

Comparative study of electrolessly deposited Pd/Ag films onto p-silicon (100)-activated seed layers of Ag and Pd

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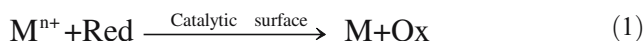
Abstract Pd/Ag films were electrolessly deposited onto p-silicon (100)-activated seed layers of Ag and Pd, respectively, in the solution of $0.005 \text{ mol l}^{-1} \text{ AgNO}_3 + 0.005 \text{ mol l}^{-1} \text{ PdCl}_2 + 4.5 \text{ mol l}^{-1} \text{ NH}_3 + 0.16 \text{ mol l}^{-1} \text{ Na}_2\text{EDTA} + 0.1 \text{ mol l}^{-1} \text{ NH}_2\text{NH}_2$ (pH 10.5) at room temperature. The morphology and composition of the films were studied comparatively by using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Cathodic polarization curves for hydrogen evolution were recorded in $0.5\text{-mol l}^{-1} \text{ H}_2\text{SO}_4$ without illumination, in which the obtained films served as working electrodes. The experimental results show that the film obtained on the Ag seed layer was rather a pure Ag film and not a Pd/Ag film, and the Ag deposition rate on Pd sites was much faster than that on Ag sites.

Keywords Electroless · Deposition · Silicon-seed · Hydrogen evolution

Introduction

Electroless deposition (ELD) technology is promising and attractive for fabricating uniform metal coatings on any kind of substrates in the absence of the external electric current. The technology is simple in operation, low cost in equipment, and allows mass production in many suitable cases [1–5]. The technology is also used to produce multicomponent films with fine quality.

The basic principle of ELD based on the mixed-potential theory could be employed in electroless co-deposition of two or more metals, although the system involving multiple reactions is much more complicated. From the electrochemical point of view, the ELD process can be considered as simultaneous reactions of cathodic metal deposition and anodic oxidation of reductants. The overall reaction for ELD of a metal with a reducing agent from an aqueous metal complex solution can be expressed as:



Therefore, it is necessary to initiate ELD on the entire surface simultaneously upon immersion in the plating solution and, thus, obtain a uniform and adherent metal plate, activation of the surface. Particularly on a semiconductor surface, which is polished, ELD is difficult without the activation step. Activation is acquired by depositing small amounts of metal particles, which are called seeds. Typically, palladium and silver are used as seed elements. Several activation techniques exist, namely, ion implantation [6], laser-assisted decomposition of spin-coated metallorganic films [7], and either photo-aided or simple immersion from a solution. Of these, the immersion plating without illumination is the simplest activation procedure [8–11].

For electroless co-deposition of Pd and Ag on Ag and Pd sites, respectively, Chen et al. [12] simulated the deposition behaviors of Ag and Pd with I–V measurement, but they did not depict clearly the differences of the morphology and composition between the films deposited on the Ag and the Pd sites. In the present work, we attempt to compare the catalytic activation of between Ag and Pd. The Ag and Pd activation surfaces were obtained before electroless co-deposition. To ensure the morphology and elemental composition of the films, atomic force microscopy

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(AFM), X-ray photoelectron spectroscopy (XPS), and cathodic polarization for hydrogen evolution were employed.

Experimental

Instrumentation

An AFM (AFM Explore, Veeco, USA) in contact mode and a PHI-5702 multifunctional XPS (USA) were used; the instrument was calibrated by the measurement of the XPS spectrum of $C1s$ at 284.6 eV binding energy with a $Mg_{K\alpha}$ excitation source; the accuracy of band-energy measurements is ± 0.3 eV).

A CHI-614A electrochemical workstation (made in Shanghai, China) was used for cathodic polarization. A 40-ml homemade electrochemical Teflon cell was used in a three-electrode configuration [13]. The silicon wafer served as the working electrode with a disc area of 0.071 cm^2 , which was mounted to a small hole at the bottom of the cell. A platinum wire was the counter electrode, and the reference was a saturated calomel electrode (SCE). They were dipped directly into the electrolyte.

Chemicals and materials

A 0.1000-mol l^{-1} $AgNO_3$ stock solution was prepared by dissolving 4.2470 g $AgNO_3$ in 250 ml water in a brown flask. The $PdCl_2$ stock solution was obtained by dissolving 1.000 g $PdCl_2$ powder in 250 ml 0.2-M HCl solution in a flask. The chemicals NH_4OH (61%), HCl (36%), H_2O_2 (31%), HF (40%), H_2SO_4 , NH_2NH_2 (80%), NH_4F , and Na_2EDTA were used. Milli-Q water ($Millipore$, $18.2\text{ M}\Omega\text{ cm}^{-1}$) was used throughout. Nitrogen was purged for solution deaeration. A p-type silicon (100) wafer with a resistivity of $15\text{--}20\ \Omega\text{ cm}$ and a thickness of $650\pm 25\ \mu\text{m}$ (Beijing Youyan silicon villa semiconductor) was used. The dopant of the wafer is B (boron), and the doping level is $5 \times 10^{15}\text{ cm}^{-3}$.

Wafer treatment

The silicon wafer was cut into square samples, each with a surface area of 1 cm^2 . The wafers were firstly cleaned in an ultrasonic cleaner in absolute alcohol for 10 min, then immersed in a hot ($80\text{ }^\circ\text{C}$) solution of $H_2O_2/NH_4OH/H_2O$ (1:1:5) for 10 min and, next, in another hot ($80\text{ }^\circ\text{C}$) solution of $H_2O_2/HCl/H_2O$ (1:1:6) for 10 min to remove possible contaminants. Finally, they were etched in a solution of 10 ml HF (40%)+100 ml NH_4F (40 g NH_4F in 100 ml H_2O) for 2 min at room temperature to remove the silicon native oxide. The wafers were rinsed with water and dried with dry nitrogen flux after each cleaning step.

Preparation of the seed layers of Pd and Ag

The Ag (Ag activation) and Pd (Pd activation) seed layers were obtained by immersing the etched silicon wafer into the solutions of 0.005 mol l^{-1} $AgNO_3+0.06\text{ mol l}^{-1}$ HF and 0.005 mol l^{-1} $PdCl_2+0.12\text{ mol l}^{-1}$ HF for 5 s at room temperature, respectively.

ELD of the Pd/Ag films

The films were prepared on the seed layers of Pd and Ag, respectively, for 180 s at room temperature. The host solution was 0.005 mol l^{-1} $AgNO_3+0.005\text{ mol l}^{-1}$ $PdCl_2$ with 0.1 mol l^{-1} NH_2NH_2 . At the same time, 0.16 mol l^{-1} Na_2EDTA and 4.5 mol l^{-1} NH_3 were added to complex silver and palladium ions. Then, the films were rinsed with water and dried with dry nitrogen flux to do the measurements of AFM and XPS.

Characterization of cathodic polarization

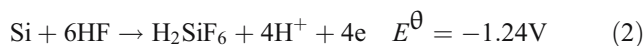
The as-prepared samples were mounted to the cell. As the electrolyte solution of 0.5 mol l^{-1} H_2SO_4 was added and was ensured that there were no bubbles on the surface of the wafer, cathodic polarization curves were recorded without illumination until reproducible signals were obtained. The scan rate was 20 mV s^{-1} .

Results and discussion

AFM characterization of the Ag and Pd seed layers

Figure 1a shows the 3D AFM images of the etched silicon surface taken before the seed layer deposition of Ag and Pd. It can be seen that the silicon itself is flat so that the AFM signal was almost at noise level. Because the wafer underwent an initial oxide removal etching in the solution of 10 ml HF (40%)+100 ml NH_4F , the images present the surfaces of a hydrogen-terminated silicon substrate [14].

The silicon surfaces were covered with small Ag (Fig. 1b) and Pd (Fig. 1c) particles that had a large variety of cluster sizes, indicating gradual nucleation. This is because the growth of nuclei on the silicon wafer and the displacement reaction are unbalanced. According to the mechanism for the displacement reaction [9, 15] under the condition of HF, the deposition of silver and palladium particles occurred by the following reaction of silicon oxidation. All potentials refer to the standard hydrogen electrode (SHE).



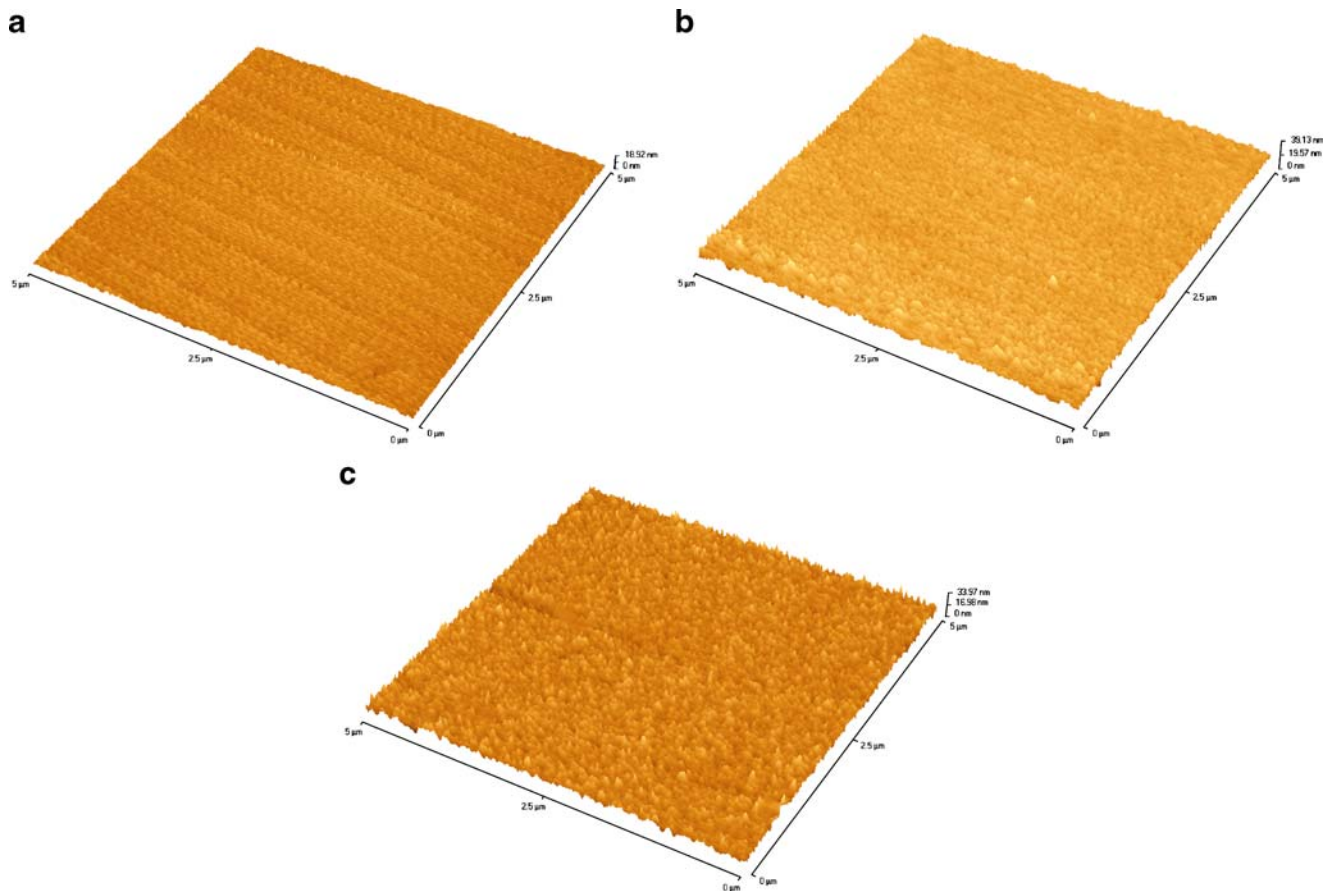
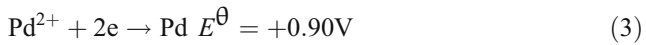


Fig. 1 3D AFM images for the etched silicon (a), the seed layers of Ag (b), and Pd (c)

The formation of the Pd and Ag seeds can be described by the following reduction reactions in which the electrons are offered by reaction 2:



ELD of Pd/Ag films on the seed layers of Ag and Pd

The 3D AFM images of electrolessly deposited Pd/Ag films on the Ag and Pd activation surfaces are shown in Fig. 2. By comparing Fig. 2 with Fig. 1, the Pd/Ag films became thicker and denser, which indicates that the Ag and Pd seeds are of catalytic activation. It is found that the initial deposition kinetics could be described by a mode involving

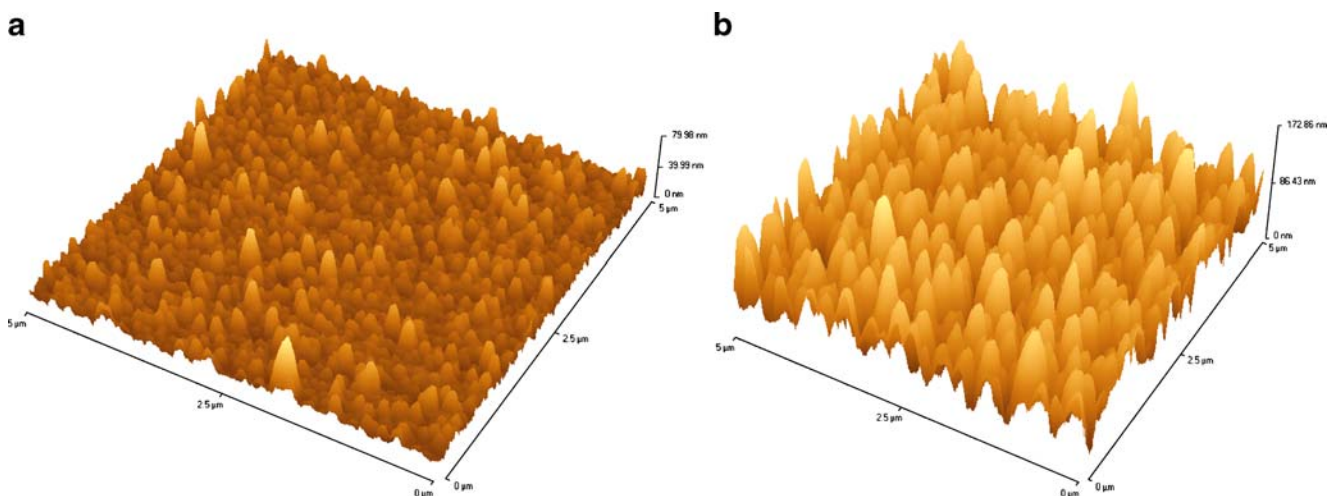
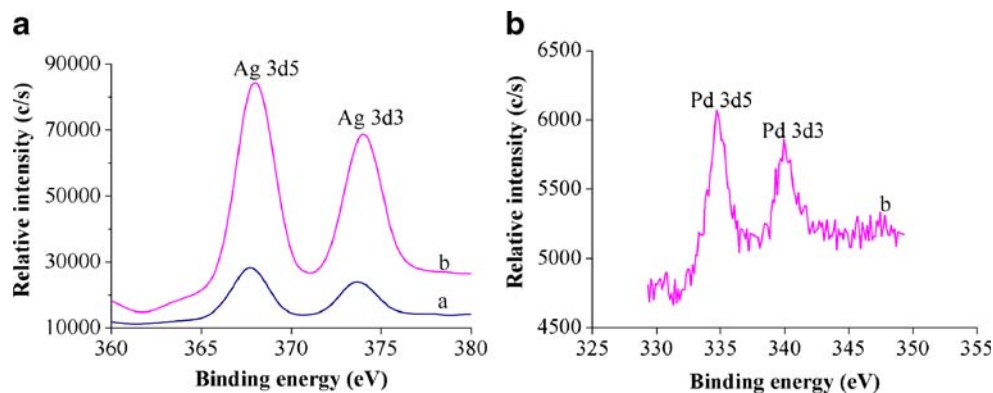


Fig. 2 3D AFM images of Pd/Ag films prepared on the seed layer of Ag (a) and Pd (b)

Fig. 3 XPS spectra of the Ag 3d (a) and Pd 3d (b) regions for the Pd/Ag films deposited on the seed layers of Ag (curve a) and Pd (curve b)



progressive nucleation on the active sites, i.e., the sites in which the Ag or Pd seed particles exist, and followed by the diffusion of silver and palladium ions toward the growing 3D nucleus islands. Many small pellets are also observed.

However, it is clear that the size of the pellets based on the seed layer of Pd (Fig. 2b) is much larger than that on the Ag seed layer (Fig. 2a), 220 vs 65 nm. From the images, it is also observed that the 3D growth of the grains based on the seed layer of Pd was more favorable than that on the seed layer of Ag. The average surface roughness degree (R_a) of the Pd/Ag film on the Pd seed layer is 22.3 nm, whereas the R_a based on the Ag seed layer is only 9.9 nm. The results indicate that the deposition rate of the grains on the Pd seed layer is much faster than that on the Ag seed layer.

Figure 3 shows the XPS spectra of the Ag 3d (a) and Pd 3d (b) regions for the as-prepared films deposited on the seed layers of Ag (curve a) and Pd (curve b). As seen in Fig. 3a, the XPS spectra in the Ag 3d5 and Ag 3d3 binding energy region with a spin-orbit separation of 5.8 eV are centered at 368.4 and 374.2 eV, respectively, for the films deposited on both seed layers. The values are very close to those of pure Ag phase [11]. Analyzing the XPS data, the silver peak intensity for the Pd seed layer is as about four times high as that for the Ag seed layer, indicating that Ag deposited on Pd is much more preferable than Ag deposited on Ag. In Fig. 3b, the XPS Pd 3d core energy peaks are only observed in the films deposited on the Pd seed layer. This suggests that Pd particles could not be deposited on Ag sites, which is in good agreement with the conclusion that only Ag can be deposited on the Ag sites, whereas Pd^{2+} cannot be reduced [12]. That is to say, the film prepared on the Ag activation surface is rather a pure Ag film and not an electrolessly co-deposited Pd/Ag film. Two Pd energy peaks assigned to the 3d5 and 3d3 energy level are located at 334.8 and 339.9 eV, respectively. Compared with Fig. 3a, it is clear from the XPS energy peak density that the amount of Pd is much smaller than the amount of silver corresponding to the Pd/Ag films prepared on the Pd seed layer, which is also consistent with the work of Chen et al. [12].

According to XPS data, we can make the conclusions that the film based on the Ag seed layer is only an Ag film rather than a Pd/Ag film, and Ag is more preferentially deposited on Pd seeds compared with Pd deposited on Pd seeds.

Cathodic polarization for hydrogen evolution

It is well known that cathodic polarization for hydrogen evolution is very effective to examine the electrocatalytic activity, depending on the composition of the electrode and the electrolyte and plating conditions [16, 17]. The cathodic polarization curves for hydrogen evolution in sulfuric acid were recorded as shown in Fig. 4. It is remarkably apparent that the cathodic current density of the films obtained on Pd seeds (curve b) is much larger than that on Ag seeds (curve a). For example, as the potential was -1.0 V, the current density of curve a was 0.34 mA cm^{-2} , whereas the current density of curve b reached up to 1.0 mA cm^{-2} . As the potential was -1.5 V, the current density of curve b was about four times higher than that of curve a (5.1 vs 1.3 mA cm^{-2}). To identify the composition of the electrode, we prepared the

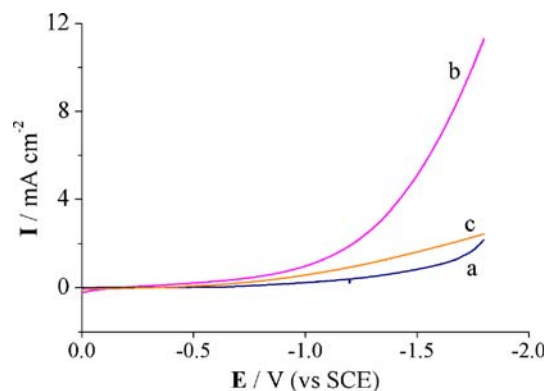


Fig. 4 Cathodic polarization curves of the Pd/Ag films for hydrogen evolution without illumination. The films were prepared on the Ag-activated (curve a) and Pd-activated (curve b) surfaces. Curve c corresponds to the Ag film on the Pd seed layer, in which the plating bath was $0.005 \text{ mol l}^{-1} \text{ AgNO}_3 + 4.5 \text{ mol l}^{-1} \text{ NH}_3 + 0.16 \text{ mol l}^{-1} \text{ Na}_2\text{EDTA} + 0.1 \text{ mol l}^{-1} \text{ NH}_2\text{NH}_2$. Scan rate was 20 mV s^{-1}

silver film deposited on the Pd seed layer for 180 s in the solution of $0.005 \text{ mol l}^{-1} \text{ AgNO}_3 + 4.5 \text{ mol l}^{-1} \text{ NH}_3 + 0.1 \text{ mol l}^{-1} \text{ Na}_2\text{EDTA} + 0.1 \text{ mol l}^{-1} \text{ NH}_2\text{NH}_2$ and used it as a working electrode for hydrogen evolution reaction, corresponding to curve c. It is seen that the cathodic current density of curve c was very close to that of curve a. Consequently, the results of XPS could be proved by the cathodic polarization measurement.

Conclusions

We studied the effect of the Ag and Pd seeds on the morphology and composition of the electrolessly deposited films, which were prepared in the solution of $0.005 \text{ mol l}^{-1} \text{ AgNO}_3 + 0.005 \text{ mol l}^{-1} \text{ PdCl}_2 + 4.5 \text{ mol l}^{-1} \text{ NH}_3 + 0.16 \text{ mol l}^{-1} \text{ Na}_2\text{EDTA} + 0.1 \text{ mol l}^{-1} \text{ NH}_2\text{NH}_2$ (pH 10.5) at room temperature. AFM and XPS were used to characterize the films, and the obtained films served as the working electrodes to carry out the cathodic polarization for hydrogen evolution in $0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ without illumination. The experimental results show that the film deposited on the Ag seed layer was rather a pure Ag film and not a Pd/Ag film, and the deposition rate of Ag on the Pd seed layer is much faster than the Pd deposition rate on the Pd-activated surface.

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