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

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MILESTONE REPORT

Executive Summary:

Under this grant, we pursue two different routes that may help increase the efficiency and lower the cost of thin film silicon solar cells. Our first approach (Track 1) 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 (Track 2), 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.

During the current project period, efforts under track 1 have focused on understanding the role of embedded nanocrystals on the electronic transport in amorphous silicon. We studied the thermopower of seeded films and conclude that hopping conduction is the main conduction mechanism in our films.

In track 2, we developed a model for the formation and propagation of voids in nanocrystal seeded films. The voids lead to enhanced crystallization, providing an interesting pathway to fast formation of nanocrystalline silicon films. We conclude that surface diffusion along the inner surface of the voids from the amorphous to the crystalline phase is the likely mechanism for the shape of the observed voids.

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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 embedded silicon nanocrystallites on the optical and electronic properties of hydrogenated amorphous silicon (a/nc-Si:H). This quarter we have investigated the Seebeck coefficient, that is the thermoelectric power or thermopower of doped a/nc-Si:H thin films measured from room temperature to 450K. So far, we have completed measurements on films with crystalline fractions XC of 0, 29 and 36%, as determined by Raman spectroscopy. As solar cells require both an n- and p-type layer in order to form the junction that separates the charge carriers, studying the transport in doped a/nc-Si:H films is also an important step on the way to producing a/nc-Si:H photovoltaic devices. 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 the second plasma chamber.

Thermopower measurements on undoped hydrogenated amorphous silicon (a-Si:H) and undoped mixed-phase (nc/a-Si:H) samples, as well as details of the thermopower measurement technique, were reported in the Q7 summary. Briefly, for thermopower measurements, a temperature gradient \((T_1 - T_2 = \Delta T)\) is maintained across a thin film sample on a glass slide, while the resulting voltage \((\Delta V)\) is measured. This is done for several temperature differences at the same average temperature \((\frac{T_1 + T_2}{2})\). A linear fit is computed for a plot of \(\Delta V\) vs \(\Delta T\); the slope is the thermopower.

Measurements of the thermopower can reveal changes in electronic transport mechanisms that are not obviously deduced from simple conductivity experiments. Over a limited temperature range, hopping conduction can be mistaken for activated conduction, particularly for doped films where the activation energy is already quite small and is comparable to the energy scales seen in hopping conduction. Both would appear as a straight line on an Arrhenius plot over a limited temperature range. However, the thermopower for hopping conduction is quite different from that of activated conduction. Activated conduction leads to a thermopower that is linear on a plot of thermopower against inverse temperature (written as \(1/k_B T\), where \(k_B\) is Boltzmann’s constant and \(T\) is the temperature in Kelvins). The slope of the line should be negative for conduction by electrons as is expected in n-type doped a-Si:H. In contrast, hopping conduction leads to a thermopower that has a much shallower slope than for activated conduction and what little slope remains may be either positive or negative, depending on the curvature of the density of states near the Fermi level. The absolute value of the thermopower for hopping conduction also tends to be much smaller than what one would measure for activated conduction.

Looking at the data in figure 1, we see immediately that the mixed-phase films (purple and red circles, 29% and 36% respectively) are much flatter than their purely amorphous counterpart (orange dots, 0%). The absolute values of the thermopower data are also smaller and the slope of the line is slightly positive, the opposite of what one would expect for activated conduction by electrons. In figure 2, we compare the thermopower of our mixed-phase films to an unhydrogenated amorphous silicon (a-Si) sample, a sample where hopping is known to occur. Notice the similarity in the shape of the curves for \(1/k_B T\) greater than about 30, corresponding to a
temperature of 390K. Above this temperature (corresponding to the left side of the graph), activated conduction begins to dominate in a-Si films. This confirms results from the Q9 report, describing the identification of hopping conduction via detailed conductivity measurements over an extended temperature range.

Figure 1: Thermopower measurements for the two doped mixed-phase films, along with a doped, purely amorphous film. Notice the very different functional form of the mixed-phase films as compared to the purely amorphous film.

Figure 2: Thermopower measurements for the two doped mixed-phase films, along with an unhydrogenated silicon film (a-Si). The change in shape for the a-Si film above 390K (1/k_BT ~ 30) corresponds to a known change in the conductivity of a-Si from hopping to activated conduction.
Track 2: Large-grain re-crystallized Si

The second track of the project aims at developing a method for reproducible control over grain structure in polycrystalline films created from solid-phase-crystallization of amorphous silicon.

In quarter 10, efforts were focused primarily on applying a macroscopic growth model to films with different seed density, as well as studying the effect of furnace annealing on stresses within films. The grain growth rate and the intrinsic tensile stress were shown to decrease as the seed density increases. Furthermore, the evolution of intrinsic stress with crystal growth indicated a trend with two stages: an initial increase of tensile stress corresponding to the volume contraction during crystallization, and a following stress decrease possibly caused by the movement of intra-grain defects.

In this quarter report, a microscopic continuous model is proposed to explain the void propagation observed during heated-stage TEM studies of seed growth. This was carried out by describing each void as being defined by a curved amorphous surface. At equilibrium, a void bordered entirely by amorphous material should form a spherical geometry. However in the situation observed in TEM, in which voids appear at seed crystal surfaces, the system is in non-equilibrium due to the difference of chemical energy between the amorphous and crystalline phases that exist at the seed surface. The driving force for the propagation of the voids is thus believed to be inner surface diffusion of silicon atoms from the amorphous side to the crystalline side. This provides a much faster crystallization mechanism than the normal solid phase epitaxy (SPE) that drives the more traditional growth observed as an expansion of the seed volume. The surface diffusion along the inner surface of the seeds causes the amorphous side to deplete while the crystalline surface to grow. At steady state, the depleting rate at the amorphous side must balance the growth rate at the crystalline side of the voids, which infers that the propagation speed at the amorphous side must be the same as at the crystalline side along the propagation direction, and thus that the volume of the void is conserved.

1. Model Description

The system of nano-voids at steady state is modeled using a polar system whose origin point is set at point O (figure 3). The entire void region is above x axis, which means that the x axis serves as the boundary of the crystalline tail of the void.

Figure 3: Sketch of void at steady state during propagation.
Assuming that the surface diffusion is only governed by the local curvature as well as temperature, the increase of the chemical potential $\mu$ per atom when traveled from the center point of the front side A to a point with curvature $C$ is calculated as [1]:

$$\mu = \gamma \Omega C$$  \hspace{1cm} (1)

Where $\gamma$ is the surface free energy of the amorphous Si ($1.9 \times 10^{-4}$ J/cm$^2$) and $\Omega$ is the averaged atomic volume of amorphous Si ($1.07 \times 10^{22}$ cm$^3$).

A gradient of the chemical potential $\mu$ along the inner surface of the void creates a flux of surface atoms, which is calculated by the Nerst-Einstein relationship:

$$J_s = -\frac{D_s N_s \partial \mu}{kT \partial s}$$  \hspace{1cm} (2)

Where $s$ is the arc length along the void surface and $D_s$ and $N_s$ ($4.4 \times 10^{14}$ atom/cm$^2$ for amorphous silicon) are the surface diffusion coefficient and surface atomic density.

The diffusion coefficient $D_s$ has an Arrhenius form of:

$$D_s = D_0 e^{-E_A/kT}$$  \hspace{1cm} (3)

For amorphous silicon, the coefficients $D_0$ and $E_A$ are chosen as $4 \times 10^{1}$ cm$^2$/s and 2.38eV [2].

If assuming that there is no mass transfer in $\phi$-direction, the mass balance equation can be written as:

$$\frac{\partial h}{\partial t} = -\Omega \frac{\partial J_s}{\partial s}$$  \hspace{1cm} (4)

Where $h$ measures the depth along the direction normal to the curve. By defining the coefficient $A = \frac{D_s N_s \gamma \Omega^2}{kT}$, which is only the function of physical properties of amorphous Si and the temperature at which the void is annealed, the above equation can be written as:

$$A \frac{\partial^2 c}{\partial s^2} = \frac{\partial h}{\partial t} = V_{\text{void}} \cos \theta_s$$  \hspace{1cm} (5)

Where $V_{\text{void}}$ is the void propagation speed. The ordinary differential equation (ODE) above could be numerically solved using finite difference method (FDM) along the curve, starting from the center point of the front side of the void (point A in Figure 1), where the boundary condition is given as $C=0$ at $\theta=0$ (flat surface). At the boundary between amorphous and crystalline phases at $\theta=\pi/2$ (point B in Figure 1), all the silicon atomic flux is captured by the grains at the crystalline tail to allow SPE to occur. The growth speed of the crystalline tail ($V_{\text{tail}}$) is then calculated from the atomic flux at the interface ($J_{s,\text{inter}}$) between crystalline and amorphous region, as:

$$V_{\text{tail}} = J_{s,\text{inter}} \frac{\Omega_c}{S} \frac{L}{S}$$  \hspace{1cm} (6)

Where $\Omega_c$ is the averaged atomic volume of crystalline Si ($1.05 \times 10^{22}$ cm$^3$) and L, S are the perimeter and area of the void cross-section at the boundary of $\theta=\pi/2$, respectively.

At fixed annealing temperature and void volume, the void propagation velocity should be the only function of the void shape. An iteration method is used to solve the void system. The inputs of the simulation are a fixed value of void volume and temperature. The final outputs are $V_{\text{void}}$ and the void shape.

2. Results

This section shows the results obtained from the continuous model, with varying annealing temperature $T$ and total void volume, which are compared with experimental observation.

Firstly, the effects of void volume on the void properties are studied. At fixed annealing temperature, the voids have the same shape but different size (figure 4). Figure 5 shows the atomic flux at the inner surface of the void from $\theta=0$ to $\theta=\pi/2$, at varying void volume. The negative sign means that the atomic flux is leaving from the surface. It is clear that decreasing void
volume corresponds to increasing atomic surface flux, which is the reason that smaller voids have higher propagation speed (figure 6).

![Figure 4: Void shapes with different total void volume, where only half of the amorphous side is shown.](image1)

![Figure 5: Atomic flux at the inner surface of the void from $\theta=0$ to $\theta=\pi/2$ at 650°C, with varying volume.](image2)
At fixed total void volume, the voids however keep the same size as temperature varies (Figure 6). Figure 7 shows the atomic flux at the inner surface of the void with fixed volume of 8000 nm$^3$ but different temperature. Increasing temperature causes an increase in flux is due to the heavy temperature dependence of surface diffusivity.

Figure 7: Void shapes with different annealing temperature. All the curves overlap together.
For the coming quarter, we plan to compare results of this model to our experimental observations.

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References:


Appendix A

Novel Crystallization of Silicon for thin film Solar Cells

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A new method for reducing crystallization time of hydrogenated amorphous silicon thin films and more successfully controlling grain structure has been studied through seeding of the bulk matrix with silicon nanocrystallites. Films were deposited by a plasma enhanced chemical vapor deposition (PECVD) technique in which nanocrystallites and amorphous film were synthesized in separate RF-powered plasmas. TEM microscopy was used to determine average crystallite size to be in the range of 20-50 nm, with highly faceted surfaces. Several films with a specific crystallite population density (seeded films) were produced, along with films containing no crystallites (unseeded films). The crystallization kinetics of seeded and unseeded films were studied and compared via Raman spectroscopy throughout a staged annealing process for three separate annealing temperatures. Seeded films displayed a characteristic crystallization time less than the incubation time of unseeded control films, as well as a lower activation energy for grain growth rate.

Keywords: solar cells, thin film, poly-silicon, nanocrystal, annealing

1. 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 silicon with the cost advantage of amorphous silicon thin films is highly attractive. To achieve this, one must produce poly-Si with maximum possible crystal grain sizes; for solar cells, ideally as large as the film thickness itself. Poly-Si directly deposited from the gas-phase through PECVD methods has been extensively studied; however these films typically consist of highly defected grain clusters with sizes rarely exceeding 50nm in diameter [1-3].

Solid phase crystallization (SPC), in which hydrogenated amorphous silicon (a-Si:H) is thermally treated until a crystalline phase transition occurs, has been studied recently as a more viable route to produce large-grain poly-Si. According to classical nucleation theory [1,2], the SPC mechanism proceeds following an incubation period during which no phase transition occurs, after which a steady-state nucleation and growth of native crystal grains can be observed. Typical a-Si:H annealing processes are relatively energy intensive; being carried out between temperatures of 550 -1000 °C, for time intervals typically extending beyond 10 hours [4-7]. The resulting structure can generically be called poly-Si, and is comprised of multiple crystals of various orientations. The interfaces or grain boundaries shared by adjacent crystal grains typically consist of amorphous or defected material. These grain boundary defects are the primary cause for reduced poly-Si device performance, due to their current-carrier trapping capabilities and a-Si:H-like degradation in extended light exposure [8,9]. Subsequently, efforts in poly-Si film improvement have been focused on both reducing the required annealing time and reducing the quantity of grain boundaries (i.e. increasing average grain size). In amorphous silicon SPC, grain size is dictated by the rate at which individual crystal grains appear following the incubation period; known as the nucleation rate. However, since nucleation rate is sensitive to a variety of factors, adjusting it for reproducible grain size control can be difficult.

The present work conveys a novel approach to poly-Si production in which both a reduction of annealing time, and control of grain density can be reproducibly accomplished by embedding a limited
density of silicon nanocrystals into the amorphous film matrix. This method requires limited additional equipment or pre-annealing processing procedures, and the entire film synthesis occurs within one vacuum using a dual plasma deposition technique.

2. Experimental Procedure

Hydrogenated amorphous silicon (a-Si:H) films containing defined densities of nanocrystal seeds were grown using a plasma co-deposition system in which a-Si:H and nanocrystal components were produced in separate plasmas. The a-Si:H component of each film was deposited from 5% silane diluted in helium, using a capacitively-coupled RF discharge operating at a frequency of 13.56 MHz, a power of 5W, and a pressure of 100 mTorr. Films were grown in a chamber evacuated to a base pressure of 2·10⁻⁶ Torr, with the film growth discharge confined to a plasma box configuration of dimensions shown in figure 1.

Nanocrystals were synthesized in a separate, capacitively-coupled, quartz tube flow-through reactor operating at the same frequency, but at higher pressure (1.5 Torr) and power (140 W) using a gas flow consisting of 5% silane:helium mixed with argon. The nanocrystal reactor tube was connected to the main film growth chamber through a 1 mm diameter orifice. Aside from allowing plasma conditions in the reactor to operate at higher pressures more conducive for large particle growth, the orifice also served as the ground electrode for the reactor discharge, as well as the passageway for nanocrystals from the reactor to the substrate in the main chamber. The full schematic of the dual-plasma system is shown in figure 1, and a more in-depth description of the particle synthesis process used can be found in Bapat et al. [10].

Each film was deposited in a layer-by-layer approach in which a layer of nanocrystals were deposited between two, 100 nm thick layers of a-Si:H film on Corning 1737 glass slides at a substrate temperature of 250 °C. As is shown in figure 2, transmission electron microscopy (TEM) studies confirmed the particles to be single crystals, exhibiting predominantly cubic shapes, and having sizes ranging between 20-50 nm across. The nature of the cubic particle shape is predicted by the simulations of Hawa et al. to be the lowest energy configuration for a crystallite with a hydrogen passivated surface [11]. For studying the crystallization kinetics of these layer-by-layer films, three pairs of samples (seeded and unseeded) were deposited, with seeded films having crystallite population densities of ~4 particles/µm². Each pair was annealed in a quartz furnace under nitrogen flow at a different temperature: 600 °C, 625 °C, and 650 °C.

Films were annealed in regular intervals, with the crystal volume fraction of each film monitored in between stages using confocal Raman microscopy with the peak fitting technique of Smit et al. [12].

A preliminary growth model was used to fit the acquired seeded data and provide estimates for seeded growth rates. Growth rates were calculated for each temperature and compared to unseeded values calculated using traditional, native nucleation models. Growth rate activation energies for each film structure were estimated and subsequently compared to draw inferences on the microscopic kinetics of each structures grain growth.
3. Results

Figure 3 shows the evolution of crystal volume fraction in each film with anneal time for the three sample pairs. As shown in figure 4, each seeded sample exhibits an almost immediate onset of crystallization, while no crystallization is observed for the unseeded sample before the completion of an incubation period of ~300 min. At the conclusion of the unseeded film incubation period, crystallization for the seeded samples is mainly complete, which strongly suggests that crystallization in the seeded films is controlled by the embedded nanocrystal seeds rather than by native nucleation.

In unseeded amorphous silicon recrystallization, the progression of crystal volume fraction \( X_c \) with anneal time is typically modeled using the Avrami–Johnson–Mehl (AJM) description frequently outlined in literature [13]. Using the AJM model along with the above nucleation rate, crystal growth rates for unseeded samples were determined.

Since the grain structure of the seeded amorphous films appears to develop without the influence of any significant native nucleation events and thus without a nucleation rate, or a significant incubation period, the AJM model cannot be used to describe the annealing kinetics of the seeded film series. Instead, the model first proposed by Anderson [14] approximates the evolution of the crystal fraction of a seeded film as a constant rate, isotropic growth of an initial crystal volume, according to Eqn. 1:

\[
X_c(t) = X_{c,0} \cdot \left[1 + \frac{2 \cdot v_g}{L_0} \cdot t\right]^3 \tag{1}
\]

Where \( L_0 \) is the average edge length of a cubic seed crystal, \( v_g \) is the crystal growth speed, and the initial crystal fraction before annealing \( X_{c,0} \) is taken as the initial number of seeds times the average seed volume. Due to the inevitable competition for space that will occur between overlapping growth volumes, it is important to note that this model is applicable only for early growth stages, typically diverging from the empirical curves above crystal fractions of 0.50.

Subsequently, as is shown in figure 4 below, growth rates were determined for seeded films using data within this regime. The resulting growth rates for each film structure were plotted for each temperature in figure 5, and found to follow Arrhenius-like temperature behavior in accord with classic descriptions of thermally activated phase transition rates for amorphous silicon films. [4,5]

It is well known that the steady-state growth rate for expanding crystallite volumes in amorphous material is thermally activated according to Eqn. 2. [4,5]

\[
v_g \propto \exp\left[-\left(E_d - \Delta G' / 2\right)/kT\right] \tag{2}
\]
in which $E_d$ is described as the growth inhibiting energy barrier required to diffuse silicon atoms to the a-Si:H/c-Si growth interface, and $\Delta G'$ is the growth promoting free energy drop between amorphous and crystalline phases. From the results shown in figure 5, it is clear that the barrier to crystallite growth is much lower for seeded films than for unseeded films.

![Figure 4](image.png)

**Figure 4.** Growth model fit of seeded samples containing ~ 4 seed crystals per square micron for three separate anneal temperatures. Experimental results in symbols, with growth model fit lines overlaid.

Since the crystalline phase serves as a constant energy reference, this implies that the inclusion of seed crystals enhances self-diffusion of silicon atoms in the surrounding a-Si:H film during grain growth (lowering $E_d$), and/or increases the disorder of the a-Si:H film in the as-grown state (increasing $\Delta G'$).

### 4. Conclusion

The enhanced crystallization of hydrogenated amorphous silicon has been achieved by embedding silicon seed nanocrystals into a-Si:H films. Crystallization kinetics suggest that the final grain structure of recrystallized films is controlled by varying the initial seed density. Moreover, aside from reducing the incubation period before crystallization onset, Arrhenius plots of growth rate show seeded crystallization to exhibit reduced energy barriers to growth following onset.

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### References