a complete segregation of organic impurities accompanied by a simultaneous stress relaxation lead to a starting grain growth resulting in a coarse grain microstructure (Fig. 1).

The detection of impurities in Cu, stemming from incorporated additives in the electrolyte, is very difficult and the favored research methods are GD-OES (glow discharge optical emission spectrometry) and SIMS (secondary ion mass spectrometry). Stangl et al. [13, 14] focused the GD-OES investigations only on incorporated C in thin electroplated Cu layers. Carbon was postulated as indicator for organic impurities, however a concrete evidence is still missing. This paper intends to prove hydrocarbon molecules as incorporated impurities and to explain the effect of segregation during Cu self-annealing.

Experimental

According to common semiconductor devices we used 3 inch Si (100) blanket wafers with 1000 nm SiO₂, 50 nm Ta barrier, and

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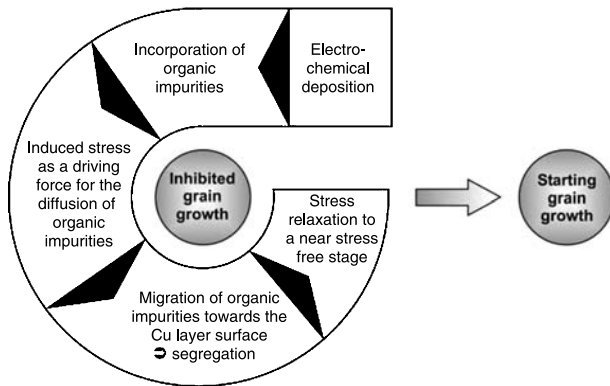


Fig. 1. Relationship between incorporated impurities, intrinsic stress and grain growth

50 nm Cu seed-layer. The electrochemical deposition was performed with a FIBROplate™ IKo™ plating station (ECSI FIBROtools Company, Denville, NJ, USA). The Cu plating electrolyte contained a typical composition of $0.25 \text{ mol L}^{-1} \text{ CuSO}_4 \cdot 5\text{H}_2\text{O}$, $1.8 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and $1.41 \text{ mmol L}^{-1} \text{ Cl}^-$ in form of KCl (all chemicals p.A., Merck, Germany) [15–17]. A prescribed amount of two commercially available additives SC MD and SC LO 70/30 (Enthone Inc., Germany) was admixed. A pump circulated the electrolyte and all Cu films were deposited by applying a dc current density of 15 mA/cm^2 .

The microstructure evolution during self-annealing is ultimately linked with a significant decrease of resistivity. This behavior of resistivity could be monitored by an in-house fabricated four-point probe resistivity measuring system. A laser-optical wafer-curvature device (Flexus, Tencor Instruments) was used for intrinsic stress measurements. Incorporated impurities in electroplated Cu metallizations were determined by analytical radio frequency GD-OES (LECO SDP-750). The detected raw signals were corrected as written in [13]. Before each analysis a 0.5 hour pre-sputtering with thermally cleaned Si samples was necessary to remove adsorbed contamination inside the GD source resulting in a low and stable over sputter time background intensity. Furthermore, a special cleaning procedure with pure hydrogen peroxide (H_2O_2 , 30%) and low concentrated sulfuric

acid (H_2SO_4 , 5%) guaranties a sufficiently cleaned sample surface [14].

Results and discussion

Previous investigations by Stangl et al. [13, 14] were focused on the detection of C in electroplated Cu metallizations. Incorporated C was proved with a maximum value of $\approx 0.04\%$ (w/w) and postulated as indicator for organic molecules. Figure 2 confirms this assumption by displaying the obviously well correlating depth profiles of C (Fig. 2a) and H (Fig. 2b) during the first 60 hours after deposition. C and H show a simultaneous transport towards the Cu layer surface and their segregation is finished within 30 hours after deposition. A joint migration of uncombined C and H can be ruled out although there are no data available for C diffusion in Cu [18]. However, it is well known that the diffusion coefficient (in solid state) of elemental H in comparison to elemental C is generally higher and would lead to a non-simultaneous diffusion. This represents the evidence for incorporated hydrocarbon molecules. Other elements stemming from incorporated additives, e.g. S and N, are not detectable by RF-GD-OES and O shows no correlating depth profiles according to C and H.

Figure 3 presents a more precise look on selective RF-GD-OES depth profiles of C and H in a 600 nm Cu layer. Short time after deposition (1 h) there is an explicit gradient of C and H towards the Cu layer surface. The C depth profile shows a significant shoulder indicating a constrict segregation of hydrocarbons. Remarkably, the corresponding C:H ratio is not con-

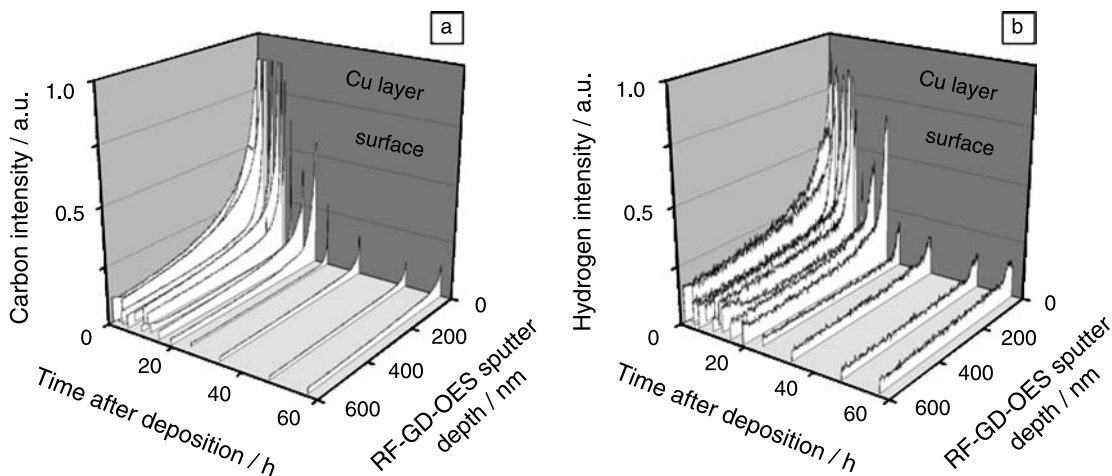


Fig. 2. Corrected RF-GD-OES depth profiles of carbon (a) and hydrogen (b) in a 600 nm Cu metallization at different times after deposition

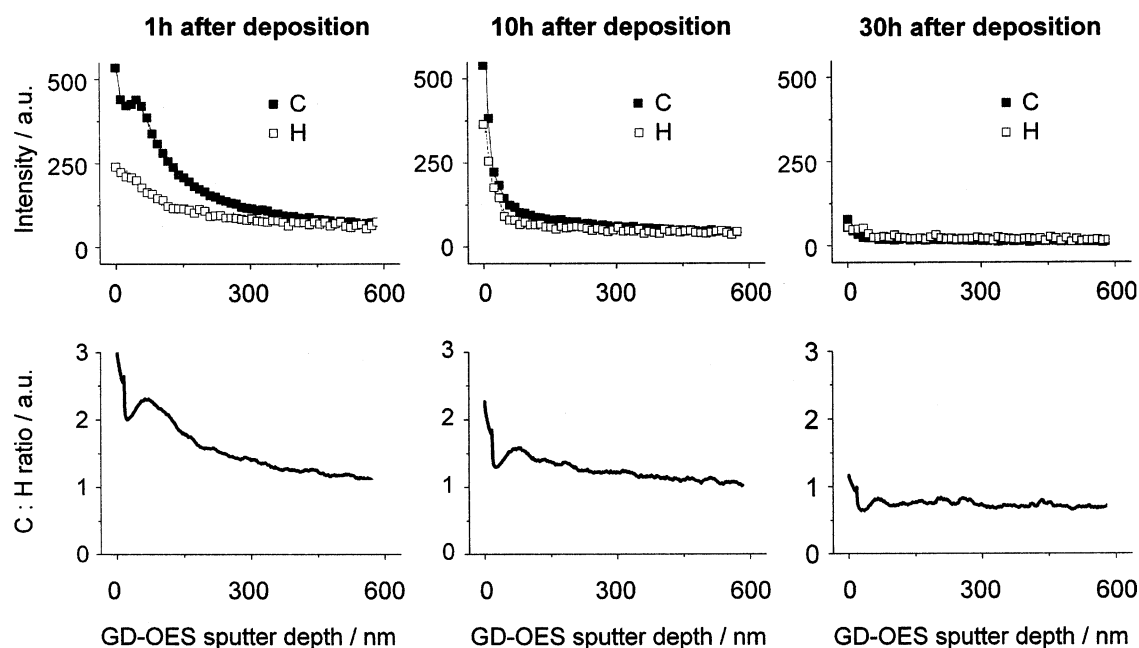


Fig. 3. RF-GD-OES depth profiles of C and H in a 600 nm Cu metallization and the corresponding C:H ratio at different times after deposition

stant and reveals an accumulation of C rich molecules near the surface. Furthermore, the C:H ratio curve denotes a fragmentation of incorporated hydrocarbons according to the results of Brongersma et al. [19]. During the subsequent segregation process (10 h and 30 h after deposition) almost all hydrocarbons leave the Cu metallization and the C and H signals as well as the C:H ratio reach a constant level near the background.

An explanation for segregation of hydrocarbon molecules is given by the Gorsky effect. The Gorsky effect represents a long-range diffusion process independently from surface processes [20]. It is an inelastic relaxation phenomenon, which occurs in metals containing mobile dilatation defects such as small hydrocarbon molecules. If a dilatation gradient is applied to a sample, for instance by uniaxial bending of a metal coating, a spatial gradient in the chemical potential of the defects will be induced. Relaxation will then occur by long-range diffusion of the defects along this gradient. Electroplated Cu in the as-deposited state exhibits compressive stress probably caused by incorporated impurities. In this regard Koch et al. [21] refer to the resulting compressive stress in thin physical vapor deposited Cr, Fe, and Al films induced by incorporation of O at interstitial sites or grain boundaries. This stress presumably entails a directed diffusion flux of hydrocarbon molecules along the grain

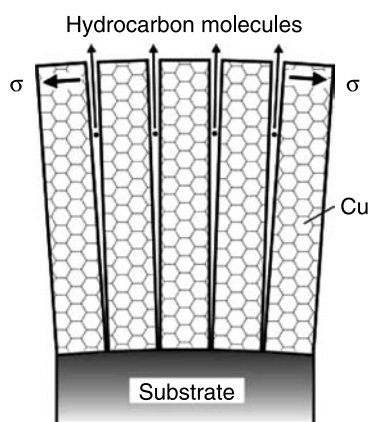


Fig. 4. Scheme of hydrocarbon segregation according to the Gorsky effect in thin electroplated Cu layers

boundaries [19] towards lattice dilatation, i.e. towards the Cu layer surface. Figure 4 illustrates the mechanism of the described phenomenon representing a quasi 'up-hill diffusion'. A similar effect is known for H incorporated at interstitial sites in Pd. The lattice expansion effect is caused by H and leads also to a directed flux of H towards lattice dilatation, which is opposing to a formation of an overall gradient of concentration [22].

The segregation of hydrocarbon molecules was proved for differently thick electroplated Cu layers. Intrinsic stress influences the segregation mechanism

Table 1. Correlation between Cu layer thickness, as-deposited intrinsic stress, and time of microstructure evolution

Thickness of electroplated Cu [nm]	Average as-deposited intrinsic stress [MPa]	Time of as-deposited microstructure evolution [h]
600	-5	900
1000	-20	50
2000	-30	15

and affects the self-annealing behavior. Table 1 summarizes findings confirming this influence for differently thick Cu metallizations. As investigated by Stangl et al. [13], only a complete segregation of organic impurities leads to a starting microstructure evolution during self-annealing. This is in accordance with the theory of grain growth in thin films described by Thompson [23]. In high purity metallic films, grain growth can occur at temperatures as low as $0.2T_m$ (T_m is the melting point). This property is connected with the mobility of grain boundaries, which is strongly temperature-dependent. As conclusion, grain growth in pure electroplated Cu films is estimated to start at a temperature around 273 K. This affirms the complete segregation of hydrocarbon molecules as a necessary precondition to get high purity Cu, which exhibits a microstructure evolution at room temperature.

Conclusion

The self-annealing of electroplated Cu metallizations is a very complex phenomenon. The different self-annealing behavior of differently thick Cu layers strongly depends on the different segregation of organic Cu impurities. These impurities are able to influence the self-annealing by inhibiting the microstructure evolution after deposition. The incorporation of organic impurities was determined by RF-GD-OES analyses. During self-annealing C and H depth profiles show a good correlation of segregation behavior revealing incorporated impurities as hydrocarbon molecules. The C:H ratio indicates a fragmentation of hydrocarbons. It was investigated that intrinsic stress strongly

influences the segregation mechanism, which can be described by the Gorsky effect.

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