Ultrasound-Assisted Pd Activation Process for Electroless Silver Plating

Chang-Myeon Lee, Min-Hyung Lee, Jin-Young Hur, Ho-Nyun Lee and Hong-Kee Lee

Abstract—An ultrasound-assisted activation method for electroless silver plating is presented in this study. When the ultrasound was applied during the activation step, the amount of the Pd species adsorbed on substrate surfaces was higher than that of sample pretreated with a conventional activation process without ultrasound irradiation. With this activation method, it was also shown that the adsorbed Pd species with a size of about 5 nm were uniformly distributed on the surfaces, thus a smooth and uniform coating on the surfaces was obtained by subsequent electroless silver plating. The samples after each step were characterized by AFM, XPS, FIB, and SEM.

Keywords—Cavitation, Electroless silver, Pd activation, Ultrasonic

I. INTRODUCTION

ELECTROLESS plating had been used for a long time as an industrial process, and Brenner and Riddell [1] did the first experiments in 1944 during the Second World War. The applications of this technique were found in the field of providing conductive or decorative coating on the surface. Before electroless plating, a palladium (Pd) activation step that introduces the catalytic sites onto the surface has to be preceded. The conventional "two-step" activation process utilizes successively the acid solutions of $SnCl_2$ then $PdCl_2$, while the "one-step" process uses a colloidal mixture of $SnCl_2$ and $PdCl_2$ [2],[3].

According to the previous results, large clusters of Pd species (Pd atom, ion) were absorbed on the surface regardless of any types of Pd activation process mentioned above. Zhu et al. [4] reported that Pd clusters with size scattering from 10 to 200 nm were absorbed on the Si wafer by one-step activation process. Chang et al. [5] showed that Pd clusters with sizes over 10 nm were loosely spread on the two-step activated $Si/SiO_2/Ta_xN$ surfaces. As the width of interconnects for semiconductor devices is decreasing under 30 nm, it is essential to develop the new activation process that can distribute small Pd clusters on the trench for the electroless gap-filling.

Previous works [6],[7] have shown a positive effect of ultrasonic irradiation on coating properties, which can be explained by several mechanisms. The goal of this study is to determine the influence of ultrasound upon the activation step

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before electroless silver (Ag) plating on Si/ SiO_2/Ru wafer and, more precisely, upon the catalysts distribution on the surface. Ultrasound is applied during the activation step at a constant frequency of 40 kHz. Then, the AFM, XPS and QCM measurements were performed to allow a better understanding of the ultrasonic effects.

II. EXPERIMENTAL PROCEDURES

The Si /SiO_2/Ru substrates were first sensitized using an acid $SnCl_2$ solution (0.5 g/l $SnCl_2$, 5 ml/l HCl) with constant agitation for 4 min. at 25 °C. The sensitized substrates were rinsed with de-ionized water subsequently. After cleaning, the Sn^{2+} ion-sensitized samples were then immersed into the activator, which was composed of 1.4×10^{-3}M $PdCl_2$ and 0.25M HCl in order to achieve surface activation. The activation of samples was carried out in 25 °C, and the activated substrates were rinsed with de-ionized water and dried. Activation was performed either with mechanical agitation or with the radiation of ultrasound for 1 min. An ultrasonic wave system (JAC 1505) with a frequency of 40kHz and a export power of 280W was used as the ultrasound source. Afterwards, the activated substrates with Pd catalysts were then electrolessly Ag plated in the solution of silver nitrate ($AgNO_3$), Ammonium hydroxide (NH_4OH) as complexing agent, and some minor surfactant of 2,2'-dipyridyl and SPS with formaldehyde (HCHO, 37%) as a reductant at 60 °C. The two methods used to examine the ultrasound irradiation effect on the electroless plating process are depicted in Fig. 1.

Scanning Electron Microscope (FEI, SIRION-400) was used to examine the surface morphologies after Pd activation process and Ag electroless deposition. 3D morphologies of the Pd activated surfaces were observed with Atomic Force Microscope (PSIA, XE-100). In order to investigate the induction time at the initial stage of electroless Ag plating, QCM measurement was carried out by immersing the sensor in electroless Ag solution. In order to obtain the cross-sectional images of 30 nm trench after Ag gap-filling, samples were milled using FIB (FEI, NOVA-600) system, and then observed by SEM.
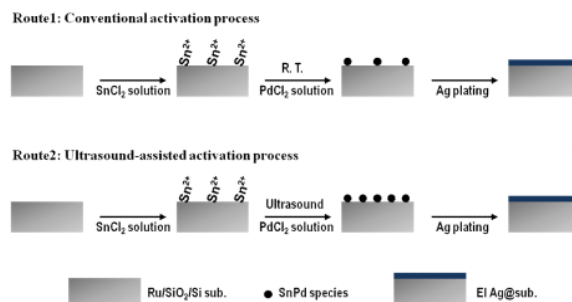

Fig. 1 Schematic diagram of the electroless plating processes using two different activation procedures

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III. RESULTS AND DISCUSSION

Fig. 2 shows the morphologies of the surfaces after activation with different methods as depicted in Fig. 1. It was shown from Fig. 2(a) that large Pd clusters with diameter over 15 nm were absorbed on the surface activated using conventional process. In contrast, when the ultrasound was applied during the activation step, the SEM image of the surface indicated smaller Pd clusters with a diameter of about 5 nm uniformly distributed on the surface. Despite the clear difference in size from the SEM results, it is insufficient to confirm the ultrasonic effect on Pd distribution.
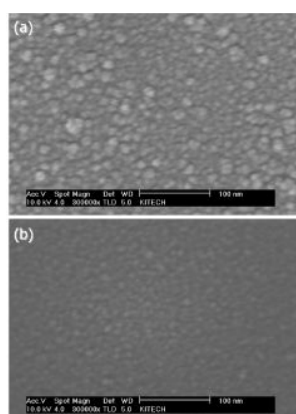

Fig. 2 SEM images of Pd activated substrates: (a) after conventional activation and (b) ultrasound-assisted activation

In order to investigate the effect of ultrasound assisted Pd activation process on the distribution of Pd clusters, AFM analysis was carried out. As shown in Fig. 3(a), large Pd clusters are not uniformly distributed after conventional activation process. On the other hand, when ultrasound assisted activation process was applied, minute Pd particles are distributed thoroughly on the surface.
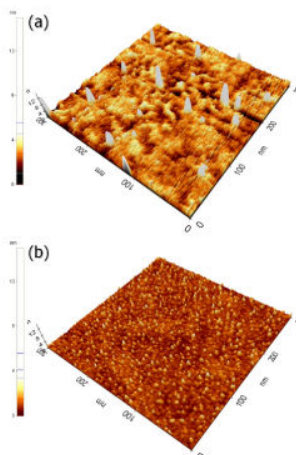

Fig. 3 3D morphologies of activated surface obtained using AFM: (a) after conventional activation and (b) ultrasound-assisted activation

Most of the ultrasonic effects in chemical processes are thought to be due to the cavitation phenomena together with micro-streaming [8]. The ultrasonic irradiation induces mass transfer enhancement throughout cavitation phenomena, which arises near inside surface just as well within the liquid. At the substrate surface, cavitation bubbles imploded in an asymmetric way, so that high speed micro-jets grow in the surface direction, inducing an enhanced mixing of the chemical species and high mass transfer coefficients values. Within the liquid, the cavitation bubbles can be considered as micro-reactors where high local temperature and pressure can be reached. In addition, some contaminant like Sn^{2+} complexes and agglomerated Pd species can be removed from the substrate surface by the ultrasonic agitation. The symmetric collapse of cavitation bubbles at the solid surface induces micro-jets that seem to be well-adapted to surface cleaning. Therefore, ultrasound assisted activation process is considered to be an effective method that can distribute small Pd clusters uniformly on the surface. Table I shows the XPS quantitative analysis of the sample surface from the conventional activation process and that from the ultrasound assisted activation process. When ultrasonic was applied during the activation step, amount of Pd adsorbed on the surface was greater. Therefore, it is confirmed that the ultrasound effectively enhances the Pd adsorption.

TABLE I
SURFACE COMPOSITIONS OF PD ACTIVATED SUBSTRATES.

Procedure	Ru(%)	C(%)	O(%)	Cl(%)	Pd(%)	Sn(%)
Route[1]	64.24	15.48	12.05	0.48	1.21	6.54
Route[2]	61.87	16.12	13.87	0.12	2.95	5.07

%: Atomic percentage
Route1: Conventional Pd activation process
Route2: Ultrasound assisted Pd activation process

In order to investigate the effect of enhanced Pd distribution by ultrasound assisted activation step on the formation of electroless Ag coating, in-situ monitoring of electroless Ag deposition at the initial stage was conducted using quartz crystal microbalance (QCM) measurement. Fig. 4 indicates the thickness (mean thickness of electroless Ag coating) calculated from the frequency change as a function of immersion time in Ag plating solution. This result shows that the incubation time for electroless Ag decreases in the ultrasonic-assisted activation step.
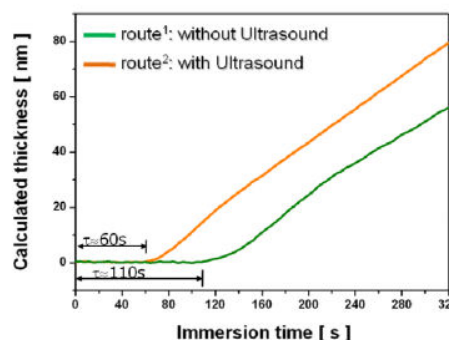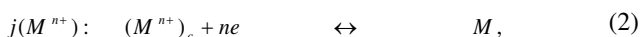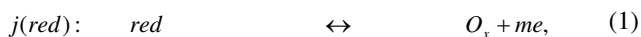

Fig. 4 Mean thickness of electroless Ag coating calculated from the frequency change obtained from Pd activated substrates using quartz crystal microbalance (QCM) method

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At relatively large surfaces, it suffices to consider mass transport and kinetics of two partial reactions, i.e., anodic oxidation of Red (reaction (1)) and cathodic reduction of $(M^{n+})_c$ (reaction (2)). However, when the Pd is isolated, it is necessary to consider O_2 reduction (reaction (3)) as well, since the nonlinear diffusion flux of dissolved O_2 to isolated Pd cluster is much larger than the linear O_2 diffusion flux to large areas [9]. Thus the following current densities (j) of three partial reactions at the surface are considered. The value of the open-circuit potential of the Pd cluster (V_{oc}) determines whether metal deposition occurs. Generally it can be stated that, at t = 0, the surface of the cluster is covered with oxygen species (O, OH). Consequently, the value of V_{oc} will be in the range (+0.7, +0.9V) vs. the reversible hydrogen electrode (RHE). This is indicated by a commonly observed induction time at the beginning of electroless metal deposition. Thus, from $t = 0$ reactions (1) and (3) occur simultaneously at the surface of the nuclei. The competition between these two reactions, i.e., the relative values of j(Red) and j(O_2), will determine whether V_{oc} is shifted to a sufficiently negative value at which metal deposition is initiated. Consequently, when minute Pd particles are uniformly distributed by ultrasound, j(O_2) becomes smaller, so the initiation of the deposition is easier, ensuing in reduced incubation time.

$$j(red): \quad red \quad \leftrightarrow \quad O_x + me, \quad (1)$$

$$j(M^{n+}): \quad (M^{n+})_c + ne \quad \leftrightarrow \quad M, \quad (2)$$

$$j(O_2): \quad O_2 + 2H_2O + 4e \quad \leftrightarrow \quad 4OH^-. \quad (3)$$

Intended to examine the influence of uniformly distributed Pd particles by ultrasound, electroless Ag plating are performed on each sample: one activated with the conventional method, and the other with ultrasonification. After 30 minutes of electroless deposition, two samples are observed using SEM and the results are indicated in Fig. 5. As shown in Fig. 5(a), the sample treated with conventional activation method exhibits rough deposit as Ag is agglomerated. However, the sample activated with ultrasound shows no agglomeration, thus showing smooth deposit.
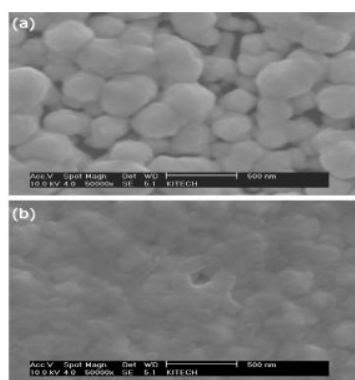

Fig. 5 Surface morphologies of electroless Ag coating on Pd activated surfaces: (a) with conventional activation (b) activation with ultrasound irradiation

Electroless Ag gap-fill is attempted on 30 nm trench prepared by two methods above. The trench samples were prepared by forming oxide layer on the Si pattern wafer with AR 3.5 and width 30 nm, and finally forming 10 nm thick Ru layer using ALD method. Indicated in Fig. 6, the sample using the conventional method reveals irregular deposition due to large Pd clusters, thus resulting void within the trench. Alternatively, gap-fill is successfully performed without void when the sample was activated with ultrasound, because simultaneous deposition was enabled.
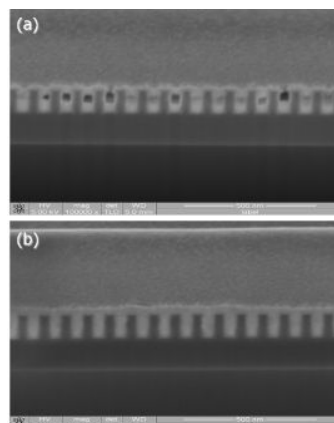

Fig. 6 Cross-sectional SEM images of 30 nm trench after electroless Ag plating: (a) with conventional activation (b) activation with utrasound

IV. CONCLUSION

This study examined how ultrasonification affects the Pd distribution, Ag deposition, and the gap-fill property. According to the SEM and AFM analysis, when ultrasound was implemented, smaller Pd particles are homogeneously distributed. Homogeneous distribution of Pd particles led decrease in induction time during Ag plating and smoother deposition surface. Using the above result 30 nm trench Ag gap-fill becomes successful.

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