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Pendant thiol groups-attached Pd(II) for initiating metal deposition

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Abstract

A new activation method has been developed for initiating electroless metal deposition on silicon substrates without $SnCl_2$ sensitization and roughening condition. Silicon wafers are first coated with thiol-terminated self-assembled monolayers (SAMs), and then catalyzed with a stable tin-free Pd(II)-based colloidal solution. Atomic force microscopy (AFM), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to characterize the step-by-step surfaces and study the binding mechanism of Pd(II) with SAMs onto surfaces. Results show that Pd(II) oligomer particles are chemisorbed on pendant thiol surfaces through S–Pd bonds. This process involves fewer steps than the conventional Sn/Pd combined activation one. Furthermore, the chemical bound initiator possesses longevity and can be stored for a long time before metallization.
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1. Introduction

Electroless metallization is a promising process for fabricating uniform metal coatings on any kind of substrates in the absence of the external electric current, by which metal ions are initially reduced at the surface of a catalytic substrate and auto-catalytic redox reactions continue for further metal deposition [1,2]. Electroless metal plating on non-metallic species requires catalytic activity of the surface to be coated. Typically, the catalytic palladium nuclei are created on the substrate surfaces via stannous chloride sensitization because of the low reactivity of the substrate surfaces [3–6]. Many studies have been focused on combined activation pretreatment of Sn/Pd system, which plays a significant role in palladium laden for initiating metallization of non-metallic species. However, the palladium nuclei formed in this way has poor adhesion to the substrate. Desorption from the substrate and invalidation of Pd catalysts occurs easily if the followed pre-reduction process or ‘‘acceleration’’ step is unsatisfactorily performed. Therefore, it should be freshly pretreated just before the effective metallization. Moreover, before the activation process the surfaces have to be chemically etched and conditioned to offer enough roughness

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to enhance mechanical cohesion between the deposit metal and the substrate.

It is desirable to develop alternative surfaces activation approaches that require less process steps, provide a highly selective, well-defined catalyst adsorption and can be applicable to a wide variety of substrates.

A process for catalysis that eliminates the acceleration step was developed by Jackson via incorporating Pd(II) into the PAA film based on ion-exchange mechanism [7]. Dressick and co-workers recently pioneered a new catalysis approach for EL metal deposition by using organosilane ultrathin films that possess ligating amine groups in conjunction with tin-free, aqueous Pd(II) catalysts [8,9]. The metal–ligand bond has served as an effective mechanism for anchoring Pd(II) catalysts to an appropriate substrate. It offers a high degree of both flexibility and control in the binding of the metal complex catalyst to the functionalized surface. Furthermore, the adhesion of the EL metal deposit can be potentially improved. Consequently, both of chemical etching and acceleration process were omitted. We also developed a similar method to activation of silicon wafers and alumina powders which performed successfully in initiating EL copper plating on them, using an amine-terminated self-assembled monolayers (SAMs) of 3-aminopropyltriethoxysilane (APTS) as the Pd(II) catalyst ligand [10,11].

In this paper, we develop another attractive method for palladium laden via covalently binding catalyst to the surfaces of silicon wafers with thiol-terminated self-assembled monolayers SAMs in the absence of $SnCl_2$ sensitization and former roughening condition. A very stable Sn-free Pd(II) colloidal solution was used as a catalyst precursor, which was prepared via precise control of sequential hydrolysis of Pd(II) species according to the hydrolysis mechanism of Pd(II) salts in a chloride-rich aqueous solution, with the colloidal particle size about 6 nm and lifetime over 9 months.

2. Experimental details

Firstly, the silicon wafers were cleaned and hydroxylated in a freshly prepared piranha solution (H_2SO_4:H_2O_2 = 70:30) at 80 °C for 15 min, and then thoroughly rinsed with deionized water and dried at 105 °C for use. Afterwards, thiol-terminated SAMs were formed on the silicon surfaces by immersing the hydroxylated wafers in a dehydrated toluene solution containing 1×10^{-3} mol/L 3-mercaptopropyltrimethoxysilane MPTS for 6 h at room temperature. After thorough rinse with toluene, acetone and water in turn, the MPTS-coated wafers were activated by dipping them in the chloride-rich Pd(II) colloidal solution for 15 min followed by rinsing with water. Finally, electroless copper deposition was carried out by introducing the activated wafers in the electroless copper plating solution, containing NaOH 12 g/L, $CuSO_4 \cdot 5H_2O$ 13 g/L, $KNaC_4H_4O_6 \cdot 4H_2O$ 29 g/L, HCHO 9.5 ml/L at ambient temperature.

Atomic force microscopy (AFM) images were obtained on a Nanoscope IIIa type atomic force microscope (Digital Instruments, Santa Barbara, CA) in the tapping mode at room temperature. X-ray photoelectron spectra (XPS) and auger electron spectra (AES) were recorded on a Perkin-Elmer PHI-550 multitechnique spectrometer using an Al Kα source. The binding energy scale was calibrated to 285.0 eV for C 1s (C–C) feature.

3. Results and discussion

As is known, organosilane MPTS, commonly used as a silanization reagent, can be quickly chemisorbed onto the surfaces of silicon wafers containing –OH groups via strong covalent bonds of Si–O–Si and can form homogeneous compact ultrathin SAMs (–Si–$CH_2CH_2CH_2$–SH) on the surfaces, with terminated thiol groups outwards. The pendant groups, –SH, are useful in surface modification strategies owing to their diversified reactions [12–16]. For example, owing to its strong affinity to the noble metal such as Au, pendant thiol can be used to capture Au nano-particles in colloidal solutions [15,16]. On the other hand, Pd(II) is noticed to covalently bind to ligands containing nitrogen, sulfur and phosphorous donor atoms [17,18]. Now we use the thiol groups to chemically bind palladium in the Pd(II)-based solution for the EL activation process on silicon wafers.

Fig. 1 shows the AFM images of silicon surfaces after successive exposure to the solutions of MPTS and Pd(II). The image of MPTS-coated silicon wafers in Fig. 1a presents a homogenous chemisorbed layer

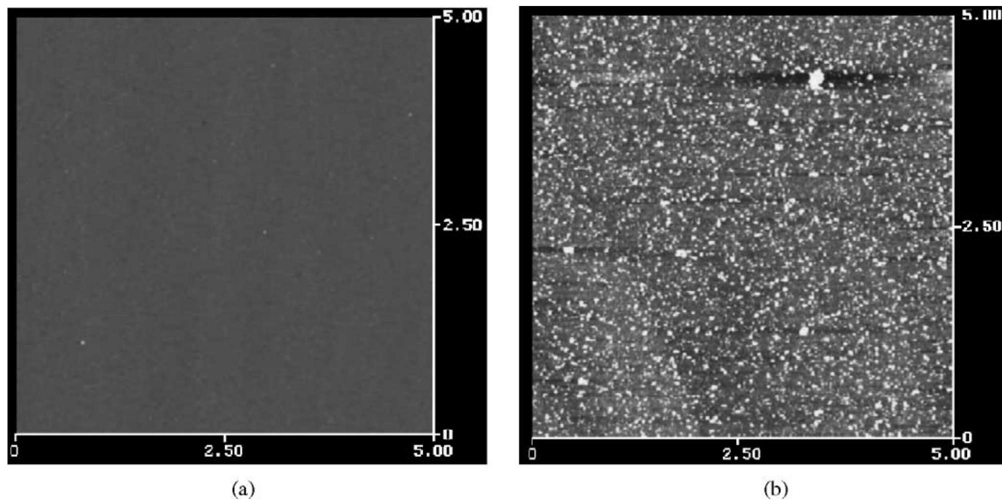

Fig. 1. AFM images (5 μm × 5 μm) of silicon surfaces after exposure to solutions of: (a) MPTS; (b) MPTS + Pd(II), respectively.

with an average surface roughness (Ra) of 0.176 nm over 25 μm^2 area. To confirm the monolayer formation, the thickness of the MPTS films was measured by AES. After 25 s of electron beam bombardment, the S, C and O peaks disappeared and only the peak of Si was left. According to the silica-etching rate of 2 nm/min, the thickness of MPTS films was estimated to be 0.8 nm, close to the length of the MPTS molecule [16]. Therefore, the morphology of the catalyst should be easily distinguishable from that of the SAMs. In fact, Fig. 1b clearly shows that treatment of MPTS-coated wafers with a Pd(II)-based activation solution results in the deposition of particles in the size range from 8 to 25 nm.

The surface element analysis by AES also confirmed the SAMs-assisted chemisorption of chloride-rich Pd(II) species. Compared with Fig. 2a, Fig. 2b presents the powerful evidence that besides Si, S, C and O, the Pd(II)-treated wafer contains Pd and Cl, which are the main components of Pd(II)-based catalytic species, similar to those chemisorbed onto amine-terminated organosilane modified wafers [10].

For comparison, we demonstrated another series of experiments on silicon wafer in the absence of MPTS SAMs modification to study Pd(II) chemisorption. If the wafers were not pre-coated with MPTS SAMs, no deposition of nano-particles was observed by AFM and no peak gains of Pd or Cl were tested after treatment of the cleaned blank wafers with the same Pd(II)-based activation solution followed by thoroughly rinsing with pure water. This suggests that SAMs play a key role in selectively attaching Pd(II) species to the surfaces. A silicon wafer itself can not bind Pd(II) strongly enough to resist the thorough water rinse.

XPS analysis were carried out to study the binding mechanism of Pd(II) to the thiol-terminated SAMs. Fig. 3 shows the S 2p XPS spectra before and after

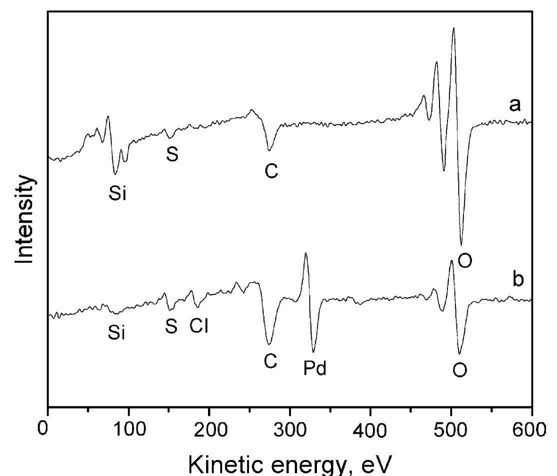

Fig. 2. AES spectra of silicon surfaces after step-by-step exposure to solutions of: (a) MPTS; (b) MPTS + Pd(II); respectively.

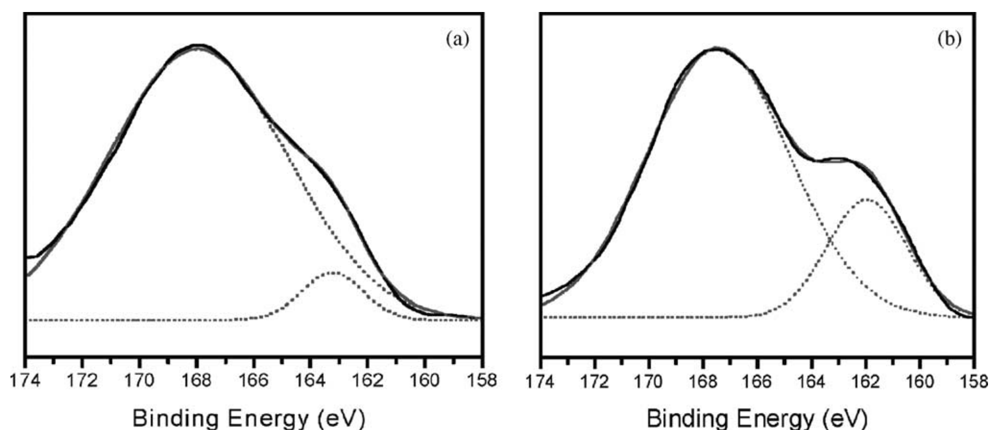

Fig. 3. S 2p XPS spectra of samples: (a) MPTS-coated silicon; (b) MPTS-coated silicon followed by the treatment with a Pd(II) colloidal solution.

dipping the MPTS-coated wafers in the Pd(II) solution. S 2p peaks of both the samples were deconvoluted into two components. The major components near 168 eV correspond to the oxidized sulfur atoms on the substrates surface, comprising 94% and 80% of the total peak area, respectively. The oxidized sulfur species maybe formed under the high-energy X-ray irradiation during XPS measurements [15] and long-term exposure to the air after treatment with solutions. The minor components at lower binding energy of the samples are assigned to low-valent S species which might belong to the original states reserved under X-ray irradiation. The peak at 163.6 eV in the MPTS-coated sample is found to be consistent with the literature value of sulfur in thiol groups of SAMs [16]. And after Pd(II) treatment, it is obvious that the minor component was shifted to 161.9 eV by comparison. The shift to lower energy side indicates the formation of S–Pd covalent bonds. However, the signal content of the minor component estimated from the integrated peak areas was found an increase from 6 to 20% of the total peak area. This confirms the Pd(II) adsorption layer which favors protection of the low-valent sulfur from the air exposure and X-ray irradiation in some way.

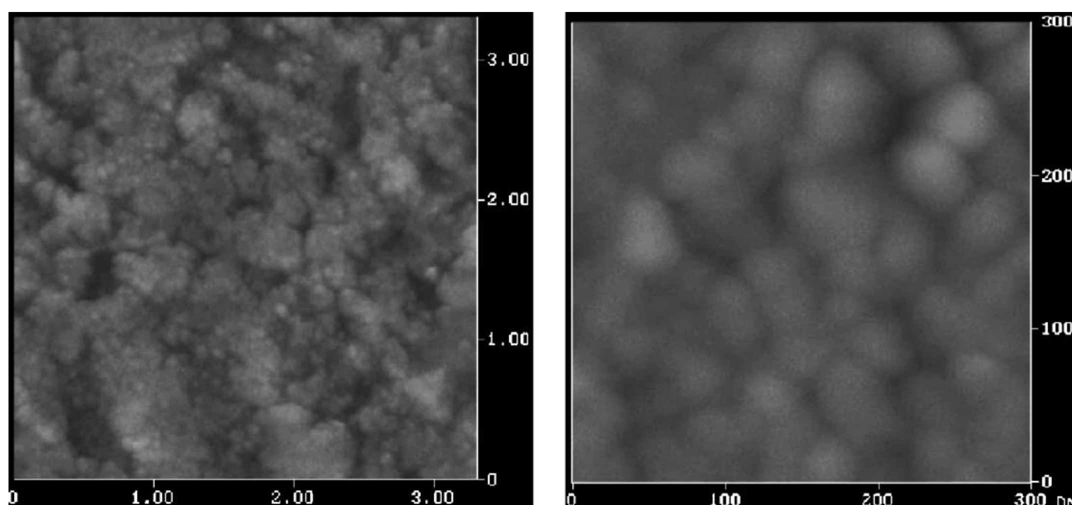

Fig. 4. The AFM images of electroless copper deposit.

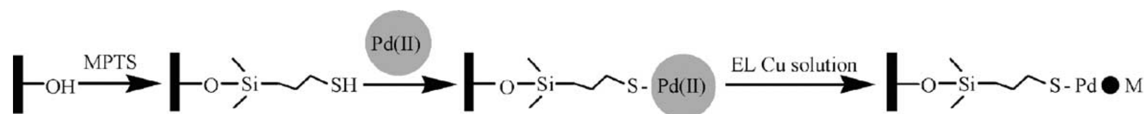

Fig. 5. Scheme of the surface attached Pd catalyst for initiating metal chemical deposition.

Dipping the activated wafers into the EL copper bath resulted in quick copper deposition and autocatalytic redox reactions at the interface between the solid substrate and the liquid solution. Fig. 4 shows the AFM tapping mode images of the copper deposit with the scale bar at 3 μm × 3 μm and 300 nm × 300 nm, respectively. The metal film is homogeneous and pinhole-free, which exhibits copper particles with an average metal particle size of 35 nm and mean roughness about 13 nm over the area range of 9 μm^2. EDXA analysis indicates the film is composed of pure copper. The results suggest that the thiol-attached catalyst ultrathin layer with smaller size and good uniformity makes for inducing good quality metal deposit.

4. Conclusions

Based on the functionalized MPTS SAMs-assisted chemisorption of chloride-rich Pd(II) species, a new approach had been developed for anchoring EL catalyst onto the non-metallic substrate surfaces in the absence of former roughening condition and stannous chloride sensitization. Electroless copper plating was quickly initiated by dipping the activated silicon wafers in the EL bath and the good quality copper deposit was obtained. The proposed chemical steps involved in the surface reactions are outlined in Fig. 5.

AFM, AES and XPS results show that thiol groups of SAMs play a key role in chemical attachment of Pd(II) involving formation of S–Pd covalent bond. This novel surface chemically bound catalysis process affords a means to control surface functionality at molecular level, improve process reproducibility and potentially enhance adhesion of the deposit to the substrates. Compared with the conventional Sn/Pd activation process, this involves fewer steps and notably improves longevity of the initiator. Therefore, it has great significance in the wide applications of electroless metal plating, especially in microelectronics, such as fabrication of microcruits or metal pattern.

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