Communication—Light-Induced Plating of Aluminum on Silicon in a Lewis Acidic Chloroaluminate Ionic Liquid

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Conventional electroplating of aluminum on silicon often requires a seed layer to overcome the high resistivity of the substrate. In this paper, light-induced plating of aluminum directly on a silicon substrate in an ionic liquid is reported. Without any seed layer, the deposited aluminum has good adhesion to the silicon surface. The resistivity of the aluminum deposits is as low as 4×10^{-6} Ω-cm, which is only about 1.5 times that of bulk aluminum. The suitable wavelength for the light source is 600 nm to 1,000 nm. The effect of plating temperature on morphology of the aluminum deposits is analyzed.
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As the consumption of silver (Ag) for the front electrode in silicon (Si) solar cells continues to grow in recent years, a low-cost low-resistivity Earth-abundant metal is likely needed to replace Ag.[1] Besides the widely-studied copper (Cu), aluminum (Al) is another candidate for front metallization in Si solar cells. Electroplating of Al in a nonaqueous ionic liquid is a low-cost method and has been carried out on different metallic substrates as well as Si.[2–6] With an electroplated Al front electrode, a Si solar cell with about 18% efficiency has been demonstrated.[7–9] However, the highly-resistive Si substrate requires a nickel (Ni) seed layer to facilitate Al electroplating on it.[6] A method to directly electroplate Al on Si without a seed layer is therefore of interest.

Light-induced plating has been developed for metallization in Si solar cells[10] and used for different metals including Ag, Ni, and Cu.[10–13] The photovoltaic current, generated across the p-n junction under illumination, drives the electroplating process. With the n side of a Si solar cell in contact with the electrolyte, the metallic ions in the electrolyte are reduced to atoms and deposit on the Si surface. Although yet to be demonstrated, light-induced Al plating in an ionic liquid should be possible using the same principle. The advantage of light-induced plating over conventional electroplating is that it enables direct Al deposition on highly-resistive Si.

In this paper, a light-induced plating process to deposit Al directly on the n side of a Si p-n junction in an ionic liquid is reported. The wavelength range for light-induced Al plating on Si is extracted from the transmission spectrum of the ionic liquid and the absorption spectrum of Si. Adhesive and dense Al is reproducibly obtained at different temperatures and the resistivity of the light-induced Al deposits is in low 10^{-6} Ω-cm.

Experimental

The ionic liquid was prepared by adding anhydrous aluminum chloride ($AlCl_3$) powder (99%, Aldrich) to 1-ethyl-3-methylimidazolium tetrachloroaluminate ((EMIm)$AlCl_4$) (≥95%, Aldrich) in a beaker on a hot plate in a dry nitrogen box to drive out any moisture in the ionic liquid. The molar ratio between $AlCl_3$ and (EMIm)$AlCl_4$ was 0.5 to keep it a Lewis acid for Al plating. The solution was stirred to dissolve all the $AlCl_3$ power.

The experimental setup for light-induced Al plating is shown in Fig. 1a. The prepared electrolyte was transferred into the glass tank. The tank was wrapped in a heating tape and placed on a stage with a round hole in the center. An array of light-emitting diodes (LEDs) with a wavelength of 620 nm shed light from the bottom of the tank. A high-purity Al mesh was placed in front of the Si sample as the anode, which was dissolved during plating to supply the depleted Al ions to the electrolyte.

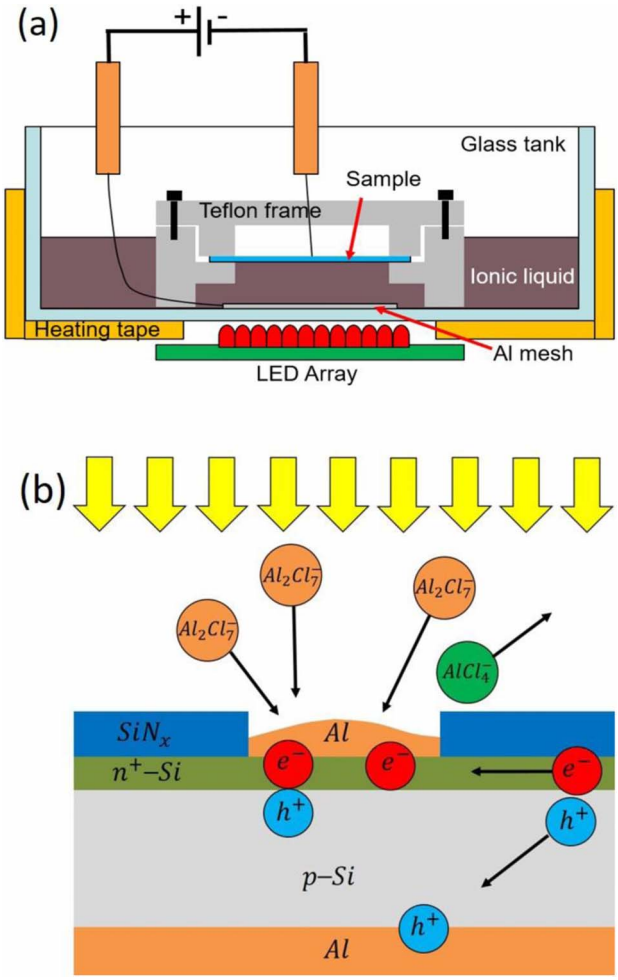

Figure 1. (a) Experimental setup for light-induced Al plating on Si. (b) Principle of light-induced Al plating on n side of a Si p-n junction.

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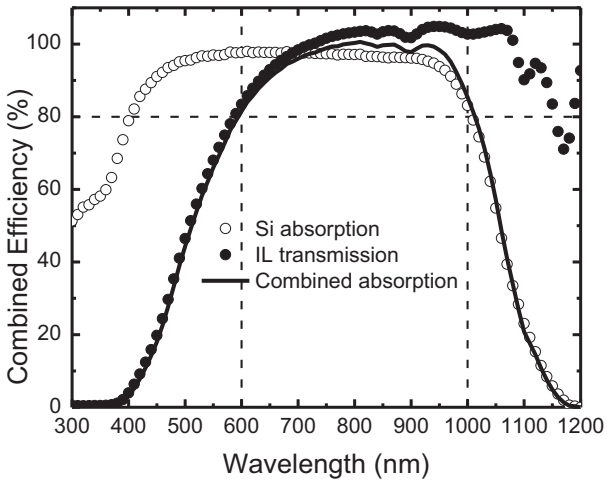

Figure 2. Suitable wavelength range for light-induced Al plating on Si.

The sample was a Si p-n junction from Canadian Solar. As shown in Fig. 1b, it had a 75-nm silicon nitride (SiN_x) layer covering the n side and screen-printed Al on the p side. The SiN_x layer was patterned with openings of 10 × 0.5 mm^2 by laser ablation where Si was exposed. The sample was cleaned in 2% hydrofluoric acid (HF) for 30 s and then immersed in 3% sodium hydroxide (NaOH) for 15 s at room temperature to remove laser damage. With a final HF dip, the sample was placed on the sample holder (Fig. 1a) with the pattern facing down and contacting the electrolyte. The back side Al on the sample served as the cathode for plating. The voltage applied between anode and cathode was controlled by a Gamry Reference 3000 potentiostat to achieve a plating current of about 40 mA/cm^2. The voltage applied by the potentiostat to achieve 40 mA/cm^2 was between 100 mV and 200 mV. The plating temperature was between 25°C and 70°C.

The photo-generated electrons in the Si sample are driven to the n side by the p-n junction. The $Al_2Cl_7^-$ ions in the electrolyte are reduced by the photo-generated electrons and form metallic Al deposit on the Si surface according to:[14]

$$4Al_2Cl_7^- + 3e^- \leftrightarrow Al + 7AlCl_4^-$$

The voltage applied between anode and cathode is to more effectively extract the photo-generated electrons to the n side surface. The plating current becomes practically zero when the light is turned off.

After plating, the sample was rinsed with methanol (CH_3OH) and distilled water before blown dry with nitrogen. The morphology and composition of the Al deposits were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Profilometry was used to measure the thickness of the Al deposits. The resistance of the Al deposits was measured with a four-probe method which eliminates the effect of contact resistance.

Results and Discussion

Light-induced plating requires a light source with a suitable wavelength. It is determined by the transmission spectrum of the electrolyte and the absorption spectrum of Si. The transmission spectrum of the electrolyte was measured in a quartz cuvette by spectrophotometry. The absorption spectrum of Si was characterized with an external quantum efficiency tester. The product of the two spectra at different wavelengths provides the suitable wavelength range for light-induced Al plating on Si in the ionic liquid. As shown in Figs. 2, the wavelength should be between 600 nm and 1,000 nm for over 80% absorption efficiency by Si. In this study, we chose red LEDs with a wavelength of 620 nm.

Figs. 3a and 3b show SEM top views of the Al deposits plated at 25°C and 60°C. In both cases, the Al deposits continuously cover the Si surface. The Al crystallites are denser and smaller at 25°C in Fig. 3a while they are larger and flake-like at 60°C in Fig. 3b. The morphologies suggest that lower temperatures produce a more compact and dense Al film on the surface in light-induced plating at 40 mA/cm^2. The strong peak at 1.49 keV in EDX verifies that the deposit is largely Al, as shown in Fig. 3c. The weak peaks of oxygen and chlorine are residues from the ionic liquid. The optimum plating conditions are still under investigation, especially as a previous report suggests that a higher temperature of 90°C improves the uniformity in conventional electroplating of Al on Cu.[15]

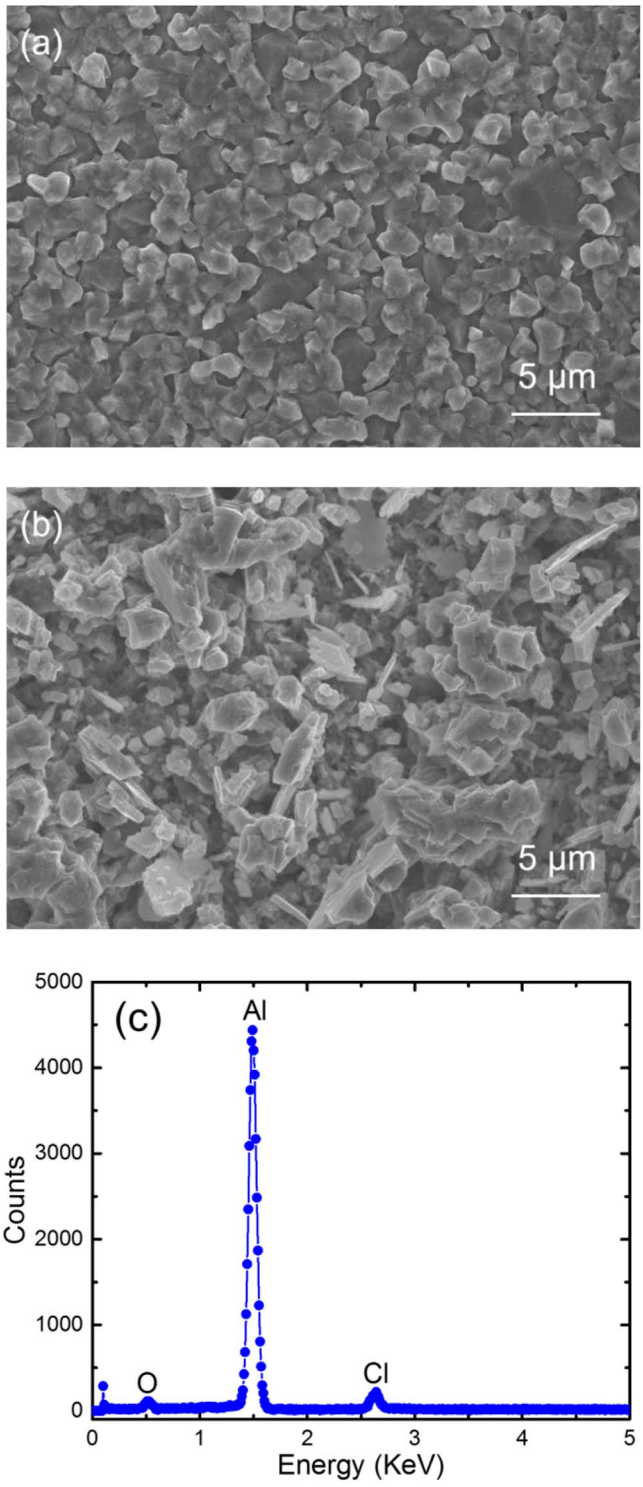

Figure 3. SEM images of light-induced Al deposits plated at (a) 25°C and (b) 60°C. (c) EDX analysis of (a).

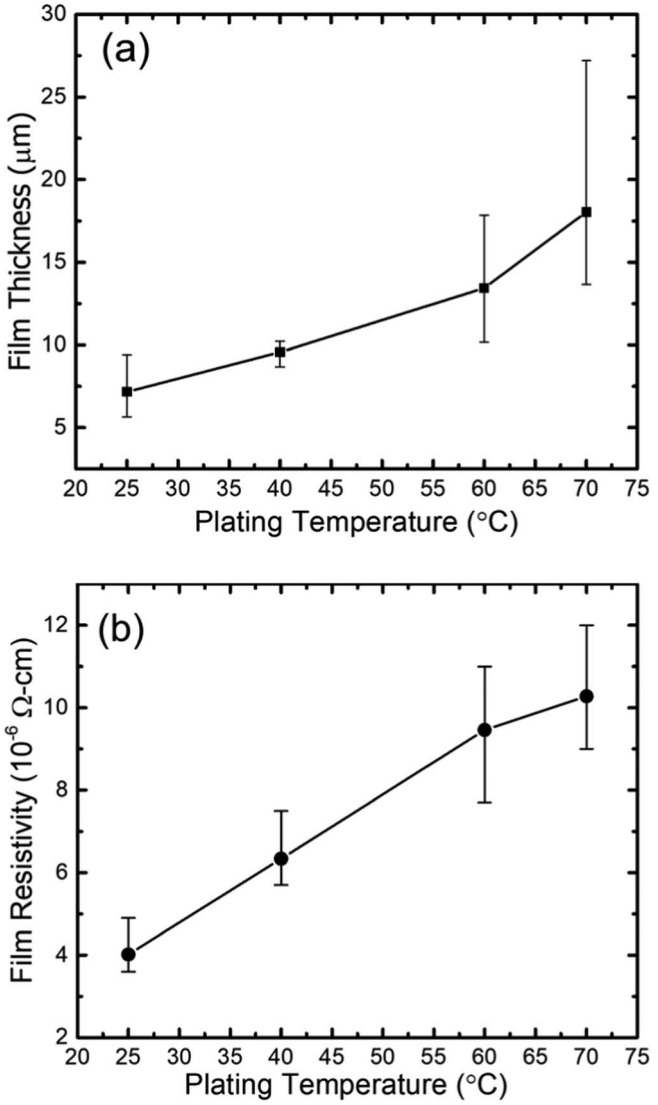

Figure 4. (a) Thickness and (b) resistivity of light-induced Al films as a function of plating temperature for 1 hour at 40 mA/cm^2.

The thickness of the Al films was measured by a profilometer. Fig. 4a shows the average thickness at different plating temperatures. Although the plating current and time were kept consistent, the average thickness and its variation increased with temperature. The resistance of the Al films was measured with a four-probe method. With the Al film dimensions of 10 × 0.5 mm^2, the resistivity of the Al films was extracted. Fig. 4b shows the resistivity of the Al films as a function of plating temperature. The lowest average resistivity is about 4 × 10^{-6} Ω-cm at 25°C, which is about 1.5 times that of bulk Al. It is lower than the resistivity of 7 × 10^{-6} Ω-cm by conventional Al electroplating as we reported before.[6] However, the resistivity becomes larger and its fluctuation also larger as the temperature increases. This agrees with the SEM images in Fig. 3. Since the Si surface is textured, light-induced Al likely grows at the tips of the pyramids and it is possible that high temperatures aggravate the nonuniformity of the Al deposits. The thicker Al deposits at higher temperatures suggest higher plating rates, but the higher resistivities indicate less dense or more porous Al deposits. Meanwhile, lower temperatures may reduce the diffusion of Al ions away from the concave positions on the surface. Another possibility is that moisture is recaptured by the ionic liquid at temperatures below 100°C. As the ionic liquid is in an open tank, it has a large surface area to absorb moisture. It is recommended that the plating process is carried out in an inert ambient or heated to above 100°C. Further investigation is underway to optimize film uniformity and density.

The setup for light-induced Al plating, as shown in Fig. 1a, can be improved. For example, the Al plating rate is proportional to the light intensity, and the light intensity can be increased by increasing the voltage and current applied to the LED array. The ionic liquid is moisture sensitive. We keep the ionic liquid in a dry nitrogen box to reduce moisture, but may also need to maintain the ionic liquid above 100°C to drive out moisture.[6]

Summary

Light-induced plating of Al on a Si substrate with a p-n junction is implemented in an ionic liquid. Adhesive and low-resistivity Al can be directly deposited on Si without a seed layer as in conventional electroplating. The lowest resistivity demonstrated is about 4 × 10^{-6} Ω-cm. Higher plating temperatures seem to increase the plating rate but have a negative effect in the current plating setup as it increases the resistivity and its fluctuation of the Al deposits. The suitable wavelength range for the light source is found to be between 600 nm and 1,000 nm.

Acknowledgments

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