Communication—Galvanic Deposition of Gold on Silicon from Au(I) Alkaline Fluoride-Free Solutions

S. S. Djokić, Ž. Antić, N. S. Djokić, and T. Thundat

Deposition of gold from alkaline fluoride-free solutions containing Au(I) ions onto the silicon surfaces has been demonstrated. This deposition takes place at room temperature and does not require the presence of a reducing agent in the solution. The results clearly show that Au(I) ions can be reduced to Au(0) by silicon and, as a consequence, gold metal can be deposited at the surface of the substrate.

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Experimental

p- (B doped) and n- (P doped) single crystal (100) silicon wafers were used as substrates in the present work. As received, silicon substrates were very carefully washed with 3:1 (H2SO4-H2O2) solution and then with water and absolute ethanol. Immersions were performed at pH 14 using a solution containing 30 g/L Na2S2O3 and 1 g/L Au2S2O3. The pH of this solution was adjusted with NaOH.

The specific immersion times are reported in the Results and Discussion section. Experiments were carried out at room temperature (about 23°C). After the immersion, substrates were removed from the solutions and carefully washed with water, ethanol and then pressure dried with air at room temperature. Coated silicon substrates were analyzed by X-ray diffraction (XRD) using the CuKα radiation and by scanning electron microscopy (SEM).

Results and Discussion

Gold was deposited on both p- and n- Si substrates after immersion into alkaline Au(I) solutions at room temperature for 2 hours. Deposition of gold was observed on both polished and back sides of the silicon wafer. A prolonged exposure of silicon wafers to the investigated solutions obviously leads to the growth of gold particles. In Figure 1 are presented SEM images of the deposited gold onto p- and n-Si substrates. The deposit of gold onto n-Si substrate is composed of agglomerated spherical particles with an approximate size of 0.7 μm. For the same time of exposure on p-Si substrate the maximum size of the individual spherical gold particle is estimated at about 2 μm in diameter.

As in previous work, silicon substrates were mechanically scratched with tweezers immediately prior to immersion into alkaline Au(I) solutions. The SEM results are shown in Figure 2 for both n- and p- silicon substrates. As shown in Figure 2, quite uniform and preferential deposition onto scratched areas occurred. In the regions outside of the scratched area there are randomly distributed particles. These results suggest a better removal of the surface SiO2 film by the mechanical scratching, leads to a more uniform gold deposition.

A prolonged exposure of silicon substrates to the alkaline Au(I) containing solutions, obviously leads to a growth of gold film deposited. Due to poor adhesion, gold film or particles can easily be separated from the surface of both p- and n- silicon wafers. The SEM images of gold separated from the silicon substrate are presented in Figure 3.

XRD patterns of the gold deposits onto silicon substrates are presented in Figure 4. As the XRD results show, the deposit is composed exclusively of gold.

The existence of SiO2 at the surface of the silicon substrate was described and attributed as a difficulty for the galvanic displacement deposition before, and notably, in the recent publications. The solution used in the present work did not contain any Au(I) ion reducing agents. Also, fluorides were purposely avoided and highly alkaline solutions (pH 14) of Au (I) were used.

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Figure 1. SEM image of gold deposited onto silicon wafer at room temperature from an alkaline Au(I) – containing solution onto n- (a) and p- (b) Si substrates. Immersion time: 5 days.

Figure 2. SEM images of gold deposits onto the scratched areas of p- (a) and n- (b) silicon substrates. Immersion time: 2 hours.

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Silicon dioxide (SiO₂) can be dissolved in alkaline solutions (KOH or NaOH) as described by the following reaction:

\[
\text{SiO}_2 + 2\text{OH}^- \rightarrow \text{SiO}_3^{2-} + \text{H}_2\text{O} \tag{1}
\]

with the standard Gibbs energy \( \Delta G^\circ = -12.108 \text{ kJ/mol} > 0 \).

Similarly, after removal of the SiO₂ film, dissolution of silicon in the alkaline solutions can be described by the reaction:

\[
\text{Si} + 2\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{SiO}_3^{2-} + 2\text{H}_2 \tag{2}
\]

with \( \Delta G^\circ = -335.236 \text{ kJ/mol} < 0 \).

The fact that the Gibbs energy, \( \Delta G^\circ \), for Reaction 1 is positive suggests that this process does not proceed under the standard physicochemical conditions. On the other hand, the value of \( \Delta G^\circ \) for Reaction 2 suggests that this process is thermodynamically favorable under standard physicochemical conditions. Dissolution of the silicon wafer in strong alkaline solutions can be described by combining Equations 1 and 2:

\[
\text{SiO}_2 + \text{Si} + 4\text{OH}^- \rightarrow 2\text{SiO}_3^{2-} + 2\text{H}_2 \tag{3}
\]

with \( \Delta G^\circ = -323.128 \text{ kJ/mol} \).

The values of \( \Delta G^\circ \) for the proposed chemical reactions were calculated according to thermodynamic data available in the literature.

Since SiO₂ film is present at the surface of the substrate, deposition of gold, as observed in this work, can be described by combining the above equations and including \( 2\text{Au(S}_2\text{O}_3)_3^{3-} \) ions by the following reaction:

\[
\text{Si} + \text{SiO}_2 + 2\text{Au(S}_2\text{O}_3)_3^{3-} + 6\text{OH}^- \rightarrow 2\text{SiO}_3^{2-} + 2\text{Au} + 4\text{S}_2\text{O}_3^{2-} + \text{H}_2 + \text{H}_2\text{O} \tag{4}
\]

with \( \Delta G^\circ = -450.276 \text{ kJ/mol} < 0 \).

Interestingly, the standard Gibbs energy (\( \Delta G^\circ \)) for Reaction 4 is \(-450.276 \text{ kJ/mol} \). Considering that this Gibbs energy is negative, the deposition of gold onto silicon from alkaline solutions should then also be possible at standard physicochemical conditions. This is experimentally confirmed by the results presented in Figures 1–4.

Generally, it was observed that a better coverage with the deposits is achieved on n- than on p- silicon substrates. This observation suggests that the impurities i.e., B and P may play some role in the rate of Si oxidation. Impurities may significantly affect the rate of many electrochemical reactions including the galvanic displacement. In this way, the rate of crystal growth is determined by the rate of substrate oxidation (dissolution) which is an anodic process and by the rate of metal ion reduction (deposition) which is a cathodic process. The half reaction describing the dissolution of silicon in alkaline solutions can be written as:

\[
\text{Si} + 4\text{OH}^- \rightarrow \text{SiO}_3^{2-} + \text{H}_2\text{O} + \text{H}_2 + 2\text{e} \tag{5}
\]

The electrons produced according to Reaction 5 are further used for the reduction of the respective metal ions i.e. Au(I).

The initial stages of gold deposition take place approximately after 1 hour upon immersion of silicon substrates into Au(I) alkaline solutions. A delayed deposition of gold onto silicon at room temperature is attributable to the Reactions 1 and 2. It seems that Reaction 1 is the rate-determining step. The results of the present work clearly show that after removal of the SiO₂ film, the deposition of gold proceeds further. Electrons, produced due to oxidation of Si (Reaction 5 are used for the reduction of Au(I) to Au(0), as described by the following reaction:

\[
\text{Au(S}_2\text{O}_3)_3^{3-} + \text{e} \rightarrow \text{Au} + 2\text{S}_2\text{O}_3^{2-} \tag{6}
\]

Based on the previous publications related to Ag, Cu and including the present experiments with Au, the results suggest that monovalent ions i.e., Ag(I) and Au(I) can directly be reduced by silicon in strong alkaline and fluoride free solutions, most preferably than Cu(II) ions. Interestingly, as shown for the case of Cu(II), the most preferable reduction process is related to the deposition of Cu₂O, rather than Cu. The observations suggest further that a “one-electron-transfer reaction” is most likely to occur in the systems investigated, as shown for Ag(I) and in the present work for Au(I). According to the results related to Cu(II), the reaction reactions to the elemental Cu probably go through “multiple steps”. The simultaneous hydrogen evolution reaction in the deposition of Ag, Cu and Au from alkaline and fluoride free solutions, as observed in experimental work with these metals, must very carefully be considered in the future, since it may affect significantly the surface morphology and adhesion of the deposited films as shown in Figure 3.

Conclusions

In spite of the existence of native SiO₂ films on silicon surface, gold can be successfully deposited via the galvanic displacement reaction from strong alkaline solutions containing Au(I) complexed ions, without a presence of any reducing agents in the aqueous phase. The deposition can take place at room temperature and at a pH close to 14. Under these conditions, the surface SiO₂ films are dissolved leading to the deposition of Au. The deposition of gold is a consequence of the reduction of Au(I) due to SiO₂ film removal and oxidation of silicon in strong alkaline solutions. Considering many potential applications, detailed studies on the effects of concentrations of Au(I), additives, complexing agents and temperature are required in the future.
Acknowledgments

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