Si thin films are employed in a variety of technologies, including microelectronic and photovoltaic devices, Li ion battery anodes, and corrosion-resistant coatings. Unfortunately, Si thin film deposition currently requires expensive vacuum methods such as chemical vapor deposition (CVD) and plasma-enhanced chemical vapor deposition (PECVD). For most materials, electrochemical thin film deposition has significant advantages of cost, scalability, and manufacturability.

However, electrochemical Si thin film deposition is notoriously difficult. Electrodeposition from aqueous solution appears to be precluded by the highly cathodic standard reduction potential of SiO$_2$ ($\sim$0.90 V vs. NHE), which is cathodic to the standard reduction potential of water ($\sim$0.83 V vs. NHE). This suggests that Si electrodeposition would be accompanied by simultaneous reduction of the solvent. Therefore, past reports of Si electrodeposition have employed either organic solvents, room temperature ionic liquids (RTILs), or high temperature molten salts. In addition, room temperature methods have to date produced Si films that are either nanoporous, or too thin for many applications (>200 nm).

We recently reported galvanic deposition of Si onto 6061 Al alloy from aqueous solutions containing 10 mM HF and 20 mM Na$_2$SiF$_6$ in 80 wt % formic acid (HCO$_2$H) by a combination of galvanic and electroless deposition. EDX measurements show that these films contain only Si, Cu, and Al.

Experimental

Semiconductor grade 10 wt % HF was obtained from J. T. Baker, Na$_2$SiF$_6$ was obtained from Sigma Aldrich, formic acid (HCO$_2$H) was obtained from JT Baker, and Al 6061 alloy was obtained from McMaster Carr. Al 6061 alloy typically contains 0.8–1.2 wt % Mg, 0.4–0.8 wt % Si, ≤ 0.70 wt % Mg, 0.15–0.40 wt % Cu, 0.04–0.35 wt % Cr, and smaller amounts of Mn, Ti, and Zn. For all Si deposition experiments, the Al sample was rotated at 850 rpm with a rotating disc electrode (RDE).

The Si film thickness and morphology were measured with a JEOL Model 7400F field emission scanning electron microscope (FESEM), following Au/Pd sputtering. X-ray diffraction measurements were performed using a Bruker Model D8-FOCUS x-ray diffractometer. Fourier transform infrared measurements were performed with a Mattson Genesis Series FTIR Model 9423-240-08061 spectrophotometer.

Results and Discussion

We recently reported galvanic deposition of Si onto 6061 Al alloy from aqueous solutions containing 10 mM HF and 20 mM Na$_2$SiF$_6$ in 80 wt % formic acid. Following emersion into laboratory air, these Si deposits contain nanoscale pores ranging in size from 3–8 nm. The nanoporous Si film appeared dark grey in solution, but gradually changed color to light grey and then white upon overnight exposure to laboratory air. This is consistent with the known color change expected with oxidation of Si to SiO$_2$. As noted above, room temperature Si electrodeposition has typically yielded porous deposits.

In order to increase the rate of SiF$_6^{2-}$ reduction, and obtain compact deposits, a series of different reducing agents were added to this electrolyte. As has been widely documented, many organic reducing agents are ineffective at low pH, since OH$^-$ is involved in the oxidation half-reaction. Reducing agents that were studied include formaldehyde, hypophosphite, borohydride, ascorbic acid, Ce(III), and formic acid. However, compact Si deposits could only be obtained using formic acid.

Dark grey deposits on Al 6061 alloy are obtained from electrolytes containing 10 mM HF and 20 mM Na$_2$SiF$_6$ in 80 wt % formic acid. Following emersion into laboratory air, these Si deposits retain their dark grey color and appearance indefinitely, indicating that Si oxidation is confined to the film surface, and does not penetrate into the bulk Si film. This is in sharp contrast to previous reports of Si electrodeposition at room temperature, which typically yield porous films that oxidize rapidly upon sample emersion. Figures 1 and 2 illustrate SEM top and side views of the Si film. In Fig. 2, the Al substrate is shown at the bottom (below line B), and the deposited Si film in the middle (between lines A and B). Following 30 h of deposition, Si films about 7–10 μm thick are obtained. Si film adhesion was not studied quantitatively, but was excellent.

The cathodic (1) and anodic (2, 3) reactions that occur during Si film deposition are likely:

\[
\text{SiF}_6^{2-} + 4e^- \rightarrow \text{Si} + 6\text{F}^- \quad E^0 = -1.37 \text{ V vs. NHE} \tag{1}
\]

\[
\text{Al} + 6\text{F}^- \rightarrow \text{AlF}_3^{3-} + 3e^- \quad E^0 = +2.07 \text{ V vs. NHE} \tag{2}
\]

\[
\text{HCO}_2\text{H} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \quad E^0 = +0.20 \text{ V vs. NHE} \tag{3}
\]

The two anodic reactions are written as oxidation reactions, so the values given above are the opposite of their standard reduction potentials. Both anodic reactions are important, since Si deposition does not occur onto Cu and Au substrates, while compact Si deposits on Al 6061 alloy cannot be obtained without formic acid. Therefore, the Si deposition process reported here is a combination of galvanic and electroless deposition, with both Al metal and formic acid serving as reducing agents. Thermodynamically, Al is a much stronger reducing agent than formic acid. On the other hand,
oxidation of formic acid may become kinetically favored as the Si film thickness, and the distance between the Si surface and the underlying Al substrate, simultaneously increase.

Figure 3 shows the open circuit potential (OCP) as a function of time during immersion of 6061 Al alloy into the same electrolyte. The OCP during Si deposition is shifted about 300 mV in the anodic direction in concentrated formic acid relative to experiments without formic acid. The overall thin film growth rate of Si is about 3–4 times slower upon addition of formic acid relative to past studies without formic acid. This is in apparent contradiction to our hypothesis that addition of formic acid yields compact Si films due to increased rate of reaction (1) above. The likely explanation is that for moderately thick Si films, the growth rate becomes limited by Al transport through the Si film, which is slower for compact films than for nanoporous films. Nanoporous Si films have additional diffusion pathways due to solution phase transport through the porous deposit, and due to the significant internal surface area for surface diffusion.

H₂ evolution might be expected at the open circuit potentials (OCP) reported in Fig. 3. Copious bubble formation is observed, both with and without formic acid. Without formic acid, bubble formation can be ascribed to H₂ evolution. With the addition of formic acid, the OCP is somewhat less cathodic and bubble formation can arise from either H₂ or CO₂ evolution, since CO₂ is a product of reaction (3). Without agitation, bubble adhesion blocks further reaction, and no Si deposit is formed. The thick Si films reported here are only obtained upon electrode rotation or some other method of forced convection.

EDX studies indicate that the film composition is about 2–3 atom % Al, 4–5 atom % Cu, and 92–94 atom % Si. The Al arises from oxidation and dissolution of Al from the substrate by reaction (2), and subsequent diffusion through the growing Si film. Cu incorporation into the growing Si film appears to arise from the 6061 Al alloy substrate itself. Some of the Si in the deposit may also arise from the 6061 Al alloy substrate.

X-ray diffraction studies show no peaks, indicating that the Si films are amorphous. This is expected for room temperature Si deposition, where diffusion is slow. FTIR studies of the Si films do not exhibit absorption peaks arising from Si-H stretching vibrations in the range 2000–2100 cm⁻¹. Therefore, the Si deposits do not contain significant hydrogen.

Several research groups recently reported the use of formic acid as a reducing agent for electroless synthesis of Pt and Ag nanoparticles, nanowires, and other nanostructures. For synthesis of nanostructures, formic acid has been suggested to promote anisotropic formation of Pt deposits, since anisotropic deposits were not obtained using other reducing agents. In some colloidal systems, a delicate interplay exists between the complexed metal ion, reducing agent, and organic additives by which the shape of nanostructures can be controlled. These arguments may suggest that the mechanism of action for formic acid is different here, since a smooth Si film is obtained.

**Conclusions**

We recently reported galvanic deposition of nanoporous Si onto 6061 Al alloy from HF-containing, aqueous electrolytes at pH 2.5. Here we report deposition of compact Si films from 10 mM HF and 20 mM Na₂SiF₆ in 80 wt % formic acid. Deposition for 30 h. yields 7–10 μm thick, dark grey Si films that do not change color upon extended exposure to laboratory air. This process is a combination of galvanic and electroless deposition, using bare Al metal and formic acid as reducing agents. X-ray diffraction studies show no diffraction peaks, indicating that the Si films are amorphous. FTIR studies do not exhibit absorption peaks in the range 2000–2100 cm⁻¹, so these Si films do not contain significant hydrogen.

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References