Fused-Salt Electrodeposition of Thin-Layer Silicon

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FUSED-SALT ELECTRODEPOSITION OF THIN-LAYER SILICON

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ABSTRACT

Electrodeposition has been employed to produce crystalline silicon layers 5–50 μm thick on heavily doped p-type (111) Czochralski Si and polished silver. Growth was also demonstrated for the first time on metallurgical-grade Si. A 50/50 mixture of KF and LiF was used as the solvent and K_2SiF_6 was the solute. The chemicals were used as received and were only ~99% pure. Nonetheless, films were obtained with relatively low impurity levels, demonstrating the self-purification effects of electrodeposition. Films were grown at temperatures ranging from 750° to 850°C, and the best film quality and deposition rates were obtained at 850°C. The film quality was also improved when a dissolving Si anode was used to replenish the Si concentration in the solution. Deposition rates onto (111) Si were higher than those previously reported and were achieved with the use of very low resistivity (0.013 Ω-cm) Si electrodes. The films in this report were deposited at current densities between 10 and 150 mA/cm^2 and as-grown layers were n-type.

INTRODUCTION

It has been known for many years that silicon films can be fabricated by electrodeposition. The first successful attempts to deposit silicon electrochemically were performed as early as 1865 using K_2SiF_6 dissolved in molten KF at temperatures in excess of 1000°C, but a detailed study of silicon electrodeposition was not performed until the 1930s [1]. In 1976, Cohen and Huggins [2] demonstrated epitaxial silicon electrodeposition on crystalline silicon substrates from a molten KF/LiF solution at temperatures as low as 750°C. Deposition rates, however, were relatively low at ~1 μm/hr, so the method could not be considered as a viable production method for photovoltaic material. Later attempts at electrodeposition have produced rates as high as 30 μm/hr [3]. Advanced solar cell designs use multiple reflection schemes to efficiently absorb incident photons [4], so Si layers can be much thinner (~10 μm) than the ~200 μm currently required. These thin layers can be effectively produced by electrodeposition and the potential exists to achieve areal throughput rates greater than those found with the ingot growth and wafering technologies currently employed by the silicon industry.

Electrodeposition is also potentially less expensive since processing temperatures are lower (~800° vs. 1400°C) and wafering is eliminated. The lower processing temperatures may also permit the use of impure and low-cost substrates. High throughput should be achievable through industrial processes currently employed for electroplating on a large scale. Furthermore, the deposition bath can be purified by pre-electrolysis, reducing the need for high-cost, ultra-pure starting materials.

Here we present our work on the deposition of thin-film silicon onto several materials, with our goal being the use of low-cost materials as substrates. We have demonstrated the highest deposition rates reported to date, and produced relatively high-purity silicon deposition on crystalline silicon (c-Si), silver, and metallurgical-grade silicon (MG-Si).

EXPERIMENTAL

The deposition system in Fig. 1 consists of a quartz vessel, a vitreous carbon crucible and graphite sample/electrode holders. These materials are stable at
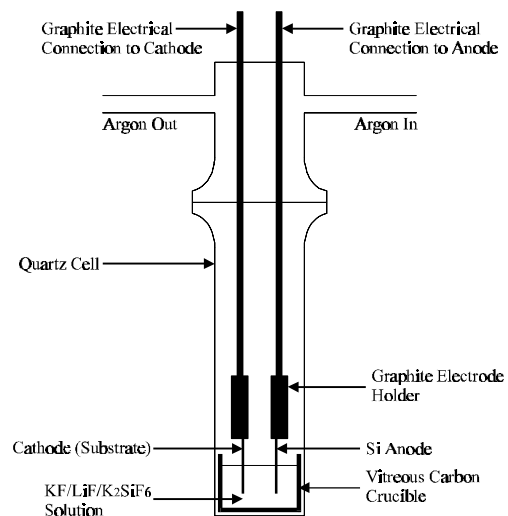

Fig. 1. Schematic of the Electrodeposition Cell

deposition temperatures and resistant to corrosion. Deposition was performed on c-Si, MG-Si or polished silver cathodes. The other electrode (the anode) could be composed of silicon or graphite, although all of the results presented here were achieved using a dissolving silicon anode. A positive argon pressure was maintained within the vessel to prevent exposure to oxygen. Silicon was deposited from a KF/LiF (1:1) mixture containing dissolved K_2SiF_6 (10 wt%) as the silicon source. This solution was heated to fixed temperatures between 750° and 850°C during deposition by inductive heating of the vitreous carbon crucible. After deposition, the samples were soaked in water and rinsed with ethanol to remove solvent salts which had adhered to the electrode. All of the experiments described in this paper were performed with low-cost, low purity chemicals (KF - 99%, LiF - 99.5%, K_2SiF_6 - 99%). This relatively low grade was used to demonstrate the purification properties inherent in the electrodeposition process.

ELECTRODEPOSITION ON c-Si

Our first experiments used silicon as the cathode. Highly doped, p-type (111) Czochralski silicon was cleaned with 10% HF and inserted into the solution at a bath temperature of 800°C. Deposition was performed with the substrate held at -0.3V with respect to the anode. Current densities between 25 and 75 mA/cm^2 were measured during the 1-4 hours of deposition. The resulting deposits were smooth silicon films, with thicknesses of 5–50 μm depending on the deposition time and electrode resistivities. The deposited silicon was found to be n-type, with a sheet resistance of ~0.3 Ω-cm, and contained fairly low levels of contaminants compared to the solvent and solute chemicals.

It was later found that deposition at 850°C produced the best films, probably due to the higher Si ion mobility and lower viscosity of the solution at higher temperatures. It was also found that the best films were produced when a silicon anode was used. This anode dissolves during deposition, maintaining a relatively constant silicon concentration in solution. Higher rates of deposition were achieved using the higher temperatures (850°C) and more conductive (0.013Ω-cm) Si electrodes, allowing more current to flow through the solution.

After deposition, samples were cleaved and then stain etched (20 HF:1 HNO$_3$) to reveal the boundary between the n-type deposit and p-type substrate. Optical and scanning electron microscopy (SEM) were used to determine the thickness of the deposited layers. Fig. 2 is a SEM micrograph showing the film/deposit interface. The roughness in the film was caused by the stain etch. Without etching, the film and substrate could not be distinguished either optically or by SEM. X-ray (Laue) diffraction determined that the deposited film was epitaxial (See Fig. 3). After a 5 minute dip in Secco etchant (4.4 g $K_2Cr_2O_7$, 100 mL dH$_2$O, 200 mL HF), an etching solution
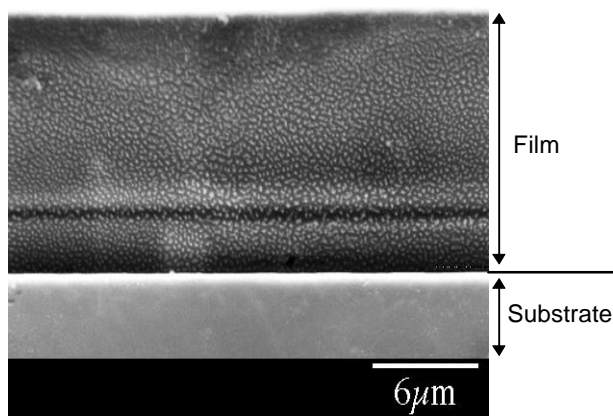

Fig. 2. SEM side view of a stain-etched silicon film deposited on c-Si. The etch was used to enhance the contrast between deposit and substrate. The striation in the deposit is due to an unintended change in temperature during deposition.
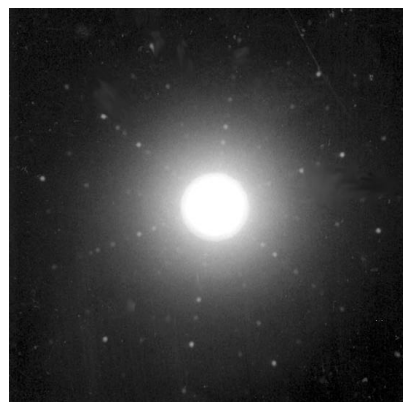

Fig. 3. Laue pattern of a 50 μm thick silicon film deposited on (111) c-Si. This pattern confirms the epitaxial nature of the deposit.

which reveals grain boundaries, the film remained featureless, confirming that it was monocrystalline.

Current densities from 10–150 mA/cm^2 have produced epitaxial films. The highest rate of deposition achieved so far has been ~45 μm/hr using 0.013 Ω-cm Si electrodes at 850°C. The higher growth rates (>35 μm/hr) produced silicon films which were faceted (See Fig. 4), while lower rates of deposition produced smooth films. These films were analyzed by Laue and θ/2θ X-ray diffraction techniques, and were also polished and Secco-etched to reveal grain boundaries. Results of these analyses were all consistent with the films being epitaxial (111) c-Si film. The high rate of deposition is apparently responsible for the faceting of this film's surface.
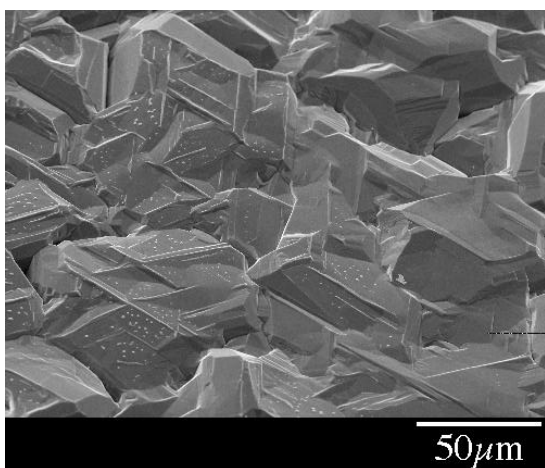
Fig. 4. Top view of epitaxial silicon deposited onto c-Si at a rate of 45 μm/hr. The high growth rate of the film resulted in faceting.
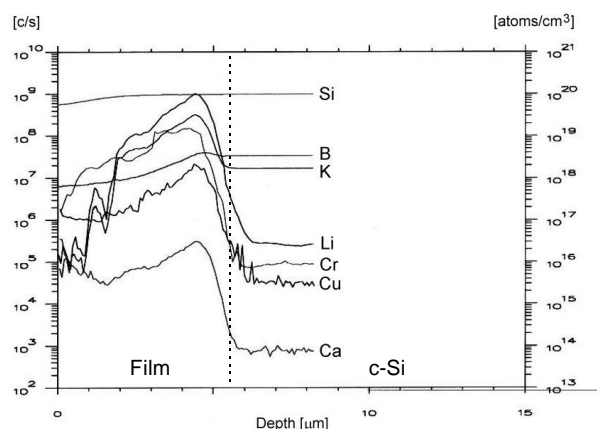

Fig 5. SIMS analysis of impurities in a film deposited onto a c-Si substrate. The epitaxial film is to the left of the dotted line and the substrate is to the right.

Fig. 5 shows the Secondary Ion Mass Spectrometry (SIMS) depth profile analysis for several elements across a film/substrate boundary. This data reveals some of the dynamics of the deposition process. During the initial stages of deposition, reactive impurity species are incorporated into the film. Since these impurities are not replaced in the solution, their concentrations fall to lower levels as more silicon is deposited. A pre-electrolysis treatment can therefore be used to remove reactive impurities from the melt. The purified solution can then be used to deposit a film with low impurity concentrations onto the desired substrate. The high levels of lithium and potassium in the c-Si substrate (Fig. 5) are likely due to diffusion from the highly impure layer which was first deposited.

DEPOSITION ON SILVER

Electrodeposition on silver substrates was performed using the same $KF/LiF/K_2SiF_6$ solution described above. The temperatures used in this experiment were slightly lower (750°–800°C) due to the relatively low melting points of silver (961°C) and the Ag-Si eutectic (845°C). The impurity levels in the silicon deposited on this substrate were much higher than in the films on c-Si. Silver levels in the film as measured by SIMS were found to be ~100 ppm due to the high mobility of silver at deposition temperatures. Lower temperatures may therefore be necessary for obtaining high-purity films on silver. The grain sizes in these films were comparable to the thickness of the deposited film. Fig. 6 shows a typical morphology of polycrystalline films deposited on silver.
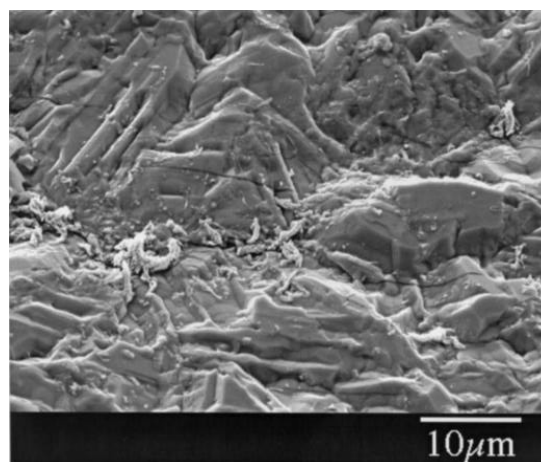

Fig. 6. Polycrystalline Si film deposited onto a polished silver substrate.

DEPOSITION ON MG-Si

Since it is desirable that this be a commercially viable process, low-cost substrates are of interest. Metallurgical-grade silicon (MG-Si) is a particularly interesting candidate, which has not been investigated in previous Si electrodeposition experiments. This substrate is polycrystalline and contains higher impurity levels than are found in c-Si wafers. The impurities in MG-Si cause it to be highly conductive, which makes it well-suited for electrodeposition.

Deposition was performed using the same $KF/LiF/K_2SiF_6$ solution described above, and resulted in silicon films 6–45 μm thick. Growth on this substrate produced epitaxial replication of the MG-Si grain structure as seen in Fig. 7. Low surface-free-energy (111) planes created the terraced morphology, which varies depending on the grain orientation.
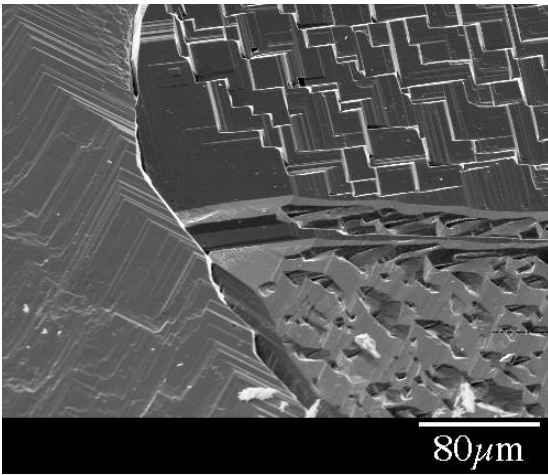
Fig. 7. Epitaxial silicon electrodeposited onto MG-Si. (111) terraced growth on adjacent grains with different orientations is shown.
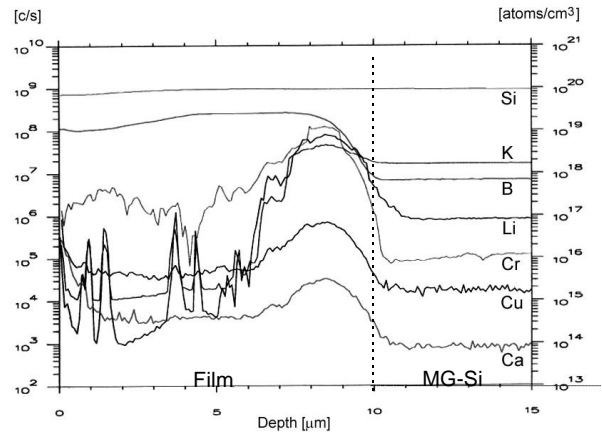

Fig. 8. SIMS analysis of Si deposited onto a MG-Si substrate. The deposited film is to the left of the dotted line and the substrate is to the right.

These films were also found to be n-type and had resistivities on the order of $0.2\,\Omega$-cm.

Fig. 8 contains a SIMS depth profile similar to the data from the film grown on c-Si. Once again, an accumulation of impurities is observed at the film/substrate interface. The silicon deposited onto this substrate was thicker than the film on the c-Si substrate which was analyzed in Fig. 5, so the impurity levels have fallen to a steady-state level near the surface of the film (at the left of the plot).

CONCLUSIONS

In this paper, we have demonstrated the use of electrodeposition in depositing thin films of silicon on several substrates. Low-cost materials, such as MG-Si or metal-coated ceramics, may also be incorporated as substrates. In addition, low-cost materials could yield high-quality silicon by utilizing pre-electrolysis treatments to purify the salts before deposition. Finally, temperatures higher than those previously reported may be utilized to accomplish much higher growth rates. Given the attractive features of electrodeposition, large-area deposition techniques could be used to make this a cost-effective method for producing c-Si films for solar cells.
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