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

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**MILESTONE REPORT**

**Executive Summary:**

More than 90% of the market share of all PV modules sold in 2005 were based on crystalline or amorphous silicon [1, 2]. 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 [2]. 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 [3]. 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% [4, 5], 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% [1, 2].

Under this grant, we study a new and radically different technique to improve the stability 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 nano-crystals 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, including the films’ crystal fraction as well as the size of the embedded nano-crystals. We study using such embedded nano-crystals as nuclei for seed-induced re-crystallization 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 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 accurately characterizing the embedded nanocrystal density in amorphous silicon thin films (track 1). In track 2, the emphasis has been on studying the crystallization kinetics during the thermal annealing of seeded amorphous silicon films as function of the seed-crystal density.

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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 nanocrystals in amorphous silicon**

Within this research track, we are continuing to study the effects of the embedded silicon nanocrystals, specifically with respect to their optical properties. 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 previous quarterly report (Q2), it was confirmed that particles do indeed come from the separate nanocrystal plasma and Raman spectroscopy was used to characterize the crystalline content of the films.

The primary focus of this quarter has been the optical characterization of the films; this was done by measuring the optical absorption of the films as a function of photon energy and then characterizing the defect density as a function of crystal fraction. The optical absorption was measured using a technique that is common to thin film semiconductors called the Constant Photocurrent Method [4]. This technique exploits the changes in the photocurrent that occur at different photon energies in order to ascertain the optical absorption coefficient. Detection is accomplished with a low-frequency lock-in detection scheme using an SR530 Lock-in Amplifier. The defect density is often characterized by measuring the optical absorption at 1.2 eV, a typical figure of merit in the literature [5]. We have used 1.4 eV due to limitations of our detection range described below, which we are working to overcome. Actual defect densities are not calculated, as the required range in subgap absorption regime is not available due to the low photo-sensitivities of the high crystal fraction (E) samples. Work is under way to improve the sensitivity of the CPM apparatus in order to achieve a range suitable for defect density calculations.

As described in the Q1 report, the particle concentration is varied by placing substrates at different positions in the system, resulting in three films per run, which are labeled A, C, and E from lowest to highest particle concentration. The optical absorption spectra were measured for two complete runs, an example of which is plotted in Figure 1. As can be seen, the crystalline concentration has a strong effect on the optical properties. Most notable is the defect density, as measured by the subgap optical absorption at 1.4 eV.
What is observed is a non-monotonic dependence of the subgap optical absorption on the crystal fraction, with the C film having the lowest absorption by about a factor of two. Additionally in the C film, there is an anomalous absorption peak at 1.9 eV, which has been observed in approximately half of the C films measured. The exact nature of this peak is as of yet undetermined.

As mentioned above, two complete series have been characterized and the subgap absorption data are presented in Figure 2. The same trend of C, A, E from lowest to highest absorption was observed for both runs, suggesting an optimum crystal fraction of approximately 1.5 – 3%. Further studies are underway to ascertain whether this trend holds for other runs.

Furthermore, a referred journal article has been submitted for publication. The paper discusses the electrical and structural characterization of these novel mixed-phase films. It is currently in the hands of the referees and we are awaiting their responses.

Figure 1: The optical absorption curves for a complete A, C, E series of films. For this series, the $X_c = 0.8\%$, 1.4\% and 17.7\% for the A, C, and E respectively.

Figure 2: Optical absorption at 1.4 eV as a function of crystal percentage. Each color/shape corresponds to one run.
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 focused on the annealing of films deposited by a “co-deposition” process in which the seed crystallites and the amorphous film were produced simultaneously in separate plasmas. This unique set-up allowed for independent control over crystallite and amorphous film synthesis parameters. The process was designed such that a continuous stream of crystallites were swept from a particle producing plasma, into a region occupied by an amorphous film producing plasma, thus resulting in deposition of a continuous mixture of crystallites and amorphous film. As results from the Q2 report conveyed, co-deposited films consisted of crystallites, roughly spherical in shape, on the order of 2-5nm in diameter, dispersed throughout the volume of the amorphous film. Films of various crystallite concentrations were produced and annealed to study the effect of seed concentration on crystallization kinetics. As predicted, the results showed that the introduction of even small concentrations of seed crystals within the amorphous film noticeably reduced the re-crystallization time.

During this past quarter, efforts were focused on enhancing this effect by increasing the crystallization rate, improving control over particle concentration and size, improving control over grain structure, and gaining a clearer understanding of the crystallization kinetics, grain structure and electronic transport properties. Upon annealing at high enough temperatures, amorphous silicon film (without seeds) will naturally form small crystalline clusters from rearranging bonds. Traditional crystallization theory dictates that clusters above a certain critical size will grow to form larger crystalline regions, a tendency which increases with initial cluster size [1]. Thus it follows that crystallization of seeded films should be enhanced by increasing crystallite size.

What more, a larger particle would provide a larger image for observing the crystallization kinetics occurring at the crystallite/amorphous interface under TEM. Larger particle production requires higher gas pressures and slower gas flow rates, such that particles are allowed to remain in the reactive plasma environment long enough to grow to substantial size. As such, the deposition system was re-configured such that the particle-producing plasma was further isolated from the conditions of the amorphous film producing plasma. This was accomplished by placing an orifice between the two regions which, aside from allowing for higher pressure conditions, also focused the exiting particle stream into a spray pattern easily stopped by a sliding shutter; permitting a more manual control over particle concentration (see figure 3).
As can be seen in the TEM images in figure 4 below, this design resulted in the consistent production of single crystallites of cubic shape averaging 25nm in edge length. However, particles of this size are unable to travel far enough through the plasma to reach the substrate, due to aerodynamic restrictions. Subsequently, unlike the co-deposition films, seeded films with the larger particles were deposited in layers, in between successive depositions of amorphous film.

In studying the microscopic crystallization kinetics of the new seeded structure, layered films were annealed under TEM. These studies were conducted on films in which the seed crystals were deposited onto a 20nm layer of amorphous silicon film and then covered by another layer of 100 nm amorphous silicon film. The samples were annealed under observation in TEM, thus allowing for a unique, real-time monitoring of the crystal growth. A time series of images recorded under 610°C annealing are shown in Figure 5. The first image (0:00) was recorded after ramping to 610°C in about 20 minutes. While the embedded seed crystals were already observed to grow, some clearly defined light-contrast regions indicating missing material (interpreted as
“voids”) formed at the interface between the particles and the amorphous film. The second image (0:15) was recorded 15 min later, in which the voids coalesced into bubble-like structures and began to propagate into the film. Each crystal appeared to have produced several voids, with the size 10-30 nm across. After one hour of annealing (1:00), the voids have moved several tens of nm from their original location. As this occurred, the “tail” region in the wake of the void motion has left behind crystallized silicon. The speed of the voids through the film was noticeably faster than the grain growth speed of the embedded nano-crystals. In the final images, several voids appeared to stop moving and became completely surrounded by crystalline material. It is assumed that these voids were most likely trapped at the interface between the film sample and the carbon support film on the grid. Additionally, native nucleation was not observed during the measurement.

Figure 5: Time series of bright-field TEM images for layered film structure annealed at 610°C in the heated stage.

High-resolution TEM imaging after partial annealing is used in order to reveal the structure of the voids. In Figure 6, the red arrow indicates the direction of the void motion away from the seed crystal. The “front” region of the void is amorphous, while the “tail” region behind the void is crystalline, evidenced by the (111) lattice plane spacing. The structure of the voids provides evidence for the mechanism of void movement: the surface diffusion of silicon atoms along the free inner surface from the amorphous to the crystalline side of the voids. By creating the part amorphous-part crystalline inner surface, we effectively replaced the mechanism of normal crystal growth through a mechanism of diffusion along a free internal surface. To confirm this mechanism, we designed another set of experiments in which we managed to seed amorphous
silicon particles into the amorphous matrix, and observed the crystallization process in heated-stage TEM (Figure 7).

![Figure 6: High-resolution TEM images of void structure at high magnification.](image)

The first image (0:00) was recorded when the temperature stabilized after ramped to 650°C. The embedded seeds were not able to clarify in TEM because both the seeds and the background film are amorphous. While we did not observe any growth of the amorphous seeds, we started to notice the voids formed at the boundary of the seeds. The second image (1:30) was captured after one hour and a half annealing. During the amorphous incubation period, the seeds remained amorphous and the voids stayed in their original position. After two hours of annealing (2:00), the voids began forming the bubble-like shape and propagating throughout the film. The select-area diffraction pattern showed crystalline structure within the seeds region when voids movement started. At the following stages, the voids moved further distance into the amorphous film from their original locations, while left behind crystalline silicon in the wake region. It is interesting to point out that several voids were observed to get trapped inside the film when they reached another crystalline region. In the final image, all the voids stopped movement as in Figure 5.

In conclusion, by embedding seeds of several tens of nanometers in size, voids with a partly crystalline and partly amorphous surface are formed at the seeds. The voids move through the film with high velocity while “pulling” behind them a trail of crystalline material which acts as additional crystallization site, leading to significantly enhanced crystallization kinetics. Also the motion of the voids can be explained by the diffusion of Si atoms at their inner surface from the amorphous “front” side to the crystalline “tail” side. Last the voids with fully amorphous surface do not propagate through the film until the “tail” region does crystallize.
Figure 7: Time series of heating stage TEM images for a-Si:H film embedded with a-Si particles annealed at 650°C.

**Project Presentations:** An oral presentation about the work performed in track 2 was presented at the 2009 ASME conference on Energy Sustainability. The associated conference paper is attached in Appendix A.

**Additional Milestones:** Work is in progress towards milestone 4.

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

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Milestone 3

To be completed 9 months after the Contract Start Date

Track 1: Embedded nanocrystal amorphous Si - Continue to establish conditions that yield films with suitable microstructure for high-quality embedded nanocrystal amorphous films. Determine electronic defect density as function of nanocrystal density.

Track 2: Large-grain recrystallized Si - Continue characterization of recrystallized Si produced through high-temperature annealing of nanocrystal-seeded amorphous Si. Study microstructure, including grain sizes and void fraction. Study impact of seed-crystal density and amorphous film thickness.

Deliverable 3

Submission of Conference paper or technical lecture. Submission of Milestone Report detailing completion of Milestone 3 requirements to RDF representative.

References:


Conference paper published in the proceedings of the
2009 ASME Energy Sustainability Conference
San Francisco, July 19-23, 2009
BUBBLY SILICON: A NEW MECHANISM FOR SOLID PHASE CRYSTALLIZATION OF AMORPHOUS SILICON

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ABSTRACT

This paper describes the rapid formation of polycrystalline silicon films through seeding with silicon nanocrystals. The incorporation of seed crystals into amorphous silicon films helps to eliminate the crystallization incubation time observed in non-seeded amorphous silicon films. Furthermore, the formation of several tens of nanometer in diameter voids is observed when cubic silicon nanocrystals with around 30 nm in size are embedded in the amorphous films. These voids move through the amorphous film with high velocity, pulling behind them a crystallized “tail.” This mechanism leads to rapid formation of polycrystalline films.

INTRODUCTION

Applications of polycrystalline silicon (poly-Si), including thin-film transistors and solar cells, have become popular in the last several years. The possibility to combine the stability and excellent electronic properties of single crystal Si with the cost advantage of Si thin films is highly attractive. To achieve this, one must produce poly-Si with the maximum possible grain sizes, ideally as large as the film thickness itself. Solid phase crystallization (SPC) of hydrogenated amorphous silicon (a-Si:H) has been studied extensively as a route to produce large-grain poly-Si. The SPC mechanism proceeds following an incubation period, after which a steady-state nucleation and grain growth rate of native crystals can be observed. The resulting structure can generically be called poly-Si, and is noted by the lack of any remaining amorphous phase.

METHODS

We previously proposed an approach to enhance the crystallization kinetics of amorphous silicon films by embedding small nanocrystal seeds. Crystalline Si nanoparticles with a specific mean diameter were produced by a plasma process, and injected into the second plasma deposition process for the a-Si:H film. We used a novel dual-plasma-reactor co-deposition process, shown in Figure 1, 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, silicon nanocrystals ranging in size from 5-30 nm in diameter are created in a synthesis plasma which was described in detail in refs. [1, 2]. 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.

RESULTS

Seeded amorphous silicon films were annealed in a furnace at temperatures of 600-650 °C. We observed that these nanocrystal “seeds” grow immediately upon furnace annealing without any incubation period, thus significantly enhancing the crystallization.

By embedding seeds of several tens of nanometers in size, voids with a partly crystalline and partly amorphous inner surface are formed at the seeds. The voids (bubbles) move through the film with high velocity while “pulling” behind them a trail of crystallized material, Figure 2. The void velocity exceeds the regular grain growth velocity around the embedded seeds by almost a factor of ten. The so produced crystalline trail acts as additional crystallization site, leading to significantly enhanced crystallization kinetics.

The mechanism of void movement is consistent with surface diffusion of silicon atoms along the free inner surface from the amorphous to the crystalline side of the voids. By creating the part amorphous-part crystalline inner surface, we effectively replaced the mechanism of normal crystal growth through a mechanism of diffusion along a free internal surface.

ACKNOWLEDGMENTS

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REFERENCES


Figure 2: TEM image of a silicon crystal embedded in an amorphous silicon film. The bright dots correspond to voids that move through the amorphous film. The visible “tails” are crystalline silicon.