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**Project Title:** Embedded Nanocrystal Silicon Films: A New Paradigm for Improving the Stability of Thin-film Silicon

**Contract Number:** RD-3-25 **Milestone Number:** 1 **Report Date:** 01 Mar 2009

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**Congressional District:** (Corporate office) Minnesota 5th

**Congressional District:** (Project location) Minnesota 5th

# MILESTONE REPORT

**Executive Summary:**

The world is expected to require carbon-free energy generation capacity at a rate of 15 terawatt (TW) to satisfy humanity's growing energy needs due to global population growth and economic development [1]. This compares to a total global consumption of primary energy of 11 TW in the year 1990. This tremendous need for carbon-free energy sources will likely require a mix of energy generation schemes, including nuclear, wind, geothermal, and hydro power, and direct solar-to-electric energy conversion, also known as photovoltaics.

While the vast majority of current photovolatics (PV) technologies are based on silicon technology, extensive research is under way into new, non-conventional PV approaches. Compared to many of the newly proposed non-conventional PV schemes, silicon technology has a number of indisputable advantages: silicon is a material that is abundant, non-toxic and environmentally benign. Moreover, silicon PV cells offer (relatively) stable efficiencies over decades of use, and the knowledge-base and infrastructure of manufacturing silicon PV cells is well developed. More than 90% of the market share of all PV modules sold in 2005 were based on crystalline or amorphous silicon [2, 3]. This market share is unlikely to decrease in the near future, since current worldwide investments in new PV cell factories are mainly in the area of silicon technology [3].

The problem faced by silicon (Si) PV technology, as well as any other PV-technology, is that the electricity generated is about a factor of ten too expensive to be competitive with that obtained from conventional coal-fired power plants [4]. One route pursued to reduce the production cost of Si PV cells is to move from wafer-based single-crystal cells to thin-film technology utilizing amorphous or microcrystalline Si as the active photovoltaic material. While the introduction of thin-film technology has reduced the materials cost in the overall cost of the cell to about 10% [5, 6], this saving is negated by the lower efficiencies and stability of thin-film Si cells as compared to single-crystal cells. For this reason, single-crystal Si PV cells still hold more than 75% of the market share of all PV devices, while thin-film Si cells have a market share of ~ 16% [2, 3].

Increases in the efficiency and improvements in the stability of amorphous Si thin-film cells have been achieved by controlling the micro-structure of the amorphous hydrogenated silicon. This has been achieved by finding new recipes and optimizing the deposition conditions of films during plasma enhanced chemical vapor deposition (PECVD). The stability problems of amorphous silicon were also addressed by moving to more stable microcrystalline silicon. How-

ever, at present the crystal grain sizes of microcrystalline silicon are too small to rival the electronic quality of wafer-based single-crystal silicon.

Under this grant, we study a new and radically different technique to control the microstructure of hydrogenated amorphous silicon and to improve the grain size of microcrystalline silicon thin films. Our approach is based on our unique ability to produce silicon nanocrystals in a low-pressure plasma-based synthesis reactor and to embed these nanocrystals in amorphous silicon films. Our novel deposition process enables us to independently control the properties of the amorphous matrix and of the crystalline phase, including the films' crystal fraction as well as the size of the embedded nanocrystals. We propose using such embedded nanocrystals as nuclei for seed-induced recrystallization of amorphous silicon films. We expect that controlling the seed concentration will enable us to grow microcrystalline Si films faster and with grain sizes larger than possible with other deposition approaches.

We expect that our research will lead to two avenues for improving current thin-film produced Si PV cells. These avenues are pursued under two tracks of research: **Track 1:** Amorphous Si films with embedded Si nanocrystals may have a better stability with respect to light-induced defect creation, leading to improvements in the conversion efficiency of amorphous Si PV cells. Use of such stabilized amorphous Si films may lead to PV cells which retain more of their initial conversion efficiency even after long-term exposure to sun light. **Track 2:** Seed-induced recrystallization of amorphous silicon films may lead to a faster, more economic production of microcrystalline Si films with grain sizes approaching the thickness of the deposited films. PV cells produced from such films may exhibit the stability and efficiency of wafer-based single-crystal PV cells with the large-area deposition advantages and low-cost of thin-film based cells.

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**Technical Progress:**

Both tracks of the project have made good progress and achieved the milestone set in the contract. The progress made on both tracks will be discussed below.

**Track 1:** ***Embedded nanocrystal in amorphous Silicon***

Under this track, we are investigating the improvement of amorphous silicon films that are currently used in thin film amorphous silicon solar cells. Thin film silicon is cheaper to produce that crystalline silicon, but solar cells produced from this material have a lower solar-to-electric conversion efficiency. Moreover, the properties of amorphous silicon deteriorate over time when illuminated with solar light due to a process known as light-induced defect creation. As a result, the conversion efficiency of thin film solar cells based on amorphous silicon degrades quickly on light exposure before leveling out at a level known as "stabilized efficiency", which is significantly lower than the efficiency of new solar cells.

One way to reduce the degradation of amorphous silicon films and to improve the final stabilized efficiency of amorphous silicon solar cells is to incorporate small silicon nanocrystals into the amorphous films. Different from amorphous silicon, crystalline silicon does not suffer from light-induced defect creation. A material that contains both phases appears to have properties that are some kind of an average between the properties of the purely amorphous and crystalline phase. Prior to our work, amorphous silicon films with embedded nanocrystals had been deposited by operating the plasma deposition process for the amorphous silicon in a regime that led to the formation of small crystals that were deposited into the film. This mode of operation, conducted in a single chamber reactor, allowed for limited control of the properties of the amorphous and the crystalline silicon film.

During the first quarter of this project, we have used a novel dual-reactor co-deposition process that decouples the amorphous silicon film deposition from the crystal formation process by conducting it in two different chambers. This approach enables us to independently control the properties of the amorphous film and of the embedded silicon nanocrystals. In the dual plasma reactor process shown in figure 1, small silicon nanocrystals, about 5 nm in diameter are created. These silicon crystals contain a few thousand silicon atoms. The crystals are injected into a second plasma reactor, in which amorphous silicon films are deposited. By changing the crystal injection rate and placing substrates at different positions on the deposition electrode (shown as positions A, C, and E in figure 1), films with various levels of nanocrystal inclusions can be produced.

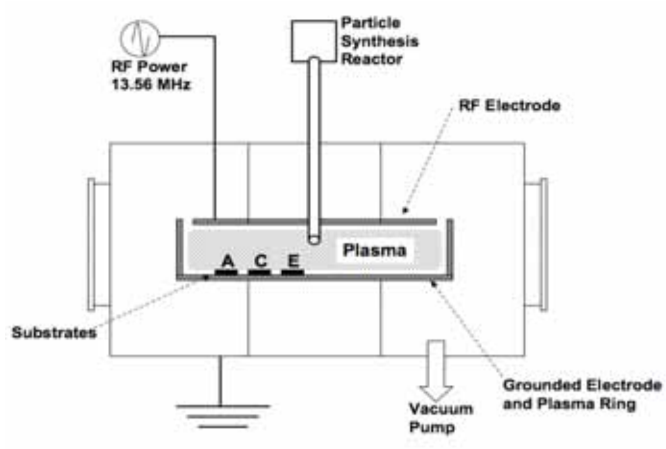


Fig. 1: Schematic of the dual-plasma co-deposition system that is employed in the current project.

In first experiments, we confirmed that the nanoparticle concentration in the amorphous silicon films is sensitive to the substrate position relative to the nanocrystal injection tube shown in figure 1. We used a technique known as atomic force microscopy (AFM) to analyze the deposition of nanocrystals during amorphous film deposition. Figure 2 shows AFM images for particles deposited for one minute under plasma conditions similar to the film growth conditions, with the exception that no silane ($SiH_4$, our silicon film precursor) was used so that no surrounding amorphous silicon film is deposited. Figure 2 shows results of these measurement. The observed area density of particles was the lowest in the periphery region of the electrode (the substrate position labeled A in Figure 1), around 80 $\mu m^{-2}$ at 5 cm. The density increased by 50% to 120 $\mu m^{-2}$ at 2.5 cm, for the substrate labeled C in Figure 1. The difference in particle deposition rate is apparently not linear with electrode distance, as the center sample (Fig. 2 (c)), labeled substrate E in Figure 1, appears to contain up to one monolayer of particles. This suggests that deposition by direct impaction may also play a role for films deposited near the electrode center. The larger features seen in the AFM images could likely be due to particle agglomerates that formed in the gas phase upon leaving the synthesis plasma.

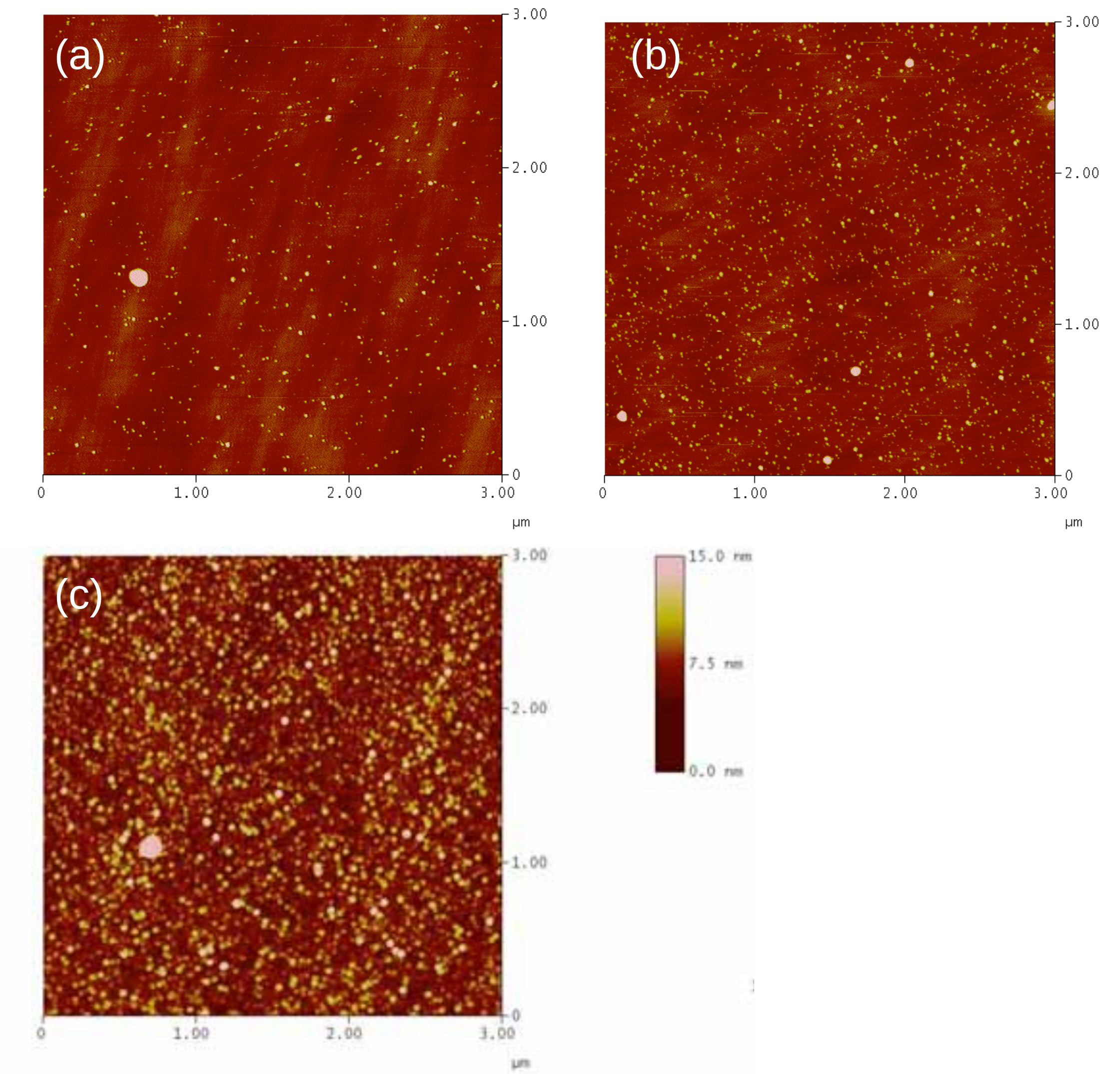


**Figure 2:** AFM images of nanoparticles deposited under typical plasma conditions for 1 minute onto c-Si substrates located (a) 5 cm, (b) 2.5 cm, and (c) 0 cm from the electrode center.

We currently started to perform first measurements of the optical absorption properties of the films as a function of the nanocrystal concentration. These measurements are ongoing and will be reported in the next progress report.

### Track 2: *Large-grain recrystallized Si*

As the properties of amorphous silicon are generally inferior to those of crystalline silicon, resulting in significantly more efficient solar cells from crystalline silicon, there are significant efforts underway to try to combine the cost advantage of amorphous silicon with the efficiency advantage of crystalline silicon. The cost-efficient formation of microcrystalline silicon films seems to be an attractive route to achieve this objective. For this purpose, researchers have proposed to deposit at high deposition rates amorphous silicon and then turn it into microcrystalline silicon through thermal annealing.

In order to improve the properties of this annealed, also known as “recrystallized” silicon, two issues need to be addressed: 1) the size of the crystalline grains needs to be optimized and 2) the time until the first silicon crystals form in the annealed films, also known as incubation time, needs to be minimized. Our new approach to addressing both of these issues involves implanting seeds for the microcrystalline film into the amorphous silicon film matrix. By implanting nanocrystal seeds, we hope to remove the incubation time, as crystalline regions already exist in the film at the start of the annealing process. By controlling the density of the initial seeds, we also hope to control the size of the microcrystals in the final films.

In a first set of experiments we studied the crystal growth of small numbers of embedded seed crystals, as shown in the sequence of transmission electron microscope (TEM) images in Figure 3. A synthesis plasma was used to create seed crystals of about 30 nm in diameter (darker dots in Figure 3). These seed crystals were deposited onto a layer of ~ 100 nm of amorphous silicon and then covered by another layer of ~100 nm of amorphous silicon. The samples were than heated up in the TEM and crystal growth was monitored in regular intervals. The sequence of images shows that each of the embedded seeds starts to grow into a bigger crystal grain. The different levels of brightness of these grains correspond to different orientations of the crystals with respect to the electron beam in the TEM. The TEM image series demonstrates that the transformation of the amorphous silicon into microcrystalline silicon is almost complete after 2 hours and 30 minutes. The growth observed over the first 30 minutes also demonstrates that by embedding seed crystals we can eliminate the incubation time.

Studies of the grain size distribution have begun and will be continued in the second quarter of the grant. We will also commence characterization of the electronic properties of the microcrystalline films as well as measurements of the optical absorption properties.

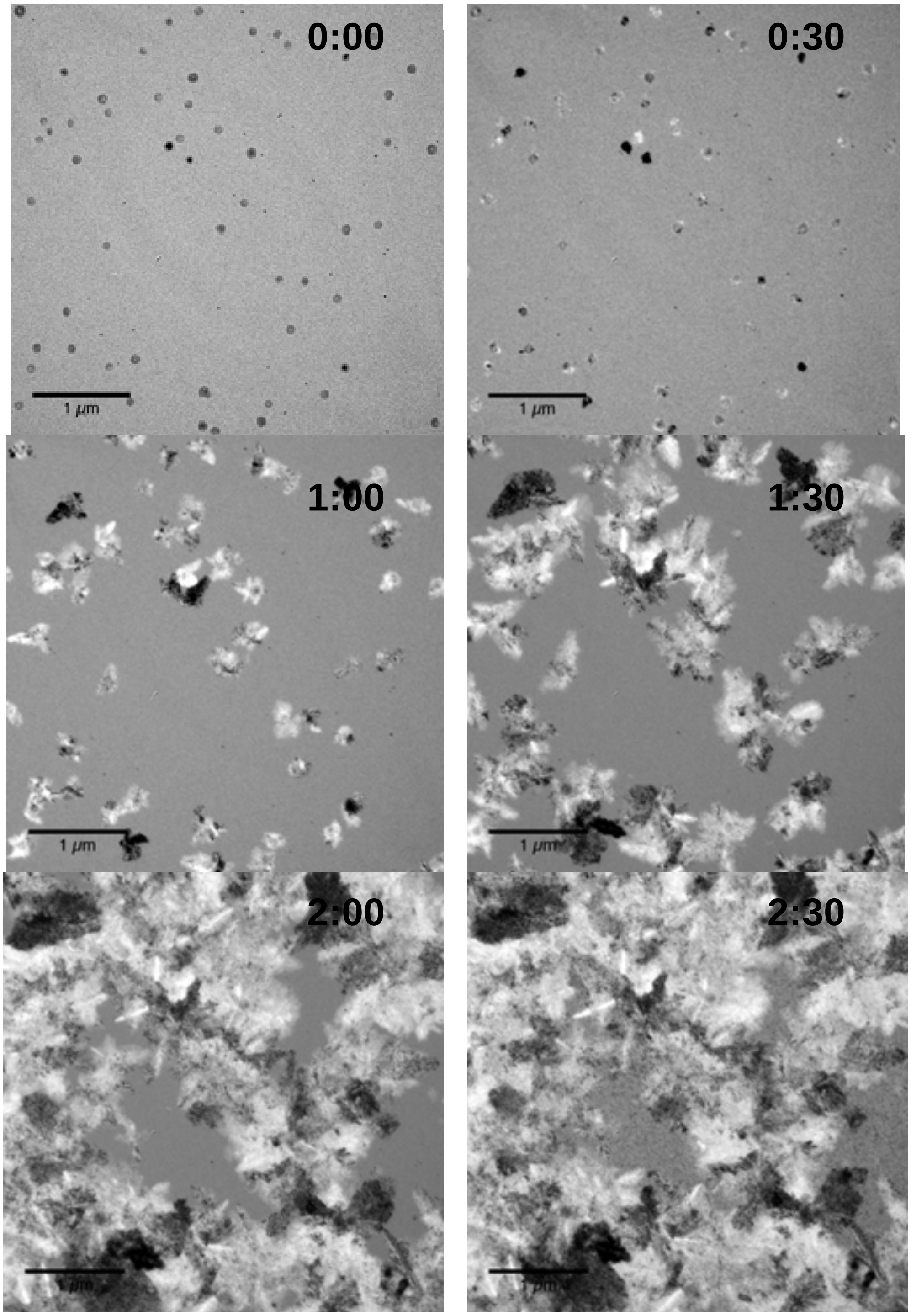

*Figure 3: Bright-field TEM images for successive annealing times (indicated as [hr:min]) using heated stage at 625˚C.*

**Additional Milestones:** Work is in progress towards milestone 2.

**Project Status:** The project is on schedule.

## LEGAL NOTICE

**Appendix:** Milestone 1

According to the contract, the following milestones were to be achieved by the end of the first quarter of the grant.

**Milestone 1**

To be completed 3 months after the Contract Start Date.

*Track 1:* *Embedded nanocrystal in amorphous Si* - Begin to establish conditions that yield films with suitable microstructure for high-quality embedded nanocrystal amorphous films. Begin determination of relation between optical absorption and nanocrystal density.

*Track 2:* *Large-grain recrystallized Si* - Begin initial characterization of recrystallized Si produced through high-temperature annealing of nanocrystal-seeded amorphous Si. Study microstructure, including grain sizes and void fraction. Begin to establish parameters amenable for producing material suited for seed-controlled recrystallization.

**Deliverable 1**

Submission of Milestone Report detailing completion of Milestone 1 requirements to RDF representative.

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