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Reduction of Pd catalytic particle size by a double activation process

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ABSTRACT

We have used a double activation method to reduce the size of Pd catalytic particles commonly used as an activation layer for electroless Cu deposition. The method produces Pd particles with sizes reduced by a factor of 4 and density increased by a factor of 10 compared to the single activation method. The first activation and the Pd etching process in the double activation removes the native Ti oxide on TiN surface and largely increase the nucleation sites for Pd. With more nucleation sites, nucleation events outrun ripening events throughout the deposition time range. However, excessive etching of Pd and the underlying TiN layer could lead to rougher electroless Cu films. Secondary ion mass spectrometry data show that the double activation step does not increase the net amount of Pd deposited on TiN surface; it only changes its particle size and density. Electroless Cu deposited on a doubly Pd activated surface has a larger grain size and appears to have a lower resistivity.

1. Introduction

Electroless (EL) Cu used in microelectronic interconnections is commonly deposited onto substrates previously activated by Pd deposition. The Cu film morphology, grain structure, and surface roughness are dependent on the Pd activation process [1,2] and the nature and distribution of Pd particles [3,4]. Large Pd nuclei lead to rapid localized electroless Cu growth, causing uneven growth over the substrate [1]. Roughness of electroless Cu can be lowered if the density of Pd particles increases and agglomeration of Pd particles is reduced [5]. We have demonstrated previously that optimum roughness in electroless Cu can be obtained with controlled Pd deposition leading to better via filling capability [6]. Furthermore, a rough Cu seed is not desirable because the electric field during Cu electrodeposition tends to be high at the sharp edges of the rough film, leading to rapid plating at those regions. As such, smaller and higher number density of Pd catalyst is required to achieve smoother EL Cu film.

Double zincation methods have been used for decades to achieve small size, high density zinc for electroless Ni deposition [7]. In double zincation, the first layer of zinc formed on the Al surface is removed with nitric acid, followed by a second step of zinc deposition. The small, high density zinc nuclei result in a more uniform EL Ni. We adapted this method for Pd activation in an effort to improve the quality of EL Cu. Here, we report the effect of this double activation method on both the characteristics of the Pd particles as well as the electroless Cu.

2. Experiments

A TiN barrier film of 25 nm thick was deposited by chemical vapor deposition (CVD) on a 500 nm thick plasma enhanced CVD (PECVD) SiO_2/Si (100) substrate. Before the substrate was treated, removal of organic and inorganic contaminants was done with the following solutions: (i) H_2O:H_2O_2: NH_4OH 5:1:1 and (ii) H_2O:HCl:H_2O_2 6:1:1, respectively, at room temperature. The HF involved in RCA cleaning etches away the oxide and allows the Pd to be deposited in-situ. The palladium chloride activation solution (concentration ~0.001 M) was prepared using a recipe proposed by Patterson et al. [1,2]. In our Pd double activation process, we first activate the substrate, remove the Pd with a Pd etchant, and activate the substrate for the second time. The composition of the Pd etchant is shown in Table 1.

Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) profiling was carried out with a ION-TOF system, with a 25 kV, ~2.8 pA Ga beam for analysis and a 3 kV, 60 nA Ar beam for sputtering. Oxygen flooding was used to enhance the intensity of the secondary ions with the chamber pressure at ~5.0×10^{-5} mbar. All data obtained were normalized with the Ga spectrum.

The EL Cu solution consisted of formaldehyde as reductant, ethylenediamine tetraacetic acid as complexing agent and Triton-X (poly(ethylene glycol) mono [p-(1,3,3-tetramethylbutyl)phenyl]ether) as surfactant and wetting agent. Tetra-methyl ammonium hydroxide was used to adjust the pH of the solution to 12.8. The EL Cu deposition was carried out at 62 °C for 8 min.

The root-mean-square (RMS) roughness value of EL Cu film was measured using TappingMode™ atomic force microscopy. X-Ray Diffraction (XRD) patterns were obtained using Shimadzu X-Ray Diffractometer (XRD)-600. XRD data were used to calculate the EL Cu

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Table 1
Composition of Pd etchant

HCl	32 mL/L
HNO_3	320 mL/L
CH_3COOH	320 mL/L

grain size using Scherrer's equation [8]. The Pd nucleus distribution behavior and size were observed using field emission scanning electron microscope (FESEM). The analysis of Pd particle size and density was performed using the UTHSCSA *ImageTool* software. The microstructures were investigated by scanning electron microscope. The thickness of EL Cu film was measured with cross-sectional transmission electron miscroscope (TEM) on JOEL JEM-2010. The sheet resistivity of EL Cu film was measured using the four-point probe method. The resistivity was calculated with the following equation:

$$\rho = R_s \cdot t$$

where R_s is EL Cu film sheet resistance and t is EL Cu film thickness.

3. Results and discussion

3.1. Pd deposition study

FESEM micrographs in Fig. 1(A) and (B) show how the Pd particles are distributed on TiN surface during the process of double activation. Fig. 1 (A) is the sample after the first 1-minute Pd activation showing a small number of Pd particles. After a 30 s Pd etching step, the TiN surface appears to be free of Pd particles in Fig. 1(B). In order to confirm if all the Pd particles were etched away, SIMS depth profiling was carried out and the result is shown below. By comparing the FESEM micrographs of Pd particles deposited on TiN surface by single and double activation methods in Fig. 1(C) and (D), one can see that a larger number and smaller Pd particles are deposited using the double activation method. But, the substrate surface appears to have more etch pits in the double activation case. It is due to the strong Pd etchant used.

Fig. 2 shows the evolution of Pd particle size distribution by double activation method. From 1-min to 3.5-min of second activation time, only partial normal distribution shows in the size distribution curves. As activation time gets longer, full curve of normal distribution shows up. This is due to the limitation of the resolution of FESEM. When the particles are smaller than the resolution, only part of the size distribution can be observed.

From the Pd size distribution curves in Fig. 2, the Pd size distribution peaks increase slowly from 1-min to 3-min of second activation time. After 3 min, the Pd size distribution collapses and the peak slowly shifts towards a bigger size range. This evolution of the size distribution is similar to that of the single activation case reported earlier [9]. This indicates that deposition of Pd on TiN surface will always go through stages of nucleation, growth, and ripening. However, the time frame for each stage to dominate the deposition process depends on the conditions of deposition. For the double activation case, ripening of the Pd particles dominates the nucleation from the deposition time of 3.5 min onwards.

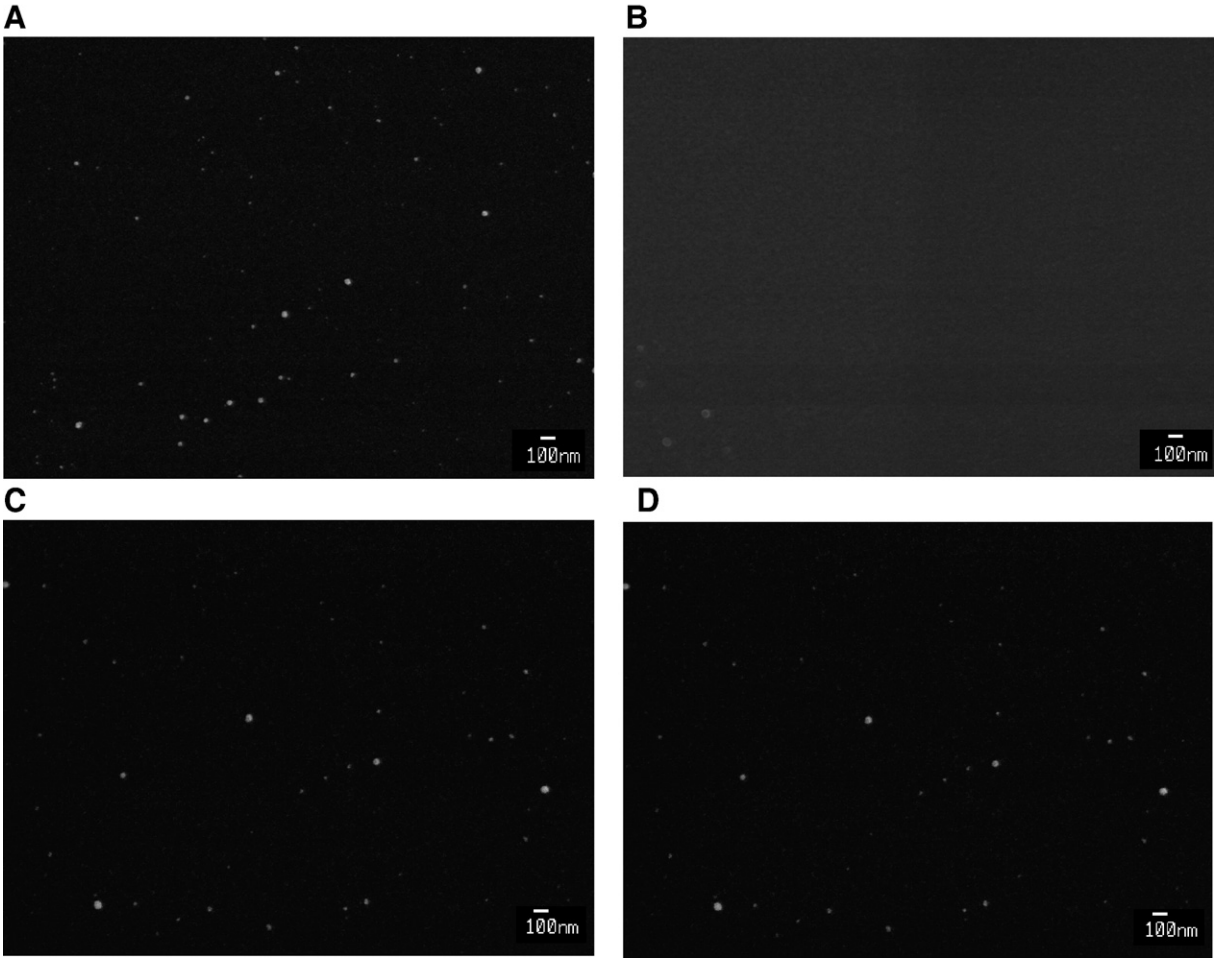

Fig. 1. FESEM micrographs of (A) TiN surface after 1 min of Pd activation and (B) TiN surface after 1 min Pd activation and 30 s Pd etch (C) Pd particles on TiN surface by 3.5 min single activation and (D) 3.5 min double activation.