Extended Abstracts of the 2008 International Conference on Solid State Devices and Materials, Tsukuba, 2008, pp. 918-919

C-9-4

Materials Engineering for future Interconnects: "Catalyst-free" electroless Cu deposition on self-assembly monolayer alternative barriers

Silvia Armini and Caroline M. Whelan

IMEC, Kapeldreef 75, B-3001 Leuven, Belgium
Phone: +3216288617 E-mail: silvia.armini@imec.be

Cu is the interconnect material of choice in the metallization step for advanced semiconductor device manufacturing. A typical interconnect structure is composed of Cu/Ta/TaN/dielectric where the Ta/TaN layer is required as a barrier to prevent interdiffusion between Cu and the underlying dielectric resulting in electrical shorting. Due to the poor electrical conductivity of the barrier, relative to Cu, the barrier layer thickness must be minimized while maintaining high performance diffusion barrier properties and good adhesion strength with neighboring layers. Nevertheless, barrier layer formation has become increasingly difficult as the technology node is reduced. An alternative to the conventional barrier process is an organic "self-assembling" system, so-called self-assembled monolayer (SAM). This inherently bottom-up process involves the anchoring of bi-functionalized organic molecules on the inter-layer dielectric (ILD) surface. There are many potential advantages of SAMs vs. metal-based barriers: i) conformality, ii) coverage in high aspect ratio (HAR) structures, iii) selectivity, iv) tailored surface functionalization to control reactivity, v) modulation of line resistance.

The current approaches to Cu metallization include physical vapor deposition (PVD) of the seed layer and filling of the recess by electroplating. Due to the need for applied power and non-uniform current distribution of Cu electroplating, Cu Electro Less Deposition (ELD) is especially emphasized for future interconnect technologies. A conventional ELD approach suffers some shortcomings such as the high price of typical metal catalysts (Pt, Pd…) and possible damage to the electric properties of the Cu film due to the presence of catalyst as a contaminant.

In the work reported here, an alternative bottom-up Cu ELD method without other catalyst material activation was developed by reducing the Cu ions in solution via standard reducing agents, such as dimethylamine borane (DMAB) or formaldehyde (FA). The reaction pH and ionic strength values can be modulated in order to impart to the metallic Cu particle surface an opposite charge with respect to the deposition substrate functionalized by the 3-aminopropyltrimethoxysilane (APTS) self-assembly monolayer (NH_2-SAM) used as diffusion barrier. The Cu particles are stabilized by a typical Cu complexing agent such as citrate, whose concentration can be varied in order to minimize their size. At neutral/basic pH the negatively-charged Cu particles are electrostatically attracted by the positively-charged NH_2-groups and they can form covalent bonds if the required activation energy budget is supplied.

A design of the experiment has been carried on in order to optimize the critical deposition parameters such as temperature, time, Cu ion concentration and pH. The level of incorporated impurities and surface roughness was improved upon performing the ELD at 60 °C, for deposition times less than 1.5 h and for pH values in the range 7 to 8. Furthermore, the optimized concentration of the Cu ions was in the range 0.05 to 0.1 M. The atomic concentrations of the Cu vs. Si background determined by X-ray fluorescence (XRF) measurements for different combination of the reaction parameters are shown in Figure 1. The optimized set of experimental conditions leads to the maximum Cu/Si ratio.

In Figure 2 the film sheet resistance (Rs) is shown in the range of 200-450°C.

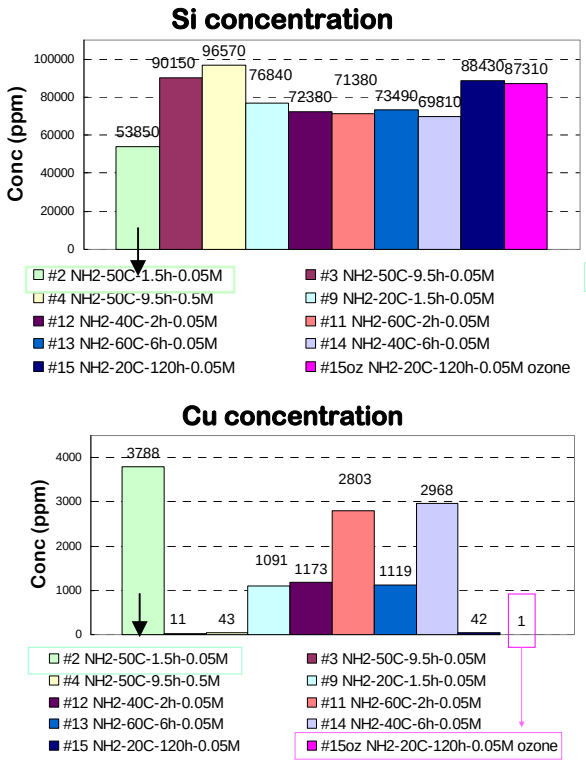

Fig. 1. XRF analysis of Si and Cu atomic concentration after Cu ELD on NH_2-SAM barrier.

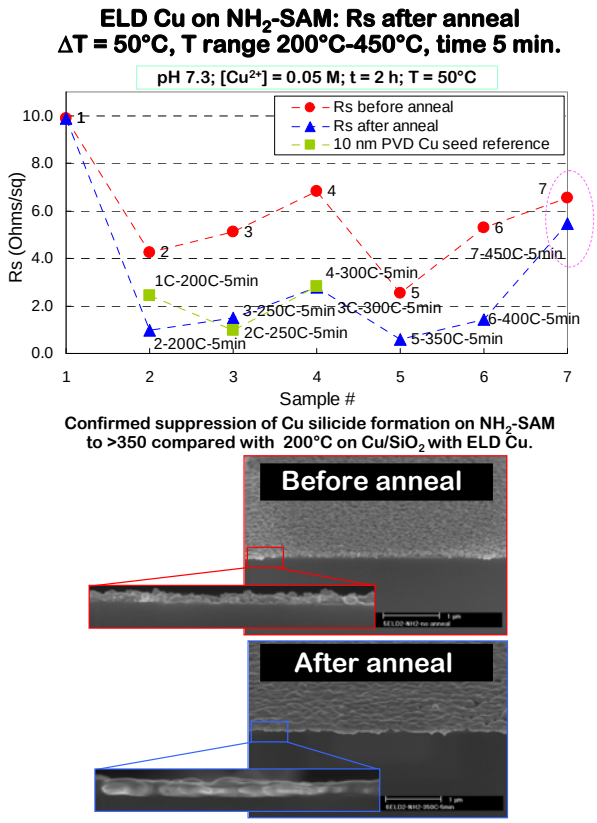

Fig. 2. Rs vs. anneal temperature after Cu ELD on NH_2-SAM barrier. The corresponding data from a blank sample is shown for comparison. The cross-section SEMs show the good barrier properties of the SAM upon annealing.

The initial decrease in Rs upon anneal x-y and the increase observed only when the temperature reaches 450°C, confirm that the Cu silicide formation is suppressed on NH_2-SAM for temperatures higher than 350°C [1].

A conformal ELD Cu layer was deposited on patterned structures (vias and trenches), as evident from the SEM pictures shown in Figure 3. The effect of the deposition time on the Cu ELD on NH_2-SAM barrier in the features is an increase in the Cu layer thickness. Lower roughness and higher adhesion strength are expected upon anneal.

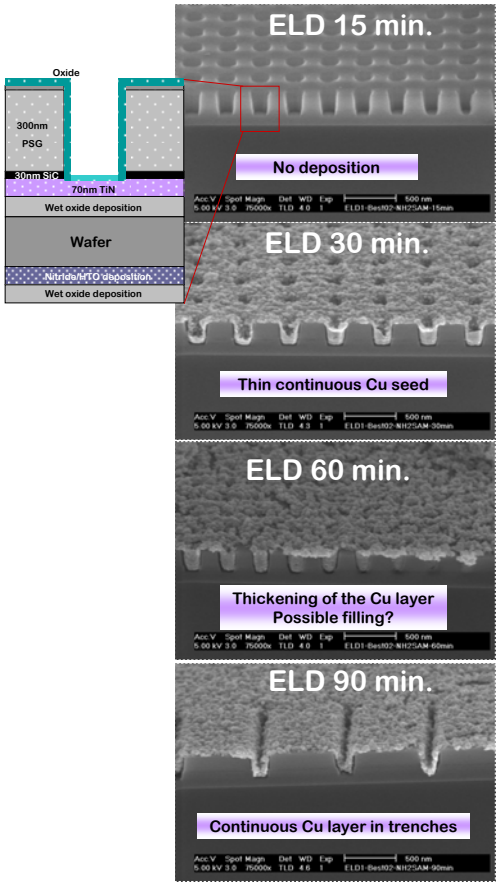

Fig. 3. Effect of the deposition time during Cu ELD on NH_2-SAM barrier in patterns.

References

[1] A. Maestre Caro, G. Borghs, G. Maes, and C. M. Whelan., *Microelectronic Eng.*, in press (2008).