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Electroless deposition of Ru films on Si substrates with surface pretreatments

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ABSTRACT

Electroless Ru depositions on Si substrates undergoing surface pretreatments such as hydrogen fluoride (HF) etching, HF etching and activation, as well as HF etching, sensitization, and activation are explored. The plating bath contains $K_2RuCl_5 \cdot xH_2O$, NaClO, NaOH, and $NaNO_2$ at appropriate ratios. Continuous electroless Ru film is unable to obtain on the as-received Si wafer because the native oxide inhibits the process of nucleation and growth. In contrast, after surface pretreatments, dense and continuous Ru films are observed at reasonable growth rates. Contact angle measurements indicate a relatively hydrophilic surface after sensitization and activation, which leads to faster Ru film growths and larger surface roughness as compared to the HF-etched sample. X-ray photoelectron spectra confirm the formation of Sn and Pd nuclei and their presence promotes the heterogeneous growth of Ru films as evidenced by images from scanning electron microscope. In addition, depth profiling from Auger electron spectrometer suggests a uniform composition across the film thickness despite part of the Ru exists in an oxidized form.

1. Introduction

Ruthenium (Ru) and ruthenium oxide (RuO_2) have attracted considerable attention recently because of their unique physical and chemical properties for many industrial applications. For example, Ru is explored as a diffusion barrier layer and as an electrocatalyst in semiconductor and electrochemical devices, respectively [1,2]. In addition, RuO_2 is widely studied as a promising pseudocapacitive material [3]. Conventional synthetic routes for Ru and RuO_2 involve vacuum-based and solution-based approaches. The vacuum-based technique includes physical vapor deposition [4], chemical vapor deposition [5,6], and atomic layer deposition [7–9]. Unfortunately, these processes often require expensive equipment and they are known for unnecessary precursor waste. In contrast, the solution-based approach such as sol–gel synthesis [10], electroplating [3,11,12], and electroless deposition [13–19] are credited with simple setups, efficient use of precursors, as well as scalability in outputs. In the solution-based approach, the electroplating technique can be conducted via an externally applied driving force in potentiostatic or galvanostatic mode to direct deposits on conductive substrates. In contrast, the electroless deposition technique can be applied on both conductive and non-conductive platforms as reducing agents in the plating bath are responsible for reducing ions on the substrates instead.

In principle, the electroless deposition approach involves an autocatalytic reaction to form deposits via a heterogeneous nucleation and growth [20]. Notable advantages for the electroless deposition technique are wide substrate selection, sophisticated shape tolerance, and free of externally applied driving force. To date, electroless deposition of metals including Ni, Cu, Ag, Au, Pd, and Pt have been demonstrated in various formulations and their formation mechanisms are well-established [21–25]. On the other hand, metals such as Ru, Rh, Re, Os, and Ir have received few attention and functional electroplating baths still require further investigation [26]. In the case of Ru, preliminary experiments have been carried out on substrates including Cu, C, Pd-InGaAs, Si, and acrylonitrile butadiene styrene [13–19]. It is realized that for non-conductive substrates, selective surface pretreatments are rather necessary to ensure a uniform film formation. Earlier, Chang et al. attempted Ru electroless deposition on Si substrates but surface pretreatments were not discussed [15]. Recently, we have developed an oxidative–reductive Ru electroless plating bath and demonstrated its applicability on a Cu substrate [18,19]. Since Cu is known as a conductive surface for electroless plating, it becomes our interest to explore identical formulation on non-conductive surface such as Si. Preliminary study using as-received Si substrates concluded that a dense Ru film was unable to form. Hence, in this work, we investigate the effect of surface pretreatments on Si substrates for the formation of continuous Ru film via an electroless route.

2. Experimental details

A 6-inch boron doped p-type single crystalline Si wafer with (100) orientation was broken into small pieces ($2 \times 2\ cm^2$) and they were used as the substrates for Ru electroless deposition. The resistance and thickness for the Si wafer were 1–30 Ω cm and 625 ± 25 μm, respectively. Prior to surface pretreatment, the Si samples were rinsed

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with deionized water and acetone to remove any debris and possible contaminant. Afterward, it was immersed in a hydrogen fluoride (HF) solution at 25 °C for 10 min. The HF solution contained HF (J.T. Baker; Buffered Oxide Etch 6:1) and H_2O_2 (SHOWA; 35 wt.%) at a 1:50 volume ratio. Subsequently, the Si samples were further subjected to two different steps including activation, as well as sensitization and activation, respectively. The activation step involved immersing the Si substrate in a mixture of 0.1 wt.% $PdCl_2$ and 1 wt.% HCl in deionized water at 40 °C for 10 min. The sensitization step engaged the Si substrate in a solution containing 0.3 wt.% $SnCl_2$ and 2.5 wt.% HCl in deionized water at 25 °C for 3 min. Upon completion of surface pretreatments, the samples were submerged in a Ru electroless plating bath at 40 °C for different times. The chemical ingredients in the plating bath contain $K_2RuCl_5{\cdot}xH_2O$, NaClO, NaOH, and $NaNO_2$ at appropriate ratios, and the relevant oxidative–reductive mechanism for Ru film formation has been reported elsewhere [18].

A field-emission scanning electron microscope (FE-SEM; JEOL-JSM-6500F) with 15 keV operating voltage was used to observe morphology and thickness for the deposited films. We took the cross-sectional SEM images and selected three different locations to estimate their respective heights. An energy dispersive spectrometer (EDS; Oxford 7557) was utilized for elements detection. The acceleration voltage was 15 keV and the acquisition time was 70 s for the EDS measurement. A contact angle set-up consisting of lens, light source, and a power supply was adopted to determine hydrophilicity of Si substrates before and after surface pretreatments. An atomic force microscope (AFM; Vecco Dimension 5000 Scanning Probe Microscopy) was involved to determine roughness for the deposited films. Tapping mode was utilized for AFM measurement for $1\times1\ \mu m^2$ scanning area. An Auger electron spectrometer (AES, Thermo Microlab 350) was employed to perform depth profiling for the deposited films. The depth profile was divided into 100 layers with Ar ions bombardment at 5 s per layer. An X-ray photoelectron spectrometer (XPS; Thermo Microlab 350) with Mg target was used to identify oxidation states of Sn and Pd on Si substrates after surface pretreatments. For the XPS measurements, additional Pt particles were sputtered on the Si surface serving as a standard for correction with metallic Pt binding energy at $4f_{7/2}$ at 71.2 eV. The Si surface was bombarded with Ar ions which were operated with 3 kV and 1 μA for 30 s before recording the XPS.

3. Results and discussion

Table 1 provides the contact angles for Si samples before and after surface pretreatments, as well as the roughness before and after Ru electroless depositions. As listed, the removal of native oxide from the as-received Si wafer after HF etching rendered a relatively hydrophobic surface. However, after further pretreatments of activation or sensitization and activation, the Si surfaces were transformed to hydrophilic again. The roughness values were consistent with what we expected as activation steps produced Pd nuclei that led to a larger roughness especially for the sample undergoing sensitization and activation steps. In addition, after Ru electroless deposition, more Pd nuclei on the Si surface resulted in a larger thickness variation for the deposited Ru.

Table 1
Contact angles for Si samples before and after surface pretreatments, as well as roughness before and after 30 min Ru electroless depositions.

	Contact angle (°)	Roughness (nm)	
		Before Ru deposition	After Ru deposition
As-received Si substrate	37.97	0.2	N/A
HF etching	79.75	0.3	3.72
HF etching + activation	17.08	3.6	11.61
HF etching + sensitization + activation	12.84	4.3	11.79

Fig. 1 demonstrates the XPS profiles for the Si samples after surface pretreatments. As shown in Fig. 1(a), the Pd $3d_{5/2}$ and $3d_{3/2}$ were identified at 334.4 and 339.9 eV, respectively for the Si substrate after activation pretreatment. These values agree well with what was reported earlier for metallic Pd 3d lines [27]. Hence, we realize that the activation step is effective in distributing Pd nuclei on the Si surface for subsequent Ru deposition. Fig. 1(b) and (c) exhibits the Sn 3d and Pd 3d lines after sensitization and activation pretreatments, respectively. As shown in Fig. 1(b), the profile revealed notable signals at 484.5 and 493.4 eV, which are consistent with metallic Sn from literature [27]. In addition, there were presence of Pd 3d lines at 335.4 and 341.1 eV, and these values are slightly larger than those in Fig. 1(a), indicating that moderate Pd oxidation to PdO was possibly occurring [28,29]. The shoulder at 332 eV in Fig. 1(c) is from Pt $3d_{3/2}$ which is

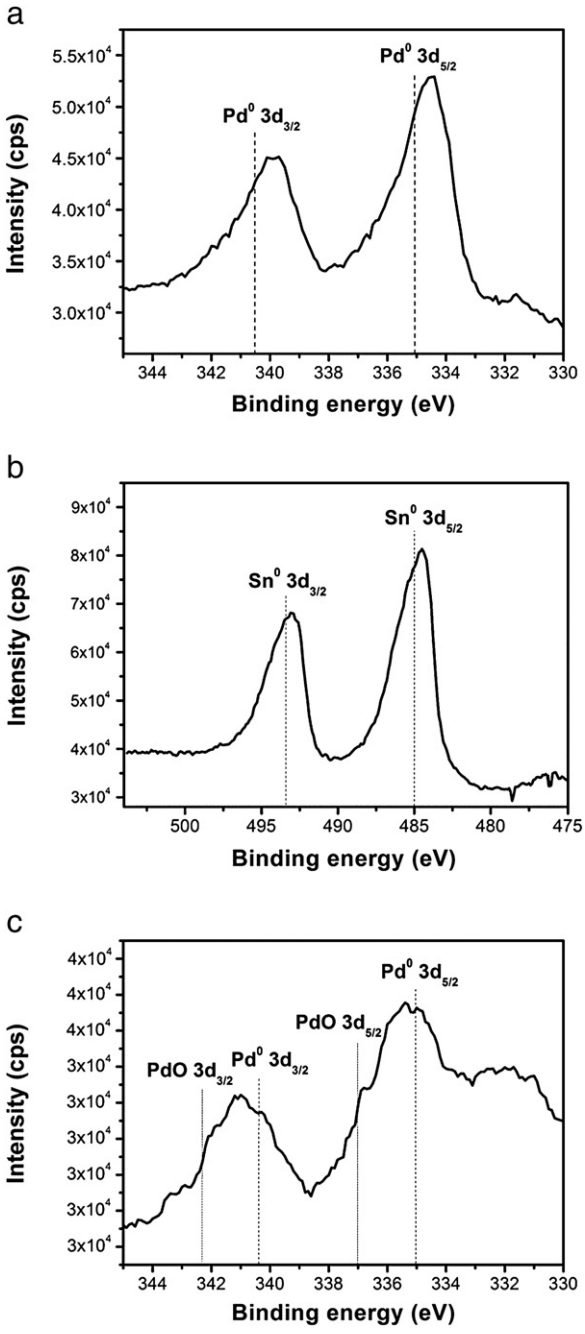

Fig. 1. XPS profiles for Si samples (a) after activation pretreatment for Pd 3d lines, as well as (b) after sensitization and activation pretreatments for (b) Sn 3d lines and (c) Pd 3d lines.