Applied Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Ultrathin cobalt-alloyed barrier layers for copper metallization by a new seeding and electroless-deposition process

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ARTICLE INFO

Article history:
Received 27 October 2014
Received in revised form 15 February 2015
Accepted 8 March 2015
Available online xxx

Keywords:
Copper metallization
Electroless deposition
Barrier layer
Agglomeration
Seeding

ABSTRACT

Pioneering activation-seeding processes grow catalytic particles with sizes exceeding 10 nm due to agglomeration, and thus are unable to act as a template for electroless deposition of a barrier layer with a thickness of 10 nm or less, which is desperately needed for the incoming ULSI copper interconnecting technology. In this work, the capacity of a seeding process to grow a continuous Co-P barrier layer of 8-nm thickness on thermally oxidized SiO_2 layers using electroless deposition will be demonstrated. The Co-P barrier layer works effectively in retarding (a) Cu agglomeration and (b) Cu diffusion into the dielectric layer subjected to thermal annealing. Evidently, thermal stability of the Cu film on SiO_2 is markedly strengthened by interposing the 8-nm-thick barrier layer. The mechanism of the interposed barrier layer in enhancing thermal stability of the metallization layer is currently under investigation.

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1. Introduction

Electroless deposition has been integrated into commercialized electroplating tools for almost a decade to directly form (or repair sputter deposited) copper-seeding layers, and recently has received intensive attention due to its potential for the sequential deposition of a nanostructured cobalt-based diffusion barrier and copper wire into sub-100-nm trenches in a conformal and in-line manner [1].

A catalyst, typically palladium, has to be deposited on dielectric layers prior to electroless deposition of the diffusion barrier layer. Conventionally, the catalyst is produced as colloidal particles by either sensitization-activation or displacement-activation in an aqueous chemical solution that contains palladium species [2,3]. However, the palladium particles tend to agglomerate into clusters of sizes typically exceeding tens to hundreds of nm [4,5], and thus are inappropriate to initiate electroless deposition of the copper metallization layer for the sub-60-nm integrated circuits. Obviously, a perquisite for employing electroless deposition to grow a barrier layer with a thickness of less than 10 nm on dielectric layers is to develop a seeding method, which has the capacity to grow catalytic seeds with a size of only a few nm without agglomeration.

We had previously developed a seeding process that grew 3-nm-sized catalytic particles (e.g., Co or Ni) on SiO_2 and HOSP^{TM} dielectric layers [6]. It involved a sequence of wet-processing steps, including chemical-solution surface functionalization and seed-adsorption treatments. A vacuum-plasma surface pre-treatment was late incorporated into the wet-processing steps, dramatically increasing the seed density by a magnitude of over 20 times [7]. The purpose of this work is using the refined seeding process to sequentially initiate electroless deposition of an ultrathin (<10 nm) Co-P barrier and copper metallization layer on the Si/SiO_2 underlying substrates. Enhancement of thermal stability of the metallization layer by interposing the barrier layer will be demonstrated, and the mechanism of the seeding refinement will be investigated by surface-bonding analysis.

2. Experimental procedure

(1 0 0)-oriented, p-type silicon wafers with a 100-nm-thick thermally oxidized SiO_2 layer were used as substrates. First, cobalt catalytic particles were grown on one type of the SiO_2 dielectric layers without surface plasma pre-treatment by the processing steps presently previously [6], referred as the reference samples. Briefly, the dielectric samples were immersed into an ammonia-hydrogen peroxide aqueous solution, the so-called SC-1, to modify the surfaces into a negatively charged state, which had the capacity to attract metallic cations (Co^{2+}) from a metal-salt ($CoSO_4$) aqueous solution. The adsorbed metallic cations were reduced to neutral species (Co) in a reducing agent and used as a catalyst for electroless deposition. Then, the catalyst-bearing dielectric samples were immersed into an electroless-deposition solution (80 °C and pH

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http://dx.doi.org/10.1016/j.apsusc.2015.03.035
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Please cite this article in press as: S.-T. Chen, et al., Ultrathin cobalt-alloyed barrier layers for copper metallization by a new seeding and electroless-deposition process, Appl. Surf. Sci. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.03.035

8.5) to trigger the growth of Co-P deposits; the times of deposition ranged from 10 s to a few minutes.

For another type of the dielectric samples, the as-prepared dielectric layers were pre-treated by N_2/H_2 vacuum plasma at a total pressure of 50 Pa. The change in surface-bonding states was elucidated by X-ray photoelectron spectroscopy (XPS). It is worth noting that the dielectric layers have to be treated by the plasma with a proper N_2/H_2 flow ratio and dosage so that their surfaces are effectively activated to increase the seeding density. The dielectric layers after the plasma pre-treatments were then subjected to the seeding and electroless-deposition treatments using the bath and deposition conditions that were identical to those of the reference samples. Then, the differences in the seeding and progress of the Co-P deposit-plating, ultimately leading to the formation of a continuous Co-P barrier layers, between the two types of the dielectric layers were compared by field-emission scanning electron microscopic (SEM) top-view imaging. Distribution of the seed particles was analyzed by transmission electron microscopy (TEM); thickness of the barrier layers was measured by cross-sectional SEM, reconfirming by a step profilometer (±10% accuracy).

The Co-P barrier layers were then used as catalysts to promote electroless deposition of copper layers using a cupric sulfate-formaldehyde based solution. Thermal stability of the Si/SiO_2/Co-P (8 nm)/Cu (40 nm) sample layers after isothermal annealing (≥400 °C) at argon atmosphere for 30 min, using Si/SiO_2/Cu (40 nm) layered structures as the competing samples, was evaluated by SEM, X-ray diffractometry (XRD), and the changes of overall sheet resistances of the metallization layers.

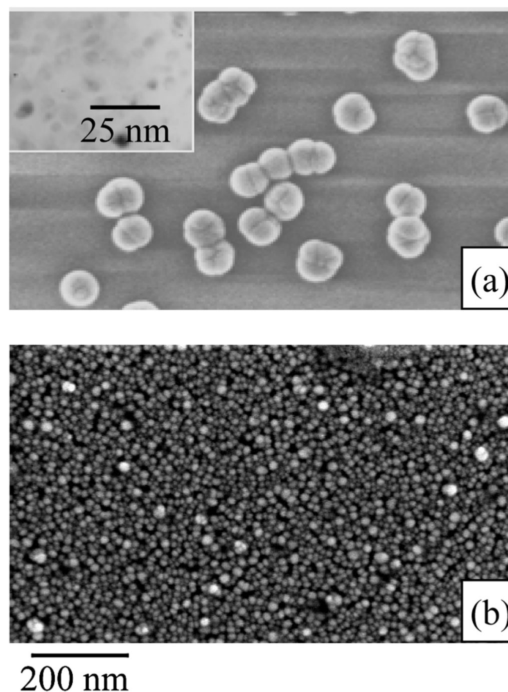

Fig. 1. (a) Top-view SEM micrograph showing the morphology of Co-P deposits on SiO_2 layers without plasma pre-treatment after 10 s of electroless deposition catalyzed by the Co seeds shown in the inserted TEM micrograph; (b) the corresponding Co-P deposits on plasma pre-treated SiO_2 layers.

3. Results and discussion

Plan-view TEM and high-resolution SEM images were used to characterize the distributions and surface morphologies of the seed (Co) particles and Co-P deposits on the two types of the catalyst-bearing SiO_2 dielectric layers. It can be seen from the plan-view TEM micrograph inserted in Fig. 1(a) that the Co seeds, with a tiny size of typically 3 nm, were sparsely dispersed on the reference SiO_2 dielectric layers which were free of the plasma pre-treatment. Importantly, the size of 3 nm obtained herein is yet to be achieved by both the ordinary and other refined activation processes [4,5,8]. The seeds presented in the inset of Fig. 1(a) provided a platform for electroless deposition of Co-P barrier deposits, evolving from equiaxed islands finally into a continuous film structure [6]. However, after electroless deposition for 10 s, the scarcity of the seeds, as observed in the inset of Fig. 1(a), catalyzed a scattering distribution of the Co-P islands with an average size of ~25 nm [see Fig. 1(a)]. It could be referred from the number of the isolated particles in Fig. 1(a) that the density of the catalytic particles was approximately 1.2×10^{14} m^{-2}. Therefore, prolonged deposition for duration greater than 60 s was required for the Co-P islands to coalesce into a continuous barrier layer, whose grain size and thickness were both greater than 40 nm.

Fig. 1(b) displays an SEM micrograph of the Co-P deposits, formed on another type of the catalyst-bearing SiO_2 dielectric layers by electroless deposition for 10 s. Prior to the seeding treatment which was identical to that of the reference SiO_2, the dielectric surfaces were pre-treated optimally by the N_2 (80%)/H_2 (20%) vacuum plasma. This high-magnification SEM micrograph demonstrates that the plasma surface pre-treatment is a key factor for the considerable increase in the seed density to 5.0×10^{15} m^{-2}, as compared to that of the reference samples (1.2×10^{14} m^{-2}); the increment is by more than 40 times. Cross-sectional SEM imaging, as presented later in Fig. 5(b) indicated that the refinement of the seeding process ultimately led to the achievement of a continuous barrier layer with a thickness of 8 nm (±10%).

The N_2/H_2 plasma surface pre-treatment is the crucial experimental step to cause a significant increase of the seed density. To clarify the mechanism of the seeding improvement by the plasma pre-treatment, surface-bonding structures of the SC-1 treated SiO_2 layers without and with the plasma pre-treatments were investigated by examining the oxygen (1s) and nitrogen (1s) XPS core-level spectra. The spectrum (dotted line) in Fig. 2 shows that the reference SiO_2 layers only subjected to the SC-1 solution treatment clearly exhibited a symmetry peak at 533.0 eV which corresponded to the O 1s (O—Si—O) bonds purely from SiO_2 [9]. As expected from the dotted plot inserted in Fig. 2, the N (1s) signals associated with the reference samples were at the background level. The spectrum (solid line) in Fig. 2 presents that the plasma pre-treated SiO_2 layers after the SC-1 solution treatment yielded an asymmetric peak with the tail toward the low-energy side, implying changes in surface bonding structures. The significant chemical shift in the O (1s) peak is due to the breakdown of the O—Si—O intrinsic bonds (533.0 eV) by the N_2/H_2 plasma treatment. Deconvolution of the newly formed asymmetric peak (see the deconvoluted solid lines in Fig. 2) revealed that the surfaces contained

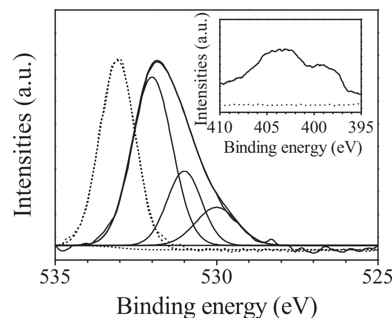

Fig. 2. O 1s and N 1s (insert) XPS spectra for the SiO_2 layers after the solution treatment without (dotted lines) and with (solid lines) the N_2/H_2 plasma pre-treatment.

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