Galvanic processes on silicon surfaces in Cu(II) alkaline fluoride-free solutions

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Fluoride-Free Solutions

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Metallization of silicon with copper, silver and gold can be realized using electrochemical methods such as electrodoposition or electroless deposition from aqueous solutions. These methods are very attractive since they are simple and relatively easy to scale up. Practical difficulties arise due to the fact that at the surface of silicon wafers, oxide films of SiO₂ are present. SiO₂ films are non-conductive, and consequently, they must be removed prior to direct metallization. Although the metallization of silicon substrates can be achieved via autocatalytic deposition through surface activation with SnCl₂/PdCl₂ catalysts, this process would not remove the SiO₂ film leading to unacceptable electronic device performance. In order to remove the SiO₂ film and to deposit metals such as copper or silver from aqueous solutions directly onto silicon, pre-treatment steps are required during processing. These pre-treatment steps may involve fluoride-containing solutions, which have deleterious effects on the environment. The direct deposition of copper, silver or gold from aqueous fluoride-containing solutions onto silicon substrates via the galvanic displacement reaction can be quite unsuccessful. According to recent investigations, silver can be successfully deposited onto silicon substrates from fluoride-free aqueous solutions. Reports on the deposition of copper onto silicon substrates via the galvanic displacement reaction from fluoride-free aqueous solutions have not been found in the literature. In an attempt to further explore the behavior of silicon in fluoride-free solutions without a presence of reducing agents in the aqueous phase, the present communication describes preliminary observations on galvanic reactions on silicon substrates using Cu(II) containing alkaline fluoride-free aqueous solutions.

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 ethanol. After the cleaning procedure, silicon substrates were immersed into respective proprietary fluoride-free solutions containing Cu(II) ions. Immersions were performed at pH 14 using a CuCl₂H₂O₄ (copper tartrate) complexed solution. The pH of this solution was adjusted with NaOH. The concentration of Cu(II) ions in alkaline solutions was 3.54 g/L. The immersion solutions in the present work were used as prepared. Consequently it should be assumed that O₂ was present in the solutions during the immersion.

The specific immersion times are reported in the Results and Discussion sections. Experiments were carried out at 90°C or at room temperature (about 23°C). After the immersion, the 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

Deposition of a reddish-orange film on both p- and n-Si substrates was observed visually after immersion into alkaline Cu(II) solutions at 90°C for 1 hour. Although the adhesion was poor, the coverage of silicon substrate with deposited film appeared uniform. In Figure 1 are presented SEM images of the deposited film onto p- and n-Si substrates. For deposits onto p-Si substrate (Figures 1a and 1b) a non-uniform coverage of the surface is visible. A higher magnification (Figure 1b) shows that the deposit consists of agglomerated particles. Also, individual cubic particles with an approximate size up to a maximum of 2 μm are noticeable. On n-Si substrates (Figure 1, bottom) less porous deposits are obtained. Due to the poor adhesion and sample preparation, the coatings peeled off. In Figure 1 (bottom left), individual cubical particles with a size of 2 μm and below are clearly visible. The size of the majority of deposited particles with multifaceted morphology is estimated to be below 500 nm.

Additionally, in some experiments silicon substrates were mechanically scratched with tweezers immediately prior to immersion into alkaline Cu(II) solutions at 90°C. The SEM results with two different magnifications are shown in Figure 2 for both n- and p- silicon substrates. As shown in Figure 2, preferential deposition onto scratched areas occurred where particles of 20 μm or larger, are visible. In the regions outside of the scratched area there are randomly distributed cubic particles with a majority being approximately 2 μm in size. These results suggest a better removal of the surface SiO₂ film by the mechanical scratching, leading in this way to a better deposition, which is addressed in more details in the Discussion section.

When both p- and n- silicon substrates were immersed into alkaline solutions at room temperature the deposition was not observed within a reasonable period of 8 hours. However, after three days, reddish deposits onto the scratched areas of silicon substrates were observed. The SEM results for this experiment are shown in Figure 3.

As the SEM images in Figure 3 show, deposition onto both p- and n- silicon substrates is possible at room temperature. The preferential deposition onto scratched areas is clearly visible. In the regions outside of the scratched area there are randomly distributed solid particles, however not to a significant degree.

What are the reddish deposits formed on the silicon surface upon an immersion into alkaline Cu(II) fluoride free solutions? XRD patterns of the reddish deposits onto silicon substrates are presented in Figure 4.
As the XRD results show, the reddish deposit is composed predominantly of Cu$_2$O. Elemental copper was detected in the deposit as well.

**Discussion**

It is common knowledge that at the surface of silicon substrate a thin oxide film of SiO$_2$ unavoidably exists. The solution used in the present work did not contain any Cu(II) ion reducing agents. Also, fluorides were purposely avoided and highly alkaline solutions (pH 14) of Cu (II) were used.

It is known that SiO$_2$ can be dissolved in alkaline (KOH or NaOH) solutions, which is described by the following reaction:

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

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

Similarly, after removal of the SiO$_2$ film, dissolution of silicon in the alkaline solutions can be described by the reaction:

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

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

The fact that the standard Gibbs energy, $\Delta G^0$, for Reaction 1 is positive suggests that this process will not proceed under the standard physicochemical conditions. On the other hand, the value of $\Delta G^0$ for Reaction 2 suggests that this process is thermodynamically favorable under the standard physicochemical conditions. However, the sum of the Gibbs energies for the Reactions 1 and 2 is negative, suggesting that the overall process is possible. The values of $\Delta G^0$ for the proposed chemical reactions were calculated according to thermodynamic data available in the literature.\(^8\)

Since the deposition onto silicon is carried out at 90°C, it is reasonable to assume that the SiO$_2$ film is dissolved in strong alkaline conditions (according to the Reaction 1) and a reduction of Cu(II) to Cu(I) or Cu(0) by silicon proceeds further. As the XRD results in Figure 4 show, Cu$_2$O and Cu(0) are formed on the silicon surface upon an immersion in the Cu(II) alkaline fluoride free solutions. Also, it is very important to note, that a formation of bubbles was observed while the Si substrates were immersed into the solution, especially at elevated temperatures. This bubble formation is attributed to the hydrogen evolution reaction. Formation of Cu$_2$O, deposition of Cu and hydrogen evolution, as cathodic reactions under the conditions of the present work can be represented as:

$$2\text{Cu}^{2+} + 2\text{OH}^- + 2\text{e} \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad [3]$$

$$\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu} \quad [4]$$

$$2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2 + 2\text{OH}^- \quad [5]$$

Since SiO$_2$ film is present at the surface of the substrate, deposition of Cu$_2$O and Cu(0), as observed in the this work, can be described by combining the above equations:

$$\text{SiO}_2 + 2\text{Si} + 3\text{Cu}^{2+} + 12\text{OH}^- \rightarrow 3\text{SiO}_3^{2-} + 4\text{H}_2\text{O} + 2\text{H}_2 + \text{Cu}_2\text{O} + \text{Cu} \quad [6]$$

with $\Delta G^0 = -1245.696 \text{ kJ/mol}$.

Interestingly, the standard Gibbs energy ($\Delta G^0$) for Reactions 6 is $-1245.696 \text{ kJ/mol}$. Considering that this Gibbs energy is negative, the deposition of Cu$_2$O or Cu onto silicon from alkaline solutions should then also be possible at the standard physicochemical conditions. This is experimentally confirmed by the results presented in Figure 3 (SEM data) and Figure 4, right (XRD data).

A prolonged immersion of silicon substrates into Cu (II) alkaline solutions at 90°C leads to the deposition of Cu$_2$O powders, which separate from the surface easily. In Figure 5 are shown SEM images of Cu$_2$O powders separated from silicon substrate. Based on the SEM images obtained, copper particles have a regular geometric shape, with the largest achieving about 6 \(\mu\)m in size.
The powders presented in Figure 5 represent Cu$_2$O, as found by the XRD analysis. Since the powders peel off and they are not anymore in contact with silicon, their further reduction to elemental copper is not possible to achieve under the conditions of the present work.

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.

Additionally, the deposits are quite porous as observed for other galvanic displacement processes. 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:

$$\text{Si} + 4\text{OH}^- \rightarrow \text{SiO}_2^{2-} + \text{H}_2\text{O} + \text{H}_2 + 2e^- \quad [7]$$

The electrons produced according to Reaction 7 are further used for the reduction of the respective metal ions i.e. Cu(II). Dissolution of the silicon wafer in strong alkaline solutions can be described by combining the Equations 1 and 2:

$$\text{SiO}_2 + \text{Si} + 4\text{OH}^- \rightarrow 2\text{SiO}_2^{2-} + 2\text{H}_2 \quad [8]$$

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

A delayed deposition of Cu$_2$O and Cu onto silicon at room temperature is attributable to the Reactions 1 and 8. It seems that Reaction 8 is the rate determining step. At higher temperatures this reaction is more thermodynamically favorable and consequently, the deposition is significantly faster. On the other hand, the results of the present work clearly show that, after removal of the SiO$_2$ film, the first step of the galvanic displacement is a one electron transfer reaction, due to oxidation of silicon, i.e. reduction of Cu(II) to Cu(I):

$$\text{Cu}^{2+} + e \rightarrow \text{Cu}^+ \quad [9]$$

Due to the high concentration of OH$^-$ ions (pH14), Cu$^+$ is further converted into Cu$_2$O according to the reaction:

$$2\text{Cu}^+ + \text{OH}^- \rightarrow \text{Cu}_2\text{O}^+ + \text{H}^+ \quad [10]$$

In this way Cu$_2$O is produced, as it is clearly confirmed by the XRD analysis. In the next step, due to the dissolution of Si and the porosity of deposited Cu$_2$O, the produced electrons are further used for its (Cu$_2$O) reduction from Cu(I) to Cu(0) and therefore to production of copper metal as described by the overall Reaction 6.

Importantly, the results of the present work suggest that the deposition of copper and Cu$_2$O onto silicon substrate in alkaline fluoride-free and Cu(II) containing solutions is possible. Additional experiments are suggested in order to find the most appropriate conditions for direct or selective deposition of copper onto silicon substrates, which could lead to further developments and/or improvements in the electronic industry. Perhaps oxygen-free or some Cu(I) containing alkaline and fluoride-free solutions could produce a direct deposition of metallic copper onto silicon in the galvanic mode, however additional studies are required to clarify these issues in the future.

**Conclusions**

In spite of the existence of surface SiO$_2$ films on silicon, Cu$_2$O and Cu can be successfully deposited via the galvanic displacement reaction from strong alkaline solutions containing Cu(II) complexed ions, without a presence of any reducing agents in the aqueous phase. The deposition can take place at room or, preferably, at elevated temperatures and at a pH close to 14. Under these conditions, the surface SiO$_2$ films are dissolved and deposition of Cu$_2$O and Cu can occur. The deposition of Cu$_2$O is a consequence of the reduction of Cu(II) due to SiO$_2$ film removal and oxidation of silicon in strong alkaline solutions. Considering many potential applications detailed studies on the effects of concentrations of Cu(II), additives, complexing agents and temperature are required in the future.

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References

1. S. S. Djokic and L. Magagnin, Metallization of Semiconductors and Nonconductive Surfaces from Aqueous Solutions, in Modern Aspects of Electrochemistry: Electrodeposition and Surface Finishing: Fundamentals and Applications, Volume 57, S. S. Djokic, Editor, p.341, Springer, New York, (2014).
2. K. W. Kolasinski, Nanoscale Research Letters, 9, 432 (2014).
3. L. Maganin, R. Maboudian, and M. Carraro, Electrochem. and Solid State Lett., 4(1), C5 (2001).
4. Y.-Y. Song, Z.-D. Gao, J. J. Kelly, and X.-H. Xia, Electrochem. and Solid State Lett., 8(10), C148 (2005).
5. C. P. da Rosa, E. Iglesia, and R. Maboudian, J. Electrochem. Soc., 155(3), D244 (2008).
6. S. Y. Sayed, F. Wang, M. Malek, P. Li, D. Wang, and J. Buriak, Cryst. Eng. Comm., 14, 5230 (2012).
7. S. S. Djokic and K. Cadien, ECS Electroche. Lett., 4(6), D11 (2015)
8. A. J. Bard, R. Parsons, and J. Jordan Editors, Standard Potentials in Aqueous Solutions, Marcel Dekker Inc., New York (1985).
9. J. O’M. Bockris and A. K. N. Reddy, Modern Electrochemistry, Plenum Press, New York (1998).
10. S. S. Djokic, "Electroless deposition of metals and alloys", Modern Aspects of Electrochemistry, No. 35, B. E. Conway, R. White, and J. O’M. Bockris, Editors. p.51, Kluwer Academic/Plenum Publishers, New York (2002).
11. S. S. Djokic and N. S. Djokic, J. Electrochem. Soc., 158, D204 (2011).
12. S. S. Djokic, Production of Metallic Powders from Aqueous Solutions without an External Current Source, in Modern Aspects of Electrochemistry: Electrodeposition of Metal Powders from Aqueous Solutions, Volume 54, S. S. Djokic, Editor, p.369, Springer, New York, (2012).
13. S. S. Djokic, N. S. Djokic, C. Guthy, and T. Thundat, Electrochim. Acta, 109, 475 (2013).