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# Electroless deposition of W-doped Ag films onto p-Si(100) from diluted HF solution

YE Wei-chun(叶为春)<sup>1</sup>, MA Chuan-li(马传利)<sup>2</sup>, WANG Chun-ming(王春明)<sup>2</sup>, ZHOU Feng(周峰)<sup>1</sup>

1. State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China;

2. Department of Chemistry, Lanzhou University, Lanzhou 730000, China

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**Abstract:** Tungsten-doped silver films were prepared by immersing hydrogen-terminated silicon wafers into the solution of 2.5 mmol/L [Ag<sub>2</sub>WO<sub>4</sub>]+0.1 mol/L HF at 50 °C. Their growth and composition were characterized with atomic force microscopy and X-ray photoelectron spectroscopy, respectively. The effect of tungstate ions on the deposition of silver was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) by comparing W-doped Ag film with Ag film. It is found that the molar fraction of tungsten in the deposits is about 2.3% and the O to W molar ratio was about 4.0 and W-doped Ag films have good anti-corrosion in air at 350 °C. The doping of tungsten cannot change the deposition of silver. **Key words:** autocatalytic electroless deposition; W-doped Ag film; silicon; HF

# **1** Introduction

Electroless deposition has been widely used in a variety of applications of the electronic and semiconductor industries such as selective depositing on patterned substrates, making ohmic contacts, preparing electrodes, and ulta-large-scale integration (ULSI) metallization[1]. This technology has three fundamentally different mechanisms: autocatalysis, substrate catalysis, and galvanic displacement[2]. Immersion plating of noble metals such as Cu, Ag, Pd, and Pt, on hydrogen-terminated silicon surface from a HF solution belongs to autocatalytic electroless deposition (AED)[3-7]. The autocatalytic process uses a complex electrolyte composition to allow the reduced metal itself to serve as a catalyst for further reductive deposition. Therefore, much research has gone into improving and utilizing this plating process.

With the development of ultra-large-scale integration (ULSI) and microelectromechanical system (MEMS), some metals with better electronic and physical properties are required. Compared with other metals such as Al and Cu, silver has been recently promoted as a potential candidate due to its low room temperature bulk resistivity (1.59  $\mu\Omega$ ·cm), relatively high melting point and expected high electromigration resistance[8–9]. However, electroless or electroplated Ag films have some drawbacks such as thin film, high resistivity and corrosion in the atmosphere. One simple way is to use the incorporation of tungsten into silver to form silver-tungsten binary system. It is assumed that refractory metals can stabilize silver layers, while increase the resistivity by a very small margin, and yield layers with high mechanical strength and good corrosion resistance[10].

About the doping of tungsten into silver, we have proposed a novel doping mode[11] different from induced co-deposition of W with iron-group metals [12–14]. We thought that the doping of tungsten occurs during silver deposition through chemisorption– chemical bonding of oxygen atoms of tungstate with silver, and also tungstate ions cannot essentially affect the growth of silver. Based on this, electroless deposition of tungsten doped silver films was firstly demonstrated by immersing H-terminated silicon wafers into a diluted HF solution containing  $Ag^+$  and tungstate ions. And the

Corresponding author: YE Wei-chun; Tel: +86-931-4968079; E-mail: xiewch03@lzu.cn

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effect of tungstate ions on the silver deposition was investigated.

## 2 Experimental

#### 2.1 Wafer treatment

The silicon wafers used in this experiment were p-Si (100) with resistivity of 15-20 Ω·cm and thickness of  $(650 \pm 25)$  µm (Beijing Youyan silicon villa semiconductor). Prior to the deposition, the wafers were cut into square samples each with a surface area of  $1 \text{ cm}^2$ . The wafers were first cleaned in an ultrasonic cleaner in absolute alcohol for 10 min, then immersed in a hot (80 °C) solution ( $\varphi$ (H<sub>2</sub>O<sub>2</sub>): $\varphi$ (NH<sub>4</sub>OH): $\varphi$ (H<sub>2</sub>O)=1:1:5) for 10 min and next in another hot (80 °C) solution ( $\varphi$ (H<sub>2</sub>O<sub>2</sub>):  $\varphi(\text{HCl}):\varphi(\text{H}_2\text{O})=1:1:6)$  for 10 min to remove possible contaminants. Finally, they were etched in a solution of 10 mL HF (40%) +100 mL NH<sub>4</sub>F (40 g NH<sub>4</sub>F in 100 mL H<sub>2</sub>O) for 2 min at room temperature, to prepare a clean, hydrogen-terminated surface. The wafers were rinsed with water and dried with dry nitrogen flux after each cleaning step. All chemicals were of analytic grade. Milli-Q water (Millipore, 18.2 M $\Omega$ /cm) was used throughout.

#### 2.2 Electroless deposition of W-doped Ag films

The W-doped Ag films were prepared by immersing the hydrogen-terminated silicon into 2.5 mmol/L  $[Ag_2WO_4]+0.1$  mol/L HF at room temperature for different time. The detailed formation of the acidified tungstate solution is very complicated[15]. There are monomeric species  $[HWO_4]^-$  and  $W(OH)_6$ , dimeric anion  $[HW_2O_7]^-$ , and polyanions  $[W_6O_{20}(OH)_2]^{6-}$ ,  $[W_7O_{24}]^{6-}$ ,  $[HW_7O_{24}]^{5-}$ ,  $[H_2W_{12}O_{42}]^{10-}$ . So, the formation of 0.11 g Ag<sub>2</sub>WO<sub>4</sub> dissolving into 0.1 mol/L HF is written as 2.5 mmol/L  $[Ag_2WO_4]^+0.1$  mol/L HF. After deposition, the samples were thoroughly washed with deionized water and then dried in air.

#### 2.3 Measurements

Surface morphology was characterized with atomic force microscope (AFM Explore, Veeco Inc. USA, in contact mode). The sample was annealed up to 350 °C in air for 1 h, and then its composition was determined by a PHI–5702 multifunctional X-ray photoelectron spectroscope (XPS, USA, the instrument was calibrated by the measurement of the XPS spectrum of C 1s at 284.6 eV binding energy with a Mg K<sub> $\alpha$ </sub> excitation source; and the accuracy of band-energy measurements is ± 0.3 eV). A field emission type scanning electron microscope (FE-SEM, XL30 S-FEG, FEI Corp. at 10 kV) equipped with energy dispersion spectroscopy (EDS) analysis tool and a X-ray diffractometer (XRD, Rigaku D/max–2400, Cu K-Alpha radiation,  $\lambda$ =0.154 1 nm) were used. To avoid the high intensity of silicon diffraction peak (at about 69°), the  $2\theta$  was selected from 35° to 65°.

#### **3 Results and discussion**

#### 3.1 Characterization of W-doped Ag films

The 3D AFM image (5  $\mu$ m $\times$ 5  $\mu$ m) for the etched silicon is shown in Fig.1. We can see the wafer itself is flat enough, so the signal is almost at noise level. Dipping a p-silicon(100) wafer into a HF solution removes the silicon native oxide and creates a silicon substrate surface with hydrogen (=SiH<sub>2</sub>) bonded perpendicular to the surface[16-18] and with a defect density of about 0.5%. Fig.2 shows the 3D AFM images (5  $\mu$ m $\times$ 5  $\mu$ m) of electroless deposited W-doped Ag films on the etched silicon wafer after deposition for 30-120 s. It is found that the surface images of the films gradually change with increasing deposition time. The films in the form of islands become thick and dense; so, no blank regions are found. The maximum value of the as-prepared grain size for 120 s deposition is approximately 200 nm as measured by the AFM profile. The relationship between surface roughness degree  $(R_{\alpha})$ and deposition time is displayed in Fig.3.  $R_{\alpha}$  increases with prolongation of the deposition time; however, its increasing slope decreases with the deposition time.



Fig.1 3D AFM image of etched silicon wafer

Here, we only consider the deposition of silver because tungsten ions cannot change the growth mode of silver which has been proved by the AFM images. The results show that the initial deposition kinetics could be described by Volmer-Weber (VW) mode, that is, the growth process includes the following steps. Silver on surface defects which nucleus starts are thermodynamically favorable for deposition[19]; and once a stable silver metal nucleus is formed, it acts as a cathode; thus, silver ions are continually reduced to neutral atoms, which are clustered around the nuclei.



**Fig.2** 3D AFM images of W-doped Ag films on silicon wafers prepared by immersion plating for 30 s (a), 60 s (b), 90 s (c) and 120 s (d) at room temperature (Plating bath: 2.5 mmol/L [Ag<sub>2</sub>WO<sub>4</sub>]+0.1 mol/L HF)



**Fig.3** Relationship between  $R_{\alpha}$  and deposition time ( $R_{\alpha}$  from AFM profiles of Fig.2)

Furthermore, the discontinuous growth was observed, that is, larger grains were surrounded by smaller particles. This is because the growth of nuclei on the substrate and the displacement reaction are unbalanced. The deposition of silver onto silicon from dilute or buffered HF solutions is electrochemical in nature. Electrochemical reactions are illustrated in the following equations. While silicon is oxidized, silver ions are reduced. All potentials refer to the standard hydrogen electrode (SHE).

Anodic area:

Si+6HF=H<sub>2</sub>SiF<sub>6</sub>+4H<sup>+</sup>+4e,  $\varphi^0$ =-1.24 V (1) Catholic area:

$$Ag^{+}+e=Ag, \ \varphi^{0}=+0.80 \text{ V}$$
 (2)

The composition of the electrolessly deposited W-doped Ag film was determined with XPS. The X-ray photoelectron spectra are shown in Fig.4, corresponding to the Ag 3d and W 4f regions of the film. Curves 1 stand for their XPS signals without annealing. It can be seen that the Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$  binding energy regions with a spin-orbit separation of 5.8 eV, are centered at 368.4 and 374.2 eV, respectively. The values are very close to those of pure metallic Ag[20]. And the profile of W 4f energy peaks appear clearly. The XPS investigation has shown that the atomic tungsten concentration in the deposits is about 2.3% and the O-to-W molar ratio is about 4.0. This suggests that the formation of tungsten is tungsten oxides. The film was further treated under annealing up to 350 °C in air for 1 h and the relevant XPS spectra are shown in curves 2 of Fig.4. It is obvious that the two Ag energy peaks do not shift and the profile of W 4f energy peaks keeps unchanged compared with



**Fig.4** XPS spectra for Ag 3d (a) and W 4f (b) of W-doped Ag films before and after annealing in air up to 350  $^{\circ}$ C for 1 h

that without annealing. The results indicate that tungsten element is doped on silver film in the formation of tungsten oxides and the film has good anti-corrosion in the atmosphere.

# 3.2 Effect of tungstate ions on deposition of W-doped Ag film

According to our proposed doping mode, the bonding energy of oxygen of tungstate with silver is weak, and thus the effect of tungstate ions on the deposition of silver is limited. To confirm this result, Ag film was compared with W-doped Ag film by SEM, EDS and XRD. Ag film and W-doped Ag film were prepared by immersing the etched silicon wafers into the solutions containing 0.1 mol/L HF+2.5 mmol/L [Ag<sub>2</sub>WO<sub>4</sub>]+5.0 mmol/L AgNO<sub>3</sub> for 120 s at room temperature, respectively. By comparing the SEM images of the W-doped Ag film (Fig.5(a)) with the Ag film (Fig.5(b)), it is found that the growth of the W-doped Ag film is in the form of islands, which is consistent with the growth mode of the Ag film. However, the W-doped Ag film is thicker and denser than the Ag film. It can be ascribed to



Fig.5 SEM images of W-doped Ag film (a) and Ag film (b)

the strong oxidation activity of  $NO_3^-$  in acid medium, as shown in Eq.(3).

 $NO_3^- + 2H^+ + e = NO_2 + H_2O, \ \varphi^0 = +0.80 \ V$  (3)

From Eqs.(2) and (3), it is assumed that both chances of the deposition of Ag and the reduction of  $NO_3^-$  are equal during the deposition of Ag film, which is confirmed by EDS. According to the EDS data, the Ag-to-Si molar ratio for the W-doped Ag film (6.6%) is approximate twice that for the Ag film (3.5%). Fig.6 shows their XRD patterns. It can be seen that not only the Ag diffraction peaks locate at identical values of  $2\theta$ , which can be indexed to (111), (200), (220) planes, but also the intensity and shape of the peaks are almost



Fig.6 XRD patterns of W-doped Ag film (a) and Ag film (b)

unchanged. Furthermore, for the XRD pattern of the W-doped Ag film, no peak corresponding to tungsten element is observed, probably due to the low tungsten concentration. The results indicate that the effect of tungstate ions on the deposition of silver is little, which is in agreement with our previous work[11].

#### **4** Conclusions

1) W-doped Ag films were prepared by immersing the hydrogen-terminated silicon wafers into the solution of 2.5 mmol/L  $[Ag_2WO_4]$ +0.1 mol/L HF. The Volmer-Weber growth process of the films was characterized by AFM, and the composition was determined with XPS. It is found that the molar fraction of tungsten in the deposits is about 2.3% and the O-to-W molar ratio is about 4.0.

2) The effect of tungstate ions on the deposition of W-doped Ag film was investigated. The results show that the doping of tungsten cannot change the deposition of silver, which is consistent with our doping mode proposed.

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