Low-Cost Photovoltaics by Electrodeposition of Silicon PN Junctions

Investigators
The University of Texas at Austin
Dr. Allen J. Bard, Professor, Chemistry; Dr. Edward T. Yu, Professor, Electrical and Computer Engineering; Dr. Fardad Forouzan, Visiting Scientist, Chemistry; Dr. Xingli Zou, Research Fellow, Chemistry; Dr. Li Ji, Postdoctoral Researcher, Electrical and Computer Engineering; Dr. Xiao Yang, Postdoctoral Researcher, Chemistry; Dr. Jianbang Ge, Postdoctoral Researcher, Chemistry; Dr. Taeho Lim, Postdoctoral Researcher, Chemistry; Dr. Robert Villwock, Associate Director, Center for Electrochemistry (up to June 20, 2017), Dr. Cynthia Zoski, Associate Director, Center for Electrochemistry (after June 20, 2017 to date).

Massachusetts Institute of Technology
Dr. Donald R. Sadoway, Professor, Materials Science and Engineering; Dr. Junjun Peng, Visiting Scientist, Materials Science and Engineering; Dr. Huayi Yin, Postdoctoral Researcher, Materials Science and Engineering; Dr. Ji Zhao, Postdoctoral Researcher, Materials Science and Engineering.

Abstract
The goal of this research was to develop a new approach to produce Si-based photovoltaics for solar energy conversion to electricity. This process should be less expensive and environmentally friendlier than the current Siemens process based on reduction of SiO\textsubscript{2} with carbon at high temperature: SiO\textsubscript{2} + C \rightarrow Si + CO\textsubscript{2}.

Our major successes are:
1. The only demonstrated electrochemical deposition of Si films on carbon that show photo activity.
2. The development of a photoelectrochemical method for testing Si electrodeposits without producing a solid-state p-n junction.
3. The only Si synthesis process described that does not produce CO\textsubscript{2}, i.e. SiO\textsubscript{2} \rightarrow Si + O\textsubscript{2}.
4. The first preparation of solid-state p-n junctions by electrodeposition.

Reliable energy supplies that are cost-effective and environmentally-friendly are critical for sustainable energy development, especially in developing countries. Billions of people, especially in India, Africa and South America, have no to very limited access to electricity. Solar photovoltaics (PV) provide promising solutions. Crystalline-silicon solar cells have dominated the PV market for the past several decades and are most likely to continue to be the primary technology for the PV industry in the future. However, high cost and energy consumption, and the presence of a carbon footprint during PV module production prevent widespread promotion of solar PV throughout developing countries. Our major successes address these obstacles through judicious design, synthesis, and characterization of electrodeposited silicon for solar energy PVs as described briefly.
We designed a simple process for making high purity solar-grade silicon films entirely from silicon dioxide via a one-step electrodeposition process in molten calcium chloride at 850 °C for PV applications. The only input materials for this molten salt electrodeposition of crystalline silicon films are abundant and low-cost silicon dioxide, calcium oxide, and calcium chloride. Calcium oxide is added as an intermediate for continuing ionization of silicon dioxide to form silicate ions which are electrodeposited onto substrates to form crystalline silicon films. By feeding silicon dioxide into the molten salt, polycrystalline silicon films are produced continuously. In the presence of a dimensionally stable, oxygen-producing Ebonex (TiO_2) anode, pure silicon is produced in the absence of CO_2 emission. We also showed that various dopants can be added into the molten salt, such as boron anhydride or alumina for p-type and antimony oxide or calcium phosphate for n-type to control the doping type of deposited silicon films. Using a periodic pre-electrolysis process to purify the molten salt system, we showed that high purity (~99.9999% pure) solar-grade silicon films can be deposited with tunable film thickness and doping type by varying the electrodeposition conditions. We also demonstrated the electrochemical formation of a silicon p-n junction, entirely by molten salt electrodeposition. These electrodeposited silicon films show about 40-50% of photocurrent density of a commercial silicon wafer by photoelectrochemical measurements. When operating in a solid state solar cell, the highest power conversion efficiency is 3.2%. A detailed cost analysis showed that the total energy consumption, carbon emission, capital costs, and leveled costs of electricity are greatly reduced, making our approach highly competitive for low-cost silicon PV production.

In a second approach, we showed that dense and uniform polycrystalline n-type silicon films with tunable film thickness can be electrodeposited on a graphite substrate in a KCl-KF-K_2SiF_6 salt bath with liquid tin as a mediator. A four-step growth mechanism for the tin-doped silicon film on a graphite substrate, including nucleation formation, island formation, island aggregation, and film formation was proposed. The electrodeposited silicon film has n-type behavior. Its photocurrent is about 30-44% that of a commercial n-type wafer.

**Introduction**

Electricity generation via PV cells is still expensive compared with fossil fuel-based electricity.[1] Almost 90% of the world’s PV power modules are based either on single or polycrystalline silicon. The cost of silicon, including costs for silicon crystal growth and wafer sawing, forms up to 65% of the fabrication costs because the production of solar grade silicon requires high-cost equipment and is energy-intensive.[2]

The purpose of this research is to advance the technology for electrodeposition of silicon in order to drastically reduce the cost of manufacture and to allow wide distribution of solar energy generation in the developing world. An objective of the project is to demonstrate and develop a new fundamental understanding of electrochemical pathways to low-cost, highly efficient silicon for solar cells in order to provide affordable access to solar energy. We tried to pursue this goal through development of molten salt electrodeposition processes by which large-area films of high-quality crystalline silicon can be produced at low cost. The objectives include developing a process to electrodeposit entire PV cells in molten salts—that is, electrodeposition of silicon films, electrochemically doping the deposited silicon films, and electrochemical formation of silicon p-n junctions.
Background

Currently, global energy generation still depends strongly on fossil fuels.[3] Driven by the rapidly increasing energy demands and the negative environmental impact of fossil fuels, renewable energy has attracted tremendous attention in recent decades. Solar cells utilizing sunlight to generate electricity directly have been recognized as one of the most promising technologies for solving energy issues. Crystalline-silicon solar cells have dominated the photovoltaics market for the past several decades and are most likely to continue to be the primary technology for the photovoltaics industry in the future due to its abundant raw materials supply and non-toxicity.[4] To make silicon-based solar cells more competitive, improving the power conversion efficiency and decreasing the module costs are the most direct routes. For efficiency enhancement, novel cell architectures involving complex processing procedures are usually required, often resulting in increased overall cost. Reducing the silicon production cost and silicon material usage thus offers an alternative route for continued growth of crystalline-silicon photovoltaics technology in the future.

Over the past decade, the crystalline silicon PV module price has dropped from 3.25$ W⁻¹ in 2010 to 0.63 $ W⁻¹ in 2016, mainly driven by the price drop of polysilicon, the raw material for making crystalline silicon solar cells. However, the cost of making solar-grade silicon wafers remains one of the largest portions of the total cost of crystalline silicon PV modules. Solar grade silicon wafers produced using the Siemens process require multiple high temperature, high energy consumption steps, in addition to about 40% materials waste due to kerf loss during wire sawing. Therefore, it is hard to further decline the cost of solar grade silicon wafer due to technical limitations of the traditional Siemens process. To address this problem, direct production of silicon at low temperature in liquid/molten salts has been proposed and intensively investigated since ~1980.[5,6] The major challenge for the molten salt technology is impurity control. Chloride molten salt has been considered to be a promising alternative molten salt for silicon electrodeposition in recent years.[7-10]

Nohira et al. systematically investigated the electrochemical reduction behavior of solid SiO₂ in molten CaCl₂ and proposed a new production process for solar silicon feedstock.[7,8] However, there are few reports on electrodeposition of high quality silicon film in CaCl₂-based molten salts found in the literature. In 2012, PI Bard’s group first reported the direct electrodeposition of photoactive silicon.[9,10] The new method is based on electrodeposition of silicon from SiO₂ nanoparticles in molten CaCl₂ on a silver electrode. However, the silicon deposit was not pure enough to show good photoactivity, and the morphology of the deposits was still poor compared to the commercial silicon solar cell materials.

During the course of this research project, PI Bard’s group further demonstrated that high-purity silicon films can be electrodeposited on a graphite substrate in molten CaCl₂; the electrodeposited crystalline silicon films exhibit high purity (99.99989% (~6N)) and exhibit 40-50% of the photocurrent response of a commercial silicon wafer. The highest power conversion efficiency (PCE) is 3.2% as a solar cell. This is the first demonstration of solar cells based on molten salt electrodeposited silicon films. There is a large margin
for improving the PCE with optimization of the electrodeposition process, making this technology promising for low-cost silicon solar cells.

**Results**

*Electrodeposition of Crystalline Silicon Films from SiO$_2$ in Molten CaCl$_2$-CaO*

Silicon dioxide is the primary source for silicon production. However, its solubility in chloride-based molten salts is generally low and inadequate for efficient electrodeposition.[7,8] Inspired by aluminum electrolysis in molten salt, efforts have been put into finding the right intermediate to facilitate the dissolution of silicon dioxide in chloride-based molten salts. Thanks to the considerable solubility (approximately 20 mol. % at 850 °C) of calcium oxide in molten calcium chloride and its reaction with silicon dioxide (Reactions (1) and (2)), the dissolution process from silicon dioxide to silicate ions is possible, which offers access to the electrodeposition of high quality silicon films in molten calcium chloride. As shown in Figure 1,[11] the only input materials for this molten salt electrodeposition of crystalline silicon films are abundant and low-cost silicon dioxide, calcium oxide, and calcium chloride. Calcium oxide is added as an intermediate for continuing ionization of silicon dioxide to form silicate ions (expressed as SiO$_{y}^{n-}$, including SiO$_3^{2-}$, SiO$_4^{4-}$, etc.), which are then electrodeposited onto substrates to form crystalline silicon films. The general reactions for the electrodeposition process can be expressed as follows:

\[
x_{2}SiO_{2} + yCaO \rightarrow Ca_{x}Si_{2}O_{(2x+y)} (yCa^{2+}, Si_{2}O_{(2x+y)}^{2y-})
\]

(1)

\[
Si_{2}O_{(2x+y)}^{2y-} + 4xe^{-} \rightarrow xSi + (2x+y) O^{2-}
\]

(2)

**Figure 1:** Schematic of the one-step molten salt electrodeposition process for crystalline silicon films production. (a) The process starts from abundant and low-cost silicon dioxide in molten calcium chloride-calcium oxide electrolyte at 850 °C. (b) Direct electrodeposition of p-type, n-type and p-n junction silicon films through a cyclic reaction mechanism. (c) Schematic of the produced p-type, n-type silicon films and the possible solar cells based on the as prepared p-n junction silicon films. [11]

The role of calcium oxide on ionizing solid silicon dioxide was confirmed by cyclic voltammetry and potentiostatic electrolysis. A cyclic voltammogram of a molybdenum wire electrode (dotted curve) was generally flat in pure calcium chloride contained in a
quartz (SiO\textsubscript{2}) crucible in Figure 2(a).[12] After addition of 1 mol. % of CaO, cathodic peaks 1, 2 and anodic peaks 1', 2' on the cyclic voltammogram (solid curve) appeared. EDS analysis of the product on a graphite plate cathode after potentiostatic electrolysis at 1.0 V vs. Ca\textsuperscript{2+}/Ca for 60 min in molten CaCl\textsubscript{2}-CaO (1 mol. %) confirmed the formation of elemental silicon (brown powder) in Figure 2(b). It is likely that O\textsuperscript{2-} cations, dissociated from CaO, reacted with the solid SiO\textsubscript{2} crucible to generate silicates ions. Therefore, we can attribute peaks 1 and 2 to the deposition of silicon from silicate ions, and peaks 1', 2' to the oxidation of silicon. Therefore, according to reactions (1) and (2) and Figures 1 and 2, the electrodeposition route is a cyclic reaction process. By periodically feeding silicon dioxide into the molten salt, crystalline silicon films can be produced continuously, which makes this method suitable for large scale production.

![Figure 2: (a) Cyclic voltammograms of a Mo wire in molten CaCl\textsubscript{2} and CaCl\textsubscript{2}-CaO (1 mol. %) in a SiO\textsubscript{2} crucible at 850 °C, (b) a photograph of a graphite plate cathode after potentiostatic electrolysis at 1.0 V vs. Ca\textsuperscript{2+}/Ca for 60 min in molten CaCl\textsubscript{2}-CaO (1 mol. %) in a SiO\textsubscript{2} crucible at 850 °C and the EDS analysis result of the product on the surface.[12] Electrodeposition of Silicon Films and Electrochemical Formation of a p-n Junction]

On the basis of the design of electrodeposition of silicon films from SiO\textsubscript{2} in molten salts, we tried to use different precursors such as calcium silicates (CaSiO\textsubscript{3}) and calcium oxide/silica (CaO/SiO\textsubscript{2}) as precursors for the electrodeposition of silicon films. Accordingly, we tried to deposit silicon films on a graphite substrate in molten CaCl\textsubscript{2} with addition of different amounts of CaO at a controlled current density in the two-electrode manner. SiO\textsubscript{2} nanoparticles (NPs) were used as the silicon precursor to favor fast ionization. The results indicated significant improvements in film thickness and quality compared with our previous work.[9,10] Judging by the quality of the deposits, we found that CaCl\textsubscript{2} with addition of ~4.8 mol. % of CaO and ~3.9 mol. % of SiO\textsubscript{2} NPs was the optimum composition.

Uniform silicon films were deposited onto a graphite substrate at a constant cathodic current of 15 mA cm\textsuperscript{-2}, as shown in Figure 3.[12] Silicates ions were reduced on the graphite substrate surface by obtaining electrons to form silicon atoms. Crystalline silicon film was formed after nucleation and crystal growth. Growth of the film with the elapse of electrolysis time indicated electrodeposition, while increase of the grain size implied crystallization. Addition of CaO improved the concentration of silicate ions which is one
of the necessary conditions for continuous film growth. Silicon films with different thicknesses were obtained by controlling electrolysis time. Generally, aluminum dissolved from the quartz crucible served as dopant for the deposited silicon film. Thus, the obtained silicon film was commonly a $p$-type silicon film. However, it has been proven that various dopants can be added into molten salt, such as boric anhydride or alumina for $p$-type and antimony oxide or calcium phosphate for $n$-type, to control the doping type of deposited silicon films. In our work, a proof-of-concept demonstration of $p$-$n$ junction formation, all by molten salt electrodeposition, has also been demonstrated as shown in Figure 4.[13]

![Figure 3: SEM images of the silicon films deposited on a graphite substrate in molten CaCl$_2$-CaO-SiO$_2$ (CaO: 4.8 mol. %, SiO$_2$: 3.9 mol. %) at 850 °C by electrolysis at a constant cathodic current of 15 mA cm$^{-2}$ for (a) 1 h and (b) 3 h.[12]](image-url)
Figure 4: (a) Cyclic voltammetry (CV) curves of the molten CaCl$_2$ dissolved with CaSiO$_3$/CaO/SiO$_2$ at 850 °C (scan rate: 100 mV s$^{-1}$). (b) Typical potential-time curve of the first step: pulse electrodeposition of a $p$-type silicon film. (c) Typical SEM image of the deposited $p$-type silicon film; the insets are photos of the silicon film before and after being polished. (d) and (e) Typical SEM images of the deposited silicon $p$-$n$ junction films (d) with and (e) without a $p$-$n$ boundary; the inset in (e) is the photo of the polished $p$-$n$ junction film. (f) Typical SEM image of the surface of the deposited silicon film; the inset shows the details of a silicon particle. (g) Typical XRD patterns of the produced $p$-type, $n$-type and $p$-$n$ junction silicon films. (h) Glowing discharge mass spectrometry (GDMS) analysis of the produced silicon film.[13]

Figure 4(a) shows the cyclic voltammogram (CV) curves of the electroreduction of calcium silicates on graphite in molten CaCl$_2$ containing CaSiO$_3$/CaO/SiO$_2$. The reduction of silicate ions starts at approximately -1.4 V versus a graphite pseudo-reference electrode, and the oxidation of silicon starts at about -0.75 V. Typically, oxygen ions generated from CaO react with SiO$_2$ to form different silicate ions, such as SiO$_3^{2-}$, SiO$_4^{4-}$, Si$_2$O$_7^{6-}$, etc., and all of these silicate ions are reduced to silicon during electrodeposition. CaO serves as an intermediate medium to the continuous ionization of SiO$_2$ to form silicate ions, and thus, the electrodeposition process for silicon film can proceed continuously. The electrodeposition process for the silicon film can be implemented via constant current density electrodeposition, constant potential electrodeposition or pulse electrodeposition. In this work, it is shown that the pulse electrodeposition process is beneficial to produce dense and smooth silicon films. The pulse electrodeposition condition is 120 s (current density: 15 mA cm$^{-2}$) for silicon electrodeposition and then 20 s (current density: 0 mA cm$^{-2}$) for silicate ion diffusion/migration, in order to maintain the concentration of silicate ions in the reaction area a relatively stable level. Figure 4(b) shows a typical potential-time plot of the pulse electrodeposition process for $p$-type silicon film. The electrodeposition process shows a constant variation trend. The stable electrodeposition process indicates that the concentration of silicate ions is constant, which could contribute to the formation of a homogenous silicon film as shown in Figure 4(c). The thickness of the film is about 40 μm, which generally depends on the deposition time. The faradaic efficiency for the formation of a silicon film is approximately 60%, and the formation of silicon powders on the film may be mainly responsible for the remaining 40% efficiency. The growth rate of
the silicon film is not constant, and commonly decreases with time and also depends on current density and silicate ion concentration. Generally, crystalline silicon films with thickness of 5 to >50 μm can be produced in a controlled manner. Different current densities, potentials, or pulse conditions could also result in different film morphologies. The insets in Figure 4(c) are photos of the deposited $p$-type silicon film before and after being polished to form a mirror finish. If the surface of the deposited $p$-type silicon film is sufficiently smooth, the obtained thin films could be used directly (without being polished) as substrate to further electrodeposit $n$-type silicon film.

After polishing to a mirror like surface, the $p$-type silicon film was used as a substrate for $n$-type silicon deposition in a second electrolytic cell. The second electrolytic cell was also composed of CaCl$_2$, CaSiO$_3$, CaO and SiO$_2$, and Sb$_2$O$_3$ was added into the bath to provide Sb as a dopant for the $n$-type silicon film. The potential-time plot for $n$-type silicon deposition is similar to that of $p$-type. Figure 4(d) and 4(e) show the scanning electron microscopy (SEM) images of typical fabricated silicon $p$-$n$ junction films. The $p$ and $n$ region can be distinguished via a clear boundary.

Interestingly, the preferred crystal growth orientation of the $p$-type silicon film can be continuously maintained during the electrodeposition of $n$-type silicon film. With the $p$-$n$ boundary gradually becoming homogeneous, a good $p$-$n$ junction film can thus be fabricated. The thickness of the $p$-type silicon film and the $n$-type silicon film can be adjusted by changing experimental conditions. Generally, the thickness of the $p$-$n$ junction film can reach up to $>50$ μm.

Figure 4(f) shows a typical SEM image of the surface of the produced silicon film. Typically, the $p$-type, $n$-type and $p$-$n$ junction silicon films show similar surface morphology. The electrodeposited silicon films have dense and uniform structure, and the size of the deposited silicon crystallites increases with the increase of electrodeposition time. The size of the silicon crystallites can reach up to about 30 μm. In addition, the crystallinity of the silicon film also increases with increasing electrodeposition time. The silicon film can be well controlled to form a relatively smooth surface with small silicon crystallites or a rough surface with large silicon crystallites (Figure 4(f)). Figure 4(g) shows the X-ray diffraction (XRD) patterns of the produced silicon films, including $p$-type silicon film, $n$-type silicon film, and silicon $p$-$n$ junction film all of which exhibit good crystallinity.

Figure 4(h) shows results of glowing discharge mass spectrometry (GDMS) analysis of the produced silicon film, which confirms that impurity levels in the films are very low. The concentrations of B and P are both lower than 1 ppm. Other impurities, except Ca and Cl, are all less than 10 ppm.[13] Ca and Cl may come from the residual CaCl$_2$ due to insufficient water washing or from entrapped molten salt at the grain boundaries. It is also possible to form a small amount of Ca-Si alloys in the silicon film. Other trace impurities such as Na, Mg, Ni, Ti and Zr may result from the molten CaCl$_2$ and from the quartz crucible. These impurities influence the device performance of the silicon film. Element Al with 10 ppm concentration was considered as the $p$-type dopant for the silicon film. It should be noted that Al mainly came from the quartz crucible (i.e., contains 14 ppm Al) used in this investigation. In order to control the dopant concentration, additional alumina can be added into the molten salt to provide Al as a dopant. For the $n$-type silicon film, it
is shown that antimony or phosphorous both can be used as dopants in our system. We note that by further optimization of the electrodeposition process, including using high-purity raw materials/quartz crucible, long time periodical pre-electrolysis, and multistep electrodeposition process, etc., we have successfully improved the purity of silicon film to solar grade (99.9999%) as shown in Figure 5. [11]

**Figure 5:** The impurity elements of a typical deposited silicon film determined by glow discharge mass spectrometry (GDMS) analysis. Ca and Cl elements come from residual calcium chloride, which can be further removed through procedure optimization. C, H, and O are not determined; C element is difficult to accurately analyze because the substrate is also graphite. Impurities below the detection limit are not listed.[11]

The silicon p-n junction devices were then characterized by I-V measurements, under AM 1.5G, 1 sun illumination, with a 0.16 mm² aperture area. As shown in Figure 6(a), in the dark (gray line), the device shows reasonably good rectifying behavior, confirming junction formation. When illuminated (red line), photocurrent and photovoltage are clearly observed with a 25 mV open-circuit potential. To confirm the efficacy of p-n junction formation by a molten salt electrodeposition process, a Sb-doped n-type silicon layer was deposited on a p-type single crystalline wafer (~1e16 cm⁻³). As shown by the I-V characterization in Figure 6(b), 400 mV open-circuit potential is obtained, further demonstrating that a p-n junction can be formed in molten salt. Therefore, facile electrochemical deposition of a silicon p-n junction film in molten salt has been successfully demonstrated for the first time. Silicon p-n junction films can be directly produced from inexpensive silicates/silicon oxide precursors through a two-step electrodeposition process, which makes this technique attractive for low-cost manufacturing for silicon solar cells. Although the photovoltaic performance is currently modest, there is still a big margin for improving the overall film quality.
Figure 6: Current-voltage characteristics of (a) A silicon p-n junction deposited in molten salt and (b) Electrodeposited n-type silicon layer on a p-type single crystalline silicon wafer, under dark (gray line) and under AM 1.5G, 1 sun illumination (red line), respectively.[13]

**Photoelectrochemical Properties of the Silicon Films and Device Characterization**

Characterization of a liquid-junction photoelectrochemical (PEC) cell enables rapid assessment of the quality of as prepared silicon films. The fabrication and test of real solar cell devices will be discussed later. Here, electrodeposited p-type and n-type silicon films were prepared to form silicon/liquid junctions with a redox agent and then characterized photoelectrochemically, as shown in Figure 7.[11] For comparison, commercial p-type and n-type silicon wafers were also characterized by PEC. The light is chopped on/off during the sweep, and the photocurrent can be clearly observed. Figure 7(b) shows the photocurrent density of the as prepared p-type silicon film and a commercial p-type silicon wafer for reduction of ethyl viologen cations (EV$^{2+}$). The photocurrent density of an electrodeposited p-type silicon film is approximately 50% that of the commercial p-type silicon wafer. Figure 7(d) shows the photocurrent density of the as prepared n-type silicon film and commercial n-type silicon wafer for the oxidation of ferrocene. The photocurrent density of the electrodeposited n-type silicon film is about 40% that of the commercial n-type silicon wafer. The PEC performance of the deposited silicon film has almost no degradation after 6 months exposure in ambient air.
Figure 7: Photoelectrochemical (PEC) characterization of the electrodeposited crystalline silicon films. (a) Schematic diagram of a $p$-type silicon film/liquid junction with a redox agent, where $E_F$ and $E_g$ are the Fermi level and bandgap energy of silicon. (b) Photocurrent density-potential characteristics of the electrodeposited $p$-type silicon film and a commercial $p$-type silicon wafer in darkness and under illumination at 100 mW cm$^{-2}$ with a scan rate of 10 mV s$^{-1}$. (c) Schematic diagram of a $n$-type silicon film/liquid junction with a redox agent. (d) Photocurrent density-potential characteristics of the electrodeposited $n$-type silicon film and a commercial $n$-type silicon wafer in darkness and under illumination at 100 mW cm$^{-2}$ with a scan rate of 10 mV s$^{-1}$.[11]
Figure 8: Solar cell efficiency characterization and techno-economic analysis. (A) Solar cell devices based on an electrodeposited $p$-type silicon film. The devices are tested under dark (blue dot line) and 100 mW cm$^{-2}$ illumination (brown line). (B) Module cost of electrodeposited silicon (ED-Si) PV as a function of efficiency via a bottom-up manufacturer ownership model.

To verify the high film quality and potentials for silicon photovoltaic applications, solar cell devices were fabricated on $p$-type silicon films produced via molten salt electrodeposition. A 3.26% power conversion efficiency (PCE) was achieved (Figure 8(A)) with 297 mV open circuit potential ($V_{oc}$) and 23.2 mA cm$^{-2}$ short circuit current ($I_{sc}$). It is worth noting that anti-reflection coating was not integrated, suggesting higher PCE could be achieved with improved light absorption. This is the first demonstration of functioning solar cell devices based on low-cost molten salt electrodeposited silicon films. We believe that the PCE can be further improved through further optimization. To assess the potential applicability and impact of this new technology, we have also performed a detailed techno-economic analysis. The resulting module price for electrodeposited silicon (ED-Si) PV is plotted as a function of module efficiency (Figure 8(B)). The estimated module price would be 0.35 $ W^{-1}$ at 6% efficiency and 0.20 $ W^{-1}$ at 10% efficiency, considerably lower than that of crystalline silicon PV with current technology (0.37 $ W^{-1}$ in 2017 with 21% efficiency). The inset in Figure 8(B) is the normalized PV module cost breakdown, including module, cell, and wafer production respectively. Compared to the traditional Siemens process, the cost of producing solar grade wafers with ED-Si technology is greatly reduced from 40-50% of the total module cost to 5%, assuming a 10% ED-Si cell efficiency.

In addition, our recent investigation shows that Ebonex material (Ti$_4$O$_7$) has the potential to be used as a dimensionally stable anode in molten CaCl$_2$ for silicon electrodeposition without any CO$_2$ emission; silicon wires, particles, and films can be directly deposited on a graphite cathode while the only by-product from the anode was oxygen gas. Therefore, based on these experimental results, the proposed molten salt electrodeposition (MSED) process was compared with the traditional Siemens process in Figure 9. The traditional multiple-step process has been integrated into a short-flow process. Therefore, the MSED PV technology investigated in this work holds significant promise
for low-cost implementing electrification in developing countries without any CO₂ emission.

**Figure 9:** A comparison between the proposed molten salt electrodeposition (MSED) process for silicon solar cells and the traditional process via carbon reduction and the Siemens process.

**Electrodeposition of Silicon Films from KCl-KF-1 mol. % K₂SiF₆**

As shown in Figure 10,[14] the electrolytic silicon samples were obtained in KCl-KF-1 mol. % K₂SiF₆ salt with and without adding tin metal at 650 °C. Without tin, yellow or brown powdery products were generated on the graphite substrate at a current density from 5 mA cm⁻² to 50 mA cm⁻². The morphologies of two typical samples (shown in Figure 10a and 10b) showed nanowire structures. These nanostructured products were elemental silicon, which were verified by XRD (Figure 11). After adding tin metal in the molten salt, dense films of blue grey color were obtained, and the films consisted of up to tens of micron-sized crystal grains. As the electrolysis was conducted at 5 mA cm⁻² for 4 h in the molten salt with 0.02 wt. % tin, a dense film (in Figure 10c and Figure 10d) with about 10 µm thickness was achieved. The crystal grains of 10-20 µm size were aggregated to form a dense surface. Under this condition, the electrolysis time needs to be extended to more than 1.5 hours to make a dense film fully cover the substrate. The relative weight ratio of tin to tin and silicon was 2.1% as measured by EDS, indicating that the film should be silicon-tin alloy film or tin-doped silicon film. As the current density was increased to 20 mA cm⁻², a much thicker film of about 61 µm thickness was achieved on a rigid graphite sheet substrate after a 4-hour electrolysis in the melt with 0.035 wt. % tin, as shown in Figure 10e and Figure 10f. The size of crystal grains on the surface also increased to 50-70 µm. By using this fine rigid graphite substrate, the tin-doped silicon film could be preserved with no crack or deformation during cooling and washing.
Figure 10: SEM images and corresponding photographs (the insets) of deposited products in 650 °C KCl-KF-1 mol. % K$_2$SiF$_6$ salt with different conditions as follows: (a-b) graphite foil substrate with no tin in the salt, (a) 5 mA cm$^{-2}$ for 4 h, (b) 20 mA cm$^{-2}$ for 4 h; (c-d) graphite foil substrate with 0.02 wt. % tin in the molten salt, 5 mA cm$^{-2}$ for 4 h; (e-f) Rigid graphite plate substrate with 0.035 wt. % tin in the molten salt, 20 mA cm$^{-2}$ for 4 h.[14]

Figure 11: (a) XRD patterns of as deposited products on rigid graphite sheet in 650 °C KCl-KF-1 mol. % K$_2$SiF$_6$ salt with different conditions as indicated. (b) The magnified region of the (111) peak shown in (a).[14]
Figure 11 shows the X-ray diffraction (XRD) results of typical samples deposited in 650 °C KCl-KF-1 mol. % K₂SiF₆ salt with and without tin. As seen in Figure 11a, the XRD patterns of sample obtained at 20 mA cm⁻² over 4 h in the molten salt with no tin agrees very well with the standard diffraction peaks of silicon, indicating that the deposited yellow powdery layer is elemental silicon. Under the same conditions, in the salt with 0.035 wt. % tin, the diffraction peaks of the sample could be attributed to graphite and silicon. The silicon peak intensity is much sharper than that of first silicon sample, indicating that the tin-doped silicon film possessed good crystallinity. The magnified peak (111) in Figure 11b clearly displays the difference between samples obtained with and without tin in molten salt. It was observed that silicon samples deposited with no tin have broader peaks and lower intensity while tin-doped silicon film has sharper peaks with higher intensity, accompanied by a tiny shift to a higher degree. The lattice parameter was calculated to be 5.411 Å, which was slightly smaller than that of pure silicon, 5.430 Å.

Effect of Tin on the Electrodeposition of Silicon Films from KCl-KF-1 mol. % K₂SiF₆

Figure 12: Cyclic voltammograms of different working electrodes: (a) A graphite rod working electrode in 650 °C KCl-KF-1 mol. % K₂SiF₆ salt with and without 0.02 wt. % tin metal. The inset is the magnification of the blue dash-lined box. Scan rate is 20 mV s⁻¹. (b) Tin metal assembled in boron nitride crucible (shown in the inset) as the working electrode in KCl-KF-1 mol. % K₂SiF₆ salt. Scan rate is 20 mV s⁻¹.[14]

To investigate the effect of tin in the salt, cyclic voltammograms of a graphite rod as the working electrode in KCl-KF-1 mol. % K₂SiF₆ salt with and without tin were performed, as shown in Figure 12a. The reduction current started at −0.9 V, and a reduction peak c₁ was at −1.05 V, indicating that this process is the electroreduction of SiF₆²⁻ to silicon on a graphite electrode. Upon the reverse sweep, an oxidation current peak a₁ was present at −0.73 V. This should be due to anodic oxidation of the deposited silicon. However, in the positive potential range, a small redox wave appeared in the salt with 0.02 wt. % tin, showing a very low cathodic current wave c₂ at −0.4 V and a large anodic current peak a₂ at −0.25 V respectively, which should be related to the electrochemical behavior of tin. To confirm this wave, cyclic voltammetry of a liquid tin electrode, contained in a boron nitride crucible and used as a working electrode (Figure 12b), was carried out in KCl-KF-1 mol. % K₂SiF₆ salt. During the negative sweep, redox peaks c₃ and a₃ occurred in the potential
range from \(-0.9\) V to \(-1.1\) V, which was the same as observed for the graphite electrode in Figure 12a and indicated that the electrodeposition of silicon was carried out on the liquid tin metal substrate. During the positive sweep, an anodic wave formed at \(-0.3\) V, and thereafter the current gradually increased with increasing positive potential. This anodic wave can be attributed to the electro-oxidation of liquid tin metal to tin ion in molten salt. These results were in accord with the CV of the graphite rod working electrode in KCl-KF-1 mol. % \(K_2\text{SiF}_6\) salt with added tin.

**Growth Mechanism of the Electrodeposition of Silicon Films from KCl-KF-1 mol. % \(K_2\text{SiF}_6\)**

![Figure 13: Schematic of the growth process of a tin-doped silicon film from electrodeposition on a graphite foil substrate in 650 °C KCl-KF-1 mol. % \(K_2\text{SiF}_6\) salt with added 0.02 wt. % tin metal, and corresponding morphologies of samples at different times at 5 mA cm\(^{-2}\): a) in 5 minutes, nucleation formation; b) in 15 minutes, island formation; c) in 30 minutes, island aggregation; d) more than 90 minutes, film formation.[14]](image)

To understand the growth mechanism of a tin-doped silicon film, a schematic growth process with four steps and the various morphologies of a sample at different stages is shown in Figure 13. At the beginning, in the first 5 minutes with a current density of 5 mA cm\(^{-2}\), numerous discrete sub-micron particles are distributed on the surface of a graphite sheet. This step is for nucleation formation (Figure 13a). It was found that a thin and porous yellow layer was formed on the graphite foil in 5 minutes, and this layer, consisting of silicon nanowires, was coherently covered on the substrate. This indicated a different growth mechanism for nucleation formation with tin present in the molten salt. With the electrolysis time increased to 15 minutes, many small particles grew and connected to form islands with a size range of 5-10 microns. EDS mapping demonstrated that the micron-size islands consisted of silicon and tin elements. This second step is island formation and growth (Figure 13b). In this step, there are two contributions to island formation and growth: the attachment of a new tin-doped silicon nucleus to the island, and the surface diffusion of a tin-doped silicon nucleus. It was assumed that the tin-doped silicon islands epitaxial growth probably predominated, so that a dense film could be formed. The tin element in silicon should act as a good mediator for attaching silicon atoms and initiating...
island epitaxial growth. Similar behavior of thin film growth has been verified by electrochemical defect mediated growth for a silver film. When time was increased to 30 minutes, tin-doped silicon islands were interconnected and formed aggregated islands, shown as step c (Figure 13c). As the electrolysis time increased to 90 minutes, tin-doped silicon island aggregation continued and gradually formed a dense and coherent film. This step is shown as the film formation step d (Figure 13d).

**Photoelectrochemical Properties of the Silicon Films Produced from KCl-KF-1 mol. % K$_2$SiF$_6$**

The photo current response of different films was tested in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte and 0.05 M ferrocene as a redox reagent. When a silicon sample was used as a semiconductor immersed in the electrolyte to form a semiconductor-liquid junction, the redox reaction occurred with a potential scan and under irradiation with UV/Vis light. Figure 14 shows a recording of photocurrent for the oxidation of ferrocene *versus* the applied potential. The Sn-doped silicon film of 8.3 µm thickness obtained at 10 mA cm$^{-2}$ for 2 h, a silicon nanowire film (NW film) on a rigid graphite substrate with no deposited tin, and a commercial $n$-type polycrystalline silicon wafer were measured, respectively. An increase in the oxidation current (photocurrent) of the Sn-doped silicon film under light illumination with a potential shift in the positive direction was observed, similar to that of a commercial $n$-type polycrystalline silicon wafer. No photocurrent was observed for silicon NW film. The average photocurrent of the Sn-doped silicon film at 0.4 V *vs.* Ag/AgNO$_3$ was about 1.47 mA cm$^{-2}$, which is about 30-40% of that found for a commercial $n$-type silicon wafer.

![Figure 14](image-url): Photocurrent response of a Sn-doped silicon film, silicon nanowire (Si NW) film and commercial $n$-type silicon wafer *versus* the applied potential with light on and off measured in a photoelectrochemical cell (PEC). [14]
Conclusions
We demonstrated a simple molten salt electrodeposition process for preparing crystalline silicon films for low-cost solar cells. \( p \)-type, \( n \)-type, and \( p-n \) junction silicon films with tunable thicknesses can be directly produced from abundant and inexpensive silicon dioxide, all in molten salts. The electrodeposited crystalline silicon films exhibit high purity (99.99989\% (~6N)) and clear photovoltaic effects with PEC as high as 3.2\%. There is a large margin for improving the PEC with optimization of the electrodeposition process. Cost analysis further confirms that a module cost lower than 0.20 \$ W\(^{-1}\) can be achieved with PEC higher than 10\%, making this technology promising for low-cost silicon solar cells. By using a non-carbon inert anode, this molten salt electrodeposition process has the potential to produce silicon films for PV applications without any carbon emission. The carbon footprint of an ED-Si PV module proposed in this work can be greatly reduced compared with current monocrystalline-silicon (mono-Si) and polycrystalline-silicon (poly-Si) PV technologies due to significant reduction in energy consumption. In addition, tin can assist to form a good \( n \)-type silicon film in molten KCl-KF-1 mol. \% \( K_2SiF_6 \) electrolyte, and the Sn-doped silicon film possesses about 30-40\% of the photocurrent density of a commercial \( n \)-type silicon wafer.

Publications and Presentations

Publications

Presentations


References


Contacts
Allen J. Bard: ajbard@cm.utexas.edu