Electrochemical investigation of the surface energy: Effect of the HF concentration on electroless silver deposition onto p-Si (1 1 1)

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Abstract

Electroless silver deposition onto p-silicon (1 1 1) from $0.005 \, \text{mol} \, l^{-1}$ AgNO$_3$ solutions with different HF concentration was investigated by using an electrochemical direct current polarization method and open circuit potential-time (Ocp-t) technique. The fact that three-dimensional (3D) growth of silver onto silicon is favored with increasing the HF concentration was ascribed to the drop of the surface energy and approved by electrochemical direct current polarization, Ocp-t technique and atomic force microscopy (AFM). The drop slope of open-circuit potential, $K_{-\Delta E(\text{OCP})/t}$, was educed from the mixed-potential theory. $K_{-\Delta E(\text{OCP})/t}$ as well as the deposition rate determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES), increased with the HF concentration, yet was not a linear function. Results were explained by the stress generation and relaxation mechanisms.
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Keywords: Electroless silver deposition; Surface energy; Direct current polarization; Open circuit potential-time (Ocp-t) technique; Stress generation and relaxation; HF
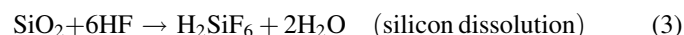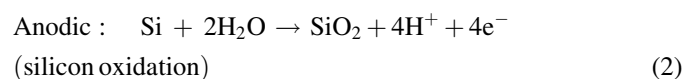
1. Introduction

In the past 10 years, electroless metal deposition (EMD) is one technique that has been widely used in a variety of applications of the electronic and semiconductor industries such as selectively depositing on patterned substrates, making ohmic contacts, preparing electrodes and ulta-large scale integration (ULSI) metallization, due to its selectivity and purity, low operating temperature, simplicity and lost cost [1–3]. Unlike conventional electrodeposition processes, in the case of electroless deposition, electrons for the reductive deposition of metal species are supplied via electron transfer between metal ions and reducing agents in electrolytes. Especially, the EMD from HF solution was often explained by the electrochemical redox reaction process in which both anodic and cathodic processes occur simultaneously at the silicon surface, while the charge is exchanged through the substrate [4–6]. Hence, much research has gone into improving and utilizing this plating process.

Noble and transition metals such as Ag and Cu are known to deposit on silicon during wet chemical processing in hydrofluoric acid (HF) solutions. In the case of electroless silver deposition onto silicon, we have reported that the silver layer deposited onto silicon from an aqueous solution without HF is only a monolayer from calculating the surface coverage (Γ) for 1 s, 10 min, or 1 h immersion based on the CV curves [7]. The result shows that the function of HF is to remove any residual oxide on the surface and aid more importantly in metal deposition through direct displacement of the silicon [8,9]. The electrochemical reaction in the presence of HF can be illustrated in the following chemical reaction formulation.

The global chemical reaction can be formulated as

$$4\text{Ag}^+ + \text{Si(s)} + 6\text{HF} \rightarrow 4\text{Ag(s)} + \text{H}_2\text{SiF}_6 + 4\text{H}^+ \quad (1)$$
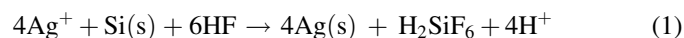
which can be separated into two half-cell reactions (2), (3) and (4)

$$\text{Anodic:} \quad \text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}^+ + 4\text{e}^-$$
$$\text{(silicon oxidation)} \quad (2)$$

$$\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \quad \text{(silicon dissolution)} \quad (3)$$

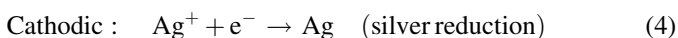
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$$\text{Cathodic}: \quad Ag^+ + e^- \rightarrow Ag \quad \text{(silver reduction)} \quad (4)$$

During the growth of Volmer–Weber (VW) thin films on substrates, stresses are commonly generated and there exits a complex dynamic competition between mechanisms for stress generation and stress relaxation leading to island zipping and island growth [10–12]. The competition depends sensitively upon whether the films were continuous or discontinuous, on the process conditions, and on the film/substrate interface. Therefore, the effect of stress could be analyzed by studying the variation of the surface energy level of silicon substrates in this work.

Electrochemical methods as conventional methods, have been employed to investigate the characteristics of metal deposition onto silicon from HF based solutions, which not only are of high sensitivity but also can record in situ the interfacial properties of silicon/electrolyte. For example, electrochemical impedance spectroscopy (EIS) [13] and open circuit potential-time (Ocp-t) technique [14] were used to probe the mechanism of copper deposition on silicon from HF solutions. In this paper, the influence of the HF concentration on electroless silver deposition onto silicon from HF solutions has been investigated by using an electrochemical dc polarization measurement and the Ocp-t technique. Atomic force microscopy (AFM) is used to investigate the three-dimensional (3D) growth of silver on silicon. Summarily, our aim is to give some fundamental aids in electroless silver deposition onto silicon.

2. Experimental

The silicon wafers used in this experiment were p-Si (1 1 1) with resistivities of 15–20 Ω cm and a thickness of 650 ± 25 μm (Beijing Youyan silicon villa semiconductor). Prior to the experiments, the wafers were cut into square samples each with a surface area of 1 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 of H_2O_2:NH_4OH:H_2O (1:1:5) for 10 min and next in another hot (80 °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 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 Ω cm^{-1}) was used throughout.

Silver deposition onto etched silicon was detected in situ with electrochemical methods allowing the electrode/electrolyte interface to be characterized. These experiments were performed in a homemade electrochemical Teflon cell with a three-electrode configuration [7] in the dark. 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, dipping directly into the electrolyte. The reference was a saturated calomel electrode (SCE), connected to the electrolyte by means of a saturated KCl-agar salt bridge made of a Teflon tube.

A CHI-614A electrochemical workstation (made in Shanghai, China) was used for the measurements of Ocp-t technique and electrochemical dc polarization, which yield valuable information since their results are directly related to the process thermodynamics and kinetics. All experiments were carried out at room temperature. The electrolyte was purged by pure nitrogen prior to each electrochemical experiment and protected by the nitrogen during the experiment. Polarization curves were obtained at a scan rate of 5 mV/s.

The amount and morphology of the Ag films were measured by an IRIS advantage ER/S inductively coupled plasma atomic emission spectrometer (ICP-AES, TJA, USA, wavelength 328.0 nm) and an atomic force microscope (AFM Explore,
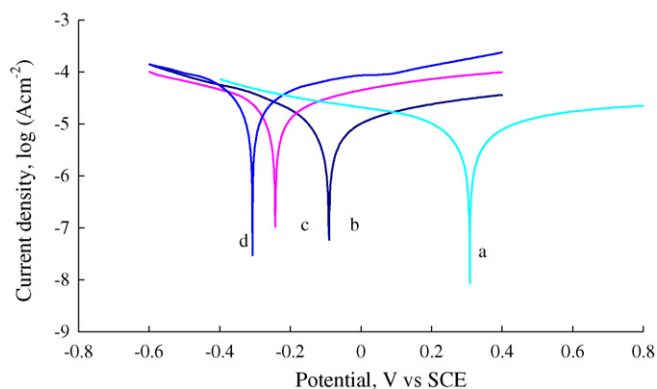
Fig. 1. Polarization curves obtained with p-Si (1 1 1) in 10 ml 0.005 mol l^{-1} AgNO$_3$ solution and 5 ml HF solution: (a) in the absence of HF; (b) 0.06 mol l^{-1} HF; (c) 0.6 mol l^{-1} HF; (d) 6.0 mol l^{-1} HF. Scan rate was 5 mV s^{-1}.

Fig. 2. Ocp-t curves of p-Si (1 1 1) in 10 ml 0.005 mol l^{-1} AgNO$_3$ solution. After scanning for 50 s, 5 ml HF solution was added fast. (A) 0.06 mol l^{-1} HF; (B) 0.6 mol l^{-1} HF; (C) 6.0 mol l^{-1} HF.

Veeco Inc., USA) in contact mode, respectively. Prior to the measurements, the Ag films were obtained by immersion in the 0.005 mol l^{-1} AgNO$_3$ solution with 0.06, 0.6 and 6.0 mol l^{-1} HF, respectively, for 10 s at room temperature. The Ag deposits were dissolved with a 50% HNO$_3$ solution at 80 °C.

3. Results and discussion

3.1. Electrochemical dc polarization analysis

To understand the EMD process, an electrochemical dc polarization method was conducted. Fig. 1 shows polarization curves of p-Si (1 1 1) in 10 ml AgNO$_3$ containing no added HF (curve a), or 5 ml solution with 0.06 (curve b), 0.6 (curve c) and 6.0 (curve d) mol l^{-1} HF. It is apparent that the corrosion potential (E_{corr}) is sensitive to the addition of HF. E_{corr} became less negative by about 400 mV even when the added HF concentration was 0.06 mol l^{-1}, which suggests that HF is favorable to the Ag deposition.

In the case of adding HF solutions, the result that the cathodic polarization curves were not remarkably different is due to the experiment process that AgNO$_3$ solution was first introduced, then HF was added quickly, and the scanning started immediately. However, the current density in the anodic polarization zone increased with the increase of the HF concentration, which is ascribed to the silicon dissolving. According to a Tafel extrapolation method, as depicted in Table 1, the corrosion current density, J_{corr}, increased as the HF concentration increased (shown in Table 1). E_{corr} became
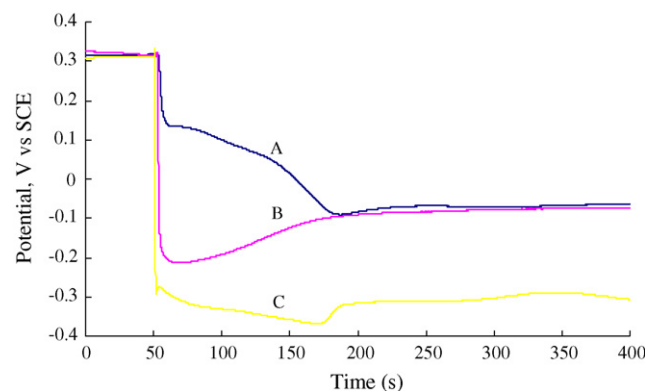
more negative with the increase of the HF concentration. For curves b–d, E_{corr} was −0.09, −0.24 and −0.31 V, respectively. So, it can be calculated that the surface energy level of the silicon (ϕ) for adding 0.06, 0.6 and 6.0 mol l^{-1} HF are 0.40, 0.55 and 0.62 eV lower, respectively, than that for no added HF.

One parameter governing the growth mode is the substrate surface free energy. 3D growth is favored when the substrate surface free energy is low [15]. As a result, the electroless silver deposition is thermodynamically favorable with increasing the HF concentration.

3.2. Ocp-t measurement

The Ocp-t technique is quite interesting because this parameter is characteristic of the anodic and cathodic surface sites reactivity, the results being dependent on the electrolyte components and the surface states of the electrode material [14,16,17]. The obtained Ocp-t curves are shown in Fig. 2. Our aim is to understand the effect of the HF concentration on electroless silver deposition onto p-Si (1 1 1). The variation of open-circuit potentials with time was investigated in the solutions adding 0.06 (curve A), 0.6 (curve B), and 6.0 (curve C) mol l^{-1} HF. Before the addition of HF, the short horizontal lines at the beginning of the curves confirmed our previous work [7] that once silicon is oxidized to silicon dioxide, the silicon dioxide becomes a barrier which prevents silver ions from being further reduced (Reaction (2)). The open circuit potentials (E_{OCP}) were all about 0.31 V, which is consistent

Table 1
The electrochemical parameters with the HF concentration

HF concentration (mol l^{-1})	E_{corr} (V)	J_{corr} (μA cm^{-2})	$\Delta\phi$[a] (eV)	$K_{-\Delta E(OCP)/t}$[b] (V s^{-1})	The deposition rate[b] (μg cm^{-2} s^{-1})
0.06	−0.09	12.6	0.40	0.0145	2.22
0.6	−0.24	26.3	0.55	0.0532	10.1
6.0	−0.31	33.9	0.62	0.0592	12.8

[a] $\Delta\phi$ is the drop of the surface energy barrier of the silicon for adding HF compared with that for no added HF.
[b] The deposition time is 10 s.

with E_{corr} of no added HF. The addition of HF was observed to result in a steep shift of the potential toward negative values. However, with the increase of HF concentration, the drops of the steep shift potential ($-\Delta E$ (OCP)) increased. It was found that the values of the surface energy level drops ($\Delta\phi$) compared with no added HF agreed with those by the electrochemical dc polarization measurement, which indicates that E_{OCP} is the measured mixed potential at the electrode in equilibrium with the solution.

It must be pointed out that the silicon electrode used in the electrochemical experiments was the contaminated silicon electrode rather than bare silicon electrode because a silver monolayer adhered on the silicon from an aqueous solution. We called it the contaminated silicon here. As a result, the open circuit potential, $E_{OCP(contam)}$, based on the contaminated silicon did not equal that based on the bare silicon.

To bare silicon, $E_{OCP(bare)}$ may be correlated to the surface energy level of the solution redox couple by the relationship [18]

$$E_{OCP(bare)} = \phi_{S(bare)} + V_{FB(bare)} \qquad (5)$$

where $\phi_{S(bare)}$ is the potential difference at the bare silicon surface due to band bending and $V_{FB(bare)}$ is the flat band potential of bare silicon.

To the contaminated silicon, however, since the amount of silver adhered on the silicon is minute [19] and the conditions in this experiment were fixed except the HF concentration, the flat band potential of the contaminated silicon, $V_{FB(contam)}$, is stable, and the potential difference at the contaminated silicon, $\phi_{S(contam)}$, can be written as

$$\phi_{S(contam)} = \phi_{S(bare)} + K \qquad (6)$$

where K is a constant. It was calculated from Eqs. (5) and (6) that the variation of OCP based on the contaminated silicon, $\Delta E_{OCP(contam)}$, was equal to that based on the bare silicon, $\Delta E_{OCP(bare)}$. Namely, the measured $\Delta\phi$ can stand for $\Delta\phi$ based on the bare silicon.

The positions of the bandedges at the surface and, hence, the energy of surface electrons in conduction or valence band, are dependent on the partitioning of the applied potential between the semiconductor space-charge layer and the Helmholtz layer at the interface. Therefore, the band edge position does not shift with variation of HF concentration in this paper. And the redox potential of the silver system, which is the component of the mixed potential, is constant during the displacement reaction, so $V_{FB(bare)}$ is constant. These experiments were performed in the dark. This means the charge transfer process of metal deposition is governed by hole injection to the valence band. The shift of OCP toward the negative potential with HF concentration will result in the increase in the band bending. Consequently, the increase of HF concentration promotes the drop of the surface energy level of the silicon.

3.3. Investigation of the deposition rate

It may be interesting to note that the Ocp-t profiles were distinctly different as different concentration HF was added.

Especially, for curve A, there is an apparent declivity (from 0.13 to −0.09 V) except the steep potential drop while for curves B and C the declivity is less than 0.1 V (in potential) and less apparent.

To interpret the change in E_{OCP}, on the basis of the mixed potential theory [20], the following expression was proposed [14]:

$$E_{OCP} = \frac{\alpha E_1 + \beta E_2}{\alpha + \beta} + \frac{RT}{nF(\alpha + \beta)} \ln \frac{j_C}{j_A} \qquad (7)$$

where E_1, E_2, α and β are, respectively, the equilibrium potentials and the transfer coefficients of the anodic and cathodic electrochemical reactions. j_A and j_C are the exchange current densities, characteristic of the rate the electronic transfer proceeds on anodic and cathodic sites.

Starting from Eq. (7) of the mixed potential, provided j_C is not changed as confirmed from Fig. 1, we can educe the equation of the drop slope of OCP, $K_{-\Delta E(OCP)/t}$

$$K_{-\Delta(OCP)/t} = -\frac{E_{OCP}(t) - E_{OCP}(0)}{t} = \frac{RT}{nFt(\alpha + \beta)} \ln \frac{j_A(t)}{j_A(0)} \qquad (8)$$

where $E_{OCP}(0)$ and $E_{OCP}(t)$ are the open-circuit potential values of before and after adding HF at time t during the silver deposition.

Eq. (8) reveals that the direct measurement of the open-circuit potential gives information about the amount of silver deposit according to Reaction (1) because j_A is ascribed to the silicon dissolving. Since the high concentration and corrosiveness of the HF solution were used in the plating bath, the simplicity of j_A in the light of literature [14] makes impractical. It was found from the calculation of $K_{-\Delta E(OCP)/t}$ for the deposition time of 10 s that $K_{-\Delta E(OCP)/t}$ increased with the increase of the HF concentration whereas it was not a linear function. We also acquired the same result based on the determination of the silver deposition rate ($t = 10$ s) by ICP-AES (Table 1). It revealed that its growth included not only the nuclei stage but also all the VW growth stages—nucleation of discrete islands, island growth, island impingement and coalescence, percolation of the island array, and channel filling to eventually form a continuous thin film.

3.4. AFM measurement

The 3D AFM image (5 μm × 5 μm) for the etched silicon is shown in Fig. 3. We can see the wafer itself is flat enough, so the signal was almost at noise level. The etching method has been shown to create a hydrogen-terminated silicon substrate surface with hydrogens bonded perpendicular to the surface and with a defect density of ∼0.5% [21].

To examine the effect of HF concentration on the silver growth, Fig. 4 shows the 3D AFM images (5 μm × 5 μm) of the Ag films, which were prepared in 0.06 (a), 0.6 (b) and 6.0 (c) mol l^{-1} HF as depicted in above mentioned. It is observed that the substrate was coved with a silver thin film in the form of islands. Comparing the images of Fig. 4, Fig. 4a shows more
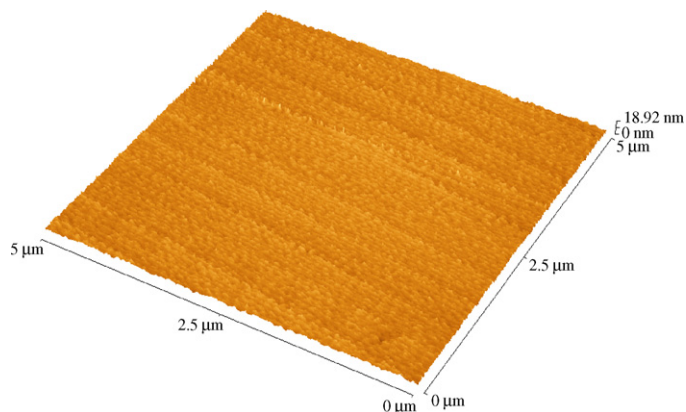
Fig. 3. 3D AFM image of the etched silicon surface.

clearly the image of silver nuclei with a diameter of approximately 30 nm, while in Fig. 4b and c, larger grains are clustered around the nuclei. The growth of the films has been proved to be in VW mode, where the growth process includes: silver nucleus started on surface defects which were thermodynamically favorable for deposition [22]; 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. This conclusion supported effectively the above results of the deposition rate. Furthermore, the discontinuous

growth was observed, i.e., larger grains were surrounded by smaller particles. This is because the growth of nuclei on the substrate and the displacement reaction are unbalanced.

Fig. 5 presents the height profile of 3D images of Fig. 4, which shows relative vertical height of the particles. The curve (a) for $0.06 \, mol \, l^{-1}$ HF has the smoothest surface and the lowest average particle height difference about 6 nm, the average vertical height difference of particle size which presents the curve (c) for $6.0 \, mol \, l^{-1}$ HF was hoisted to 16 nm, indicating that increasing HF concentration has stimulated the 3D growth of silver on silicon. This is consistent with the analysis from the electrochemical dc polarization measurement and Ocp-t technique.

According to the researchers [23–25], during the deposition of VW thin films there exits a complex dynamic competition between mechanisms for stress generation and stress relaxation leading to island zipping and island growth. And the competition depends sensitively upon whether the films were continuous or discontinuous, on the process conditions, and on the film/substrate interface. Based on the above mentioned discussion, the surface energy level (ϕ) decreased with increasing the HF concentration, which might lead to enhance the extent of stress relaxation in the competition between stress generation and stress relaxation. Consequently, the increase of the HF concentration would stimulate island growth, i.e., three-dimensional growth is favored, which demonstrated the
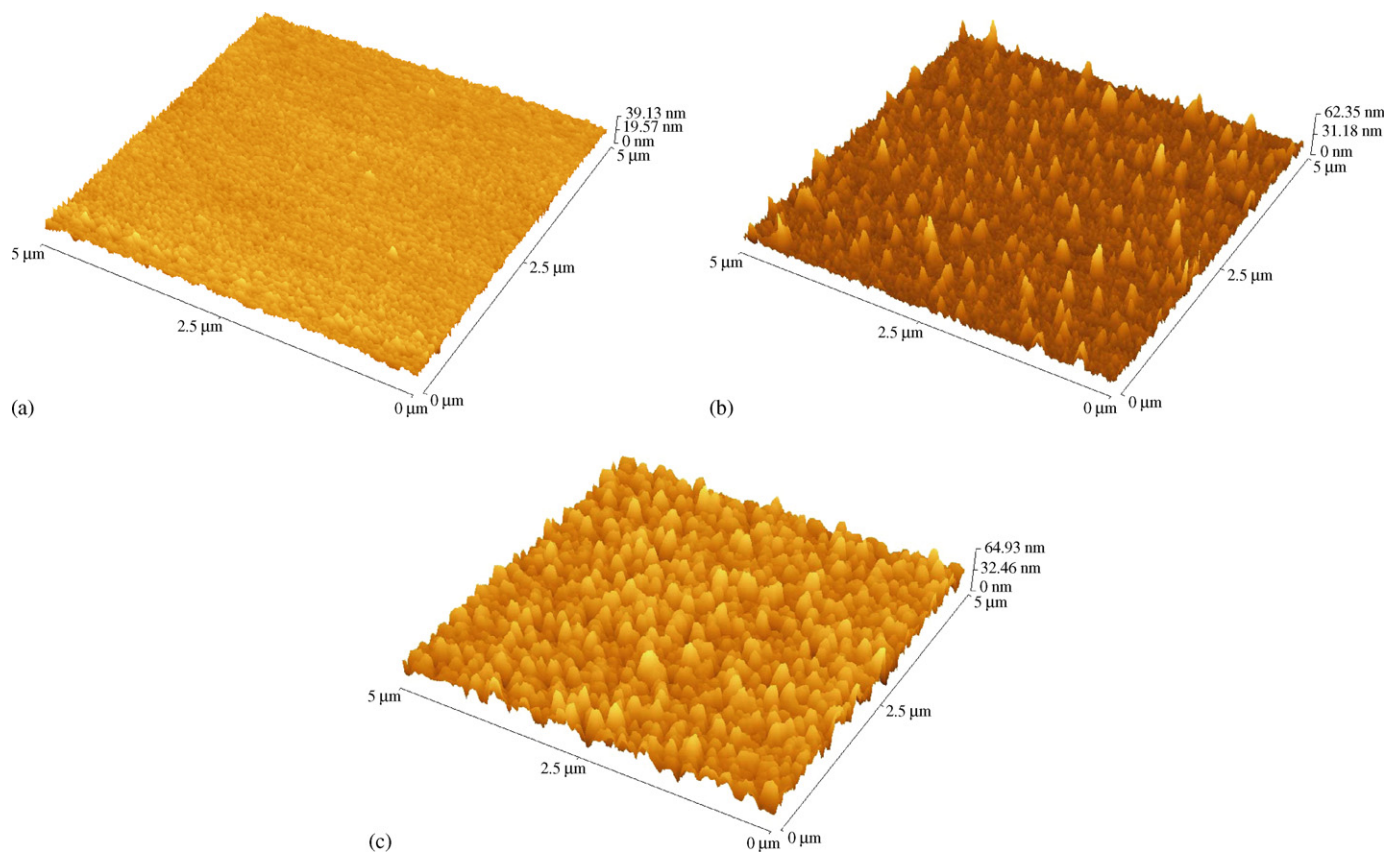

(a)

(b)

(c)

Fig. 4. 3D AFM images of the Ag films prepared by immersing in the solution of $0.005 \, mol \, l^{-1}$ AgNO$_3$ containing 0.06 (a), 0.6 (b) and 6.0 (c) $mol \, l^{-1}$ HF for 10 s at room temperature.
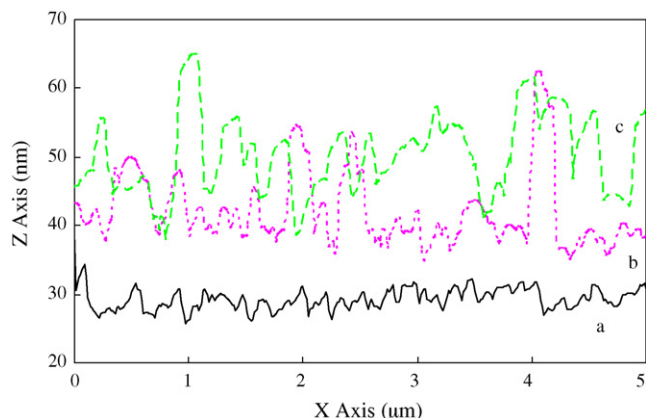
Fig. 5. Height profile of 3D AFM images of the Ag films prepared by immersing in the solution of 0.005 M $AgNO_3$ containing 0.06 (a), 0.6 (b) and 6.0 (c) mol l^{-1} HF for 10 s at room temperature.

increasing deposition rate. Furthermore, the solution temperature is another important factor. For example, Peng and Zhu [26] prepared silver dendrites on p-silicon (1 1 1) from HF solution, where the reaction temperature was 50 °C. Here it is not discussed.

4. Conclusions

The characteristics of electroless silver deposition onto p-silicon (1 1 1) from 0.005 mol l^{-1} $AgNO_3$ solutions with 0.06, 0.6 and 6.0 mol l^{-1} HF, respectively, was investigated using an electrochemical dc polarization method and open circuit potential-time (Ocp-t) technique. The same result that the surface energy levels of the silicon for adding 0.06, 0.6 and 6.0 mol l^{-1} HF were 0.40, 0.55 and 0.62 eV lower, respectively, than that for no added HF was obtained by both electrochemical methods. The drop slope of open-circuit potential, $K_{-\Delta E(\mathrm{OCP})/t}$, educed from the mixed-potential theory increased with the HF concentration, yet was not a linear function. This was also obtained by the determination of the silver deposition rate (deposition time is 10 s) by ICP-AES. 3D AFM images revealed that the 3D growth of silver onto silicon was favored with increasing the HF concentration, which was ascribed to the drops of the surface energy level. Results were explained by the stress generation and relaxation mechanisms.

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