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

Contract Number: RD-3-25   Milestone Number: 6   Report Date: 22 May 2010

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Congressional District: (Corporate office) Minnesota 5th
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MILESTONE REPORT

Executive Summary:

Under this grant, we explore 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 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, 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 nanocrystals 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. 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 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 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 quarter 6, studies under track 1 have focused on studying the absorption properties of amorphous crystalline films with embedded nanocrystals. Two different techniques were used: the constant photo current method and photothermal deflection spectroscopy. We observed significant differences between these methods for low energy photons, which are strongly sensitive to defect states in the band gap of the silicon films. We hypothesize that the photothermal deflection technique is strongly affected by surface states. Electron spin resonance measurements, which detect dangling bond defects, confirm this assumption.
In track 2 studies focused on determining mechanisms leading to film crystallization at the microscopic level. Electron microscopy studies suggest that stress fields around the embedded nanocrystal seeds play an important role in the film crystallization. We also studied whether the electronic properties of the annealed poly-crystalline films can be improved by trying to terminate defect states at grain boundaries. We were able to show that hydrogen passivation of grain boundaries increased the films’ conductivity by several orders of magnitude.

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 on the opto-electronic properties of silicon nanocrystals embedded in a hydrogenated amorphous silicon matrix. This quarter, our continuing focus has been on the examination of the influence of nanocrystalline inclusions on the optical absorption of these mixed-phase films using the Constant Photocurrent Method (CPM) [1], described in the Q3 report. We have increased the number of films characterized using CPM. In addition, in order to corroborate the trends with nanocrystalline inclusion observed via CPM, we have initiated a collaboration with scientists at the National Renewable Energy Laboratory in Golden, Colorado, attempting two new techniques; photothermal deflection spectroscopy (PDS) [2] and electron spin resonance (ESR).

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 Q5 report, we reported improved optical absorption spectra for two films and this quarter we report improved measurements of four additional films as well as attempts to measure the films’ properties using PDS and ESR.

The additional CPM spectra can be found in figure 1; figure 1a and 1b are both complete series of co-deposited films, labeled the 436 and 736 series respectively. We can see that both series are in qualitative agreement. There is little change in the optical absorption for the A and C films, the low and medium nanocrystalline content films respectively, while we see a dramatic increase in subgap absorption for the E films, the high crystalline concentration film, as well as a broadening of the Urbach slope.
Photothermal deflection spectroscopy (PDS), as described in ref [2], is a bolometric technique to measure the absorption coefficient in thin films that is complimentary to CPM. Whereas CPM only sees electronic transitions that contribute to the photoconductivity, PDS sees all transitions that end in non-radiative recombination. In amorphous silicon at room temperature, this includes virtually all transitions. Thus, by having both spectra, differences in the spectra can help one to learn about the density of states of the material. In addition, electron spin resonance (ESR) provides complimentary information, in that detection of paramagnetic spins is sensitive to the density of uncharged defect states. Comparisons of these measurement techniques for identical samples provide us with useful information.
Figure 2: Optical absorption spectra for each film in the 436 series measured using Photothermal Deflection Spectroscopy (PDS) (solid symbols) and the Constant Photocurrent Measurement (CPM) technique (open symbols).

We present the first attempt at PDS in figure 2 (solid symbols), where their respective CPM spectra (open symbols) are plotted on the same graph for the 436 series. There is a significant difference in the low photon energy optical absorption coefficient, associated with the density of mid-gap defect states obtained from the two techniques. We believe that these differences are due mainly to surface state absorption, which CPM is not sensitive to, but plays a significant role in PDS. We believe that the ESR data also suffered from a similar problem, as all the films displayed approximately the same spin density, $10^{17}$ cm$^{-3}$. This will be remedied by growing thicker films such that the surface plays a reduced role in these measurements. However, the deposition system has had several parts out for repair over the past several months, which has limited our ability to grow new films.

**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 “seeds” for crystal grain growth. The previous quarter’s report included studies carried out on the new structure of seeded films consisting of single layers of relatively larger (25-35nm) crystallites embedded between two amorphous film layers in a sandwich-style construction. Several films of varying initial seed densities were annealed simultaneously with unseeded films and their crystallization rates were compared via...
Raman spectroscopy. After achieving full crystallization, electrical conductivity measurements were taken on each film to assess transport performance as well as to draw inferences on the relative grain sizes between samples. As expected, the results of the crystallization study showed that films with higher initial seed densities exhibited an earlier onset of crystallization, and the results of the conductivity study showed films with lower initial seed densities (and thus hypothetically larger final grain sizes) to have greater electrical conductivities. These two sets of data give strong support to the idea that enhancements in both crystallization time and electrical performance can be achieved over unseeded amorphous films with the current seed film construction.

Since, as discussed in quarters 3 and 4, this new film structure has been observed to exhibit crystallization behavior not discussed in literature to date, in quarter 6, studies were conducted on both microscopic and macroscopic fronts. Microscopic studies focused on analyzing the effect of seed inclusions on the surrounding amorphous film before annealing, while macroscopic studies focused primarily on further enhancing the electrical conductivity of the fully annealed films studied in quarter 5.

The main component of fully crystallized films which acts to limit their electrical performance is the existence of boundaries between adjacent crystal grains. These highly disordered regions consist largely of strained as well as broken or “dangling” bonds. Strained or stretched bonds may pose a hindrance to current flow by introducing geometric obstacles to charge flow, however dangling bonds pose a more substantial hindrance since they typically exhibit a charge capable diverting passing current. As briefly discussed in quarter 5, if introduced into the films after crystallization, hydrogen atoms can readily diffuse along grain boundaries and potentially serve to neutralize or “passivate” these grain boundary charges and thus enhance current flow [3, 4]. In order to achieve this, the fully annealed seeded samples were placed back into the deposition chamber and exposed to a hydrogen plasma.

Since the successful diffusion of hydrogen into the film grain boundaries is extremely sensitive to plasma power, chamber pressure, substrate temperature, and exposure time, several different recipes were tested on different samples until noticeable enhancements in conductivity were achieved. The recipe yielding the most significant enhancements was then implemented on the samples used in the electrical conductivity studies of quarter 5. Figure 3 below depicts a plot of each samples’ electrical conductivity before and after hydrogen treatment, in which a several order of magnitude increase in conductivity is observed for each sample after hydrogen treatment.
In order to confirm that the treatment process was successfully introducing hydrogen into the films, forward-recoil scattering (FReS) measurements were performed on all samples before and after treatment to quantify the change in atomic percentage of hydrogen within each film following treatment. The data which results from FReS measurements typically consists of a peak whose height can be correlated with the amount of hydrogen present within the film. The FReS results from one sample is shown in figure 4 below, in which the hydrogen signature peak is seen to increase dramatically after hydrogen treatment. The FReS data from each of the other treated samples showed similar increases, with all samples increasing in percentage composition of hydrogen by almost 6%.
Figure 4: Forward-recoil scattering of nanocrystal-seeded amorphous film before and after hydrogen plasma treatment. The hydrogen plasma increases hydrogen content in the films, serving to passivate dangling bond states.

Transmission electron microscopy (TEM) was utilized to study the nanoscale environment involving the nanocrystal seeds in the amorphous crystalline matrix. The kinetic processes dictating the crystal growth at elevated temperatures must be understood to optimize the crystal growth process. TEM of as-deposited specimens prepared for cross-sectional analysis revealed what appears to be a parabolic strain or defect field surrounding the incorporated nanocrystal seeds, which extends to the film surface. The effect of this field at high temperatures may be to promote the reorganization of the amorphous film, resulting in crystallization. Further work is ongoing to prepare sufficiently thin cross-sectional specimens of films for variable anneal times to study the evolution of this region.
Figure 5: Cross-sectional transmission electron microscope images of two individual nanocrystal seeds embedded in an a-Si:H film (a) as-deposited and (b) after 20 minutes of annealing at 650 °C.

In conclusion, the results obtained in quarter 6 have shown success in developing a hydrogen treatment process for enhancing the electrical performance of films re-crystallized from the second-generation seed structure, as well as success in uncovering new details regarding the relatively new mechanism of crystallization they exhibit. Studies on secondary trends within quarter 5 data regarding conductivity variation across the film and seed-competition-based growth rates are near completion. In order to further enhance the crystallization rate, studies are also underway to observe the effect of seed shape and chamber conditions on crystallization kinetics. In parallel to these studies aimed at macroscopic enhancement of film performance, efforts to develop an atomic-scale understanding of the crystallization mechanism is ongoing.

**Project Presentations:** Results of the recent studies were presented at the Materials Research Society spring 2010 symposium.

**Additional Milestones:** Work is in progress towards milestone 7.

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

**Milestone 6:**

To be completed 18 months after the Contract Start Date

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

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

**Deliverable 6:**

Provide 1 x 2 cm² film sample. Submission of Milestone Report detailing completion of Milestone 6 requirements to RDF representative.
References


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