

Surface-bound nanoparticles for initiating metal deposition

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Abstract

An alternative activation method was developed via binding electroless catalysts onto silicon substrates with 3-aminopropyltriethoxysilane (APTS) self-assembled monolayers (SAMs). Atomic force microscopy, Auger electron spectroscopy and X-ray photoelectron spectroscopy were used to characterize the laden of tin-free Pd(II)-based nanoparticles on silicon surfaces. The results indicate that the formation of coordination bonds between Pd ions and nitrogen atoms of APTS SAMs serves the important binding mechanism. Electroless copper deposition was successfully initiated by the catalyzed substrates and high quality Cu deposition was obtained. Owing to the chemically bound catalyst, this approach has advantages over the conventional Sn–Pd combined activation process, including reduced steps and improved longevity of initiator and enhanced adhesion of the deposition to the substrates.

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1. Introduction

Catalytic sites should be created on the surface for initiating electroless plating on non-metallic species [1]. Typically, the catalytic palladium nuclei are obtained on the substrate surfaces via stannous chloride sensitization due to the low reactivity of the substrate surfaces [2–6]. The Sn–Pd combined activation process plays a significant role in initiating electroless metallization on any kind of non-metallic species. However, it has some drawbacks. Firstly, it requires multifarious steps. Previously, the surfaces have to be chemically roughened to enhance mechanical cohesion between the deposited metal and the substrate. A pre-reduction step or an ‘acceleration’ step is also needed after the activation process. Secondly, the palladium nuclei itself formed in this way has poor adhesion to the substrate because of the absence of chemical conjunction between palladium catalysts and substrates. Desorption of the catalysts from the substrate may cause failure in initiating uniform

metal deposition or result in decomposition of the concerned electroless plating solution. Thirdly, the metallic palladium initiator is unstable and easily oxidized in the air. Therefore, the substrates need to be freshly pretreated just before effective metallization. Finally, adsorption of the catalysts onto surfaces is non-specific, which is not in favor of well-defined metallization.

Pd(II) is noticed to chemically bind ligands containing nitrogen, sulfur and phosphorous donor atoms [7,8]. Recently a new catalysis approach was pioneered for electroless metal deposition by using organosilane ultrathin films that possess ligating amine groups in conjunction with tin-free, aqueous Pd(II) catalysts [9,10]. The organosilanes mainly applied were 2-(trimethoxysilyl)ethyl-2-pyridine, (aminoethylaminomethyl)-phenethyltrimethoxysilane, *N*-(2-aminoethyl)-3-amino propyltrimethoxysilane, phenethyltrichlorosilane and 4-chloromethylphenylsiloxane. 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 controllability in the binding of the metal complex catalyst to the function-

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alized surface. Furthermore, it can potentially control the adhesion of the electroless metal deposition by improved control of the interfacial chemistry. Consequently, both chemical etching and acceleration process were omitted.

We developed a similar activation method with an amine-terminated molecule of 3-aminopropyltriethoxysilane (APTS) as the Pd(II)-based catalyst ligand [11], which performed well in initiating electroless copper plating on non-metallic species. Organosilane APTS is well known to be quickly chemisorbed onto the surfaces of silicon wafers containing $-OH$ groups via strong covalent bonds of $Si-O-Si$. It forms homogeneous compact ultrathin self-assembled monolayers (SAMs), with terminated amine groups pendant from the surfaces, which are useful in surface modification strategies due to their diversified reactions [12,13].

In this paper, we pay more attention to the study of palladium laden on silicon wafers with APTS SAMs by atomic force microscopy (AFM), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). A catalyst precursor, chloro-/hydroxo-bridged Sn-free Pd(II) colloid, was prepared via precise control of sequential hydrolysis of Pd(II) species in a chloride-rich aqueous solution according to the hydrolysis theory of transition metal ions and the hydrolysis model of Pd(II) [14,15]. The colloidal particle size is approximately 6 nm observed by TEM and its lifetime is at least 9 months.

2. Experimental details

Firstly, the silicon wafers were pretreated with a freshly prepared piranha solution ($H_2SO_4/H_2O_2=70:30$, v/v) at $80^\circ C$ for 15 min, then thoroughly rinsed with deionized water and dried by nitrogen flow for use. Amine-terminated SAMs were formed on silicon surfaces by immersing the hydroxylated wafers in an alcohol solution containing 1×10^{-3} mol/l APTS for 40 min at room temperature. After thorough rinsing with alcohol and water in turn, the APTS-coated wafers were activated by dipping them in the chloride-rich Pd(II) colloidal solution for 15 min and rinsed with water. Finally, electroless copper deposition was carried out by introducing the activated wafers into 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.

AFM characterization was performed with a Nanoscope IIIa type atomic force microscope (Digital Instruments, Santa Barbara, CA) in the tapping mode at room temperature. The typical conditions of the tapping mode AFM were as following. The scan speed was 1.489 Hz. The integral gain and the proportional gain were 0.2536 and 2.321, respectively. The tip driving frequency was 266.673 kHz and the engagement ratio was 0.723. AES

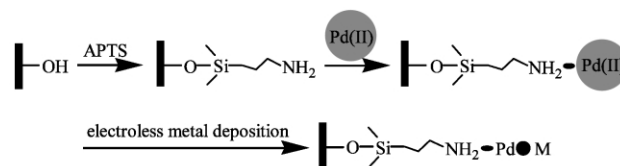


Fig. 1. Scheme for electroless metal deposition initiated by the surface-bound catalysts.

and XPS spectra were recorded on a Perkin–Elmer PHI-550 multi-technique spectrometer using an Al $K\alpha$ source. The binding energy scale was calibrated to 285.0 eV for C 1s (C–C) feature.

The proposed chemical steps involved in the surface reactions are outlined in Fig. 1.

3. Results and discussion

Fig. 2 shows the AFM images of silicon surfaces after step-by-step exposure to the solutions of APTS and Pd(II) colloid. Fig. 2a indicates that a homogenous ultrathin layer was coated on the APTS-treated silicon wafers, with an mean square roughness (RMS) of 0.048 nm over a $0.25 \mu m^2$ area. Therefore, the morphology of the catalyst should be easily distinguishable from that of the SAMs. AFM images in Fig. 2b clearly shows that treatment of APTS coated wafers with a Pd(II) based activation colloidal solution results in the deposition of particles. The particles size is approximately 12 nm, larger than that observed by TEM. There are two reasons for this large broadening of the AFM images. One reason can be expounded by the defects of AFM itself [16]. As was expected, there was some broadening due to the finite size of the AFM tip. Besides, smaller particles might be undercounted by AFM due to the movement of small material by the AFM tip and/or below the detection limit of AFM in the presence of much larger particles. Another probable reason is that the original chemistry equilibrium of the colloidal solution was broken by the quick surface adsorption reaction involving recombination of Pd(II) bonds. Surface attached basic amine groups may cause subsequent hydrolysis of the attached Pd(II) colloid at the interface and tend to form larger particles.

The surface element analysis by AES confirmed the chemisorption of chloride-rich Pd(II) species in assistant with APTS SAMs. Compared with Fig. 3a,b presents the powerful evidence that the Pd(II)-treated wafer gains elements of Pd and Cl, which are the main components of Pd(II)-based catalytic species.

For comparison, we demonstrated another series of experiments on silicon wafers without APTS SAMs to study the chemisorption of chloride-rich Pd(II)-based catalysts. No deposition of nanoparticles was observed by AFM and no peak gains of Pd and Cl were tested

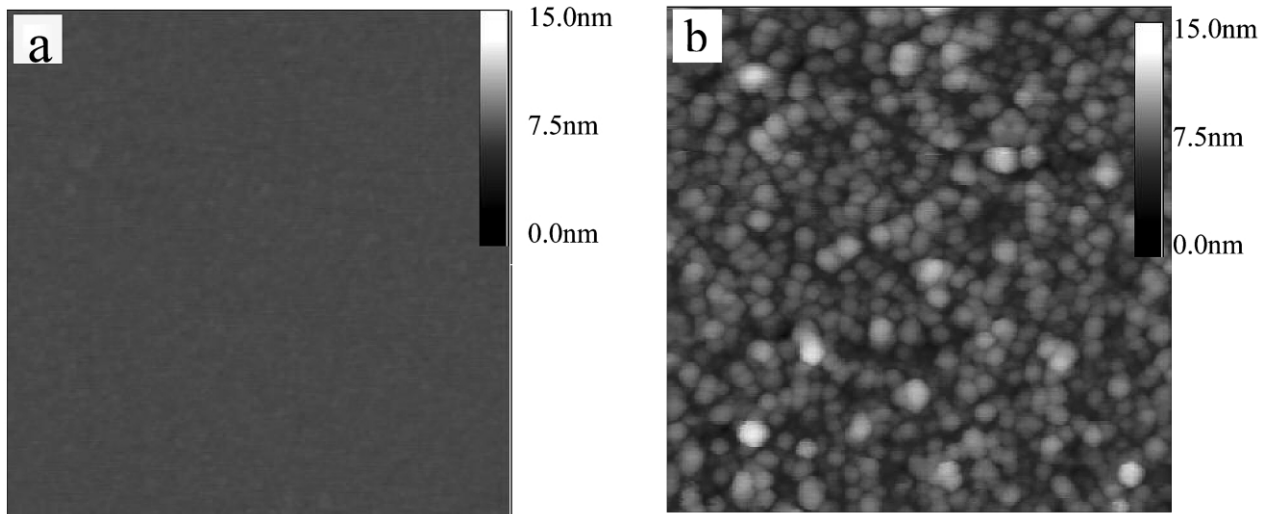


Fig. 2. AFM images (500×500 nm) of silicon surfaces after step-by-step exposure to solutions of: (a) APTS; (b) APTS + Pd(II). The maximum z and the RMS value in Fig. 2a were 0.794 and 0.048 nm, respectively; In Fig. 2b, these values were measured to be 9.227 and 1.044 nm.

after treatment of the cleaned blank wafers with the same Pd(II) based activation solution and pure water. Its morphology and surface component elements hardly showed any difference with the cleaned blank wafers. This suggests that the laden of Pd(II) catalysts on silicon surfaces is not a simple physisorptive process. SAMs actually play a key role in selectively anchoring Pd(II) species to the surfaces.

The binding mechanism of Pd(II) to the amine-terminated SAMs was further studied by XPS. Fig. 4 shows the N1s XPS spectra before and after dipping the APTS coated wafers in the Pd(II) solution. By comparison, it is obvious that the N 1s peak was shifted to higher binding energy position after Pd(II) treatment. The positive shift indicates the decrease of electron

cloud density around N atoms, which suggests forming chemical bonds between Pd ions and N atoms of APTS SAMs. As is well known, the amine group is a strong electron donor and possesses great ligand capability to transition metal ions due to lone pair electrons of nitrogen atom. On the other hand, Pd(II), as a soft metal ion, whose outermost electron is configured as $4d^8 5s^0 5p^0$, possesses empty lower energy orbit for accepting electron. Its coordinary chemistry is satisfactory for forming stronger bonds with nitrogen than those with oxygen and chloride [17]. For example, H_2O molecules in the $[Pd(H_2O)_4]^{2+}$ can be favorably replaced by amine ligands, forming complexes with

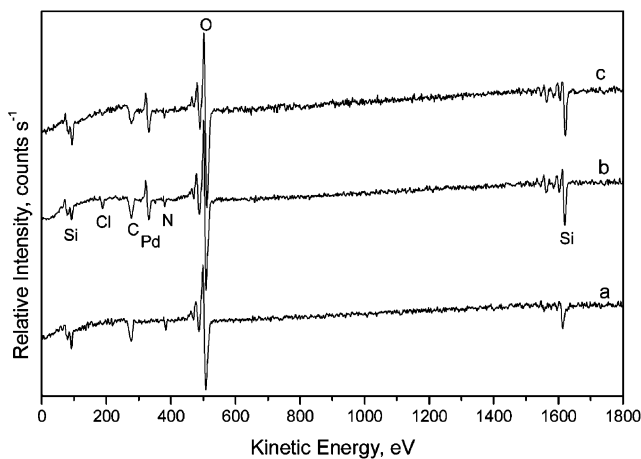


Fig. 3. AES spectra of silicon surfaces after step-by-step exposure to solutions of: (a) APTS; (b) APTS + Pd(II); (c) APTS + Pd(II) + HCHO.

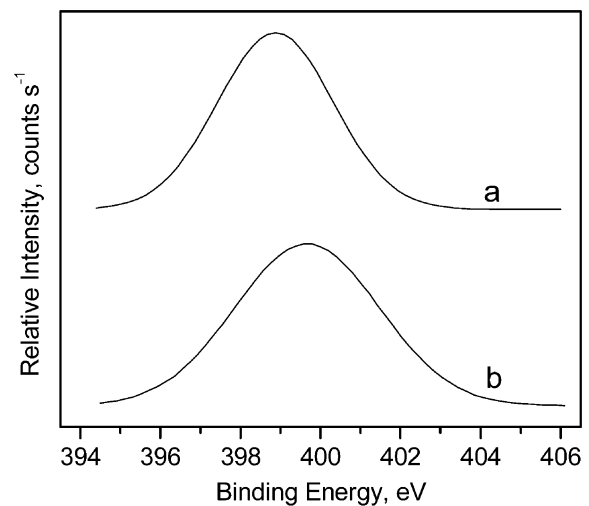


Fig. 4. N1s XPS spectra of samples: (a) APTS coated silicon; (b) APTS coated silicon followed by the treatment with a Pd(II) colloidal solution.

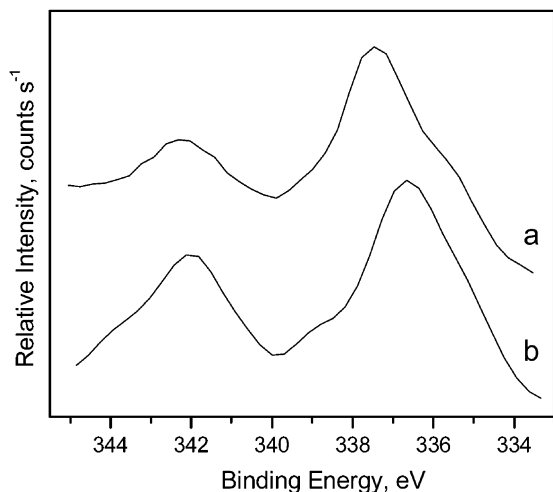


Fig. 5. XPS spectra of Pd 3d spinorbit doublet of samples before (a) and after (b) reduction with formaldehyde.

stability constants too high to be determined by direct conventional methods in many cases. Consequently, chloride and hydroxy groups, ligating with Pd(II) colloid in aqueous solution could be easily replaced by amine groups pendant from surfaces. Relative theoretical consideration along with XPS results strongly suggests that there involves the formation of N–Pd coordination bonds.

Based on the analysis above, it is clear that the particles are attached to the substrates as Pd(II) species. However, it is Pd(0) that functions as the actual electroless catalyst. One possible reason is that lower valent Pd species were quickly formed after the activated wafers were dipped into the electroless copper bath. In order to confirm the deduction, Pd(II)-bound surfaces were treated with a diluted formaldehyde aqueous solution, which acted as a reducing agent in the electroless bath, for 1 min, and then rinsed with water and dried by nitrogen flow for characterization. AES analysis confirms distinct decrease of Cl element compared Fig. 3c with Fig. 3b, indicating that reduction of Pd(II) was achieved by formaldehyde. Pd 3d XPS spectra further provide powerful evidence for the formation of low-valent Pd species after exposure to the reducing agent. Both the Pd 3d signals appear as a spinorbit doublet in Fig. 5. Fig. 5a clearly shows the characteristic of chloride-rich Pd(II) species, with a lower Pd 3d_{5/2} peak at 337.3 eV. While in Fig. 5b, the Pd 3d peak is obviously shifted to the lower energy side. However, its main component has higher binding energy than that of Pd(0), which suggests there exists newly formed Pd–O bonds in addition to the residual N–Pd coordination bonds and chloro-/hydroxyl bridged bonds with palladium which was not completely reduced. Pd–O bond signal is probably assigned to PdO, the re-oxidized product of active Pd(0) by both exposure to the air and

the high-energy photoelectron bombardment during XPS measurement.

After the activated wafers were dipped into the electroless copper bath, electroless copper deposition was quickly initiated at the interface between the solid substrate and the liquid solution in seconds. Fig. 6 shows the AFM tapping mode images of the copper deposition. The metal film is homogeneous and pinhole-free, with the copper particle size approximately 30 nm and RMS approximately 2.975 nm over the area range of 0.25 μm^2 . The results suggest that the surface-bound catalytic ultrathin layer makes for inducing high quality metal deposition.

4. Conclusions

A convenient approach was developed for anchoring Pd-based electroless catalysts onto the silicon substrate with functionalized APTS SAMs. It avoids former roughening condition and stannous chlorate sensitization. Electroless copper plating was quickly initiated by dipping the activated silicon wafers in the electroless bath and high quality copper deposition was obtained. AFM, AES and XPS were used to study the binding mechanism of Pd(II) with SAMs onto surfaces. The results indicate that there involves the formation of N–Pd coordination bonds. Consequently, this process has many advantages over the conventional Sn–Pd combined one, such as reduced steps and increased longevity of the activated initiator and improved adhesion of metal deposition to substrates. This well-defined catalyst attachment mechanism can be extended to other substrates with hydroxylated surfaces. It has great signifi-

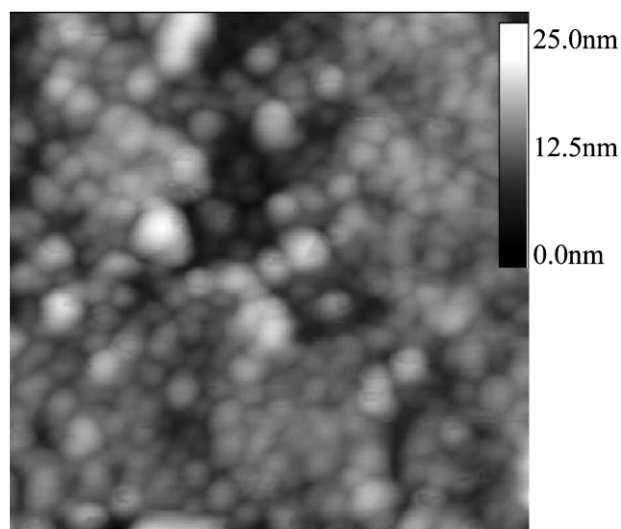


Fig. 6. AFM image (500 \times 500 nm) of electroless copper deposition. The maximum z and the RMS value were 22.473 and 2.975 nm, respectively.

cance in the fields of electroless metal plating, microelectronics and metallic circuit fabrication.

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