In-Situ Characterization of Growth and Interfaces in a-Si:H Devices

**Annual Subcontract Report
1 May 1992 – 30 April 1993**

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National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of the U.S. Department of Energy
Operated by Midwest Research Institute
for the U.S. Department of Energy
under contract No. DE-AC02-83CH10093

Prepared under Subcontract No. XG-1-10063-10

February 1994

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Printed in the United States of America

Available from:

National Technical Information Service

U.S. Department of Commerce

5285 Port Royal Road

Springfield, VA 22161

Price: Microfiche A01

Printed Copy A05

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issue of the following publications which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

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SUMMARY

- Individual Goal:** The interfaces of the "top junction" will be investigated for defects using the spectroscopic ellipsometry technique. This will include an evaluation if specific defects can be associated with C, B, Sn (diffusing from the TCO) or Na (diffusing from the glass). It may include an assessment of the function of a graded a-SiC:H buffer layer. As defects are identified and characterized, their influence on the transport properties will be assessed. This should lead to better parameters used as input to models for the electronic materials and device performance.
- Wide Gap Team Goal:** Demonstrate, characterize, and understand improved doped and undoped "wide gap" materials for use in achieving 15% stabilized photovoltaic modules. (Note: "wide gap" materials are defined by this team as those materials with a band gap ≥ 1.9 eV.)

Here, we enumerate the major conclusions of our research in meeting the above goals.

(1) In order to prepare amorphous silicon-carbon alloys having optimum microstructural characteristics, one must use the maximum possible $H_2:(CH_4+SiH_4)$ dilution ratio that can sustained without entering the regime of microcrystallinity. In studying a-SiC:H ($E_g=1.95$ eV) as a function of H-dilution level at fixed reactive gas ratio $CH_4:SiH_4$ (2:3), substrate temperature (250°C), plasma power (130 mW/cm²), and reactive gas partial pressure (0.085 mTorr), we find that a number of features of the microstructural evolution improve consistently with increasing $H_2:(CH_4+SiH_4)$ gas flow ratio up to 25:1. These include a reduction in the nucleation density, an increase in surface smoothening during coalescence, an enhancement of the long term smoothening trends, and a reduction in the ultimate void density in the thick film. At dilution levels above 25:1, some of these trends reverse suggesting microstructural instability associated with etching, as the regime of microcrystallinity is approached.

(2) The conditions under which optimum microstructural characteristics are observed in the a-SiC:H alloys [see (1)] also correspond to the conditions of optimum photoelectronic performance, at least over the range of parameters explored here. For alloys prepared as a function of $H_2:(CH_4+SiH_4)$ gas flow ratio from 0:1 to 20:1 and measured in the annealed state, the Urbach tail steepens, the density of midgap states decreases, and the electron mobility lifetime product increases, while retaining the same optical band

gap. These trends with H-dilution are also apparent in the light-soaked state, but the overall improvements with H-dilution are not as large as those in the annealed state. We have proposed a causal relationship between the optimum microstructural development on the monolayer scale (as observed by real time spectroscopic ellipsometry) and the optimum photoelectronic properties in the ultimate material. We further propose that the observed microstructural trends are associated with increasing film-precursor diffusion length on both substrate and film surfaces with increasing H-dilution. This latter proposal is supported by the results of a number of continuum models of film growth that predict the behavior observed by real time spectroscopic ellipsometry.

(3) Microcrystalline SiC:H films show optical properties that can be understood in terms of a mixture of a-SiC:H and microcrystallites. Although the microcrystallites in the films exhibit overall critical point features in the joint density of states consistent with single crystal Si, the features exhibit significant energy shifts relative to those of Si. Such energy shifts may be due to C in the crystallites or strong quantum size effects, both of which would modify the electronic band structure of the material. In our system uniform microcrystalline films ($\mu\text{c-SiC:H}$) can be prepared on either metal or Si substrates with a $\text{H}_2:(\text{CH}_4+\text{SiH}_4)$ gas flow ratio of 80:1.

(4) Device grade amorphous silicon-carbon alloys ($E_g=1.94$ eV), prepared by Solarex as a baseline material for the Wide Gap Team, exhibit excellent optical absorption characteristics in the annealed state; however, the improvements in the material characteristics tend to be lost in the fully light soaked state. In the annealed state, the material exhibits an Urbach tail as steep as that of high quality a-Si:H (~ 50 meV) and a low sub-gap absorption coefficient [$\alpha(1.2\text{eV})=0.1\text{ cm}^{-1}$]. The corresponding values for typical material prepared at Penn State are $E_0=53$ meV and $\alpha(1.2\text{eV})=0.3\text{ cm}^{-1}$. In the fully light-soaked state, the corresponding values are (56 meV, 7 cm^{-1}) and (57 meV, 10 cm^{-1}) for the baseline material and our material, respectively. A full complement of measurements is being performed on the baseline material by the Wide Gap Team.

(5) Calibration techniques have been developed in order to implement alloy band gap grading in devices under real time control. For ease of implementation, we have developed a functional relationship between the room temperature optical gap and the dielectric function, measured in situ at a fixed photon energy / deposition temperature. The implicit parameter in this relationship is the $\text{CH}_4:\text{SiH}_4$ gas flow ratio which is varied in the experiment to control the grading. The way band gap grading would be automated is to (i) measure the dielectric function in the near-surface (top $10\text{ \AA}$) of the film at one photon energy during film growth, (ii) calculate the corresponding room temperature optical gap using the functional relationship developed in calibration, (iii) compare the gap to a target value established through optimization of solar cell models, and (iv) adjust the $\text{CH}_4:\text{SiH}_4$ gas flow ratio in an attempt to hit the target, based on the resulting error between the observation and target. These four steps can provide the basis of a

feedback-control loop.

(6) **Metal contamination at the a-SiC:H/SnO₂ interface due to reduction of the SnO₂ in the initial stages of alloy growth is influenced by the concentration of gas phase H, by the substrate temperature, and by the bulk layer induction time, i.e., the time it takes for the a-SiC:H nuclei to coalesce and fully cover the SnO₂.** For a substrate temperature of 250°C and a H₂:(CH₄+SiH₄) dilution ratio of 0 (no H-dilution), we find no detectable reduction of the SnO₂ substrate (<0.5 Å mass thickness of metal) during the initial stages of alloy growth. Under optimum conditions of alloy growth (20:1 H-dilution ratio), about 5 Å mass thickness of metal is present at the the interface. The metal content at the interface can be decreased by more than 50% by decreasing the substrate temperature to 170°C. In general, we find that the a-SiC:H/SnO₂ interface structure is not stable as a function of time, and the metal at the interface is either reoxidized into the TCO, or (more likely) diffuses into the a-SiC:H alloy over a period of weeks to months. This latter possibility is a very important one which needs further study, since metal diffusion into the top of the solar cell may be a source of cell instability, distinct from the light-induced defects observed in materials. For example, if even one monolayer of metal diffuses from the interface into the p-layer region (throughout a thickness of 200 Å), then this results in a concentration of metal atoms in the layer of about 1 at.%. The fact that metal diffusion occurs over longer time scales after the deposition process rather than during deposition suggests that the diffusion coefficient has a relatively low activation energy (i.e., <0.4 eV).

(7) **Although ZnO substrates are resistant to chemical reduction in the initial stages of a-SiC:H alloy growth, atomic H diffuses into the ZnO during interface formation, widening its gap (by as much as 0.2 eV) and decreasing its index of refraction in the visible.** The process of H-incorporation in the ZnO occurs in a diffusion-limited fashion in the early stages of a-SiC:H growth when the TCO is not fully covered by the semiconductor. Future work needs to be undertaken to assess the effects of H-incorporation on the electrical properties of the TCO. One interesting observation of relevance in the future development of TCO layers is that the ZnO can be deposited very uniformly in thin layers in the sputtering process.

The future directions in each one of these seven individual research areas initiated in Phase II will be discussed in the final section of this report.

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1. Introduction, Motivation, and Overview

Because of the complexity of amorphous semiconductor device structures, the complexity of the processes used to fabricate them, as well as the stringent demands on their specifications, techniques for real time monitoring of materials and interface characteristics during preparation and processing have gained considerably in importance. If the data collected in real time can also be interpreted in real time, then it becomes possible to control materials characteristics through closed-loop adjustment of process variables, such as gas flow ratios that establish alloy composition. Even if real time data interpretation is not possible, the information deduced in post-process analyses of real time measurements is especially important for understanding the process. In addition, reproducibility can be assessed, problems identified and better understood, and new processing procedures designed with an expeditious arrival at appropriate process variables. In contrast, the fundamental mechanisms underlying processing-(device performance) relationships may be hidden from post-process measurements because of the complexity of the final structure.

Obtaining any useful information at all from real time observations is a challenge, however, considering that the probe must be non-invasive, non-perturbing, and, hence, contactless. Traditionally, diffraction techniques have been used most widely to provide feedback on the growth of materials by molecular beam epitaxy under ultrahigh vacuum conditions. Surface probes involving either electrons or ions, however, cannot be used in the high pressure reactive environments associated with plasma-enhanced chemical vapor deposition (PECVD) of amorphous semiconductor devices. Thus, we are left with probes based on photons as the only possibilities for non-invasive, real time measurements. At first glance, it may appear that any optical probe will not be sufficiently powerful to extract information on the material and interface characteristics. However, studies using single wavelength and spectroscopic ellipsometry over the last five years or more have demonstrated its sensitivity and power [1].

For example, from real time ellipsometry at one wavelength, the kinetics of the interaction of $B_2H_6:SiH_4$ doping gas mixtures with the a-Si:H surface was better understood [2]. The steps involved initial, rapid adsorption of B at the a-Si:H surface which activated the surface for subsequent CVD of SiH_4 at the typical substrate temperatures of 150-250°C. The speed of the initial activation step was found to depend on the nature of the bonds at the starting surface; it is fastest for a-Si:H and very slow for $In_2O_3:Sn$ (ITO), for example. When both SiH_4 and B_2H_6 gases are present at the activated surface, self-sustained CVD of a-Si:H:B occurs at a rate of several Å/min. If the SiH_4 flow is terminated in this process, the surface becomes rapidly poisoned with B and no further B_2H_6 decomposition occurs. As long as there continues to be an adequate supply of B_2H_6 in the gas phase, CVD continues; but if the B_2H_6 is terminated then CVD halts because the surface loses its activity. Such observations, which have important implications for dopant gas

handling and designing p-layer preparation in devices, would be impossible to uncover from ex situ measurements of materials or devices.

More recently, we have developed a real time spectroscopic ellipsometer with much more powerful characterizational capabilities [3]. It has a minimum acquisition time of 16 ms for a full spectrum from 1.5 to 4.5 eV; thus, film growth and etching processes at effective rates up to 60 Å/s can be monitored while retaining monolayer resolution and sensitivity. With the spectroscopic capability, we have been able to (i) extract the monolayer-scale features of the nucleation of a-Si:H [4], (ii) obtain the band gap of an amorphous semiconductor as thin as 20 Å from real time measurements during deposition [5], (iii) determine the evolution of H-content in the near surface region (top 200 Å) during in situ H treatment [6,7], and (iv) extract the evolution of the crystallite size and absorption properties of μ c-Si:H from real time measurements during the growth [8,9]. This and other work was completed in Phase I of our Subcontract.

In Phase II, we are concentrating on issues related to the "top contact" of the amorphous silicon solar cell. Namely, we are interested in the growth of a-Si:H/a-SiC:H/B/TCO and a-SiC:H/a-SiC:H/B/TCO structures, using our new capabilities to better understand the materials and interfaces, and the processing-(device performance) relationships. The motivation for studying the first structure (a-Si:H i-layer) was developed in our initial proposal; the motivation for studying the second structure (a-SiC:H i-layer) has arisen from recent Wide Gap Team activities.

Here we enumerate the separate sections of the report in order to provide background on the logical framework. In Sec. 2, details regarding our a-SiC:H preparation and real time measurement procedure are presented. In Secs. 3 and 5, we describe the optimization of intrinsic a-SiC:H alloys using H-dilution as a parameter. In Sec. 3, the microstructural evolution of the materials will be described, and in Sec. 5, a summary of the photoelectronic properties of these materials will be presented. Since it is found that the optimum photoelectronic properties of a-SiC:H are obtained at the highest H-dilution levels, while stopping short of the phase boundary associated with the onset of microcrystallinity, in Sec. 4 we briefly describe the microstructural and optical properties of μ c-SiC:H films which are prepared beyond this boundary. In future efforts, it is possible that our real time probe, with its sensitivity to crystallinity and electronic structure through the interband critical points of Si, can provide insights into the preparation of p-type μ c-SiC:H on TCO's. Correlations between the microstructural evolution and the electronic properties of a-SiC:H will be discussed in detail in Sec. 6, and process-properties relationships will be generalized for the alloy materials. The important goal for the optimization of our a-SiC:H, as discussed in Secs. 3 and 5, is to prepare films with properties comparable to those measured for solar cell grade materials prepared by Solarex. This is required to establish the relevance of our information in processes used by the industrial partners of the Wide Gap Team. The optical properties of the Solarex materials, measured as part of the Wide Gap Team effort are presented in Sec. 7.

In Sec. 8, we describe an approach, to be further developed in the future, that will allow for

automated band gap grading, based on feedback and control established by a single wavelength optical probe. In the future, we plan to use solar cell modeling and establish the optimum functional dependence of band gap with depth into the i-layer of the cell, and then to use the real time feedback and control to obtain the desired profile experimentally. Then simulation can be compared to experiment for the actual device. In Secs. 9 and 10, we describe our initial studies of TCO stability in atomic H environments, as well as the modification that the TCO undergoes when a-SiC:H is deposited on top of it. In this study, we focus on TCO's prepared at Solarex (R. D'Aiello and B. Fieselman) and at USSC (S. Guha). Because of the difficulties of the a-SiC:H:B/TCO interface problem, we have performed experiments of increasing complexity in order to obtain a clearer picture of the (assumed) independent processes: (i) TCO modification by atomic H (Sec. 9); and (ii) concurrent growth of intrinsic a-Si(C):H and TCO modification (Sec. 10). In the near future, we will attack the entire problem of a-SiC:H:B/TCO, including the possibility of TCO modification, B-contamination of the interface, and concurrent doped alloy growth. Section 11 describes future work in this and in other areas, and also describes our planned efforts on correlating interface properties with device performance, proposed as part of the Phase III of our research.

2. Experimental Details

All films studied here were deposited by rf plasma-enhanced chemical vapor deposition (PECVD) in the conventional parallel-plate electrode configuration. The stainless steel vacuum chamber was ultrahigh vacuum-compatible and pumped by turbomolecular pump to a base pressure of 10^{-8} Torr. The films were deposited at a power of 5 W (38 cm^2 electrode area). Unless otherwise stated, the substrate temperatures for our films were in the range of $240\text{--}250^\circ\text{C}$. In our studies of the effect of C incorporation on the evolution of microstructure, the total reactive gas flow was $(\text{SiH}_4 + \text{CH}_4) = 5 \text{ stand. cm}^3/\text{min}$ (sccm) and the $\text{CH}_4:\text{SiH}_4$ ratio was set at either 0:5, 1:4, 2:3, or 3:2. For these depositions, the $\text{H}_2:(\text{SiH}_4 + \text{CH}_4)$ ratio was set at 4:1. In our studies of H_2 -dilution, the $\text{CH}_4:\text{SiH}_4$ ratio was set at 2:3. In varying the H_2 dilution level, the $\text{H}_2:(\text{SiH}_4 + \text{CH}_4)$ ratio ranges from 0:1 to 20:1 at high reactive gas flow $(\text{SiH}_4 + \text{CH}_4) = 5 \text{ sccm}$, and from 10:1 to 80:1 at low reactive gas flow $(\text{SiH}_4 + \text{CH}_4) = 2.5 \text{ sccm}$. Thus, some films with $\text{H}_2:(\text{SiH}_4 + \text{CH}_4)$ ratios of 10:1 and 20:1 were prepared under otherwise identical conditions but with high and low gas flows for comparison purposes. No detectable differences were observed in the measured properties for the samples prepared at the two flow levels, at least within the typical run-to-run variations encountered. In spite of this, we still distinguish between the two types of samples in the presentation below.

In these studies, the partial pressure of the total reactant gas (rather than the total pressure) was kept constant (at 85 mTorr) as the dilution level was changed. The reason for this approach is that at the highest total gas flows ($\sim 200 \text{ sccm H}_2$), the minimum achievable chamber pressure (with

the process gas pump full-throttle) was 0.8 Torr. If this pressure was maintained as the H-dilution is reduced, we might expect degradation of film properties due to effects such as gas phase reactions that can lead to undesirable precursors or powder formation. This degradation may be interpreted erroneously as being caused directly by the reduction of H in the plasma.

By fixing the partial pressure of the reactive gases, we avoid this problem in our experiments. Thus, the total pressure decreases to 0.085 Torr as the H-dilution ratio decreases to 0:1. This pressure is lower than that typically used in PECVD and may result in the reduced thermalization of charged species in the plasma, so that they impact the film at higher energies. It is not clear however that such an effect is detrimental to the properties of the alloys. In fact, higher energy impact may be needed to break C-H bonds in the near surface and prevent the incorporation of bond-terminating CH_3 structures in the film. In such an experimental approach, we propose that any degradation in film properties with decreasing H-dilution can be attributed directly to the reduction of H in the plasma. To further support this point, we need to study the properties of a-SiC:H prepared without H-dilution, as a function of total reactive gas pressure and power (see Sec. 11).

Real time spectroscopic ellipsometry studies were performed using a novel rotating polarizer multichannel ellipsometer. Raw spectra obtained from four scans of the photodiode array detector were sufficient to calculate a single pair of spectra in (ψ, Δ) from 1.5 to 4.5 eV. The four scans were performed over one half-rotation (optical cycle) of the polarizer and were triggered by the output of an optical encoder attached to the polarizer. Thus, with a typical motor speed of 12.5 s^{-1} , a single pair of (ψ, Δ) spectra can be collected in 40 ms. To eliminate alignment errors and improve the signal-to-noise ratio, spectra from an even number of half-rotations are accumulated and averaged. The number of spectra chosen for signal averaging depends on the desired time resolution. For example, in studies of the evolution of microstructure and optical properties for a-SiC:H thin films during growth, spectra from 2 full rotations of the polarizer were averaged, leading to an acquisition time of 160 ms. The repetition time for the collection of successive spectra was chosen to be $\sim 1 \text{ s}$. Thus, at the highest film growth rates, obtained with pure SiH_4 and no H-dilution (see Fig. 3), 0.5 Å of material was deposited during the acquisition of a single pair of (ψ, Δ) spectra, and successive pairs were collected every $\sim 3 \text{ Å}$. In contrast for a $\text{H}_2:(\text{SiH}_4 + \text{CH}_4)$ dilution ratio of 20:1, 0.08 Å of material was deposited during data acquisition, and successive pairs of (ψ, Δ) spectra were collected every $\sim 0.5 \text{ Å}$.

3. Monolayer-Scale Nucleation/Growth Behavior and Structure of Intrinsic a-SiC:H Alloys

In this Section, we describe a study of the microstructural evolution at the monolayer level for a series of amorphous silicon-carbon alloy samples prepared by PECVD onto solvent-cleaned,

native oxide-covered (18-23 Å thick) c-Si wafers. It is to be expected that prior to full coalescence of the film (i.e., before the substrate is fully covered), the substrate chemical characteristics should play an important role in the nucleation process. Although this subject will not be addressed here for the alloys, earlier studies that have compared PECVD a-Si:H nucleation on different substrates are probably also relevant for the a-SiC:H nucleation process. Real time spectroscopic ellipsometry results for a-Si:H growth on both oxidized c-Si and oxidized metals of Cr and Mo (ion beam sputtered in thin film form to achieve ultra-smooth surfaces), reveal similar nucleation densities for all substrates, consistent with a homogeneous nucleation behavior. In spite of this similarity, the geometry of the nuclei are different in the first few monolayers. Plasma deposition on oxidized c-Si yields disc-shaped a-Si:H nuclei which appear to grow so as to *maximize* the film/substrate interface area, whereas deposition on oxidized metals yields hemispherical nuclei which appear to grow so as to *minimize* the interface area. This is consistent with a relatively low interface free energy for a-Si:H/SiO_x and a high interface free energy for the a-Si:H/MO_x (M: Cr or Mo). Thus, in the case of metals, it is energetically favorable for the nuclei to increase their surface free energy somewhat (i.e., form curved surfaces) in order to avoid forming an interface with the metal. Once the first bulk-like monolayer of a-Si:H forms, the coalescence pattern is identical on the different substrates (as long as they are nearly atomically smooth), yet this pattern depends very sensitively on the plasma deposition conditions. Because we expect a-SiC:H to show similar general behavior as a-Si:H with regards to substrate-dependent effects, we have not repeated the substrate-dependent study for the alloys. Here, we focus on the nucleation density and coalescence characteristics since these are relatively insensitive to the substrate, again as long as the substrate is smooth on an atomic scale. Thus, solvent-cleaned (but not oxide-etched) c-Si is a convenient, reproducible substrate for a monolayer-scale microstructural study of the alloys.

As in our earlier studies on PECVD a-Si:H, we have interpreted real time spectroscopic ellipsometry data using a two-layer model for the film. The top layer simulates (i) the isolated nuclei prior to bulk film formation and (ii) the surface roughness layer on the film after the first bulk-like monolayer forms and the film becomes continuous. The void volume fraction in this top layer is allowed to vary, and it stabilizes to ~0.5 after the film becomes continuous. The underlying layer simulates the bulk layer, and is not present in the initial stage of film growth when isolated nuclei are present.

Figure 1 shows typical results for two films deposited onto native oxide-covered single c-Si substrates, one with CH₄:SiH₄ flows of 2:3 (in sccm) and a H₂:(SiH₄+CH₄) flow ratio of 4:1 (solid symbols) and the other with a CH₄:SiH₄ flows of 1:1.5 (in sccm) and a H₂:(SiH₄+CH₄) flow ratio of 20:1 (open symbols). The differences between the microstructural evolution for the two samples in Fig. 1, which represent extremes in behavior as a function of H-dilution, can be quantified with two important pieces of information as described next.

- (1) The thickness of the surface layer when the first bulk density monolayer forms, $d_s(t_b)$,

Fig. 1 Closed symbols: low density surface layer (triangles) and underlying bulk layer (circles) plotted as a function of time for an a-SiC:H film prepared on c-Si at 250°C with a $CH_4:SiH_4$ ratio of 2:3 (in sccm) and a $H_2:(SiH_4+CH_4)$ ratio of 4:1. Open symbols: corresponding results for a film prepared on c-Si at 250°C with a $CH_4:SiH_4$ ratio of 1:1.5 (in sccm) and a $H_2:(SiH_4+CH_4)$ ratio of 20:1. Four features derived from such data have been compared for our samples (i) the thickness of the nucleating layer when the bulk layer reaches 2-3 Å (1 ML); (ii) the magnitude of smoothening in the first 50 Å; (iii) the longer term smoothening/roughening trends (100-240 Å) and (iv) the deposition rate (from the bulk layer growth).

provides a measure of the nucleation density. When $d_s(t_b)$ is low, the nucleation density is high and vice versa. In fact, if the nucleation geometry is such that the nuclei are hemispherical and located on a square grid, then the nucleation density is given by $N_d = [2d_s(t_b)]^{-2}$. Generally, the nucleation density can be high for three possible reasons: (i) the precursors have a high sticking coefficient and short diffusion length on the surface of the substrate, (ii) the film material exhibits a small stable cluster size (critical nucleus), or (iii) the precursors have sufficient energy to generate substrate defects that serve as sites for nucleation.

(2) The magnitude of the surface smoothening or roughening, Δd_s , that occurs as the bulk layer increases from the monolayer level to 50 Å in the coalescence regime provides information on the diffusion length of the precursors on the film surface. If the precursor surface diffusion length is shorter than the average spacing between the nuclei, it is expected that roughening and void propagation will occur. If the diffusion length is longer than the average spacing, then smoothening and coalescence will occur. [Such considerations are based on capillarity-driven surface diffusion. Since the chemical potential μ_c of an atom on a curved surface is greater than that for an atom on a flat surface, the velocity of the atom is $v = -(D_s/kT)\partial\mu_c/\partial s$, where D_s is the surface diffusivity, and s is an element of arc along the surface.] Previous studies of the surface smoothening or roughening, Δd_s as a function of preparation conditions for PECVD a-Si:H prepared from pure SiH_4 , have shown that the maximum surface smoothening occurs at the lowest rf power and a substrate temperature of $\sim 250^\circ\text{C}$ [4]. These are the same conditions that are generally known to give optimum photoelectronic-quality material. Thus, one might propose a causal connection between surface processes and the ultimate quality of the material. It is of interest, therefore to characterize similar possible connections that occur in the a-SiC:H alloy system as a function of $\text{CH}_4:\text{SiH}_4$ ratio, H-dilution, and other parameters such as substrate temperature and pressure. Because H-dilution has the potential for improving the photoelectronic quality of the alloys and the solar cell performance, more extensive results will be presented versus H-dilution.

We begin by showing $d_s(t_b)$ (circles) and Δd_s (triangles) in Fig. 2 for a series of a-SiC:H depositions on native oxide-covered c-Si as a function of the $\text{CH}_4:\text{SiH}_4$ flow ratio. Other process parameters were kept constant, including a substrate temperature of 250°C , a total reactive ($\text{SiH}_4 + \text{CH}_4$) gas flow of 5 sccm, and a dilution ratio $[\text{H}_2:(\text{SiH}_4 + \text{CH}_4)]$ of 4:1. The monolayer-level microstructural effects of gas phase carbon species are relatively weak over the range of CH_4 flow from 0.5 to 3:2 for these conditions. However, there does appear to be a trend toward increasing nucleation density and reduced surface smoothening with increased carbon incorporation. The maximum $\text{CH}_4:\text{SiH}_4$ flow ratio of 3:2 used here leads to an increase in the room temperature optical gap by ~ 0.35 eV (from ~ 1.75 eV to ~ 2.1 eV, via the conventional Tauc method) over material prepared without CH_4 , and also leads to a decrease in deposition rate from ~ 1.5 Å/s to ~ 1.1 Å/s. (See Figs. 3 and 4).

Fig. 2 Magnitude of surface smoothing occurring in the first 50 Å of bulk film growth, Δd_s (triangles), and the thickness of the nucleating layer when the first bulk monolayer forms, $d_s(t_b)$ (circles), both plotted as a function of the $CH_4:SiH_4$ gas flow ratio. In this series of experiments, the substrate is c-Si at 250°C, the total reactive gas flow is 5 sccm, and the $H_2:(SiH_4+CH_4)$ ratio is 4:1.

The trends in Fig. 2 are consistent with a detrimental effect of C-bearing precursors on the processes at the growth surface. An increase in nucleation density, especially occurring as the deposition rate is reduced, suggests that some C-bearing species in the plasma can stick more readily onto the substrate surface. This is reasonable considering the wider range of bond hybridizations accessible to it. It is also possible that the critical nucleus size for a-SiC:H is smaller as a result of the stronger Si-C bonding. Similar arguments appealing to a reduced diffusion length of C-bearing precursors on the *film* surface can be applied to explain the weaker smoothing effect in Fig. 2.

Figures 3 and 4 show further information of interest extracted from either real time, in situ, or ex situ ellipsometry for these depositions. The linear slope of the bulk layer thickness plotted versus time as shown in Fig. 1 provides an accurate (real time) measurement of the deposition rate. These results are plotted in Fig. 3 as a function of the CH₄:SiH₄ flow ratio. The deposition rate decreases by about 30% with increasing CH₄ flow. This may be attributed the lower total reactive radical flux to the surface as a result of the greater difficulty of dissociating CH₄ relative to SiH₄. The trend may also be related to the observed ability of a CH₄ plasma to etch a-C:H surfaces. Etching by the plasma is dominant at low plasma powers (low plasma sheath potentials) and high pressures, whereas deposition from the plasma occurs at high plasma powers and low pressures. Clearly C incorporation in the a-C:H surface requires energetic particle impact at the surface to generate free bonds for crosslinking, otherwise the incoming radical reacts with a saturated surface CH_x and leaves as a stable hydrocarbon such as acetylene. Similar processes may also occur between gas phase C-containing radicals and CH_x on the a-SiC:H surface. Such features also account for the fact that 1:1 CH₄:SiH₄ reactive gas mixtures typically lead to <0.1 atomic fraction of C in the final film.

In Fig. 4 the optical gaps as a function of CH₄:SiH₄ gas flow ratio are presented for the same set of samples depicted in Fig. 3. One series of results was obtained from real time spectroscopic ellipsometry measurements (sample thickness: 150 Å; see Fig. 23) and, thus, are representative of a 250°C substrate temperature. The other two series of results were obtained from in situ SE measurements after terminating deposition and cooling the sample, or from ex situ measurements immediately after removing the sample from the reactor. Because the gaps were derived from SE measurements which are most accurate in the very high absorption coefficient region (>2.25 eV), we used the approach of Cody to determine the gaps. This consists of plotting $\epsilon_2^{1/2}$ versus $h\nu$ and finding the energy axis intercept of the linear fit to the data. The results of Fig. 4 are consistent with an average temperature coefficient of the gap of 6×10^{-4} eV/K. In plotting these results, it is apparent that a ~0.25 eV gap shift occurs (from 1.65 eV to 1.9 eV according to the Cody method) when the CH₄:SiH₄ gas flow ratio increases from 0:5 to 2:3. This result, coupled with the fact that the Cody method tends to give a gap 0.08-0.09 eV systematically lower than the conventional Tauc approach (which uses the linear, high energy part of the transmission and reflection spectra with

Fig. 3 Deposition rate of a-SiC:H obtained from real time spectroscopic ellipsometry and plotted as a function of the CH₄:SiH₄ gas flow ratio. In this series, the substrate temperature is 250°C and the H₂:(SiH₄+CH₄) ratio is either 0:1 (open circles), 4:1 (closed circles), or 20:1 (open triangle).

Fig. 4 Optical gaps for the samples of Fig. 3 with a dilution ratio of 4:1, obtained by the Cody method using real time spectroscopic ellipsometry measurements at the substrate temperature of 250°C (open circles) and using in situ and ex situ measurements at 25°C (closed circles). The broken line is an estimate of the optical gap that would be obtained by the conventional Tauc method using transmission and reflection measurements at the highest accessible energy.

$5 \times 10^3 < \alpha < 1.5 \times 10^4 \text{ cm}^{-1}$; see Fig. 15), suggests a standard Tauc gap of $\sim 1.95\text{--}2.0 \text{ eV}$ would be obtained with a 2:3 $\text{CH}_4\text{:SiH}_4$ gas flow ratio. Thus, we use the 2:3 $\text{CH}_4\text{:SiH}_4$ ratio in studies of H-dilution of a-SiC:H alloys. It should be noted that if the Tauc gap is obtained by fitting to a wider range of the transmission and reflection spectra, with α spanning the order of magnitude range centered at $\alpha = 10^4 \text{ cm}^{-1}$, then an optical gap close to that of the Cody method is obtained [10].

Before presenting and discussing the results corresponding to Fig. 2 for H-dilution, it is useful to consider the variation in the bulk void volume fraction as a function of the dilution ratio, $\text{H}_2\text{:}(\text{SiH}_4 + \text{CH}_4)$ [11]. The void fraction is extracted by fitting the dielectric functions deduced from the real time or ex situ ellipsometry measurements using the Bruggeman effective medium theory (correcting for surface roughness in the analysis). In the fitting, we scaled the void volume fraction relative to that of a high density film; it should be stressed that ellipsometry cannot provide an absolute measure of material density. In addition, the analysis is only valid as long as the C content of the film remains reasonably constant. This is substantiated by the fact that the peak energies of the imaginary parts of the dielectric functions (ϵ_2) shift by no more than 0.02 eV. Figure 5 shows the dielectric function for a representative sample, along with the fit that provides the void volume fraction. The oscillations at low energy are interference fringes that appear in the region of semitransparency (photon energies less than 2.25 eV in this case). The resulting void volume fractions for a series of samples are plotted in Fig. 6. For the films of Figs. 5 and 6, the $\text{CH}_4\text{:SiH}_4$ ratio is maintained at 2:3, resulting in a conventional Tauc optical gap $\sim 0.20 \text{ eV}$ higher than that of a-Si:H from pure SiH_4 ($\sim 1.75 \text{ eV}$ at room temperature) as noted above. In Fig. 6, the solid points were obtained with a total flow of $(\text{SiH}_4 + \text{CH}_4)$ of 5 sccm and the open points were obtained with a flow of 2.5 sccm.

For the samples of this study, the void volume fraction in Fig. 6 shows a decreasing trend with increasing dilution ratio over the range at least from 0:1 to 20:1. As will be discussed shortly, samples over the range of dilution from 0:1 to 30:1 appear to be fully amorphous. Films deposited with 30:1 deviate from the trends with H-dilution in some aspects of the growth behavior (see Figs. 7 and 9), indicating that the regime of microcrystallinity is being approached. For a 40:1 dilution ratio, photoelectronic measurements of thick films suggest that a small volume fraction of crystallites may be present and influence the properties. No evidence of crystallites are observed in thin films ($< 800 \text{ \AA}$) prepared under these conditions, however, indicating that the crystallites develop only in the thick films and thus may be non-uniformly incorporated with depth in the film. Films deposited with an 80:1 H-dilution ratio exhibit clear evidence of microcrystallinity in the optical functions of thin and thick films, as discussed in greater detail below.

The reduction in void fraction in Fig. 6 may be attributed to the ability of H in the gas phase to remove H more effectively from the C-H or C=H bonds at the film surface, allowing the network to crosslink. Thus, the H-dilution may prevent the formation of terminating (CH_3) and polymeric $(\text{CH}_2)_x$ structures. In general, with more effective H-exchange between the surface and gas phase,

Fig. 5 The dielectric function obtained from real time measurements (broken lines) for a representative sample of a-SiC:H prepared on c-Si at a substrate temperature of 250°C, with no H₂ dilution, and a CH₄:SiH₄ gas flow ratio of 2:3 (in sccm). The lines represent a fit to the data that provides the void volume fraction within the film. The dielectric functions here are characteristic of a substrate temperature of 250°C.

Fig. 6 Void volume fraction relative to the highest density material for a series of a-SiC:H films, obtained from analyses such as that of Fig. 5, plotted as a function of the $\text{H}_2:(\text{SiH}_4 + \text{CH}_4)$ gas flow ratio. In this series, the $\text{CH}_4:\text{SiH}_4$ gas flow ratio is either 2:3 (in sccm; solid points) or 1:1.5 (in sccm; open points).

the microstructure has a better opportunity to coalesce into a dense film. This mechanism is discussed more fully in connection with the results of Fig. 7. As can be seen in Fig. 6, there appears to be a run-to-run variability in the void volume fraction at the level of about ± 0.02 . The origin of this problem is not clear at present, but may be related to the variability in the nucleation behavior as noted in conjunction with Figs. 7 and 8.

Figure 7 shows $d_s(t_b)$ and Δd_s deduced from real time SE for a series of a-SiC:H depositions on native oxide-covered c-Si as a function of the $H_2:(SiH_4+CH_4)$ gas flow ratio. The results for $d_s(t_b)$ have been converted directly to nucleation density, N_d , using the approximate expression $N_d=[2d_s(t_b)]^{-2}$, which is exact for the ideal case of hemispherical nuclei on a square grid. The results for N_d as a function of H-dilution for the series of samples of Fig. 7 appear in Fig. 8.

The results in Fig. 7 can be compared with the corresponding values for optimum a-Si:H prepared from pure SiH_4 (horizontal broken lines), and discussed in terms of the two extremes of behavior that tend to occur at the lowest ($<5:1$) and higher dilutions (20:1 to 25:1). For dilution levels less than 5:1, the nucleation density is significantly greater than for optimum a-Si:H from pure SiH_4 , and there is a weak smoothening effect by one or two monolayers (3-4 Å). In fact, the nucleation density is similar to that for sputtered a-Si without hydrogen. The behavior for the alloys prepared without dilution indicates that some component of the plasma, presumably a C-bearing species, bonds more readily onto the substrate surface in comparison to pure SiH_4 plasmas. The fact that the void density tends to decrease with H-dilution from 0:1 to 4:1 in Fig. 6, even though the microstructural features of coalescence remain about the same in Fig. 7, suggests that the voids eliminated with H-dilution in this regime are associated with point defects (e.g., Si-CH₃) within the nucleating clusters (rather than extended void structures associated with incomplete coalescence that may also occur in this regime).

As the dilution level increases to 20:1 in Fig. 7, the nucleation density becomes lower than that for optimum a-Si:H prepared from pure SiH_4 , whereas the smoothening effect for the 20:1 dilution level, 8-10 Å, is comparable to that for optimum a-Si:H. The reduction in nucleation density means that the H in the plasma is very effective at either (i) scouring the substrate, eliminating the high sticking coefficient species that serve as nucleation centers; (ii) preventing the formation of such species from occurring in the plasma in the first place; or (iii) passivating sites for nucleation that exist on the substrate surface. The larger smoothening effect at the higher dilution is attributed the corresponding conditioning of the film surface during growth or an elimination of high sticking coefficient radicals in the gas phase. The fact that the increase in smoothening in Fig. 7 is accompanied by a continued reduction in void volume fraction with dilution in Fig. 6, suggests that the high dilution effectively eliminates extended microstructural defects (e.g. columnar voids) that are related to a low precursor surface diffusion length. The smoothening trend becomes weaker for a film prepared at the highest dilution (30:1) shown in Fig. 7. This appears to be related to the onset of H-etching reactions that tend to break the weaker bonds connecting neighboring

Fig. 7 Magnitude of surface smoothening occurring in the first 50 Å of a-SiC:H bulk film growth on native oxide-covered c-Si, Δd_s (triangles), and the thickness of the nucleating layer when the first bulk monolayer forms, $d_s(t_b)$ (circles), both plotted as a function of the $H_2:(SiH_4+CH_4)$ gas flow ratio. In this series, the $CH_4:SiH_4$ gas flow ratio is either 2:3 (in sccm; solid points) or 1:1.5 (in sccm; open points). The horizontal lines indicate values obtained for optimum a-Si:H prepared from pure SiH_4 .

Fig. 8 Nucleation density obtained from real time SE measurements of a-SiC:H thin film growth on native oxide-covered c-Si substrates, plotted versus the dilution ratio over a range from 0:1 to 30:1. In this series, the $\text{CH}_4:\text{SiH}_4$ gas flow ratio is either 2:3 (in sccm; filled points) or 1:1.5 (in sccm; open points). These results were obtained by manipulation of the $d_s(t_b)$ values from Fig. 7, as noted on the ordinate label.

microstructural units. At the 30:1 dilution level, such an effect leads to gradual surface roughening over time (see Fig. 9) but no apparent degradation in the density of the underlying material (see Fig. 6).

Finally, we note in Fig. 7 that there tends to be significant scatter in $d_s(t_b)$, the thickness at which nuclei make contact (± 2 Å). In contrast, the trend in the magnitude of surface smoothening is more clearly defined (± 0.5 Å). This may be related to the fact that the nucleation density can depend on the condition of the substrate, which may not be identical from run-to-run. In contrast, the degree of surface smoothening depends on the a-SiC:H surface and the plasma conditions which are more reproducible.

Figure 9 shows the change in surface roughness on the film measured over the bulk thickness range from 100 to 240 Å. The positive values indicate roughening of the surface over time, behavior that is clearly observed for H-dilution ratios less than 10:1. The negative values indicate surface smoothening which tends to be observed only at the higher dilution levels of 20:1 and 25:1. The film prepared with 30:1 is well away from the general trend observed as a function of dilution, and shows clear roughening. The overall behavior in Fig. 9 is consistent with that in Fig. 7. For low H-dilution ratios, the precursor surface diffusion length tends to be low, and any roughness with spatial wavelength greater than the diffusion length tends to be enhanced with continued growth. In contrast, the much longer precursor surface diffusion lengths, proposed for the higher H-dilution ratios, leads to a dampening of the corresponding roughness features that originate in the nucleation process. At the 30:1 dilution ratio, as noted earlier, the roughening may be attributed to the effects of H-etching as the microcrystalline regime is approached.

To summarize this section, we find that the optimum microstructural development, as well as ultimate film density, are obtained under conditions of high H-dilution level, while avoiding the regime representing the onset of microcrystallinity. For our system, this corresponds to a dilution level of 20:1-25:1. Under these conditions, the nucleation density is a factor of 5 lower than for no H-dilution, the coalescence phenomenon is more extensive, the film exhibits a longer term smoothening trend, and the ultimate film density is highest. For practical reasons, Figure 10 shows the accumulated results for the deposition rate as a function of H-dilution, obtained from the linear increase in bulk film thickness with time deduced in analyses of real time spectroscopic ellipsometry data (see Fig. 1). Under the conditions of optimum microstructural development the deposition rate is between 0.3 and 0.6 Å/s, depending on the total reactive gas flow. We have not attempted to optimize the films versus plasma power, and thus do not know if improvements in rate can be made without sacrificing structural and electronic properties. We also seek more quantitative information on how the structural properties, observed by real time methods, influence the fundamental electronic properties of the material, as well as the electronic properties in the device configuration. A discussion of the former properties is presented in Sec. 5; the latter research is currently in progress.

Fig. 9 Change in surface roughness amplitude during growth (positive values meaning roughening) over the thickness range from 100 to 240 Å for a-SiC:H films prepared as a function of H-dilution. In this series of samples, the $CH_4:SiH_4$ gas flow ratio is 2:3 (in sccm; solid points) and 1:1.5 (in sccm; open points).

Fig. 10 Deposition rate of a-SiC:H plotted as a function of the $H_2:(SiH_4+CH_4)$ gas flow ratio from 0:1 to 30:1. In this series, the $CH_4:SiH_4$ gas flow ratio is either 2:3 (in sccm; solid points) or 1:1.5 (in sccm; open points). The deposition rate of μc -SiC:H prepared with a H_2 dilution ratio of 80:1 is plotted at the far right.

4. Microcrystalline SiC Prepared at Very High Hydrogen Dilution Levels

For films prepared on native oxide-covered c-Si substrates with a fixed $\text{CH}_4:\text{SiH}_4$ ratio of 1:1.5 (in sccm) and H-dilution levels at 40:1 and 80:1, there is evidence for microcrystallinity in the alloy films. Spectroscopic ellipsometry measurements on thin films prepared with a 40:1 H-dilution ratio exhibited a gradual roughening over time, similar to the behavior of the 30:1 dilution sample, but more extensive (see Fig. 9). However, the final thin film (800 Å thick) did not show any evidence of crystallinity (i.e., critical point structure) in the above-gap dielectric function. Thicker films (0.9 μm) prepared for electrical measurements exhibited sub-gap absorption behavior significantly different than that of the a-SiC:H alloys (see Sec. 5 and Fig. 21). Based on these observations, it is possible that the films evolve with thickness during growth from an amorphous structure to a two-phase amorphous-microcrystalline structure. Because of the potential complexity of such samples, we did not study them further.

In contrast, the real time SE measurements of the film prepared at 80:1 suggest a more uniform microcrystalline structure throughout the deposition process. After deposition, the ellipsometric spectrum was measured at room temperature and analyzed in detail. In this analysis, we attempted to fit to the data using a mixture of pure Si microcrystallites (bulk Si dielectric function) and a-SiC:H (reference dielectric function from a sample with 20:1 dilution). Figure 11 shows the fit (solid lines) to the pseudo-dielectric function measured ex situ at room temperature (points), that yields a bulk layer thickness of 1780 ± 50 Å, a roughness layer thickness of 95 ± 15 Å, and a bulk layer composition of 0.42 ± 0.11 c-Si, 0.50 ± 0.12 a-SiC:H, and 0.08 ± 0.01 void (volume fractions). These volume fraction values should be viewed with caution for two reasons. First, size effects in microcrystallites are known to broaden the electronic transitions relative to bulk, single-crystal Si. This broadening may be simulated by the introduction of additional a-SiC:H component in the model. Thus, the volume fraction of the crystalline component may be underestimated as a result of the size effects. Second, the choice of the c-Si dielectric function (rather than, say, β-SiC) is an assumption of questionable validity. We performed further optical analysis in an attempt to understand the properties of this material.

In fact, in Fig. 11, the fit (solid lines) exhibits relatively sharp peaks at the critical points of c-Si (near 3.3 eV and 4.2 eV) that do not appear clearly in the data, and this may be related to either or both of the two problems noted in the previous paragraph. To obtain more information, we first extracted the amorphous component from the dielectric function of the μc-SiC:H by analytical inversion. The resulting dielectric function of the crystallites alone is compared to that of bulk single crystal Si in Fig. 12. A simple inspection of the spectra, particularly ϵ_1 , suggests that the $E_0'-E_1$ transition complex has shifted to higher energies whereas the E_2 transition has shifted to lower energies. This leads to a single broad structure, centered near 3.9 eV. Next we performed critical point analysis on the dielectric function of Fig. 12 in order to study the electronic transitions

Fig. 11 A comparison of the experimental pseudo-dielectric function (points) and best fit model (lines) for $\mu\text{c-SiC:H}$ prepared on c-Si with a 80:1 H-dilution ratio and a $\text{CH}_4\text{:SiH}_4$ gas flow ratio of 1:1.5 (in sccm). In the model, the film is assumed to consist of a physical mixture of a-SiC:H, c-Si, and void. The lack of good agreement in the region of the critical points is attributed in part to a microcrystallite size-induced reduction in the excited state lifetime of the electrons, which leads to a broadening of the electronic transitions. The energies of the critical points are also shifted, indicating a possible effect of C-incorporation on the electronic structure of the crystallites (see Table I).

Fig. 12 A comparison of the room temperature dielectric functions of bulk single crystal Si with the crystalline component of the $\mu\text{c-SiC:H}$ film of Fig. 11. The latter result was obtained from the pseudodielectric function of Fig. 11 by mathematical inversion, assuming the best fit structural parameters of the film (deduced by linear regression analysis).

of the crystalline component of the $\mu\text{c-SiC:H}$. An excitonic lineshape, found to be appropriate for single crystal Si, was assumed in this analysis. In Fig. 13, we show an example of the excellent fits to the second derivative lineshape spectra for both ϵ_1 and ϵ_2 which provide the critical point parameters of energy E , linewidth Γ , and phase ϕ . The results for this particular sample are shown as the second row in Table I, which compares the critical point parameters for the $E_0'-E_1$ and E_2 transitions of bulk c-Si and the crystalline component of three 80:1 $\mu\text{c-SiC:H}$ films prepared under identical conditions. For two of the three $\mu\text{c-SiC:H}$ films, the substrate is c-Si, whereas for the third film the substrate is Cr.

The results in Table I for the two $\mu\text{c-SiC:H}$ films on c-Si substrates are quite consistent. It is clear that the $E_0'-E_1$ transition complex has shifted to higher energy by 0.10-0.12 eV and has broadened significantly, by a factor of three, relative to that of single crystalline Si. In addition there is a factor of two increase in the phase angle, suggesting that the nature of the electronic transitions is changing. For the E_2 transition, a shift to lower energies by 0.04-0.05 eV has occurred and the broadening effect is similar.

From Heisenberg's uncertainty principle, the linewidth Γ of an electronic transition can be expressed in terms of the excited state lifetime of the electron τ , by $\Gamma = h/\tau$, where h is Planck's constant. It turns out that in high quality crystallites the electron lifetime is limited by scattering at the surface of the crystallites. Thus, the linewidth decreases monotonically with crystallite radius R according to $\tau = R/v$, where v is the electron velocity. From our earlier study of this effect [8], we have determined the broadening parameter as a function of crystallite size for the $E_0'-E_1$ transitions. As shown in Table I, the $E_0'-E_1$ broadening parameter of the crystallites in the $\mu\text{c-SiC:H}$ films on c-Si substrates is ~ 0.37 eV, as compared to 0.12 eV for bulk, single-crystal Si. For such a value of Γ_1 , the crystallite radius is estimated to be ~ 80 Å. This appears to be large enough so that quantum size effects on the energy of the transitions can be neglected. Thus, it is possible that the differences in the energy positions of the $E_0'-E_1$ and E_2 from the bulk, single crystal values may be related to C-incorporation, that modifies the electronic density of states. Further work is needed to support this supposition.

One final comment needs to be made concerning these films. Our initial studies were performed on the two $\mu\text{c-SiC:H}$ films in Table I that were prepared on c-Si substrates. For these depositions, we considered it possible that the H in the growth plasma may etch away the substrate native oxide, which then allows the microcrystals to nucleate on the c-Si in an initial epitaxial process. To assess this possible substrate-dependent effect, we deposited a $\mu\text{c-SiC:H}$ film on a Cr substrate under the same conditions for comparison. Although some of the values in Table I are different, all of the same general features are observed for the $\mu\text{c-SiC:H/Cr}$ structure (second row, Table I) as for $\mu\text{c-SiC:H/c-Si}$ (third and fourth rows). This indicates that the substrate is not playing a dominant role in the crystallite nucleation process.

Fig. 13 Second derivative spectra for the crystalline component dielectric function of Fig. 12, along with a best fit assuming an excitonic lineshape. The results of this analysis are the critical point energy, broadening parameter, and phase for both the E_0' - E_1 and E_2 transitions. The best fit values are given as the second row entry in Table I.

Table I

	$E_0'-E_1$			E_2		
	E (eV)	Γ (eV)	ϕ (°)	E (eV)	Γ (eV)	ϕ (°)
c-Si	3.376 ± 0.002	0.120 ± 0.002	-37.6 ± 3.1	4.275 ± 0.003	0.078 ± 0.003	106.9 ± 4.2
$\mu\text{c-SiC:H}$ (Cr substrate)	3.494 ± 0.008	0.171 ± 0.008	-89.1 ± 7.3	3.961 ± 0.089	0.473 ± 0.090	95.1 ± 18.5
$\mu\text{c-SiC:H}$ (Si substrate)	3.494 ± 0.017	0.367 ± 0.017	-74.5 ± 7.4	4.237 ± 0.020	0.267 ± 0.021	134.6 ± 8.0
$\mu\text{c-SiC:H}$ (Si substrate)	3.475 ± 0.054	0.374 ± 0.054	-79.0 ± 23.5	4.228 ± 0.053	0.265 ± 0.053	127.0 ± 20.7

Table I A comparison between the critical point parameters of energy (E), broadening (Γ), and phase (ϕ) for both the $E_0'-E_1$ and E_2 transitions for bulk, single-crystal Si, and for the crystallites in two-phase $\mu\text{c-SiC:H}$ films. For the three $\mu\text{c-SiC:H}$ films, the $\text{CH}_4:\text{SiH}_4$ ratio was 1:1.5 (in sccm) and the $\text{H}_2:(\text{SiH}_4+\text{CH}_4)$ ratio was 80:1. For the first $\mu\text{c-SiC:H}$ film, the substrate is Cr, and for the second two the substrate is native oxide-covered c-Si.

5. Electrical and Optical Measurements of Wide Gap Materials

Conventional electrical and optical measurements were performed on a-SiC:H samples prepared at different H-dilution ratios. These samples were deposited to thicknesses of ~ 0.5 - 1.5 μm in the same chamber under identical conditions as those studied by real time spectroscopic ellipsometry. At this point, we have characterized the absorption spectra from 0.8 to 5.0 eV using a combination of dual beam photoconductivity, transmission and reflection, and spectroscopic ellipsometry measurements. The former results were obtained in annealed and fully light soaked states (accelerated soaking to saturation). We have also measured the dark and photo-conductivity characteristics.

Figure 14 shows the absorption spectra in the annealed state, measured from 0.8 to 5.0 eV for two films, one prepared with a H-dilution ratio of 20:1 and the other without dilution under the conditions described in the discussion of the experimental details. It is clear, at least in the annealed state, that the sample prepared with H-dilution exhibits a lower density of midgap states and a steeper exponential Urbach tail than the sample without dilution, in spite of nearly identical E_{04} optical gaps.

Values that characterize the optical gap, deduced from spectra such as those in Fig. 14 are summarized in Fig. 15. The conventional method for determining the gap is to apply the Tauc relationship $[(\alpha E)^{1/2} = B(E - E_g)]$ to the strongest absorption regime that is accessible to the transmission and reflection (T&R) measurement (typically $5 \times 10^3 < \alpha < 1.5 \times 10^4 \text{ cm}^{-1}$). However, the Tauc relationship exhibits upward curvature and the accessible α values decrease as the optical density of the measured film increases, and this approach ultimately leads to a gap that spuriously depends on the optical density of the film. The curvature in the Tauc relationship becomes a much more serious problem in our situation since our data span a much larger range in α , owing to the availability of ellipsometry data. Figure 15 shows the conventional Tauc gap measurements which range from about 1.99 to 1.95 eV with increasing dilution. A weak trend to decreasing gap is observed with increasing H-dilution for these measurements; however, the trend is within the range of experimental error.

Figure 15 also includes three other energy gap measures: (i) the Cody relationship $[\epsilon_2^{1/2} = B'(E - E_g)]$ which uses the assumption of a constant dipole matrix element and is less sensitive to the energy range over which the linear fit is made; (ii) the Tauc relationship, in which a lower range of α (the order of magnitude centered at 10^4 cm^{-1}) is used for the fit; and (iii) E_{03} , the energy at which $\alpha = 10^3 \text{ cm}^{-1}$. For a given sample, these three approaches provide a common value for the gap within the typical experimental uncertainties (± 0.02) [10]. When this common value is considered, then we conclude that H-dilution has little effect on the gap. In fact, if there may be a slight increase in the gap value from 1.85 to 1.87 eV with increased dilution. We believe that these values better characterize the energy gap of the material, in spite of the fact that they are typically ~ 0.1 eV lower

Fig. 14 Absorption spectra over a wide range for a-SiC:H samples in the annealed state prepared with 20:1 H-dilution and without H-dilution. The CH₄:SiH₄ gas flow ratio was 1:1.5 (in sccm) for the H-diluted material and 2:3 (in sccm) for the undiluted material. These results were obtained from a combination of dual beam photoconductivity, transmission and reflection (T&R), and spectroscopic ellipsometry measurements.

Fig. 15 Optical gap as a function of H-dilution obtained by four different methods: E_{03} from T&R, the Cody gap $[\epsilon_2^{1/2}$ vs. E] from SE, and the Tauc gap $[(\alpha E)^{1/2}$ vs. E] from both wide energy range and high energy range T&R/ellipsometry measurements. The high energy range Tauc gap extrapolation is the one most commonly used in the literature.

than the conventionally deduced optical gap. The fact that the gap is nearly constant over a wide range of dilution suggests that both the hydrogen and carbon contents of the material do not change with dilution. However, it is possible that a decrease in C content is compensated by an increase in H content. Infrared absorption and electron microprobe measurements to assess such a possibility are currently in progress.

Figures 16 and 17 show other information extracted from absorption spectra such as those in Fig. 14, namely the absorption coefficient at 1.2 eV [$\alpha(1.2\text{eV})$] and the inverse exponential slope of the Urbach tail, respectively. Figure 16 shows that in the annealed state, $\alpha(1.2\text{eV})$ decreases by a factor of 3-6 (from 1.5 to 0.6-0.25 cm^{-1}) as the dilution increases from 0:1 to 20:1. Unfortunately, much of this significant improvement with dilution is lost in the fully light-soaked state. For the film prepared without H-dilution, $\alpha(1.2\text{eV})$ increases by a factor of 10 with light-soaking, whereas for the film prepared with a 20:1 ratio, $\alpha(1.2\text{eV})$ increases by a factor of 30. As a result in the light-soaked state, the improvement with H-dilution is only 50% (from 15 to 10 cm^{-1}). Thus, we find it interesting that films exhibiting greater homogeneity, i.e., a lower volume fraction of voids, exhibit a lower stability when the midgap density of states is considered. Thus, the instability may be related to overconstrained or weak Si-C bonds that are susceptible to breaking by free H. These bonds may exist in lower concentration when the void volume fraction is high. Figure 17 shows the slope of the Urbach tail for the same set of samples. In the annealed state, the sample prepared with a dilution ratio of 20:1 appears to exhibit the narrowest valence band tail, with an inverse exponential slope of 51 meV. This value is quite close to that obtained for our best a-Si:H prepared from pure SiH_4 (~48 meV). Under fully light soaked conditions, the band tail broadens, and a trend with H-dilution is seen more clearly. The data in the fully light-soaked condition must be viewed with caution, however, since the range over which the band tail is exponential is quite narrow.

Figure 18(a) shows the dark conductivity versus T^{-1} for selected samples of different H-dilution level, and Figure 18(b) shows the room temperature conductivity and the activation energy plotted as a function of H-dilution ratio. For H dilution ratios less than 5:1, the Fermi level resides somewhat below midgap and the room temperature conductivity is very low. For higher dilution ratios, the Fermi level is somewhat above midgap, and the conductivity is 1-3 orders of magnitude higher.

Figure 19 shows the photoconductivity versus generation rate for two samples, one prepared without H-dilution and the other with a 20:1 H-dilution level. Results are presented in both light-soaked and annealed states. At a generation rate G of $10^{19} \text{ cm}^{-3}\text{s}^{-1}$, the photoconductivity of the sample prepared with H-dilution is about a factor of three higher than that prepared without dilution. For $G=10^{19} \text{ cm}^{-3}\text{s}^{-1}$, the reduction in the photoconductivity with light soaking is somewhat larger for the sample prepared without dilution. Thus, the poorer stability of the a-SiC:H prepared using H-dilution (relative to the undiluted preparations), as noted from the increase in the

Fig. 16 Absorption coefficient in the subgap region at 1.2 eV for annealed (circles) and fully light-soaked (triangles) states of selected a-SiC:H films prepared with different H-dilution ratios but a fixed $CH_4:SiH_4$ gas flow ratio of 2:3 or 1:1.5 (in sccm). The result for a Solarex (SLX) sample with a 25:1 H-dilution ratio, deposited at a substrate temperature of $\sim 300^\circ\text{C}$, is given as the horizontal broken line.

Fig. 17 Urbach tail inverse slope for annealed (circles) and fully light-soaked (triangles) states of selected a-SiC:H films prepared with different H-dilution ratios but fixed $CH_4:SiH_4$ gas flow ratios of 2:3 or 1:1.5 (in sccm). The result for a Solarex (SLX) sample with a 25:1 H-dilution ratio, deposited at a substrate temperature of $\sim 300^\circ C$, is given as the horizontal broken line.

Fig. 18 (a) Dark conductivity versus $1000/T$ (K^{-1}) in the annealed state for selected a-SiC:H films prepared with different H-dilution ratios and a fixed $\text{CH}_4:\text{SiH}_4$ ratio of 2:3 (in sccm).

Fig. 18 (b) Room temperature conductivity (solid points) and activation energy (open points) plotted as a function of H-dilution for a series of films with fixed $CH_4:SiH_4$ ratio of 2:3 (in sccm).

Fig. 19 Photoconductivity as a function of generation rate for two a-SiC:H films prepared with (triangles) and without (squares) H-dilution in both light soaked (solid points) and annealed (open points) states. The H-dilution level in this case was 20:1 and the $\text{CH}_4:\text{SiH}_4$ gas flow ratio was 2:3 (in sccm) for both films.

midgap defect density (see Fig. 16), does not translate into a greater degradation of the photoresponse.

Figure 20 shows the electron mobility-lifetime product for three a-SiC:H samples prepared in this study: one without H-dilution, one with 2:1 dilution ratio, and the third with 20:1 ratio. The results for a fourth film received from Solarex is also included for comparison. This latter film was prepared with a 3:2 CH₄:SiH₄ ratio, leading to a conventional energy gap of ~1.95 eV. In addition the substrate temperature was ~300°C; the H₂:(SiH₄+CH₄) ratio was 25:1; the pressure was 0.5 Torr; and the rf power was 110 mW/cm². This is the same sample whose subgap absorption characteristics are included in Figs. 16 and 17 (horizontal broken lines). In the annealed state, the Solarex sample exhibits the highest $\mu\tau$ -product. At a generation rate of 10¹⁹ cm⁻³s⁻¹, our a-SiC:H sample with 20:1 is only slightly lower than the Solarex sample. The results for the low dilution materials are another factor of 5 lower still. The $\mu\tau$ -products in the fully light-soaked states are also provided and reveal that the film with the 20:1 ratio now exhibits the best electron photoresponse among the four samples.

Table II compares some of the properties of the Solarex sample with one of our 20:1 H-dilution samples. The point to be made from such a comparison is that the material properties are quite similar. The main difference between the preparation conditions, other than the CH₄:SiH₄ ratio which controls the optical gap, is the higher substrate temperature for the Solarex sample: 300°C versus 250°C for our material. We must stress, however, that the Solarex sample is no longer considered to be the best possible 1.95 eV (conventional Tauc gap) alloy material for incorporation into solar cells. More recent research at Solarex has led to a new generation of alloys prepared at much lower temperature that shows improved fundamental materials parameters (e.g., sub-gap absorption and Urbach tail slope), and (more importantly) when incorporated into solar cells, leads to improved performance. (See Section on the Solarex Baseline Series). Thus, in future optimization of our alloys for devices, we must also perform depositions as a function of substrate temperature.

To conclude this section, it is pertinent to emphasize that the improvements in the electronic properties of the alloys through enhanced H-dilution (and attributed to improved microstructure; see Sec. 6) are achieved in both *fully light-soaked* and *annealed* states. However, these improvements are, in fact, smaller than those obtained upon annealing the alloys in the fully light-soaked state (see Figs. 19 and 20). An obvious practical implication of this latter observation is that, in comparing samples prepared under different conditions, it is important to ensure that the materials are in the same state (i.e., either fully light-soaked or fully annealed, as has been done here). Furthermore, because of the magnitude of the instability of the alloys (and its potential variability with alloy preparation conditions), it is important to seek improved properties in the light-soaked state. Another more fundamental implication also follows from the observations. Because the microstructure of the film does not change upon annealing from the fully light-soaked state, the

Fig. 20 Electron mobility-lifetime product as a function of generation rate for four a-SiC:H films at different H-dilution ratios in both light-soaked (solid points) and annealed (open points) states. The H-dilution levels for our samples were 20:1, 2:1, and 0:1 and the $\text{CH}_4:\text{SiH}_4$ gas flow ratio was 2:3 (in sccm). For the Solarex (SLX) sample the H-dilution ratio was 25:1, and the $\text{CH}_4:\text{SiH}_4$ ratio was 3:2.

Table II

Sample Number	$E_{\text{Tauc}}(\text{eV})$ 2.0-2.4eV	$E_{\text{Tauc}}(\text{eV})$ 2.3-2.6eV	$E_{\text{Cody}}(\text{eV})$ 2.0-2.9eV	E_0 (meV)		$\alpha(1.2\text{eV})$ (cm^{-1})		$\sigma_{\text{ph}} (\Omega^{-1}\text{cm}^{-1})$		$\mu\tau$ ($\text{cm}^2 \text{V}^{-1}$)		E_{σ} (eV)	σ_{RT} ($\Omega^{-1}\text{cm}^{-1}$)	σ_0 ($\Omega^{-1}\text{cm}^{-1}$)
				ann.	sat.	ann.	sat.	ann.	sat.	ann.	sat.			
SLX	1.90	1.96	1.88	55		0.32	9.80	1.4E-6	8.0E-9	2.9E-7	1.7E-9	1.00	1.0E-11	6.3E+5
EC1B	1.87	1.94	1.90	54	60	0.61	9.59	9.4E-7	2.3E-8	2.0E-7	4.0E-9	0.88	2.8E-11	5.3E+4

Table II A comparison of some of the properties of our typical a-SiC:H film prepared in this study with a 20:1 H-dilution ratio, and one prepared by Solarex with a 25:1 ratio. Included are three measures of the gap (the higher-energy-range Tauc extrapolation corresponding to the conventional method), the Urbach tail inverse slope, the absorption coefficient at 1.2 eV, the photoconductivity and electron mobility-lifetime product at a generation rate of $3 \times 10^{19} \text{ cm}^{-3}\text{s}^{-1}$. The latter four parameters are given in annealed (ann.) and fully light-soaked states (sat.). The conductivity activation energy, room temperature conductivity, and conductivity intercept are given in the last three columns.

electronic structure of the material (as measured, for example, by the light induced defect concentration) appears to be a more important factor controlling material transport properties than is microstructure, at least over the range of microstructural variation explored here. The importance of the stability issue will be treated again in Sec. 7.

6. Growth and Properties of a-SiC:H: Discussion

A general conclusion based on the results of the previous two sections is that the favorable surface processes in the initial nucleation and growth stages that lead to a dense microstructure for alloys prepared with increasing H-dilution, are also accompanied by improvements in the electronic characteristics. These improvements include a lower midgap density of states, a steeper Urbach edge, and a higher electron photoresponse, all achieved while maintaining the same optical gap. However, there is some evidence that the alloys prepared with high H-dilution ratios are more susceptible to light induced degradation than the alloys prepared without dilution: the subgap absorption coefficient increases by a factor of 30 for the former films whereas only by a factor of 10 for the latter. This may be related to a higher concentration of strained bonds in the H-diluted films. In fact, such films tend to be highly stressed and special procedures and care must be taken to improve film adhesion to prevent spalling which destroys the film. [For example, if the very edges of the substrate are scribed with scratch lines for stress relief, then it tends to prevent the film from spalling from the edges of the substrate, the most commonly observed failure mode. (For the same reason similarly-prepared films on textured transparent conducting oxides tend to show no adhesion problems.) Atomic hydrogen treatments of glass substrates before growth have also been successful in promoting adhesion.]

It is of interest to discuss the relationship between the improved monolayer level growth characteristics and the improved electronic properties. It is not unreasonable to propose that the two observations are unrelated causally, since the growth process involves the movement of a majority of species on the surface, whereas only a fraction of the atoms control the observed electronic characteristics. However, the growth of single crystal layers is one application in which the connection between surface processes and defect concentrations is well established. This has even led to new techniques such as migration-enhanced epitaxy, a technique in which precursors are given more time to diffuse on the surface and bond at the desired sites of the crystal. In the case of amorphous semiconductors a similar connection can be made. When the average surface diffusion length for precursors is high, for example through an increase in passivation of the surface or a reduction in high sticking coefficient precursors in the plasma, a reduction in the density of void structures may occur. This may, in turn, reduce the width of the band tails, for example. A causal connection between surface processes during growth and ultimate electronic properties is supported not only by this study of a-SiC:H alloys, but also by a similar study of a-Si:H prepared from pure

SiH_4 , as a function of substrate temperature, plasma power, and inert gas dilution [1,4]. In the study of [4], maximum surface smoothening after thin film coalescence and hence maximum precursor surface diffusion was observed to occur under the conditions that lead to optimum electronic quality.

We must also consider the possibility that the deposition conditions influence the electronic properties through the processes of near- and sub-surface equilibration of H, rather than through the processes of precursor surface diffusion that establishes the ordering of the SiC network. Although both processes may be equally important in the ultimate electronic properties of the material, it is of interest to ask whether one or the other of the two processes are dominant in their effects on the electronic properties. At least in our studies of a-Si:H, we have found that H interacts and equilibrates with the a-Si:H surface in the growth environment on a faster time scale than previously estimated [6]. The previous estimates were based on H-diffusion coefficient measurements obtained from secondary ion mass spectrometry (SIMS) studies of a-Si:H/a-Si:H:D multilayers which are found not to be relevant for atomic H injected at the surface during growth. Thus, H appears to be in equilibrium with the near-surface even for growth rates known to provide poor electronic quality a-Si:H. Based on these considerations we suggest that the surface processes of Si network formation exerts a dominant influence on the electronic properties. Further studies of H-interaction with the near- and sub-surface a-SiC:H is required before coming to such conclusions for the alloys as well.

Finally, it is of interest to assess the implications of the results so far for alloy preparation. The results for the electronic properties suggest that 20:1 H-dilution ratio leads to the most desirable properties, such as a steep Urbach tail and a low $\alpha(1.2 \text{ eV})$ (see Figs. 16-17). Thus, it seems reasonable to state that the optimum H-dilution condition for amorphous alloy preparation is the maximum level prior to the onset of crystallite formation. For our system this appears to occur at H-dilution ratios between 20:1 and 40:1. For example, Fig. 21 shows the absorption spectrum for a film prepared with a 40:1 H-dilution ratio. One can see that $\alpha(1.2\text{eV})$ for this film is more than an order of magnitude larger than that for the films prepared with a 20:1 ratio (see Fig. 16). The shape of the absorption edge is clearly different than that of the alloys prepared at lower ratios, thus indicating a microcrystalline structure.

Based on the real time ellipsometry-deduced structural properties alone, one would come to similar conclusions concerning the optimum H-dilution ratio for our alloys. The clearest trend is in the magnitude of the surface smoothening, which continues to increase up to a dilution ratio of 25:1. This indicates that the precursor surface diffusion continues to show improvement to this point. Insufficient statistics for the void volume fraction at a 25:1 dilution ratio, prevent us from making the corresponding conclusion based on the ultimate density of the film. However, the statistics of Fig. 6 shows that improvements in density do extend to 20:1 dilution. As noted earlier, for dilution ratios above 25:1, the films show indications of microstructural degradation due to in

Fig. 21 Absorption coefficient for an annealed SiC:H film prepared with a H-dilution ratio of 40:1 and a CH₄:SiH₄ ratio of 1:1.5 (in sccm). The unusual shape of the absorption edge suggests the presence of microcrystallites.

situ etching. This degradation presages the formation of the microcrystallites which become evident at higher dilution. This conclusion is also consistent with the available electrical measurements.

7. Optical Properties of Solarex Baseline Series

To meet the goals of the NREL Wide Gap Team, we have undertaken measurements of a series of three wide gap materials prepared by Solarex. Three samples with numerical labelling, A3006, A3018, and A3019 have been received. Although the details of the preparation have not been made available, A3006 and A3018 are a-SiC:H alloys and A3019 is a wide gap variety of a-Si:H. We have measured absorption spectra over a wide photon energy range for these materials. These measurements are a part of an extensive characterization effort performed by the Team. The results will be used as a baseline in future attempts to prepare improved wide gap materials.

Figure 22(a) shows the absorption spectra for the baseline series in the sub-gap and near-band-edge regions obtained from dual beam photoconductivity and transmission and reflection spectra of the materials in their annealed states. Figure 22(b) provides data over the full accessible range with the inclusion of spectroscopic ellipsometry data. Table III summarizes the information that was extracted from Figs. 22, as well as measurements performed in the fully degraded state, achieved through accelerated light soaking. The conventionally-defined Tauc gap is obtained from the higher energy range where $(\alpha E)^{1/2}$ from T&R spectra tend to be linear vs. E and is given in the third column.

First it is surprising that the a-Si:H material in Table III with the narrowest gap exhibits the highest subgap absorption coefficient in the annealed state, and its Urbach tail is quite shallow as well, with an inverse slope of ~ 64 meV. Because its optical gap parameters are so close to those of standard a-Si:H, this material appears to be of limited use if its subgap absorption characteristics are any indication of device performance. In contrast, sample A3006 exhibits superior characteristics in the annealed state considering that its conventional optical gap is 1.94 eV. These characteristics include an Urbach tail as steep as that of high quality a-Si:H (~ 50 meV) and a low sub-gap absorption coefficient [$\alpha(1.2\text{eV})=0.1\text{ cm}^{-1}$]. It is clear that (pending further information on this sample provided by other Team members), it provides an excellent baseline for possible future improvements in wide band gap materials, at least in the annealed state. Upon light-soaking, the subgap absorption increases greatly, however, and in this state its optical characteristics are comparable to our best sample, also in the saturated state [$\alpha(1.2\text{eV})=10\text{ cm}^{-1}$ and $E_0=57$ meV]. The results seem to underscore a general trend in the midgap absorption characteristics of a-SiC:H alloys: the better the sample is in the annealed state, the more it degrades under light-soaking. This is an issue that the Wide Gap Team needs to address in the future.

Fig. 22 (a) Absorption spectra for Solarex wide-gap materials in the annealed state from a combination of dual beam photoconductivity and transmission and reflection (T&R) spectra. These results were obtained as our contribution to the Wide Gap Team effort. (See Table III for a summary of the parameters deduced from these data.)

Fig. 22 (b) Absorption spectra for Solarex wide-gap materials in the annealed state from a combination of dual beam photoconductivity, transmission and reflection (T&R) spectra, and spectroscopic ellipsometry. These results were obtained as our contribution to the Wide Gap Team effort. (See Table III for a summary of the parameters deduced from these data.)

Table III

Sample Number	E_{03} (eV)	E_{Tauc} (eV) 2.0-2.4eV	E_{Tauc} (eV) 2.3-2.6eV	E_{Cody} (eV) 2.7-3.1eV	E_0 (meV)		$\alpha(1.2\text{eV})$ (cm^{-1})	
					ann.	sat.	ann.	sat.
A3006(a-SiC:H)	1.84	1.85	1.94	1.88	50	56	0.10	6.86
A3018(a-Si:H)	1.74	1.81	1.86	1.77	64	72	1.86	32.80
A3019(a-SiC:H)	1.94	1.92	2.02	1.92	63	70	0.62	12.47

Table III Parameters deduced from the absorption spectra $\alpha(h\nu)$ of Solarex wide gap samples in the annealed and light-soaked states: E_{03} (energy at which $\alpha=10^3 \text{ cm}^{-1}$), wide range Tauc gap (from T&R), conventional Tauc gap (from T&R and ellipsometry), Cody gap (from ellipsometry), inverse slope of the Urbach tail, and absorption coefficient at $h\nu=1.2 \text{ eV}$. The photon energy ranges used in the gap extrapolations are provided in each case. This study was performed as part of the Wide-Gap Team effort.

8. Development of Real Time Control of Alloy Grading

As the optimization of amorphous semiconductor solar cells progresses into the future, the capability of generating a prescribed gradient in the band gap of a material throughout the *i* layer may be desired. The theoretical form of the gradient required to improve cell efficiencies may be determined through solar cell modeling programs, for example. In order to put such theory into practice in a sufficiently controlled fashion for high reproducibility and yield, it is possible to use real time ellipsometry as a sensor in a monitor-control loop. There are a number of possible approaches for accomplishing this. These approaches differ in how the optical measurements collected in real time are employed to determine the optical band gap at room temperature.

The ultimate solution of course, is to obtain the gap directly from an analysis of real time spectroscopic ellipsometry measurements collected with a multichannel detection system such as the one developed in our laboratory. For example, Fig. 23 shows the optical gap determination from such measurements collected in real time in 320 ms during the growth of a-SiC:H using different CH₄:SiH₄ flow ratios from 0:5 to 3:2. For this series of samples, the H-dilution ratio, H₂:(CH₄+SiH₄), is 4:1, and the thickness of each of the films at the time of data acquisition is about 150 Å. In Fig. 23, the optical gaps are obtained by the method of Cody for the same reasons as were discussed earlier. This method involves plotting $\epsilon_2^{1/2}$ versus energy and extrapolating the observed linear behavior to the energy axis in order to read off the gap. There are a number of disadvantages to this "ultimate solution". First it involves a complex analysis that requires determining, in addition to ϵ_2 , the layered structure of the sample as shown in Fig. 1. Because this analysis is very computation intensive, it may be impossible to apply with sufficient speed to provide a control response time of about 1 second. Another less serious problem is that the optical gap determined in this way corresponds to a measurement temperature equal to the substrate temperature, 250°C in this case. Thus, an additive correction must be applied to the measured gap value to get the anticipated room temperature value.

Another much simpler way of performing real time control of the compositional profile is proposed here. For a given series of samples prepared under specific fixed conditions (e.g., substrate temperature, T_s , total pressure, p_{tot} , H-dilution etc.) such that the only variable is the CH₄:SiH₄ flow ratio, we can develop an empirical correlation between the room temperature optical gap and the dielectric function of the a-SiC:H film at a fixed photon energy, substrate temperature, etc. For example, Figure 24 shows a graphical depiction of the correlation between the room temperature optical gap and the dielectric function of the a-SiC:H at 3.2 eV and 250°C, for the fixed conditions of $T_s=250^\circ\text{C}$, $p_{tot}=0.8$ Torr, and H-dilution of 4:1. The locus of points corresponds to the values of (ϵ_1, ϵ_2) observed in real time for a continuous range of room temperature optical gaps achieved through continuous variation of the flow ratio. Because the optical gap along the curve in Fig. 24 uniquely defines the observed (ϵ_1, ϵ_2) values, the local slope of the 3.2 eV ellipsometry

Fig. 23 Optical gaps deduced from real time measurements at a sample temperature of 250°C using the $\epsilon_2^{1/2}$ extrapolation of Cody. These films were deposited to 150 Å with different $\text{CH}_4:\text{SiH}_4$ ratios and a fixed $\text{H}_2:(\text{SiH}_4+\text{CH}_4)$ ratio of 4:1.

Fig. 24 Dielectric function trajectory at 3.2 eV and a sample temperature of 250°C, corresponding to all possible flows ratios, $\text{CH}_4:\text{SiH}_4$, from 0:5 to 3:2 (in sccm) used in the preparation of a-SiC:H films of variable C-content. The conventional Tauc gaps at room temperature corresponding to the different flow ratios are noted alongside the curves. Such a calibration is needed in order to deposit graded a-SiC:H layers under real time control.

trajectory provides a unique definition of the gap. This calculation is relatively straightforward and can be done in less than a second of computer time.

Thus, with the approach described here, we can obtain an instantaneous measure of the optical gap for 20 Å increments in film thickness, and the information can be compared to a target value. If an error is detected between the measured and target value, the flow meter can be adjusted to reach the target value. In this way, any arbitrary band gap profile as a function of thickness can be obtained. Additional progress on this unique capability will be made in the third phase of our work. Although the present work focuses on the wide gap a-SiC:H system, this capability may be most beneficial for the low gap a-SiGe:H system.

9. Interaction of H with Various Transparent Conducting Oxides (TCO's)

Early in our study of transparent-conducting-oxide (TCO)-related issues, we anticipated that atomic H exposure of the TCO substrate in the initial stages of a-SiC:H/TCO interface formation was the dominant factor that controlled the modification of the TCO properties at the contact. Later, this view was supported by an extensive study of the growth of a-SiC:H on TCO's that will be discussed in the next section [11]. As a result, in our initial experimental studies, we exposed different TCO's to atomic H generated by a filament heated in H₂ gas (without concurrent film deposition). Our earlier research showed that the hot filament was an effective way of generating low energy atomic H [6]. During exposure, the TCO samples were normally held at the typical deposition temperature for a-SiC:H, 250°C. The resulting TCO modifications could be characterized easily, and the results have also provided insights into the more complex process of concurrent deposition and TCO interaction.

Our H-exposure study was performed on three TCO's, ZnO and In₂O₃:Sn (ITO) prepared by sputtering, and SnO₂ prepared by CVD. The later studies of a-SiC:H growth on TCO's described in the next section were confined to ZnO and SnO₂, materials obtained from our Wide Gap Team industrial partners (USSC and Solarex). Figure 25 shows real time ellipsometry results for the exposure of the three TCO's at 250°C to a W filament (5 cm long by 0.025 cm diam.) heated at 28 W in an atmosphere of H₂ at 8 mTorr. The filament was mounted behind the sample holder, without direct line-of-sight to the sample surface. In this experiment, thin TCO's were used; the SnO₂ and ITO were ~500 Å and the ZnO was ~300 Å. The purpose of Fig. 25, which shows the time evolution of the real part of the optical functions at 1.6 eV, is to assess the time scale and approximate magnitude of the interaction of H with the TCO. It is clear from Fig. 25 that the most rapid change in optical properties occurs for SnO₂, which appears to be the least stable of the three materials in the reducing environment. The optical conversion of this material has fully saturated after 7 min H-exposure. In contrast, ZnO shows very little change on this scale of $\langle \epsilon_1 \rangle$. The strong oscillations in the ITO and SnO₂ data are interference-related. In other words, if the real

Fig. 25 Real part of the pseudo-dielectric function at 1.6 eV, plotted as a function of time during a 25 min exposure of three different TCO's to thermally-generated atomic H: $\text{In}_2\text{O}_3\text{:Sn}$, SnO_2 , and ZnO . The TCO's were held at 250°C during exposure. The H was generated from 8 mTorr H_2 gas using a filament heated to $\sim 2000^\circ\text{C}$, without direct line of sight to the sample. This figure reveals the time scale of the reduction process.

part of the index of refraction of the film changes significantly with time, then fringe oscillations will be swept out with time. It turns out that the weaker fringe oscillations in the SnO_2 arise because the initial specular material becomes hazy with H-exposure whereas the sputtered ITO remains specular.

A further analysis of these optical changes is very helpful in a study of the more complex a-SiC:H/TCO interfaces to be described in the next section. First, we find that the optical changes associated with SnO_2 exposure are not readily interpretable because the initially specular film becomes gray and hazy upon H-exposure. Apparently the H preferentially reduces the oxide in the boundaries between grains, whose sizes appear to be comparable with the wavelength of visible light. The resulting spatial variation of optical properties, between metallic-like and insulator-like, leads to the extensive light scattering which makes the real time ellipsometry uninterpretable.

In contrast, the sputtered ITO has a very fine grain structure (grain size $<100 \text{ \AA}$), and a comparison of its optical properties before and after H-exposure is easily interpretable in terms of a decrease in thickness by atomic H-etching, along with a complete reduction of the ITO to metal throughout the thickness. Figure 26(a) provides experimental SE data, expressed as (ψ, Δ) , for the ITO film after a 24 min exposure (points). The solid line best fit, which superimposes onto the data on the scale of Fig. 26(a), was obtained by assuming that the $\sim 500 \text{ \AA}$ thick ITO film converts to a $\sim 300 \text{ \AA}$ thick Drude metal containing a high volume fraction of voids, 0.60 ± 0.02 . The characteristic parameters of the metal include (i) a plasma frequency of $\omega_p = 1.26 \times 10^{16} \text{ Hz}$, (ii) an electron relaxation time of $\tau = 1.64 \times 10^{-16} \text{ s}$, and (iii) a high frequency dielectric function of $\epsilon_0 = 2.80 \pm 0.11$. The resulting dielectric function with these parameters is shown in Fig. 26(b). We expect that these optical properties are characteristic of an In:Sn metallic alloy. Although the composition of this metal is not purely Sn, we will use the response of Fig. 26(b) as characteristic of the metallic contamination that occurs at the a-SiC:H/ SnO_2 interface, as well. Any errors generated in making this assumption appear to affect the absolute calibration of the metallic mass thickness at the interface, but do not influence the relative values and the overall conclusions of the study.

Although the changes in the ZnO in Fig. 25 are negligible in comparison to those for SnO_2 and ITO, the deduced effect on the optical properties is very interesting. Figure 27 shows the optical functions of ZnO between 2.0 and 4.5 eV at 250°C , obtained from measurements collected in real time just before and after a 45 min H-exposure. After 45 min, complete saturation of the optical change has occurred. From the analysis that led to Fig. 27, we conclude that any etching effects (reduction in the thickness of the film) are small ($< 0.005 \text{ \AA/s}$). There is a detectable change in the optical properties in Fig. 27, but it **cannot** be attributed to any reduction of the ZnO to form Zn metal. This is clear from the fact that the film retains its original transparency. Instead the optical change can be described as an increase in the band gap, a shift in the critical points in the band structure to higher energy, and a concomitant reduction in the index of refraction in the visible range. One caveat must be made here, however. In performing the optical analysis of Fig. 27, we

Fig. 26 (a) Room temperature ellipsometric spectra (ψ , Δ) measured ex situ for a 300 Å layer of ITO after exposure to thermally-generated H for 25 min (points). During H exposure, the ITO was held at 250°C. The solid line is a fit to the spectra using a dielectric function computed assuming a mixture of a Drude (free-electron) metal with voids. The dielectric function of this mixture, associated with a low density In:Sn alloy film, is shown in (b).

Fig. 27 Dielectric functions for ZnO deduced from real time SE data before and 50 min after treatment by thermally-generated H. These measurements are characteristic of the optical properties at the treatment temperature of 250°C.

have assumed that when the optical change has saturated, the film has been modified throughout the full 300 Å thickness of the ZnO film. Although this provides an excellent fit to the data, it is somewhat difficult to distinguish a small optical change throughout a larger thickness, from a large optical change throughout a smaller thickness. For example, the band gap shift in Fig. 27 is 0.02 eV; however, if we assume instead that the modified thickness is only 20 Å (rather than ~300 Å), then the band gap shift becomes ~0.1 eV. A depth profiling measurement such as high-resolution SIMS would allow us to resolve this issue. At present samples for such a study have been deposited and await further analysis (see Sec. 11).

To obtain more information on the time scale and mechanism of the optical band gap shift for the ZnO in Fig. 27, we performed further analysis of the SE measurements obtained continuously in real time during H-exposure. In this analysis, we assume that when the optical change saturates, the final film is fully modified throughout its 300 Å thickness. Starting from this initial assumption, two different models were compared. In the first model, we proposed that the modification occurred in a reaction-limited process, uniformly throughout the entire thickness of the ZnO film. In the second model, we proposed that the modification occurred in a diffusion-limited process in which a diffusion front separating the near-surface ZnO:H, from the underlying ZnO, progressed in a layer-by-layer fashion throughout the thickness. Figure 28 (top) compares the time evolution of the parameter σ , which is a measure of the quality of the best fit model to the SE data, for the reaction- and diffusion-limited processes. From the much lower initial σ value for the diffusion-limited process, we find that such a model is a better approximation to reality. In the lower part of Fig. 28, the thicknesses of the modified ZnO:H and the unmodified ZnO as a function of time during exposure are presented. These results show that the H-exposure has a significant effect (~100 Å) in the first 30 seconds of exposure. This very fast reactivity of ZnO with H suggests that the modification of the ZnO will also occur in the SiH₄ plasma deposition environment.

Although we have identified a potential problem associated with H-diffusion into ZnO, it is not clear at this point how it relates to the electrical properties of the TCO in the device configuration. An increase in the optical gap of the ZnO *per se* may not influence the electrical behavior; however, the gap shift may be accompanied by other effects such as dopant passivation. The latter would lead to a decrease in the Fermi level of the TCO, increasing the resistivity greatly. An effect such as this may account for the lack of success in using this material in the solar cells even though its nominal properties suggest that it should be superior to SnO₂. Electrical studies of doped ZnO, performed before and after H-exposure are now underway. At this point in our study, we can conclude confidently that the near surface properties of the ZnO are modified from those of the as-deposited material as a result of H-incorporation. This is in contrast to previous reports by the Ecole Polytechnique group that the ZnO is unmodified, an erroneous conclusion based on more limited single wavelength ellipsometry data.

Fig. 28 The lower panel shows the thicknesses of the top ZnO:H material and the underlying unmodified ZnO that characterize the diffusion-limited modification of the material in thermally-generated atomic H at 250°C. The top panel shows the quality of the fit to the real time SE data (σ) plotted as a function of time for diffusion- and reaction-limited models. In the diffusion-limited model, the ZnO:H develops from ZnO in a layer-by-layer mode. In the reaction-limited model the ZnO:H develops uniformly throughout the film by volume. The former model (used in the lower panel) is deemed most appropriate.

A further point of interest is whether the H-incorporation that modifies the ZnO optical properties can be avoided in the initial stages of the a-SiC:H deposition by using a lower substrate temperature, which may limit the diffusion of H. Figure 29 shows real time ellipsometry measurements at 1.6 eV, collected in the first ~15 min of H-exposure of ZnO at different temperatures. The results show that there is no advantage gained by reducing the ZnO temperature to 150°C; the H-incorporation effect appears equivalent to that at 250°C. In contrast by reducing the temperature to 25°C, it appears that the diffusion of H into the ZnO is prevented. Thus, an interesting future experiment is to deposit the p-layer on the TCO at room temperature before adding the i-layer at 200-250°C. In this way, it may be possible to check whether the as-deposited TCO conditions are retained with this procedure. Another potentially useful observation is that when the H-modified ZnO is maintained at 250°C for several hours, the H tends to diffuse out from the material and revert to its original optical state. A process test under solar cell preparation conditions based on this observation is difficult to design since the overlying p-layer will most likely cap the modified ZnO, and the high H-chemical potential of the a-SiC:H will keep the H trapped in the ZnO during any attempted annealing step.

10. Growth of a-SiC:H on Transparent Conducting Oxides

Our initial studies of the growth of a-SiC:H on TCO's has been confined to undoped semiconductor material. The rationale for this is an attempt to separate the potentially complex effects due to combined TCO-modification and B₂H₆ interaction (CVD). Based on previous research, however, it appears that B₂H₆ decomposition is very slow on TCO surfaces (see Sec. 1). This is in contrast to its rapid decomposition on doped and undoped a-Si:H surfaces, which results in the activation of the surface for low temperature CVD (250°C) of a-Si:H:B from SiH₄+B₂H₆. Thus, we believe that the dominant problem associated with the TCO interface is the modification of the TCO by H incorporation or interface properties by metal contamination. Boron contamination most likely occurs as well, but will be quantified in a separate series of experiments so that the optical problem becomes tractable.

Thus, our approach in studying TCO-related issues is a step-by-step one. We have first studied the modification of TCO by atomic H (which will always be present in a PECVD discharge). Second, we have proceeded to study the growth and interaction of undoped a-SiC:H with the TCO. The third step is to study the effect of B₂H₆ exposure at the TCO under the growth conditions (partial pressure, gas flow, T_s) used for doped a-SiC:H. Finally, the full problem of p-type a-SiC:H growth on TCO will be attacked, using pieces from the separate studies to help with the interpretation. The first two steps have been completed and are reported here. The second two steps have been delayed by the installation of safety precautions associated with the use of B₂H₆. The final results will be reported in Phase III.

Fig. 29 Ellipsometric parameter ψ at 1.6 eV versus time during a ~15 min exposure of ZnO samples to thermally-generated atomic H. In this series of experiments, the samples were held at different temperatures, 25°C, 150°C, and 250°C.

Before undertaking our ellipsometry experiments on the growth of a-SiC:H on SnO₂ and ZnO, we performed simulations in an attempt to identify features in the raw (preprocessed) (ψ, Δ) spectra for an ultrathin a-SiC:H/TCO structure that provide at least a relative measure of metallic contamination. It turns out that the metal contamination strongly increases the optical absorption of a-SiC:H in the neighborhood of the band edge, over that observed in the absence of the metal. This leads to a strong dampening of the interference fringe pattern generated by the combined a-SiC:H/TCO structure. This effect is apparent in the ellipsometric parameter ψ between 1.5 and 3.0 eV as shown in Fig. 30. This figure shows simulated ψ spectra for an a-SiC:H/SnO₂/c-Si structure, where the a-SiC:H and the SnO₂ layers are 90 Å and 500 Å thick, respectively. The different curves correspond to different levels (in volume percent) of metal contamination, dispersed throughout the 90 Å a-SiC:H. As noted above, the metal optical properties are assumed to be those deduced from the ITO study of Fig. 26. Through this effect, SE and real time SE can detect the presence of metal with fairly high accuracy for the full a-SiC:H/TCO structure.

Figure 31 shows the results of an SE analysis for an a-SiC:H film prepared under H-dilution conditions that lead to a high density material, i.e., an H-dilution ratio H₂:(CH₄+SiH₄) of 20:1. Other conditions include a CH₄:SiH₄ ratio of 2:3, and a substrate temperature of 250°C. The solid lines are the experimental (ψ, Δ) spectra, focusing on the low energy range where the effect of metal contamination is the greatest. The short-dashed line is the best fit sample structure that does not include metal contamination. Such a sample structure includes three layers (see lower inset): (i) an interface layer that simulates the roughness present at the a-SiC:H/SnO₂ interface, (ii) a bulk a-SiC:H layer, and (iii) a low density surface layer that simulates roughness at the a-SiC:H surface, which is generated in part by a conformal coverage of the rough SnO₂ surface. Although the best fit free parameters for this model are realistic (i.e., the surface and interface roughness layers are similar in magnitude, indicating the a-SiC:H conformally covers the roughness on the SnO₂), the ψ spectrum cannot be fit closely. This state of affairs is common to any model that uses a structure composed of weakly absorbing layers, and the fit to ψ can only be rectified by assuming metal contamination, as demonstrated in the simulations of Fig. 30.

The long dashed line in Fig. 31 uses the same realistic structural model [(surface roughness)/(bulk a-SiC:H)/(interface roughness)/(bulk SnO₂)/substrate], but assumes that metal is dispersed uniformly throughout the interface roughness layer. This allows for the possibility that the metal is present both in the near-surface SnO₂ and the near-interface a-SiC:H. The parameters of this model are shown in the upper inset, and again the surface and interface roughness layers are close, indicating that the a-SiC:H covers conformally an ~70 Å thick roughness layer on the SnO₂. The key to obtaining a good fit to the ψ spectrum, however, is the incorporation of 7 vol.% metal dispersed throughout the 70 Å interface roughness layer. Such metal contamination is not unexpected given the results of the previous section concerning the ease of reduction of the SnO₂ to Sn metal with atomic H exposure.

Fig. 30 Simulation of the effect on the ellipsometric ψ spectrum for $1.5 \leq h\nu \leq 3.0$ eV when the metal contamination level near the interface between SnO₂ and a-SiC:H is increased. In this simulation, the metal is assumed to be dispersed uniformly throughout a 90 Å thick a-SiC:H layer with metal volume fractions ranging from 5% (mass thickness: 4.5 Å) to 30% (mass thickness: 27 Å).

Fig. 31 Best fits to ellipsometric (ψ, Δ) spectra for a ~ 120 Å film of a-SiC:H on SnO₂, obtained in an ex situ measurement. The a-SiC:H was prepared at 250°C with a CH₄:SiH₄ ratio of 2:3 (in sccm), and a H₂:(SiH₄+CH₄) ratio of 20:1. Two different models are employed. One (a) includes metal at the a-SiC:H interface and the other (b) does not. Both models use a realistic three layer structure for the a-SiC:H film, including interface roughness, bulk, and surface roughness layers.

Before proceeding, however, we need to make some remarks on the limitations of the model developed in Fig. 31 (top inset). We find that the fit to the data is sensitive to the total mass thickness of metal (through the height of the peak in ψ), but it is not sensitive to exactly where that metal is located. For example, we cannot distinguish between a structure in which 50 vol.% metal is confined to a 10 Å layer from one in which 10 vol.% is confined to a 50 Å layer. (In both cases the mass thickness is 5 Å.) This problem arises in part because of the non-planarity of the a-SiC:H/SnO₂ interface. Another limitation is the absolute calibration of the metal content, which may be in error due to the use of an inappropriate metal dielectric function (deduced for an In:Sn alloy obtained by reduction of ITO). As noted above, such a problem does not influence the relative comparisons made below and the overall conclusions of the study.

Because of the more time consuming nature of the spectroscopic analysis of Fig. 31, we reverted to an inspection of real time single wavelength ellipsometry trajectories in order to compare the metal contamination problem from run-to-run more easily. Figure 32(a) shows the (ψ , Δ) trajectories obtained during the growth of two a-SiC:H alloy films on SnO₂. For the open triangles the film was prepared with a CH₄:SiH₄ ratio of 2:3 without H-dilution, whereas for the open squares the film was prepared with the same CH₄:SiH₄ ratio but with a H-dilution ratio H₂:(CH₄+SiH₄) of 20:1. This latter film is the same one that was analyzed spectroscopically in Fig. 31. The lower part of the figure shows the initial ~20 Å of a-SiC:H growth on an expanded scale in order to focus on the SnO₂ reduction process. The reduction process is indicated by a decreasing value of ψ with increasing metal content at the interface as in the simulations in Fig. 30. The solid lines have been calculated assuming that the film forms on the rough SnO₂ surface with the volume percentage of metal as indicated. The open circles represent 10 Å increments in this model. In the experimental trajectory, the initial decrease in ψ is clear evidence of metal contamination. By comparing to the model trajectories, we conclude that 50 vol.% metal forms within the film during the deposition of the first 10 Å of film. Because the SnO₂ is rough, however, this 10 Å layer conformally covers the substrate. We conclude then that the results of the single wavelength and spectroscopic analyses are in agreement in the important parameter, the metal mass thickness. In the latter case it is (0.07)(70 Å)~5 Å, and in the former case it is (0.50)(10 Å)~5 Å. Thus, the equivalent of a few monolayers of metal form at the rough a-SiC:H/SnO₂ under the H-dilution conditions used here.

It is also important to assess the effect of the a-SiC:H growth conditions on the extent of metal contamination. From the single wavelength trajectories in Fig. 32(a), it is clear that there is no detectable free metal at the interface between a-SiC:H and the SnO₂ when the alloy is prepared without H-dilution. We estimate that the limit of sensitivity to metal contamination is <0.5 Å mass thickness. Apparently the a-SiC:H prepared without H-dilution grows sufficiently fast in comparison to the speed of the H-interaction so that the depositing semiconductor protects the TCO from reduction. Figure 32(b) shows that this is also the case for a-Si:H prepared from pure SiH₄,

Fig. 32 (a) Experimental and simulated trajectories in (ψ, Δ) at 2.45 eV obtained in real time during the growth of a-SiC:H on SnO_2 (top panel). The lower panel is an expanded view of the initial growth stage ($\sim 12 \text{ \AA}$) for the trajectories of the upper panel. The open triangles are for an a-SiC:H film prepared with a $\text{CH}_4:\text{SiH}_4$ ratio of 2:3 (in sccm), but with no H-dilution. The open squares are for a film prepared with the same $\text{CH}_4:\text{SiH}_4$ ratio, but with a $\text{H}_2:(\text{SiH}_4+\text{CH}_4)$ ratio of 20:1. The solid lines depict models for the growth of a-SiC:H on a rough SnO_2 surface with different volume fractions of metal in the resulting SnO_2 interface layer. The open points denote $2 \text{ \AA}$ thickness increments in the a-SiC:H (from 0 to $10 \text{ \AA}$). (b) as in (a) except that the open triangles are for an a-Si:H film prepared using pure SiH_4 under otherwise similar conditions as for the alloys.

but under otherwise identical conditions as the alloys prepared without dilution. This figure is identical to that of Fig. 32(a), except that the trajectory represented by open triangles is for unalloyed a-Si:H growth on the SnO₂.

The results of Fig. 32(b) appear to be at odds with earlier published reports from the Ecole Polytechnique group, describing a strong a-Si:H/SnO₂ interaction. Either one of two possibilities explain this: (i) our a-Si:H growth conditions are gentler or generate less atomic H than those of the earlier report, or (ii) the SnO₂ used here resists reduction better than that of the earlier report. A summary of our results for amorphous semiconductor depositions on SnO₂ appears in Fig. 33 and Table IV. One additional point of interest revealed in the Table is that the metal contamination effect is reduced by about 60% (from 5 Å mass thickness to 2 Å) by reducing the substrate temperature to 170°C. This means that, for the SnO₂ employed here, it is more convenient and effective to avoid metal contamination by eliminating H-dilution in the gas formulation (rather than lowering substrate temperature) in the initial stages of a-SiC:H alloy growth on the SnO₂. Eliminating H-dilution may be difficult to do in some cases where the dopant gas is carried in H₂. The results of Fig. 33 and Table IV suggest that it may be acceptable to use H-dilution to the level of 5:1 with this SnO₂ without significant problems. In the future, we will assess whether it is feasible to prepare a µc-SiC:H alloy on SnO₂ by starting out with an a-SiC:H buffer layer to protect the SnO₂.

We have also studied the stability of the a-SiC:H/SnO₂ structures in laboratory ambients at room temperature over more extended time periods. We have focused on the structures in which free metal forms at the interface during the a-SiC:H growth process. Figure 34 shows the ellipsometric (ψ, Δ) spectra as a function of time for a-SiC prepared onto SnO₂ at 250°C with a H-dilution ratio H₂:(CH₄+SiH₄) of 20:1 and a CH₄:SiH₄ ratio of 2:3. The measurements were performed immediately after deposition, and 1 day, 2 weeks, and 3 months after deposition. It is clear from this figure that the interference-related peak in the ψ spectrum is gradually increasing over time, indicating that the near-interface absorption coefficient is gradually decreasing. A simulation has shown that this effect is not caused by oxidation of the a-SiC:H. In accordance with the simulation of Fig. 30, the effect instead appears to be caused by a "loss" of free metal at the interface. Because the a-SiC:H has reached full density with a 49 Å bulk-like layer (see top inset Fig. 31), it does not seem likely that O₂ or H₂O is diffusing from the ambient to reoxidize the interface metal. It seems more likely that (i) the metal is reabsorbed into the bulk of the SnO₂ through the diffusion of oxygen vacancies, or (ii) it diffuses into the a-SiC:H, where it is sufficiently dispersed to be invisible to the optical measurement. The effect in Fig. 34, if it does in fact represent metal reoxidation, leads to apparent full recovery after 2 months. Thus, if highly concentrated metal at the interface is detrimental to the performance of a device some improvement may be gained over time as a result of the effect shown in Fig. 34. Further study is needed to see if longer term annealing can promote the reoxidation effect.

Fig. 33 Mass thickness of metal detected at the a-SiC:H/SnO₂ interface plotted as a function of the H₂:(SiH₄+CH₄) ratio. The substrate temperature for this series of depositions was 250°C. A selected deposition with a dilution ratio of 20:1 and a substrate temperature of 170°C was also performed and analyzed. The results of this figure are summarized in Table IV.

Table IV

H ₂ -dilution ratio	0	2	5	10	20	80
Mass Thickness (Å) T=250°C	0	1	1	5	5	15
Mass Thickness (Å) T=170°C					2	

Table IV Mass thickness of metal at the a-SiC:H/SnO₂ interface, incorporated as a result of the reduction of the SnO₂, for different H₂ dilution ratios from 0:1 to 80:1 and two substrate temperatures used in the a-SiC:H preparation.

Fig. 34 Ex situ ellipsometric spectra for the sample of Fig. 31, consisting of about 120 Å of a-SiC:H on SnO₂. The a-SiC:H was prepared at 250°C with a CH₄:SiH₄ ratio of 2:3 (in sccm), and a H₂:(SiH₄+CH₄) ratio of 20:1. These measurements were obtained immediately after deposition, and then 1 day, 2 weeks, and 12 weeks after deposition.

Next, we will briefly describe aspects of the growth of a-SiC:H on ZnO. Our initial experiment was an assessment of the possibility of free metal contamination at the a-SiC:H/ZnO interface. For such a study, we concentrated on fitting the experimental (ψ, Δ) spectra for the a-SiC:H/ZnO structure at the lower energies, as in Fig. 31, where any metal is strongly absorbing and where the a-SiC:H and ZnO are weakly absorbing. The experimental results and best fit to the (ψ, Δ) spectra for a ~ 95 Å thick a-SiC:H film on ZnO are shown in Fig. 35. In this case the a-SiC:H was prepared with a substrate temperature of 250°C, a H-dilution ratio $H_2:(CH_4+SiH_4)$ of 20:1, and a $CH_4:SiH_4$ ratio of 2:3 (in sccm). It is clear from the figure that a very good fit can be obtained, in particular to the amplitude of the low energy interference fringe in the ψ spectrum, without including any metallic component in the model. Thus, the ZnO is not subject to reduction even when exposed to the 20:1 H-dilution plasma. This conclusion is consistent with the observed stability of ZnO in filament-generated H (see Fig. 25), but the conclusion is stronger since plasma H is more energetic than thermal H.

Another observation from Fig. 35 is that no interface roughness is required in the model of the a-SiC:H/ZnO structure, as in that for the a-SiC:H/SnO₂ structure. A related observation is that the final roughness on the 88 Å bulk a-SiC:H film is comparable (within ± 1 Å) to that for a-SiC:H deposited onto c-Si under similar conditions. These two observations indicate that the surface of the ZnO is very smooth on an atomic scale, and that the roughness on the over-deposited a-SiC:H is controlled, not by the substrate, but by the precursor surface processes on the a-SiC:H. This is in contrast to the observation for the SnO₂ in which the 70 Å of roughness on the over-deposited a-SiC:H surface is established by the corresponding roughness amplitude on the SnO₂ substrate. The differences between the surface structures of the TCO's may be related to the methods of deposition: ZnO by sputtering and SnO₂ by CVD.

We have also analyzed the data of the experiment of Fig. 35, assuming that the optical properties of the ZnO are modified by H incorporation from the $CH_4+SiH_4+H_2$ plasma similar to the effect observed in the H-exposure experiment (see the ZnO dielectric functions of Fig. 27). However, in Fig. 35, the overlying a-SiC:H is too thick to detect the relatively weak optical change that results (compare the magnitudes of the effects in Fig. 25). Thus, we studied the full real time data set collected during the growth of a-SiC:H on ZnO in an attempt to detect H-incorporation. In fact, a fairly large band gap shift of ~ 0.2 eV for the ZnO was apparent in the real time spectroscopic data, indicating that in the first 20-25 Å of a-SiC:H growth, the ZnO is modified in accordance with Fig. 27, but even more extensively as a result of the direct plasma exposure. We analyzed this data set assuming (as in Fig. 28) that the optical modification of ZnO by H occurs uniformly throughout the full 280 Å thick layer. Figure 36 shows the results in the first 100 s of a-SiC:H film growth during which the bulk layer grows to ~ 20 Å with a 20 Å surface roughness layer on top. The deposition conditions for the a-SiC:H were the same as those in Fig. 35.

Fig. 35 Best fit to ex situ ellipsometric (ψ, Δ) spectra for a ~ 95 Å film of a-SiC:H on ZnO. The a-SiC:H was prepared at 250°C with a $\text{CH}_4:\text{SiH}_4$ ratio of 2:3, and a $\text{H}_2:(\text{SiH}_4+\text{CH}_4)$ ratio of 20:1. The best fit model uses a two-layer structure for the a-SiC:H, including bulk and surface roughness layers. An excellent fit to the data is obtained without free metal or roughness at the a-SiC:H/ZnO interface.

Fig. 36 (a) Evolution of the low density surface layer thickness (solid points) in a one-layer model (circles) for $t < 60$ s during the initial nucleation of a-SiC:H on ZnO. The evolution of the low density surface layer (solid triangles) and the underlying bulk layer (open triangles) in a two-layer model is shown for $t > 60$ s. (b) Diffusion-limited conversion of the 280 Å ZnO substrate film from its initial as-deposited state (solid line) to a higher-gap hydrogenated state (broken line) in the first 60 s (20-25 Å) of nucleation of a-SiC:H on the ZnO. The a-SiC:H was prepared at 250°C with a $\text{CH}_4:\text{SiH}_4$ ratio of 2:3 (in sccm), and a $\text{H}_2:(\text{SiH}_4+\text{CH}_4)$ ratio of 20:1.

Figure 36(a) shows the evolution of the low density layer that simulates (i) isolated nuclei in the one layer model for the growing a-SiC:H, and (ii) the surface roughness in the two layer model. Also included is the increase in thickness of the bulk layer in the two layer model. The break between the one layer model is chosen at about 60 s, when the bulk layer thickness reaches a single monolayer ($\sim 3 \text{ \AA}$). Overall, the features in Fig. 36(a) are very similar to those of Fig. 1 for a-SiC:H growth on c-Si with 20:1 H-dilution. Isolated nuclei form, increase in thickness to about $25 \text{ \AA}$ whereupon they make contact to form the first bulk-like monolayer. After the first bulk-like monolayer forms, a process of surface smoothening sets in due to the high precursor surface diffusion length under H-dilution conditions. To be more quantitative, we can make the following comparisons between the results in Figs. 1, 35, and 36: (i) thickness of the a-SiC:H film when the first bulk monolayer forms: $25 \text{ \AA}$ for ZnO, and $21 \text{ \AA}$ for c-Si substrates; (ii) roughness thickness after $88 \text{ \AA}$ bulk film growth: $12 \text{ \AA}$ for ZnO (see Fig. 35), and $11 \text{ \AA}$ for c-Si substrate. Thus, the microstructural evolution for a-SiC:H on c-Si and ZnO substrates is identical within run-to-run repeatability.

We have observed some complications in the ZnO case, however. Figure 36(b) shows the modification to the ZnO that appears to occur in the first $\sim 1 \text{ min}$ or ($20\text{-}25 \text{ \AA}$) of a-SiC:H film growth. There is a gradual conversion of the ZnO from its as-deposited state to the hydrogenated state. It is interesting that the time scale of this conversion (1 min) corresponds to the time scale when the a-SiC:H nuclei are isolated and there is at least some surface area of the ZnO in direct contact with the plasma. However, we should not conclude that direct exposure of ZnO to atomic or ionic H is a necessary condition for ZnO modification. We have found that modified ZnO (i.e., ZnO:H) with a thin (but continuous) a-SiC:H film on top of it can be reverted to its initial state after a long term (12 hr) anneal. This suggests that H can leave (and possibly enter as well) the ZnO by way of the a-SiC:H overlayer. If this is the case, then it is difficult to avoid hydrogenation of ZnO, since it may be modified not only by direct exposure, but also by placing any hydrogenated layer on top of it. Such issues and future experiments needed to clarify them will be discussed in the next section.

11. Future Research Directions

In order to reach the goals set in our initial proposal for Phase III, as well as to redirect our work toward the future goals set by the Wide Gap Team, we must continue our efforts along the lines initiated here. The numbers in this list correspond to the topics highlighted in the Summary on the first page of this report.

(1 and 2) Our initial efforts in studying intrinsic a-SiC:H were undertaken in order to ensure that the properties of the alloys that we use in our interface structures are similar to those of

device-quality alloys of similar optical gap prepared at Solarex. Our material compares favorably to a Solarex film of similar optical gap prepared at $\sim 300^{\circ}\text{C}$ (see Table II). Since our initial studies, however, the state of the art has progressed, and more recent experience at Solarex suggests that better alloys are prepared at much lower temperatures. In future work, we also intend to optimize our intrinsic alloys as a function of substrate temperature using the 20:1 H-dilution ratio. In fact, lower substrate temperatures are preferable in forming interface structures due to the observed diminished reduction of the SnO_2 TCO at a substrate temperature of 170°C in comparison to 250°C (see Fig. 33). We will then use both temperature and gas pressure as variables in an attempt to optimize p-type a-SiC:H layers without utilizing extensive H-dilution which tends to be detrimental to the interface. The p-type layers will be characterized by sub-gap absorption spectra, void density, and dark conductivity versus temperature. In these further attempts, we will continue to correlate electronic characteristics with microstructural evolution and ultimate density for both intrinsic and p-type materials.

(3) In situ ellipsometry studies of $\mu\text{c-SiC:H}$ will be continued in an attempt to better understand the material, its properties, and its suitability for devices. We will alter the $\mu\text{c-SiC:H}$ growth environment by varying the $\text{CH}_4:\text{SiH}_4$ gas flow ratio while maintaining the H-dilution ratio constant at 80:1. In this way, we will see if the additional C-containing species in the gas phase exert any influence on the critical points in the band structure of the microcrystallites in the resulting two-phase (amorphous/crystalline) composite. The samples will also be studied by Raman spectroscopy for complementary characterization of the crystallites in the composite. Optical absorption spectra of the $\mu\text{c-SiC:H}$ thin films will be obtained and compared to the results for a-SiC:H, to assess potential advantages of the former in solar cells. If the materials show promise, they will be studied in real time during growth on ZnO, to see if the microcrystalline structure develops from the nucleation stage. In addition, such materials will be doped in attempts to place Fermi level closer to the conduction band edge than has been possible in the amorphous alloys.

(4) We will continue to collaborate with the industrial partners of the Wide Band Gap Team by assisting with optical measurements of materials and structures. Our initial work has established baseline optical properties, namely $\alpha(h\nu)$ for $0.8 \leq h\nu \leq 5$ eV in the annealed and light-soaked states, for three wide gap alloys prepared by Solarex. We have also characterized the structure of ZnO/Ag interfaces for USSC (work not described here). In the future, we intend to study pure Si-based wide gap materials at the request of ECD.

(5) Much more work needs to be accomplished in order to implement grading. We need to develop the optical equations that will allow us to convert the change in near-surface dielectric response, as measured by single-photon energy ellipsometry, to a near-surface band-gap. The equations need to be developed to take into account the 10-20 Å roughness layer that typically exists on the growing semiconductor surface. Once these equations have been developed, we need to install them in a real time monitoring and control loop, so that the calculated band gap is compared

Document Control Page	1. NREL Report No. NREL/TP-451-6135	2. NTIS Accession No. DE94000291	3. Recipient's Accession No.
4. Title and Subtitle In-Situ Characterization of Growth and Interfaces in a-Si:H Devices		5. Publication Date February 1994	
		6.	
7. Author(s) R. W. Collins, C. R. Wronski, I. An, Y. Lu, H. V. Nguyen		8. Performing Organization Rept. No.	
9. Performing Organization Name and Address Pennsylvania State University Materials Research Laboratory University Park, PA 16802		10. Project/Task/Work Unit No. PV431101	
		11. Contract (C) or Grant (G) No. (C) XG-1-10063-10 (G)	
12. Sponsoring Organization Name and Address National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393		13. Type of Report & Period Covered Technical Report 1 May 1992 - 30 April 1993	
		14.	
15. Supplementary Notes NREL technical monitor: B. von Roedern			
16. Abstract (Limit: 200 words) This report describes work to reach two goals—an individual goal and a wide-gap team goal. The individual goal was to investigate the "top junction" for defects using the spectroscopic ellipsometry technique. This will include an evaluation if specific defects are associated with C, B, Sn (diffusing from the transparent conducting oxide [TCO]) or Na (diffusing from the glass). It may include an assessment of the function of a graded a-SiC:H buffer layer. As defects are identified and characterized, their influence on the transport properties will be assessed. This should lead to better parameters used as input to models for the electronic materials and device performance. The goal of the wide-gap team was to demonstrate, characterize, and understand improved doped and undoped "wide gap" materials for use in achieving 15%-efficient stabilized photovoltaic modules ("wide gap" materials are defined by this team to have a band gap ≥ 1.9 eV). The major conclusions of the research are discussed in the report.			
17. Document Analysis a. Descriptors characterization ; growth ; interfaces ; amorphous silicon ; devices ; photovoltaics ; solar cells b. Identifiers/Open-Ended Terms c. UC Categories 271			
18. Availability Statement National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161		19. No. of Pages 80	
		20. Price A05	