In-situ Characterization of the Amorphous to Microcrystalline Transition in Hot-Wire CVD Growth of Si:H Using Real Time Spectroscopic Ellipsometry

Preprint


To be presented at the 29th IEEE PV Specialists Conference
New Orleans, Louisiana
May 20-24, 2002
NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste
IN-SITU CHARACTERIZATION OF THE AMORPHOUS TO MICROCRYSTALLINE TRANSITION IN HOT WIRE CVD GROWTH OF Si:H USING REAL TIME SPECTROSCOPIC ELLIPSOmetry

National Renewable Energy Laboratory, Golden, CO 80401

ABSTRACT

We have used in-situ real-time spectroscopic ellipsometry (RTSE) to characterize the morphology and crystallinity of hot-wire CVD (HWCVD) Si:H films as a function of hydrogen dilution $R=\frac{[H]}{[H+SiH_4]}$, substrate temperature $T_s$, and film thickness $d_f$. Transitions from one mode of film growth to another are correlated with changes in the magnitude of the surface roughness during growth. The degree of crystallinity of the film can be determined from the form of the dielectric function. We have studied the growth parameter space for $R$ from 0 to 14, $T_s$ of 250°C and 500°C, and $d_f$ from 0 to 1 um. We have mapped out the crystallinity vs. $R$, $T_s$, and $d_f$ based on our analysis of the RTSE data. These results have been corroborated using Raman scattering and atomic force microscopy to characterize the crystallinity and surface morphology of the films.

INTRODUCTION

The properties of amorphous and microcrystalline hydrogenated silicon (a-Si:H and μc-Si:H) have attracted a great deal of research interest in recent years because of their application in thin-film solar cells and thin film transistors [1]. Of particular interest are the mechanisms occurring during film growth that are responsible for the transition from amorphous to microcrystalline growth. Improved understanding and enhanced control of these mechanisms will lead to higher-performance silicon thin-film devices.

Many studies have applied ex-situ measurement techniques to structural characterization of Si:H films, yet ex-situ approaches are limited in the information they can provide because μc-Si:H nucleation usually occurs at layer thicknesses below 500Å. In addition, the properties of μc-Si:H vary with film thickness. In-situ, real time spectroscopic ellipsometry (RTSE) provides an ideal characterization tool to study the amorphous to microcrystalline transition because it is able to monitor the evolution of the film thickness, surface roughness, and optical properties in real time during the film growth.

The utility of RTSE to study growth processes of thin-film a-Si:H and μc-Si:H has been demonstrated by Collins and co-workers in numerous studies [2]. Their studies have focused on plasma-enhanced CVD (PECVD) deposition of Si:H. They have established that the surface roughness of the growing film is a sensitive indicator of changes in the mode of film growth. An abrupt increase in surface roughness indicates a transition from stable a-Si:H growth to unstable a-Si:H growth, or from a-Si:H growth to a mixture of a-Si:H and μc-Si:H, or from mixed to purely μc-Si:H growth [3]. These transition points in the properties of the growing film have been expressed on a phase diagram by plotting the bulk thickness of the film where the transition occurs as a function of process variables such as dilution ratio $R$. These points can be linked to delineate regions of different growth modes as a function of deposition parameters.

EXPERIMENTAL DETAILS

All depositions were performed using a single 0.5 mm diameter W filament operated at a 60-Hz ac filament current of 16 amps (~2200°C). The filament is wrapped in a 4 mm diameter helix and mounted 4 cm from the substrates. The silane flow was fixed to 6 sccm with a silane partial pressure of ~3 mTorr. The two main deposition parameters varied in this study were the starting $T_s$, at either 250 or 500°C, and $R$ from 0 to 14. All films were grown to a thickness of approximately 1 um. These experiments were carried out in the same chamber described in detail in [4] and under similar conditions to those in [5].

RTSE measurements were performed using a J.A. Woollam, Inc. M2000 visible and near IR rotating compensator ellipsometer and Woollam software for instrument control and data acquisition and analysis. The ellipsometer utilizes array detectors to collect spectra from 250 to 1700 nm, with an acquisition time as short as 100 ms. For this study spectra were collected from 255 to 1240 nm with an integration time of 200 to 500 ms during the nucleation phase of growth and 1 to 5 seconds during the later stages of growth, dependent upon film deposition rates. The angle of incidence was fixed at 70°.

The Raman scattering measurements were performed in a 180-degree backscattering configuration with a doubled Nd:YAG operating at 532 nm and a single grating Spex 270M spectrometer with a LN2 cooled CCD array detector. The incident laser power was 30 mW and a holographic notch filter was used to suppress the laser line. Penetration depth was approximately 96 nm for μc-Si:H and 64 nm for a-Si:H.

AFM measurements were performed using a Digital Instruments Dimension 3100 AFM, operating in tapping mode, using Si tips. RMS roughness values were calculated using the z-position of every pixel in the image.
Analysis of RTSE Data

RTSE data were analyzed in two stages. The early-time nucleation phase was modeled using a two-layer model, consisting of a bulk film with thickness $d_b$ and a surface roughness layer with thickness $d_s$, both on top of a crystalline silicon substrate with a 15 Å thick native oxide layer. Most of the growth conditions required a third layer to represent a secondary phase of Si:H which started growing shortly after the nucleation phase had coalesced. The surface roughness layer was modeled using a Bruggeman effective medium approximation (EMA) of 50% void and 50% of the underlying material. The dielectric functions of the nucleation and post-nucleation layers were determined using an iterative optimization method to minimize the overall mean squared error within a selected region of growth time. Amorphous Si:H was modeled using a Cody-Lorentz oscillator formalism, while microcrystalline Si:H was modeled using a two-oscillator Tauc-Lorentz formalism [6].

In most of the films studied the optical properties of the film evolved during deposition. Multi-layer models do not work well to analyze the data as the film grows because of grading in the optical properties. In order to analyze the data after the initial nucleation phase, we have utilized a virtual interface (VI) model. The VI model cannot be applied during nucleation because it assumes a slowly varying surface roughness. The VI model fits the data using a 3-layer model consisting of 1) a surface roughness layer on top of 2) a growing film of thickness $5r_{to}$, where $r$ is the growth rate and $t_o$ is the data acquisition interval, and 3) a pseudo-substrate with a pseudo-dielectric function $<\varepsilon>$ calculated by directly inverting the psi and delta data at time $t_{to}$. The growing film of thickness $5r_{to}$ is modeled as a 2-component Bruggeman EMA composed of a mixture of materials determined from the post-nucleation layer and the final material deposited at the end of the deposition. The growth rate $r$ is held constant while the EMA percentage and surface roughness thickness are fit using regression analysis. In general, for each film three distinct dielectric functions are determined corresponding to the nucleation layer, the mid-layer, and the final layer. In the more homogeneous films some or all of these layers may be the same.

EVOLUTION OF SURFACE ROUGHNESS WITH FILM GROWTH

As discussed above, changes in the surface roughness are indications of changes in the growth mode of the film. A universal pattern for all films in this study is the initial nucleation and coalescence sequence. Figure 1 shows the evolution of $d_s$ with time. There is a rapid initial increase in $d_s$ as film growth begins at isolated nucleation sites, followed by a rapid decrease in $d_s$ as the nucleation sites coalesce to form a continuous film. The amplitude of the initial peak in $d_s$ is inversely correlated with the density of nucleation sites. Differences in the early time evolution of $d_s$ are correlated with differences in the nucleation process of the film.

![Figure 1](image1.png)  
Figure 1. Evolution of $d_s$ and $d_b$ during nucleation and coalescence for the R=3, $T_s=500^\circ$C sample. The dashed line indicates the coalescence of nucleation centers.

Figure 2 presents the evolution of $d_s$ with $d_b$ for the films grown at $T_s=500^\circ$C. The behavior of $d_s$ during the first few hundred angstroms, corresponding to the nucleation and initial stages of growth, is essentially the same for all films except for R=14. We conclude that the nucleation density is relatively constant for all films with $Rs\leq10$ at $T_s=500^\circ$C. Analysis of the dielectric functions of the nucleation layers in these films indicates that all films with $Rs\leq10$ nucleate as a-Si:H, while R=14 nucleates as $\mu$c-Si:H. This is consistent with the relatively large values of $d_s$ that the R=14 sample exhibits throughout growth. The evolution of $d_s$ for $d_b>300$ Å indicates differences in films with different levels of dilution. The R=0 and R=3 films display almost identical behavior. Analysis of dielectric functions, as well as Raman scattering, show that both films are completely amorphous. Raman and RTSE data show that the R=4 and R=6 films are mixed-phase a-Si:H and $\mu$c-Si:H. The exceptionally large final values of $d_s$ measured in these films have been corroborated by AFM measurements. AFM also shows these films have a distinct morphology, similar to grains of rice. The R=10 film is shown by Raman and RTSE to be primarily $\mu$c-Si:H, although it nucleates as a-Si:H. The R=14 film is $\mu$c-Si:H throughout its growth.

![Figure 2](image2.png)  
Figure 2. Evolution of $d_s$ with $d_b$ for $T_s=500^\circ$C.
The broad peak at ~460 cm⁻¹ is correlated with amorphous, while the sharp peak at ~530 cm⁻¹ is correlated with microcrystalline silicon [7]. Penetration depths calculated at the 532 nm laser wavelength are 96 nm for microcrystalline and 64 nm for amorphous silicon. Because the degree of crystallinity varies with depth in the film, it is difficult to calculate an accurate ratio of amorphous to microcrystalline material based on the Raman scattering peak heights. The Raman data does provide a qualitative measure of the relative degree of crystallinity within the top 0.1 µm of these 1.0 µm thick samples. In addition, the Raman intensity scales with the degree of crystallinity, with small-grained µc-Si:H having a lower Raman intensity than large-grained µc-Si:H, and crystalline Si having a much higher intensity than any of the µc-Si:H samples measured in this study. We attribute this to final-state lifetime effects on the Raman scattering cross-section. Thus, the amplitude of the 530 cm⁻¹ peak in the Raman spectrum is an indication of the degree of crystallinity of the µc-Si:H films.

It is clear in figure 4 that the R=0 and R=3 films are purely a-Si:H, whereas the R=4 film has a slight degree of crystallinity. The R=6, 10, and 14 films are all predominantly µc-Si:H, with varying peak heights. This likely correlates with grain size in these µc-Si:H films. The trends for the Ts=250°C films are very similar to those noted for the Ts=500°C films. The R=4 film at Ts=250°C has somewhat less crystallinity than its Ts=500°C counterpart. Also, the R=6, 10, and 14 films at Ts=250°C have a larger spacing in Raman intensity than their Ts=500°C counterparts, indicating larger difference in grain sizes for the µc-Si:H films grown at Ts=250°C.

Figure 5 is a representation of the degree of crystallinity versus depth based on evaluation of the dielectric functions derived from the RTSE data. As Si:H evolves from a-Si:H to µc-Si:H, both the amplitude and the peak energy of ε₁ and ε₂ increase. The amplitudes of ε₁ and ε₂ are also influenced by the presence of voids within the material. Because of this ambiguity in tracking crystallinity using the amplitude of the dielectric function, we have focused on the peak energies for ε₁ and ε₂. We have found that the peak in ε₁ evolves from 2.5 to 3.15 eV and the peak in ε₂ evolves from 3.6 to 4.15 eV as the film evolves from a-Si:H to µc-Si:H. Hence, in figure 5 the gray scale ranges from a sum of 2.5+3.6=6.1 eV to 3.15+4.15=7.3 eV, with white = 6.1 eV and black = 7.3 eV. White corresponds to completely amorphous and black...
Figure 5. Grey scale plots of the evolution of the sum of $\varepsilon_1$ and $\varepsilon_2$ peak energies with thickness. Scale is from 6.1 eV (white, a-Si:H) to 7.3eV (black, $\mu$-c-Si:H). Numbers across the top are the ratio of the 530 cm$^{-1}$ Raman peak to highest measured in this study (≠ crystalline fraction).

As described in the section on analysis, most films required three distinct dielectric functions for analysis of the in-situ RTSE data. This consisted of one function for the nucleation phase, one for the intermediate phase, and one for the end phase. Nucleation was described as a single or double layer, with the nucleation layer thickness allowed to vary as needed to fit the RTSE data. The remainder of the film was modeled as an EMA mixture of the intermediate and final dielectric functions. Thus the EMA % value provides a continuous scale between the intermediate and final endpoints. While this is admittedly a phenomenological, semi-quantitative approach to describing the crystallinity versus thickness, we believe that the results accurately describe how the relative degree of crystallinity evolves with substrate temperature, hydrogen dilution, and film thickness.

Figure 5(a) presents the evolution of crystallinity with thickness and hydrogen dilution for $T_s=250^\circ$C. The numbers across the top give the ratio of the amplitude of the 530 cm$^{-1}$ peak in the Raman spectrum to the highest intensity 530 cm$^{-1}$ peak measured in this study. This number is roughly interpreted as the relative degree of crystallinity within the uppermost 1000Å of the film.

The homogeneous light gray shading for the R=0 and R=3 films in Figure 5(a) show that the R=0 and R=3 films are completely amorphous. This is confirmed by the Raman results. The R=4 film appears to be completely amorphous in the RTSE data, yet Raman indicates a small component of microcrystalline material at the surface. The R=6 film nucleates as a-Si:H, and grows primarily as $\mu$-c-Si:H. The R=10 film nucleates as a material that appears to be midway between a-SiH and $\mu$-c-Si:H, while the bulk of its growth is microcrystalline. Finally, the R=14 film is $\mu$-c-Si:H at nucleation and throughout its growth.

Trends are very similar for the $T_s=500^\circ$C films shown in figure 5(b). The R=0 and R=3 films are completely amorphous. Although the R=4 film nucleates as a-Si:H, it has a significantly greater $\mu$-c-Si:H component than the $T_s=250^\circ$C R=4 film. This is confirmed by the Raman results. The R=6 and R=10 films both nucleate as a-Si:H, although the R=10 nucleation layer has some microcrystalline character. An anomaly noted with the R=10 film is that it appears to become less crystalline as the film grows. We currently do not have an explanation for this behavior. The R=14 film nucleates and grows as $\mu$-c-Si:H, as did the $T_s=250^\circ$C R=14 film.

**DISCUSSION AND CONCLUSIONS**

RTSE measurements, as corroborated by Raman scattering and AFM, show that the transition from a-Si:H growth to $\mu$-c-Si:H growth in HWCVD deposition of Si:H is relatively abrupt as a function of hydrogen dilution, whereas the transition occurs gradually as a function of film thickness.

**ACKNOWLEDGMENTS**

We acknowledge Rob Collins for many useful discussions and collaborations. This work was performed under DOE contract number DE-AC36-99GO10337.

7. Guozhen Yue, J. D. Lorentzen, Jing Lin, Qi Wang and Daxing Han, APL. 75, 492 (1999).
## In-situ Characterization of the Amorphous to Microcrystalline Transition in Hot-Wire CVD Growth of Si:H Using Real Time Spectroscopic Ellipsometry; Preprint

### Authors

### Performing Organization
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

### Abstract
This conference paper provides a brief look at the current U.S. research and development (R&D) investments in photovoltaics, covering the spectrum from materials and devices through electronics and systems reliability. The program is balanced among fundamental R&D, technology development, and systems performance and reliability, with more than half the funding for university and industry partners. The major activities can be categorized into two general areas: improving current and near-term technologies toward their expected performance levels (the largest portion), and positioning the United States for technical leadership, decision making, and ownership for the host of next-technology options (including some options that have been called third-generation). The investments in these higher risk, longer-term technology generations provide options that could leapfrog into more rapid use because of their promise of potentially high payoff. Solar electricity is part of America’s present and future energy security and independence—as is the R&D that enables it.

### Subject Terms
PV; research and development (R&D); technology development; systems performance and reliability; fundamental materials and device