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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:** 5 **Report Date:** 22 Feb 2010

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

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

# MILESTONE REPORT

**Executive Summary:**

More than 90% of the market share of all photovolatics (PV) modules sold in 2005 were based on crystalline or amorphous silicon. 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 five too expensive to be competitive with that obtained from conventional coal-fired power plants. Under this grant, we pursue two different routes that may help increase the efficiency and lower the cost of silicon solar cells. Our first approach is based on our unique ability to produce silicon nanocrystals in a low-pressure plasma-based synthesis reactor and to embed these nano-crystals in amorphous silicon films. Our novel deposition process enables us to independently control the properties of the amorphous matrix and of the crystalline phase, which we hope will enable us to improve the electronic quality of amorphous silicon that is used in thin film solar cells. In the second approach, we study using such embedded nano-crystals 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. This may enable the cheaper production of solar cells based on microcrystalline silicon.

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 nano-crystals 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 re-crystallization 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.

During the current project period, efforts have focused on characterizing the optical properties of amorphous silicon thin films with embedded nanocrystals. The absorption properties of amorphous silicon films were studied with a technique known as constant photocurrent method. Unfortunately, some of the results obtained in previous quarters revealed some inconsistencies.

These led to the reconstruction and improvement of the experimental set-up. The new system is now in place and will enable a more meaningful study of the absorptive properties in the future.

In track 2 studies focused on the crystallization kinetics of films seeded with large silicon nanocrystals. The dependence of the crystallization kinetics on the density of initially deposited films was investigated. An increased seed density led to faster film crystallization. Simultaneous measurements of the electrical conductivity showed a trend of decreased conductivity with increased seed density, suggesting that a large seed concentration leads to smaller grain sizes. These results suggest that a balance between crystallization time and electrical properties needs to be found. This correlation will be further investigated in current studies.

Project funding provided by customers of Xcel Energy through a grant from the Renewable Development Fund.

**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 nanocrystals in amorphous silicon***

Within this research track, we are continuing to study the effects of the embedded silicon nanocrystals. This quarter, our focus is examining how the nanocrystalline inclusions affect the optical absorption of the films using the Constant Photocurrent Method (CPM) [1], which was described in the Q3 report. As described in the first quarterly report (Q1), a dual plasma system has been used to produce silicon nanocrystals in one plasma deposition system. The particles generated in this system are then entrained by a carrier gas and injected into a second plasma deposition system. These nanocrystals are embedded into a hydrogenated amorphous silicon film being grown in a second plasma. In the Q3 report, we reported rough estimations of the defect densities through optical absorption measurements at 1.5 eV, showing a possible minimum of the defect density at a non-zero crystal fraction. We are currently examining this effect in greater detail.

In accordance with our desire for greater sensitivity, in this quarter we have built and debugged a new chamber to house the CPM setup. It was designed to reduce noise and extraneous voltage pick-up in order to improve the sensitivity and extend the range of the experiments. A schematic of the new chamber is shown in figure 1. Cartridge heaters are employed for annealing the sample as well as tubes that can be used to cool the sample with either room temperature or liquid nitrogen chilled air. The contact arms support the wires making electrical contact with the sample and reduce stray voltage pick up due to external vibrations.

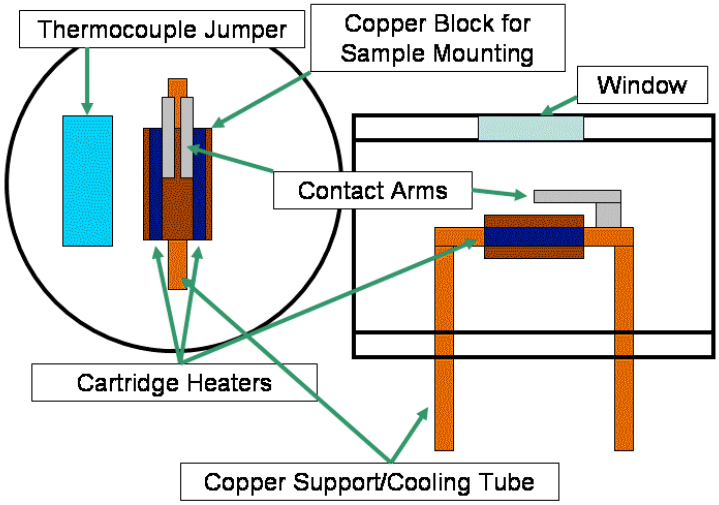


**Figure 1:** Schematic of the newly constructed Constant Photocurrent Measurement chamber.

To date, two of the films measured previously, 436A and 436C, have been remeasured in the new system. The 436A matches the spectra taken before, while the 436C no longer displays the anomalous absorption peak that was observed and described in the Q3 report. We therefore believe the excess absorption peak at 1.9 eV to be an artifact of undetermined nature, as the more accurate measurements in the new system fail to show this feature. The optical absorption spectra are shown in figure 2.

In order to continue to improve the accuracy of our results, we are currently working on several options to improve the absorption measurements for above band gap light; it is these measurements that ultimately set the scale of the CPM results. As was mentioned in the Q3 report, CPM is a relative measurement which requires an absolute measurement of the absorption coefficient to set the scale [1]. Typically this is done with a traditional transmission measurement, though care must be taken when dealing with thin films to allow for the effects of interference fringes and surface roughness, as these can have a large effect on the calculated absorption coefficients [2]. We will employ both a traditional spectrophotometer and a spectroscopic ellipsometer in order to obtain accurate absorption values to set the CPM to an absolute scale. Note that this may shift the absolute values for the absorption curves seen in figure 2. We hope to finalize the transmission measurements and report the optical absorption data for additional mixed phase amorphous/nanocrystalline silicon films for the next quarterly report.

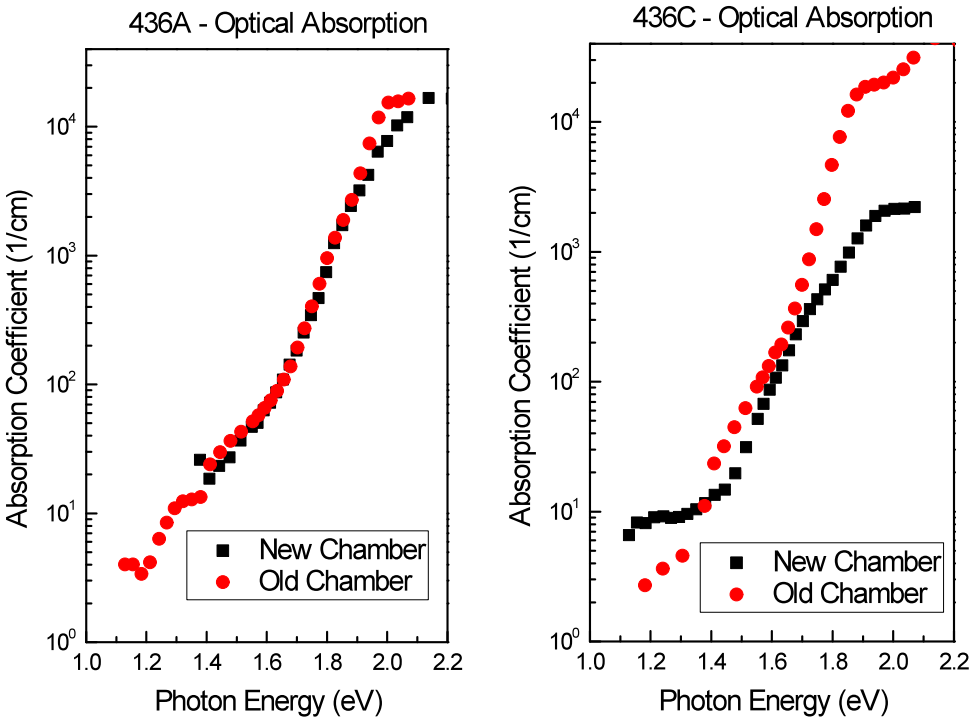


**Figure 2:** Optical absorption curves for 436A (right) and 436C (left). The results from the new chamber are in black and the old chamber in red.

Our previously submitted journal publication has now been accepted to the Journal of Applied Physics, volume 107 (in press).

**Track 2:** ***Large-grain re-crystallized Si***

The second track of the project aims at controlling the grain structure and reducing the re-crystallization time of micro-crystalline films through the annealing of amorphous silicon films in which silicon nano-crystals are embedded as crystallization "seeds". The previous quarter's report consisted of the first studies to be carried out on a drastically different film structure from those studied in quarters 1 and 2. Whereas the previous generation of film structure consisted of dispersing relatively small (2-5nm in diameter) crystallites randomly throughout the amorphous film volume with limited control over population density and reproducibility, the new generation of film structure consists of larger crystallites deposited with system that allows greater control over particle size, shape, and population density, as well as significantly enhanced reproducibility.

The results of quarter 4 showed that the crystallization rate of the new film structure increased by an order of magnitude relative to the previous structure. Relative to unseeded films, new generation films also showed a significantly reduced time required to achieve full crystallization. Specifically, for every anneal temperature studied, all seeded films achieved crystallization in roughly half the time as unseeded films, data which fit with classical thermodynamic growth models to show a reduced energy requirement for seeded crystallization. Furthermore,

electrical conductivity measurements showed a trend in which seeded films exhibited consistently superior conductivity over unseeded films when annealed above a certain temperature.

Since quarters 3 and 4 showed enhancements in crystallization time and electrical transport in quarter 5, studies were focused on exploring the degree to which the seed inclusions were capable of controlling the final grain structure of the film. This was performed by comparing the crystallization kinetics and electrical conductivities of films re-crystallized from a variety of initial seed densities.

If the final grain structure is indeed controlled by the initial seed concentration, films with higher initial concentrations should experience faster crystallization kinetics. Furthermore, if the seeds were the only active sites of crystal growth, then samples with lower initial seed concentrations should exhibit larger grain sizes and subsequently larger electrical conductivities. In exploring the hypothesis that more heavily seeded films would crystallize earlier, samples with three different initial seed population densities, along with an unseeded film, were synthesized and annealed in a quartz furnace under nitrogen flow at 650 °C, with their corresponding crystal volume fractions measured at regular time intervals via Raman spectroscopy.

The resulting data regarding volume crystal fraction vs. anneal time is depicted below in figure 3. Samples A, B, and C were confirmed via transmission electron microscopy (TEM) and atomic force microscopy (AFM) to have aerial seed densities of roughly 30, 50, and 100 seeds per square micron, respectively. As the data shows, the onset of crystallization does indeed occur earlier for films with higher initial seed densities, supporting the hypothesis that the film crystal structure can be controlled by the embedded seed population. Furthermore, each seeded film achieved full crystallization before the onset of crystallization occurred within the unseeded film, excluding the possibility that any non-seed-induced, native crystallization played any significant role in the final grain structure. Another interesting observation within this data is that the sample with lowest initial seed concentration (sample A), although having a crystallization onset which occurs the latest, seems to crystallize faster than the slightly more heavily seeded sample B. We hypothesize that, if each seed acts as a multidirectional growth site, neighboring seeds may encounter resistance from one another in higher seed density films. This is also supported by the fact that the crystal fraction at which samples A and B intersect is near the value commonly agreed to occur when neighboring growth sites in most films intersect to form grain networks [3, 4]. Studies are currently under way to explore this hypothesis further by studying the growth kinetics of films with even lower seed densities.

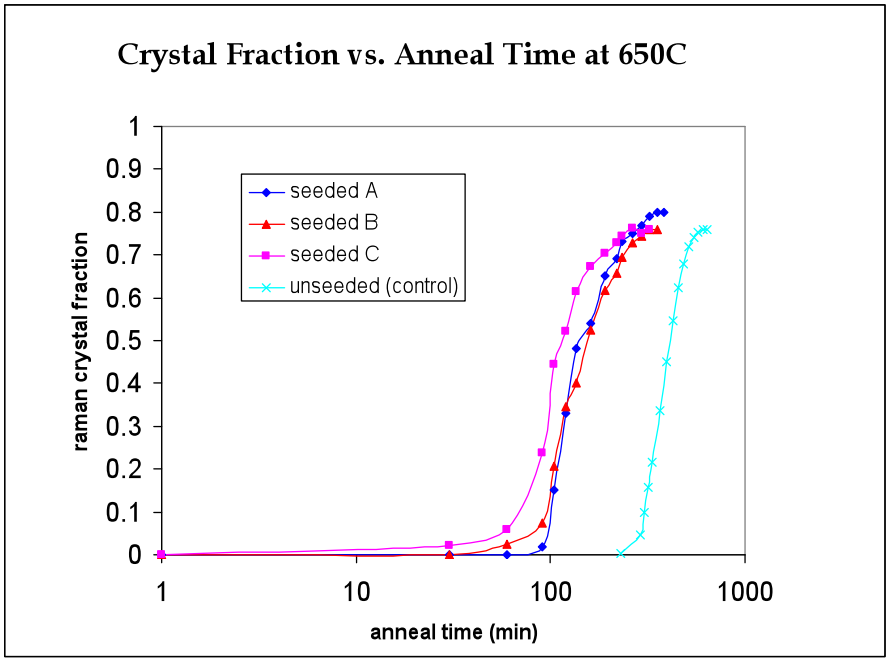


**Figure 3**: Raman crystal fraction evolution with anneal time at 650 °C. seeded samples A, B, C were initially deposited with roughly 30, 50, and 100 particles per square micron, respectively.

Since these most recent crystallization data suggests that grain structure can be controlled by varying initial seed density, subsequent studies were focused on determining whether this control could be translated into electronic performance of the films. This was performed by crystallizing films with several different initial seed densities and comparing their respective dark conductivities. Since samples with fewer seeds will have less competition for grain growth space upon annealing, the grains originating from each seed should therefore be able to grow to larger sizes. Subsequently, samples having lower initial seed densities should have a grain structure composed of fewer, larger grains than more heavily seeded samples, and thus larger electrical conductivity. In comparing the electronic transport properties of films re-crystallized from initially seeded structures, seeded films having five different seed structures and a sixth unseeded control sample, were fully re-crystallized, fitted with a chromium contact pattern, and I-V characteristics were taken to acquire dark conductivity values at several locations in each film. The samples were observed by TEM and AFM to have initial seed densities of roughly 2, 5, 30, 50, and 100 particles per square micron, respectively.

As predicted, the average dark conductivity for each sample, as shown in figure 4, depicts a trend in which conductivity decreases with increasing initial seed density. It is interesting to note that the variation in conductivity for each film also seems to follow a trend, in which films with lower seed densities seem to exhibit a larger spread of values. This variation may be potentially explained by substrate charging phenomena related effects on particle deposition; however studies are currently underway to further explore this trend.

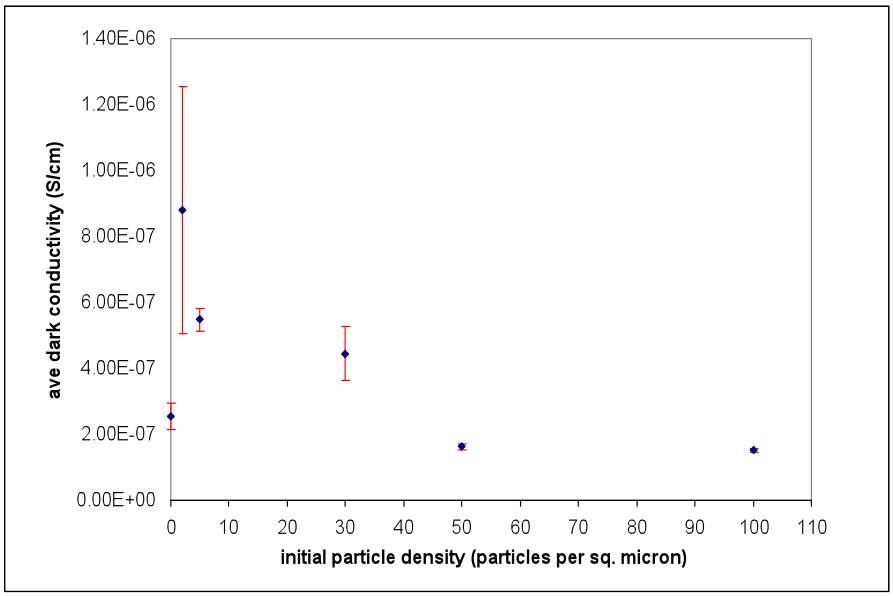


**Figure 4**: dark conductivity vs. initial seed density for five films having various initial seed densities, along with a sixth unseeded control film.

In conclusion, the results obtained in quarter 5 have shown this new process for seeded film synthesis to be successful in the context of both film performance and process control. With the successful production of larger seed crystals, and a more controllable embedding process, the data suggests that we are able to tune both the crystallization kinetics and the electronic performance of films based on seed density alone. Secondary trends within these data regarding conductivity variation across the film and seed-competition-based growth rates are currently underway in order to understand and control film parameters to an even greater degree. Due to the unique nature by which films from this process crystallize, extensive high-resolution microscopy studies are also being conducted in parallel to these macroscopic studies; data which will be utilized for developing a thermodynamic model to describe the phase-change kinetics. Furthermore, studies are also being performed to develop a post-process hydrogen treatment by which the electrical conductivity of the films can be potentially enhanced even further.

**Project Publications:** A full paper draft has been submitted to be presented at the Proceedings of the 4$^{th}$ International Conference on Energy Sustainability in May, 2010. Furthermore, the abstract for the conference publication submitted in quarter 4 has been accepted and the corresponding data will be presented to the Materials Research Society spring 2010 symposium.

**Additional Milestones:** Work is in progress towards milestone 6.

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

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**Milestone 5:**

To be completed 15 months after the Contract Start Date

Track 1: Embedded nanocrystal amorphous Si – Begin to establish main parameters affecting optical and electronic properties of the embedded nanocrystal amorphous films. Begin to determine effect of embedded nanocrystal size on optical absorption.

Track 2: Large-grain recrystallized Si – Begin to establish main parameters affecting the crystal growth kinetics, incubation time, and grain size distribution. Determine influence of seed-crystal size and recrystallization time.

Deliverable 5:

Submission of Milestone Report detailing completion of Milestone 5 requirements to RDF representative.

## References


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