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Cyclic voltammetry study of silver seed layers on p-silicon (100) substrates

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Abstract The anodic stripping behavior of the Ag seed layers on a p-silicon (100) wafer was studied by cyclic voltammetry (CV). The seed layers were prepared by immersing the silicon wafer in a solution of 0.005 M $AgNO_3 + 0.06$ M HF at room temperature. Then the layer adhered wafers were used as the work electrodes. The oxidation energy of the Ag monolayer based on the Si-Ag combination was observed and the oxidation energy of the Ag multilayer based on the Ag-Ag combination was also found.

Keywords Ag seed layer · Silicon wafer (p-100) · Cyclic voltammetry

Introduction

With the development of the manufacturing processes for ultra-large-scale integration (ULSI) and microelectromechanical systems (MEMS) [1], Ag electroless deposition onto silicon wafers has been receiving special attention, due to the potential applications of the end product arising from its excellent electronic properties [2, 3]. In previous work, we successfully prepared Ag seed layers on p-Si(100) wafers in a solution of 0.005 M $AgNO_3 + 0.06$ M HF, and then electrolessly deposited Ag [4] and Au [5] films on the seed layer. the next step in this field is to attempt to improve our understanding of the adhesion intensity and the stability of the Ag seed layer on the wafer.

In the field of electrochemistry, the underpotential deposition (UPD) method [6, 7] is often used to study the monolayer properties of a metal element on an electrode substrate. In this case, a solution containing ions of the metal is used. In order to induce an interaction between the ions and the electrode surface, a cathodic potential is generally applied. Cyclic voltammetry, used to determine the reductive (deposition) and the oxidation (stripping) behavior of the metal ions/metal, is the most frequently used tool in UPD study. The adsorption intensity between the adatom and the electrode surface is often characterized by the reductive potential difference ΔE_p, which is the difference between the monolayer deposition and the bulk deposition peaks. In the electroless deposition method, the adhesion intensity between the deposited metal and the electrode surface is characterized by the oxidation potential difference $\Delta E_{p\text{-}OX}$, which is the potential difference between the monolayer metal film stripping and the bulk metal stripping peaks. A number of previous papers have dealt with UPD-Ag on platinum and gold single crystal electrodes [8, 9, 10].

In this paper, cyclic voltammetry is used to study the anodic stripping behavior of the Ag seed layer on a p-Si(100) wafer. The Ag adhered silicon wafer was prepared prior to the electrochemical experiments. The Ag seed layer adhered silicon wafers were then used as the work electrodes. The aim of the work is to investigate the electrochemical behavior of the Si-Ag and the Ag-Ag interacting wafer surface, and to find the adhesion intensity and the stability of Ag on the wafer.

Experimental

Instrumentation

A CHI-660 electrochemical workstation (USA) was used. A 40 ml homemade Teflon cell was used in a three-electrode configuration [11]. The silicon wafer, which was mounted to a small hole at the bottom of the cell, served as the working electrode, with a disc area of 0.071 cm^2. The counter electrode was a platinum wire, dipped directly into the supporting electrolyte. The reference was a saturated Hg_2Cl_2/Hg (SCE) electrode.

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Chemicals and materials

The stock solution of 0.5 M $AgNO_3$ was prepared by dissolving 4.2468 g of $AgNO_3$ in 50 ml water in a brown flask. 0.1 M $NaClO_4$ was used as supporting electrolyte. All reagents are analytical-reagent grade. Milli-Q (Millipore, 18.2 MΩ cm^{-1}) water was used throughout. A (100) p-type silicon wafer with a resistivity of 15–20 Ω cm and a thickness of 650 + 25 μm (Beijing Youyan silicon villa semiconductor) was used.

Wafer treatment

The silicon wafer was cut into square samples each with 1 cm^2 surface area. The wafer was first cleaned in an ultrasonic cleaner in absolute alcohol for 10 min. The wafer was then immersed in a hot solution (80 °C) of H_2O_2:NH_4OH:H_2O (1:1:5) for 10 min and then into another hot solution (80 °C) of H_2O_2:HCl:H_2O (1:1:6) for 10 min to remove possible contamination. Finally, the wafer was 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 native silicon oxide. The wafer was rinsed with deionized water and dried with nitrogen flux after each cleaning step.

Preparation of the Ag seed layer on silicon

The silver seed layer was deposited onto the surface of the etched silicon wafer by immersing the wafer in a solution of 0.005 M $AgNO_3$ + 0.06 M HF for different lengths of time at room temperature [4, 5].

The CV procedure

After the seed layer was deposited on the etched wafer and the wafer was mounted to the cell, the electrolyte solution of 0.1 mol/L $NaClO_4$ was added while ensuring that there were no bubbles on the surface of the wafer. CV scanning was then immediately performed. The potentials were initially scanned in the positive direction from −0.5 V, and the oxidation peak was taken as positive current.

Results and discussion

The CV behavior of the Ag seed layers

Figure 1 shows the CV curves of the Ag seed layers on the silicon wafers. Two cycles of potential scan were performed for 1 s of Ag deposition onto a silicon wafer (Fig. 1A). When the scan was performed from −0.5 V to 6.0 V, an Ag stripping peak was found at 2.9 V (curve a). When the potential was scanned in the reverse direction (from 6.0 V in a negative direction), no reductive peak was observed. In the second cycle (curve b) there were neither stripping nor reductive peaks found. These results demonstrate that the lower coverage Ag seed layer, resulting from 1 s deposition, can be wholly stripped in a single cycle, and the Ag^+ ions

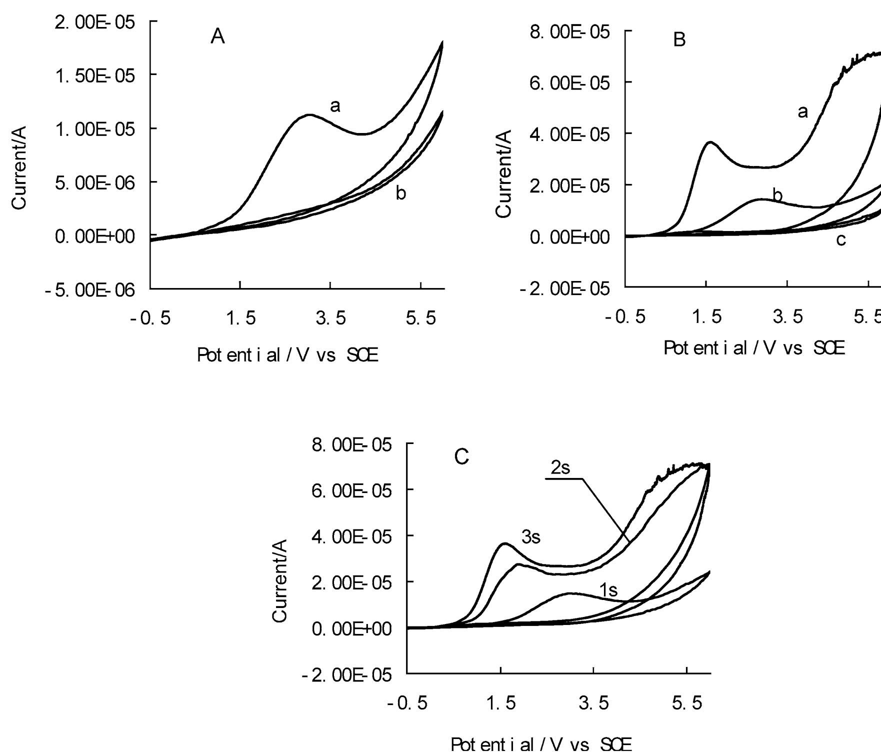

Fig. 1 Successive cyclic voltammograms of Ag deposited on wafer for 1 s (A), 3 s (B) deposition, and overlapped first cycle CV curves (C) for different deposition times. The scan sequence is marked by a, b, and c. Supporting electrolyte is 0.1 M $NaClO_4$. Scan rate is 100 mV s^{-1}

produced by the oxidation of the Ag seed layer immediately diffuse into the solution bulk without further reduction. In comparison, it needs two cycles to completely strip the Ag seed layer prepared by 3 s deposition (see Fig. 1B). The stripping peak of the Ag seed layer is located at 1.6 V in the first cycle, which is more negative than that seen in the 1 s deposition scans. The stripping potential of the Ag seed layer is 2.8 V in the second cycle, which is very close to that seen in the 1 s deposition scans (Fig. 1A). CV curves of the first cycle scan for different deposition times are shown superposed in Fig. 1C. From 1 s deposition to 3 s deposition (in other words with increasing coverage of the seed layer, see our previous work [4]), the Ag stripping peak currents increase and the peak potential shifts in the negative direction – a phenomenon that is typical of UPD [12]. This confirms that the stripping peaks observed for these shorter deposition times, 1~3 s,are caused by the oxidation of the Ag monolayers.

If the Ag seed layer can be wholly stripped out in one cycle of the CV scan, as indicated in Fig. 1A, the surface coverage (mol cm^{-2}) of Ag on the silicon wafer can be calculated by the following formula [13]:

$$\Gamma = Q/_{nAF} \tag{1}$$

Here Q is the charge from the peak area (coulombs), F is the Faraday constant, n is the number of electrons transferred in the electrode reaction, and A is the electrode area (cm^2).

For the higher coverage Ag seed layer, several cycles of CV scanning are necessary to completely strip out the Ag on the wafer. For example, Fig. 1B shows that the Ag seed layer was completely stripped out by two cycles of CV scanning. In this case, the total charge Q_{Total} should be the overall separated charge from all of the stripping peaks from every CV scan. If the CV scan must be performed x times to completely strip out the Ag seed layer, we obtain:

$$Q_{\text{Total}} = Q_1 + Q_2 + \ldots + Q_x \tag{2}$$

Here Q_1, Q_2, and Q_x represent the charges of the Ag stripping peaks from all of the CV scans needed to completely strip the Ag monolayer on the silicon wafer.

Therefore,

$$\Gamma_{\text{Total}} = Q_{\text{Total}}/_{nFA} \tag{3}$$

From Fig. 1B, the calculated Q_1 for curve a is 5.5×10^{-5} C, and Q_2 for curve b is 3.2×10^{-5} C. Therefore, the surface coverage for 3 s Ag deposition is:

$$\Gamma_{\text{Total}} = (Q_1 + Q_2)/nAF = \frac{5.5 \times 10^{-5}C + 3.3 \times 10^{-5}C}{1 \times 0.071\ \text{cm}^2 \times 96500\ C\ \text{mol}^{-1}} = 1.3 \times 10^{-8} \tag{4}$$

For most of the metal monolayers in UPD studies, the maximum surface coverage $_{\text{max}}$ is about 2×10^{-9} mol/cm [14]. In our work, we have determined to be 3.9×10^{-9} mol/cm^2 for 1 s deposition and $_{\text{Total}}$ is 1.3×10^{-8} mol/cm^2 for 3 s deposition. These values are very close to the reported monolayer coverage $_{\text{max}}$.

The CV behavior of the monolayer and multilayer Ag

Figure 2 shows another series of cyclic voltammograms for Ag seed layers on silicon wafers, but for much longer deposition time than those discussed in the previous

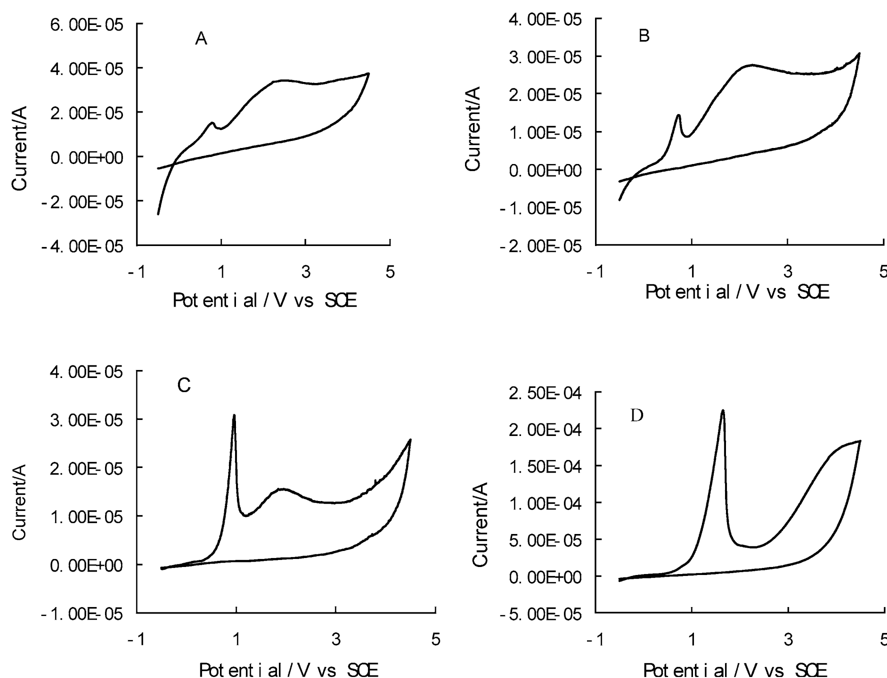

Fig. 2 Cylic voltammograms of the Ag seed layers on silicon wafer for 5 s (A), 10 s (B), 30 s (C), and 45 s (D) depositions. Only the first cycle CV curves were recorded. Supporting electrolyte is 0.1 M $NaClO_4$. Scan rate is 100 mV s^{-1}

section. Only the first cycle CV curve is recorded. In contrast to the results discussed previously, all of the CV curves in Fig. 2 show two stripping peaks. The peak located at a relatively positive potential can be assigned to the Ag monolayer stripping (MD-S) caused by the oxidation of the Ag-Si structure, while another peak located at a relatively negative potential corresponds to the bulk stripping (BD-S) from the oxidation of the Ag-Ag structure. For the stripping process of silver on silicon, the electrode reaction can be expressed as follows:

$$\text{Ag - Ag - e} = \text{Ag - Ag}^{+} \quad \text{BD - S} \tag{5}$$

$$\text{Si - Ag - e} = \text{Si - Ag}^{+} \quad \text{MD - S} \tag{6}$$

Figures 2A to Fig. 2C show that the BD-S peak height increases proportionally as deposition time is increased from 5 s to 45 s. This is due to a dramatic increase in Ag film thickness. At the same time, the peak current of the MD-S stripping maintains a reasonably constant level, which indicates that the Ag monolayer coverage is saturated on the silicon wafer. On the other hand, the peak potential ($E_{\text{p-BD}}$) of the BD-S shows a shift to the positive direction as the thickness of the Ag seed layer is increased, although it is limited to a relatively narrow potential range in the 30 s deposition. The average peak potential of Ag BD-S is 0.9 V.

For the extreme case, when the deposition time is 45 s, the stripping peak of the Ag monolayer is entirely obscured by the Ag BD-S so that the two peaks become a single peak, as shown in Fig. 2D. It is clear that the single peak has a much higher current and a wider shape than the peak for 30 s deposition. At the same time, the BD-S peak is substantially shifted in the positive direction, from about 0.9 V to 1.4 V.

Because of the MD-S and the BD-S are shifted in opposite directions, the difference in potential shift between the MD-S and the BD-S, ΔE_{p}, is not stable. The ΔE_{p} is about 1700 mV for 5 s deposition, 1500 mV for 10 s deposition, and 1030 mV for 30 s deposition. The reason that the lower coverage monolayer Ag seed layer possesses the more positive potential is that the lower coverage Ag monolayer forms a single Si–Ag bond with the silicon substrate. In other words, the Si–Ag bonds are less affected by interactions between the Ag atoms due to the lower Ag density (coverage). In this case, the Si–Ag bonds are relatively strong and need more energy to oxidize them. Usually the substrate–adatom bonds are stronger than the bonds between the adatoms themselves [15].

The negative shift of MD-S as the Ag thickness increases can be explained by the increase in the density (coverage) of Ag atoms on the Ag–Si structure: the more Ag atoms there are on the Ag–Si structure, the stronger the interaction force between the Ag atoms. This interaction force weakens the interactions between the Ag atoms and the Si atoms. On the other hand, the solid solubility of silicon in silver also affects the Si–Ag interaction [16].

A sudden change in MD-S potential and MD-S peak current between 3 s deposition and 5 s deposition is apparent. For example, the MD-S potential is 1.6 V and the MD-S peak current is 2.8×10^{-5} A for 3 s deposition. But the MD-S potential is 2.5 V and the MD-S peak current is 1.2×10^{-5} A for 5 s deposition. This behavior contradicts our previous conclusion, in which the MD-S potential should shift to a more negative value with an increase in the layer coverage. It must be pointed out that the BD-S cannot be found in the 3 s deposition, but it can be clearly observed in 5 s deposition. So we have every reason to believe that when the multilayer Ag was initially formed, say one or two layers of Ag had developed on the monolayer Ag, then because of the Ag-Ag interactions, the BD-S of the initial Ag multilayer should involve some Ag atoms of the monolayer. This leads to a decrease in the number of Ag atoms in the monolayer, and this ‘‘lower coverage monolayer’’ possesses a more positive peak potential and a lower peak current.

From the data above, we can infer that the bond energy of Ag on Si is a function of the monolayer coverage. A more positive potential of MD-S indicates that it takes more energy to oxidize the seed layer. In other words, a lower coverage seed layer will be more stable and possess much stronger bonds with the silicon substrate.

Conclusions

The anodic stripping behavior of monolayer and the multilayer Ag layers on p-Si(100) was studied using cyclic voltammetry. In the monolayer range, the potential difference between the stripping peaks of the monolayer and bulk stripping were much more than 1000 mV. The higher ΔE_{p} between the MD-S and BD-S is due to the large difference in the bond energies of Si–Ag and Ag–Ag. The bond energy combination of Ag on Si is a function of the monolayer coverage. A more positive potential of MD-S means that it takes more energy to oxidize the seed layer. In other words, lower coverage seed layers will be more stable and possess stronger bonds with the silicon substrate.

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