



Electrical properties of sub-100 nm Cu films deposited by electroless plating on amino-terminated silicon oxide activated with Au nano-particles

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ARTICLE INFO

Article history:

Received 26 October 2008

Accepted in revised form 23 August 2009

Available online 1 September 2009

Keywords:

SAM

Electroless deposition

Cu films

Resistivity

Au nano-particles

Surface activation

ABSTRACT

Self-assembled organic monolayers (SAMs) are good coupling agents and diffusion barriers at Cu/SiO₂ and Cu/low-k interfaces and are considered therefore as important elements of future *all-wet* ULSI metallization with sub-45 nm Cu deposited by *electroless plating* (ELD). We formed SAM of 3-aminopropyltrimethoxy silane (APTMS) onto SiO₂/Si substrate, activated the surface of APTMS with 5, 8, 15 and 25 nm Au nano-particles (AuNPs), deposited (30–100) nm films of Cu by ELD and measured electrical resistivity ρ of the films in the as-deposited state and after vacuum annealing at 220°C. The size of AuNPs was found to be a key factor in getting low resistance sub-100 nm Cu films by ELD. The resistivity $\rho \approx 4 \pm 0.8 \mu\Omega \cdot \text{cm}$ – considerably smaller compared to the previously reported data – was achieved with the use of 5 nm AuNPs. XPS and AFM revealed nano-pores, which can contribute to ρ but do not compromise likely the diffusion barrier properties of the SAM.

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1. Introduction

The trend towards increasing functional density in ultra-large scale integrated circuits (ULSIs) cannot be supported by the current technology of copper (Cu) metallization used relatively thick diffusion barrier to prevent Cu transport into dielectric. This fact and weak adhesion between Cu and dielectrics motivates strong interest to *self-assembled organic monomolecular layers* (SAMs) with their “near zero” thickness, tunable surface chemistry and structure. Self-assembled organic monolayers of silanes with –SH, –NH₂ and –C₃H₄N functional groups have been shown to act as excellent coupling agents, ultra-thin diffusion barriers and adhesion enhancers at the Cu/dielectric interfaces [1–9]. SAM barrier properties against Cu diffusion into dielectric have been tested upon annealing from 200°C to 400°C in several works and decomposition of the organic layers has not been reported. More recently, Caro et al. [8] have found that NH₂-SAM derived from 3-aminopropyltrimethoxy silane (APTMS) is the most promising diffusion barrier that prevented Cu diffusion into SiO₂ up to 400°C. That is why SAMs are considered as essential element of future all-wet ULSI metallization with sub-45 nm wide copper interconnects obtained by electroless deposition (ELD) or a combination of ELD and electroplating. Integration of sub-45 nm SAM assisted Cu metallization is impossible without understanding the factors that control the quality of Cu films on SAM/dielectric substrates. In particular, it's

important to understand how the ‘size effect’, which determines electrical resistivity ρ in sub-100 nm films, manifests itself in Cu films deposited by ELD on SAMs and whether continuous sub-45 nm Cu films with $\rho < 3 \mu\Omega \cdot \text{cm}$ can be obtained. It is expected that perfectly ordered, atomically flat SAMs with their tunable surface chemistry and strong covalent bonds formed with Cu can minimize surface- and interface-scattering-controlled resistivity and thus make the ‘size effect’ less pronounced. This can be achieved through surface smoothening, surface ‘cleaning’ [6], and texture improvement. All the desired actions depend on the SAM ω -functionalization, activation of the SAM surface with the catalyst metal prior to ELD, and the ELD conditions. There are some researches on catalyzed [9–11] and non-catalyzed [12–15] ELD of Cu on SAMs but too few investigations are devoted to electrical resistivity of thin Cu films for interconnects obtained by this technique. Recent literature survey [16] shows that methods, which enable formation of low resistivity ELD Cu films of sub-100 nm thickness onto SAM surface, have not been developed yet. In our view, the role of SAM underlayers in resistivity of very thin metal films, in particular Cu, is in its infancy and relations among Cu film resistivity, its microstructure and ELD conditions are still unclear.

The works of C.D. Zangmeister et al. [14,15] present an interesting description of thin Cu films ELD onto SAM *without any activation* by catalyst metal. However, the papers do not contain any information on the electrical properties of the film; moreover, in [14] it is shown that the Cu layer of 170 nm thickness obtained by the proposed technique has a *discrete*, noncontinuous structure, which cannot be tolerated in Cu interconnects of sub-100 nm thickness where low resistivity is the major requirement. Our research is aimed at obtaining *low-resistivity*, sub-100 nm Cu films by ELD on SAM. To reach this goal we activated

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APTMS self-assembling monolayer with Au nano-particles (AuNPs). Surface activation with catalyst metal is the critical stage in ELD of Cu onto dielectrics. Electrical resistivity $\rho \approx 17 \mu\Omega \cdot \text{cm}$ was reported for 40 nm Cu films deposited by ELD onto amino-terminated SAM activated with Pd; after post-deposition vacuum annealing at 200°C the resistivity was found to decrease to $14 \mu\Omega \cdot \text{cm}$ that is still too large for ULSI interconnects [11]. The minimum ρ value that has ever been published is $11 \mu\Omega \cdot \text{cm}$; it was obtained for 70 nm Cu film deposited by electroless plating on SAM [9]. Activation of the SAM surface by mono-dispersed metal Au nano-particles (AuNPs) was proposed in [16]. The (50–100) nm Cu films were deposited from boron- and phosphorus-free bath onto APTMS layer activated with 15 nm AuNPs. The resistivity of 50 nm films after post-deposition annealing at 220°C, 1 h was found to be $\rho \approx 4.5 \mu\Omega \cdot \text{cm}$. This observation looks very promising in getting the interconnect quality Cu on SAMs activated with AuNPs. The major advantage of AuNPs over Pd is the fact that ρ of Au is ≈ 4.5 times smaller; this results in smaller ρ of the “Cu + catalyst metal” films, especially in cases when thickness h of the Cu films becomes comparable to diameter of catalyst particle d . Further reduction d from 25 nm to 15 nm caused considerable increase in surface coverage θ of APTMS by AuNPs and resulted in drop of ρ of the Cu films [17]. The surface coverage is governed by the particle charge (zeta-potential) and the surface charge. C.D. Keating et al. [18] have shown that the main tool allowing the control over NP adsorption kinetics and coverage is colloid pH. Particle charge is predetermined by ionic content of colloidal solution and its pH. NH_2 -terminated surface of the substrate may also acquire charging (positive) due to protonation. Maximum coverage is a result of interplay between the inter-particle repulsion (decreasing coverage) and the particle-to-surface attraction (increasing it).

In the present paper we extended the study of electrical resistivity of sub-100 nm Cu films to smaller film thickness, 30 nm, deposited by ELD onto APTMS activated with AuNPs and achieved further reduction in ρ by the use of smaller, 5 and 8 nm, AuNPs. We studied how the APTMS surface coverage θ by AuNPs depends on the particle size d and used $\theta(d)$ as empirical parameter. It should be noted that discretization of the electron band structure caused by quantum confinement can result in losing the metallicity and catalytic activity only in case of very small AuNPs, several times smaller compared to the minimal ones used in our work [19].

For $h = (30\text{--}100)$ nm, after post-deposition annealing at 220°C, we obtained $\rho \approx 4 \pm 0.8 \mu\Omega \cdot \text{cm}$. These observations show that in this range of h the size effect $\rho(h)$ for the ELD Cu films on APTMS is rather weak, in spite of the fact that h is well comparable to the mean electron free path $l_e \approx 40$ nm in Cu. This suggests that further reduction in ρ can likely be achieved only via reduction in the ‘bulk’ resistivity, which is determined

mainly by the concentration of point defects and nano-pores in the Cu films. We applied AFM and XPS to reveal the defects in Cu/AuNPs/APTMS/ SiO_2/Si structure that can contribute to the bulk resistivity of sub-100 nm films.

2. Experimental details

Preparation of Si/SiO_2 substrate, its silanization with APTMS ($=\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$) resulted in siloxane SAM formation, activation of SAM by immersion of the samples in the aqueous colloid solution of 15 and 25 nm AuNPs, and subsequent ELD of Cu have been described recently in detail in Ref. [16,17]. Monodispersed AuNPs of the size 5 and 8 nm were synthesized by protocol where 0.25 ml of 50 mM solution of HAuCl_4 and 0.125 ml of 0.1 M solution of trisodium citrate dehydrate were added to about 10 ml DI water. Higher concentration of sodium citrate results in smaller NPs. Then the flask was filled with DI water up to 50 ml. After 1–2 min “incubation” 1.25 ml of 0.1 M NaBH_4 (0.19 g freshly dissolved in 50 ml of cooled DI water) was quickly introduced into the flask while vigorously stirred. The mixture was left stirred for 2 h [20]. For 15 and 25 nm AuNPs, citrate-based synthesis at boiling temperature was used; variation in the citrate concentration allows controlling the size of AuNPs [21].

ELD of Cu onto the activated surface was performed at room temperature from tartrate/formaldehyde bath. The average Cu deposition rate was 0.1, 0.13, 0.15 and 0.2 nm/s for the ELD performed with the use of 5, 8, 15 and 25 nm AuNPs, respectively. ELD rate was defined as the thickness of Cu deposit divided by deposition time. Thickness of Cu films was measured by profilometer Alpha-step 500 after etching the step and deposition duration was counted just after the sample immersion into the ELD solution.

Electrical resistivity of Cu films was measured using In-line Four Point Probe (Lucas/Signatone™) with the Dual-Configuration Procedure. For comparison with their ELD counterparts, we measured also the resistivity of Cu films e-beam evaporated on APTMS at vacuum better than 2×10^{-4} Pa. Post deposition annealing was performed in vacuum better than 10^{-5} Pa at 220°C, 4 h and 420°C, 1 h. All the samples were tested for adhesion in Scotch tape peeling test and have successfully passed it. Digital Instruments atomic force microscope (AFM) operating in tapping mode with a High Resolution tip (NANOSENSORS™) having 2 nm radius of curvature was applied for characterization of the surface morphology. To observe the SAM surface coverage by AuNPs, high resolution scanning electron microscopy (HRSEM) (JSM 6700F) was used.

The thickness of APTMS was measured by Woollam M2000 DUV spectroscopic ellipsometer. The ellipsometric data were acquired in

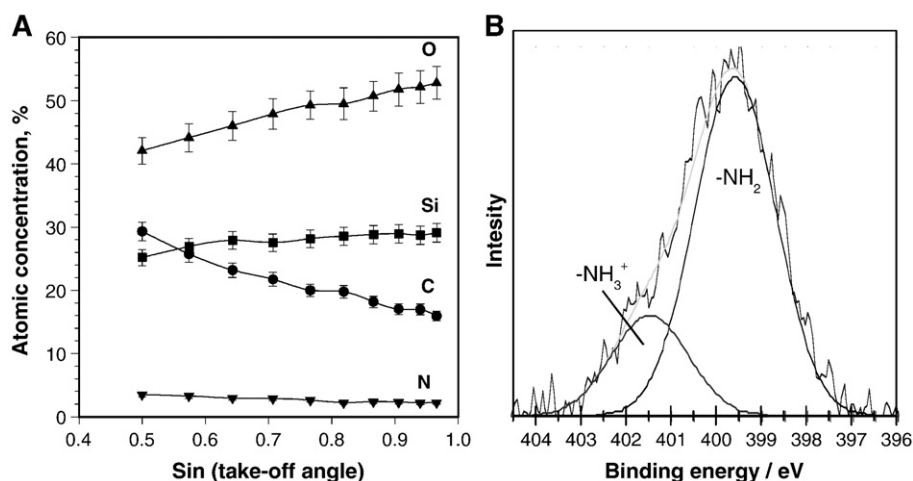


Fig. 1. Angle resolved XPS (A) and high resolution N 1s spectrum (B) for the bare APTMS on SiO_2/Si substrate.

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