Analysis of Si$_{1-x}$Ge$_x$:H thin films with graded composition and structure by real time spectroscopic ellipsometry

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Silicon-germanium (Si$_{1-x}$Ge$_x$:H) thin films have been prepared by plasma enhanced chemical vapor deposition (PECVD) processes for Si-based thin film photovoltaics. From virtual interface analysis (VIA) [1, 2] has been applied to study the structural evolution of Si$_{1-x}$Ge$_x$:H films that initially nucleate in the amorphous (a) phase, but evolve to the microcrystalline (μc) phase with accumulated thickness. The compositional evolution of alloy-graded a-Si$_{1-x}$Ge$_x$:H has been studied as well using similar methods. Both types of films are of interest for Si-based photovoltaic devices.

1 Introduction A two-layer (roughness/outer-layer) virtual interface analysis (VIA) [1, 2] has been applied to real time spectroscopic ellipsometry (RTSE) data collected during two plasma-enhanced chemical vapor deposition (PECVD) processes for Si-based thin film photovoltaics. From VIA the evolution of (i) structure or composition, (ii) deposition rate, and (iii) surface roughness layer thickness can be extracted. In the first process, films initially nucleating as hydrogenated amorphous silicon-germanium (a-Si$_{1-x}$Ge$_x$:H) evolve to the fully microcrystalline phase (μc-Si$_{1-x}$Ge$_x$:H) during PECVD under fixed growth conditions. In this case, a depth profile in the crystallite volume fraction $f_{vol}(d)$ with bulk layer thickness $d_b$ can be deduced [2]. In the second process, graded a-Si$_{1-x}$Ge$_x$:H has been prepared intendingly varying the flow ratio $G = [\text{GeH}_4]/[[\text{SiH}_4] + [\text{GeH}_4]]$ versus time, and in this case, a depth profile in Ge content $x(d)$ can be deduced [1].

In the study of the second process, the dielectric functions $\varepsilon = \varepsilon_1 + i \varepsilon_2$ of a-Si$_{1-x}$Ge$_x$:H have been obtained by RTSE for selected compositions $x$ during PECVD of (SiH$_4$ + GeH$_4$ + H$_2$). Using RTSE data, surface contamination and roughness influences can be avoided without relying on a specific analytical form for the $\varepsilon$ spectra. In fitting the data, improvements in consistency and fit quality are obtained by replacing the Tauc–Lorentz formula [3] by one that simulates a constant dipole matrix element just above the optical band gap [4]. With the resulting database, $\varepsilon$ for a-Si$_{1-x}$Ge$_x$:H can be predicted for any $x$. Another model is applied to describe $\varepsilon$ for μc-Si$_{1-x}$Ge$_x$:H prepared by PECVD at high H$_2$ dilution. In this model, additional oscillators with a common gap are incorporated to fit the broadened critical points for the ~10 nm grain-size film.

2 Experimental details

2.1 Deposition processes The Si$_{1-x}$Ge$_x$:H films in this study were deposited on native-oxide/c- Si substrates using single-chamber rf (13.56 MHz) PECVD and were measured in real time using a rotating-compensator multichannel ellipsometer [5]. The fixed parameters were selected for the most part at values used in previous studies of pure Si:H PECVD [6], including the minimum rf power for a stable plasma ($P = 0.08$ W/cm$^2$), a low partial pressure of the source gases SiH$_4$ + GeH$_4$ ($p_{tot} \sim 0.06$ Torr), and a low total pressure ($p_{tot} < 1$ Torr). Variable parameters in this study include the substrate temperature $T_s = 200–260$ °C, the electrode configuration, either conventional anode (which is grounded) or cathode (which stabilizes at a dc self-bias of $\sim$25 V), the H$_2$-dilution...
ratio \( R = \frac{[H_2]}{([SiH_4] + [GeH_4])} \), and the alloying flow ratio \( G = \frac{[GeH_4]}{([SiH_4] + [GeH_4])} \) which was varied from \( G = 0 \) to 0.167, leading to \( x \) values up to 0.4, as deduced by X-ray photoelectron spectroscopy (XPS).

### 2.2 Optical model

The most popular dielectric function parameterization for amorphous semiconductors is based on an expression for \( \varepsilon_2 \) that assumes parabolic bands and a constant maximum matrix element (CM-ME) at near gap energies according to \( G_{\text{CM}}(E) = (E - E_{\text{g}})^2/E_{\text{g}}^2 \), evolving to a Lorentz oscillator \( L(E) = \Delta E_{\text{g}}/E/(E_{\text{g}}^2 - E^2) + \Gamma^2 E^2 \) at high energies [3]. In these expressions, \( \varepsilon_2, \Delta, E_{\text{g}}, \Gamma \) are the band gap energy, oscillator amplitude, resonance energy, and broadening, respectively. Then \( \varepsilon_1 \) is given by an analytical Kramers–Kronig integration of \( \varepsilon_2(E) = G_{\text{CM}}(E) L(E) \) for \( E > E_{\text{g}} \) and \( \varepsilon_1 = 0 \) for \( E < E_{\text{g}} \). This integration introduces a fifth parameter \( \varepsilon_{\text{in}} \), the constant contribution to \( \varepsilon_1 \). More recent research has shown that simulating instead a constant dipole matrix element (CD-ME) at near gap energies according to \( G_{\text{CD}}(E) = (E - E_{\text{g}})^2/(E_{\text{g}}^2 - E^2 + E_{\text{g}}^2) \), provides a better fit in some materials systems with improved consistency [4, 7]. Thus, in order to couple the CD-ME expression to the Lorentz oscillator, the additional parameter \( E_{\text{g}} \) is required that controls the transition energy between the near gap absorption onset and the Lorentz oscillator behavior.

In general, addition of the parameter \( E_{\text{g}} \) in the CD-ME approach is compensated through improved consistency that allows fixing \( \varepsilon_{\text{in}} = 1 \). In contrast, for the CM-ME, \( \varepsilon_{\text{in}} \) decreases to negative values with increasing \( x \) in a-Si_{1-x}Ge_{x}:H, i.e., unphysical behavior [4]. Such results have been demonstrated in this study through a comparison of CD-ME and CM-ME parameterized models in fitting SE data for the specific case of a-Si_{1-x}Ge_{x}:H with \( T = 200 \, ^\circ\text{C}, R = 10, G = 0.125 \). For this fit with parameterized \( \varepsilon_2 \), the bulk and surface roughness layer thicknesses were fixed at values determined by the RTSE \( \Sigma \sigma \)-minimization analysis procedure [8], where \( \sigma \) represents the root mean square (rms) error between calculated and measured RTSE spectra and the sum is over process time. The spectra in \( \varepsilon \) were fit using a weighted estimator \( \chi^2 \) [9]. In the CD-ME fit, \( \varepsilon_{\text{in}} = 1 \), whereas in the CM-ME fit, \( \varepsilon_{\text{in}} \) is allowed to vary freely. The CD-ME approach yields a 15% improvement in \( \chi^2 \) for the fit while eliminating the unphysical behavior \( \varepsilon_{\text{in}} = -0.18 \pm 0.06 \) in the CM-ME approach.

### 2.3 Virtual Interface Analysis (VIA)

The analysis of thin films with graded structure and composition can be accomplished through the use of a four medium optical model consisting of (i) the ambient; (ii) a surface roughness layer; (iii) an outer-layer which contains the most recently deposited material; and a virtual interface to (iv) the pseudo-substrate which contains the past history of the deposition. The roughness layer is modeled using the Bruggeman effective medium theory as a 0.5/0.5 volume fraction mixture of the outer-layer material and void. The overall analysis approach is based on least-squares regression with the free parameters being the outer-layer composition, \( f \), or \( x \), the outer-layer growth rate \( r \), and the surface roughness layer thickness \( d \). In the case of films initially nucleating as a-Si_{1-x}Ge_{x}:H but evolving to \( mc \)-Si_{1-x}Ge_{x}:H during PECVD under fixed conditions, microstructural changes are observed through the crystallite volume fraction \( f_{\text{cr}} \) in the outer-layer of the film, similar to earlier reports for pure Si:H films [2]. In the case of a graded a-Si_{1-x}Ge_{x}:H alloy prepared with varying GeH_4 flow, compositional changes during deposition are observed through the Ge content \( x \) in the outer-layer of the film, similar to earlier studies of a-Si_{1-x}Ge_{x}:H [1].

### 3 Results and discussion

In the first study to be reported here, a Si_{1-x}Ge_{x}:H thin film was prepared on a Si wafer substrate mounted on the grounded anode (\( V_{\text{dc}} = 0 \, \text{V} \)), which was heated to a temperature of \( T = 260 \, ^\circ\text{C} \). The H_2-dilution was fixed at \( R = 60 \) and the GeH_4 flow ratio was fixed at \( G = 0.083 \) throughout deposition. These conditions result in a film that initially nucleates in the amorphous phase but evolves with accumulated thickness to a mixed (amorphous + microcrystalline) phase and eventually to a single microcrystalline phase as shown by transmission electron microscopy (TEM) in Fig. 1.

The growth of this film has been studied by RTSE and analyzed using a combination of the two-layer \( \Sigma \sigma \)-minimization and VIA procedures. In the early stages of film growth (\( d \leq 120 \, \text{Å} \)), the former procedure can be used for accurate determination of \( \varepsilon \) for the amorphous phase as shown in Fig. 2 and evidenced by the low stable values of \( \sigma \) in Fig. 3. After microcrystallites nucleate from the amorphous phase with continued film growth, the two-layer analysis based on the amorphous phase \( \varepsilon \) breaks down, as evidenced by the increase in \( \sigma \). The VIA is then used to obtain \( \varepsilon \) for the fully microcrystalline phase after its coalescence as shown in Fig. 2, simultaneously with the evolution of (i) the microcrystallite fraction in the mixed-phase regime, (ii) the surface roughness thickness, and (iii) the rms error \( \sigma \) as shown in Fig. 3. The onset of microcrystallite nucleation from the amorphous phase is represented by the amorphous to mixed-phase (amorphous + microcrystalline) transition \( [a \rightarrow (a + mc)] \) and appears at \( d_0 = 155 \, \text{Å} \). The onset of microcrystallite coalescence is represented by the mixed-phase to single-phase micro-

![Figure 1: Transmission electron microscopy (TEM) image of a Si_{1-x}Ge_{x}:H film prepared at \( T = 260 \, ^\circ\text{C}, G = 0.083, R = 60 \).](image)
In the second study to be reported here, a series of a-Si$_x$Ge$_{1-x}$:H films was prepared at $G = 0.083$ and $R = 60$. The amorphous film $\varepsilon$ was obtained by inversion at a bulk layer thickness of 100 Å, whereas the microcrystalline film $\varepsilon$ was obtained by inversion at a bulk layer thickness of 870 Å. The solid lines are best fits using parameterized models described in the text.

The crystalline transition [(a + μc) → μc] which appears at $d_b = 835$ Å. These thicknesses determined by RTSE are in good agreement with the $a \rightarrow (a + μc)$ transition thickness $d_a = 140$ Å and the $a \rightarrow μc$ transition thickness $d_μ = 840$ Å, estimated from the TEM image in Fig. 1. Also shown in Fig. 3a is the predicted evolution of the microcrystallite volume fraction as determined by a cone growth model based on input parameters of the bulk and surface roughness layer thicknesses at the $[a \rightarrow (a + μc)]$ and $[(a + μc) \rightarrow μc]$ transitions [6].

In the second study to be reported here, a series of a-Si$_x$Ge$_{1-x}$:H films was prepared on $T_s = 200$ °C Si wafers mounted on the rf powered cathode ($V_{sr} \sim -25$ V) using a fixed H$_2$-dilution ratio of $R = 10$. The GeH$_4$ ratio was varied from $G = 0$ to 0.167 for individual depositions in order to produce a database of $\varepsilon$ spectra for a-Si$_x$Ge$_{1-x}$:H in which the Ge content $x$ has been determined within the range 0.0 ≤ $x$ ≤ 0.4 by XPS [10]. These $\varepsilon$ spectra are then fit to a CD-ME model in order to extract the parameters {$A$, $Γ$, $E_Γ$, $E_g$} versus $x$ over its range as shown in Fig. 4. $E_Γ$ was fixed at 1 as described in Section 2.2, and $E_g$ was fixed at 3.74 eV because its variations across the series were less than the confidence limits. $A$, $Γ$, $E_Γ$, and $E_g$ were then fit to polynomial expressions in $x$ in order to obtain their values for any $x$ over the range 0.0 ≤ $x$ ≤ 0.4.

After this database development, an a-Si$_x$Ge$_{1-x}$:H film was then prepared under the same conditions as the database series, but with varying ratio $G$ in order to grade the Ge content $x$ and the optical band gap $E_g$. Before grading was initiated, an opaque film with $G = 0.042$ was deposited on the Si wafer as a substrate layer. The graded film was studied by RTSE and analyzed using the VIA technique with an average 7 Å outer-layer thickness in order to extract the time evolution of the Ge content in the outer-layer $x(t)$, the surface roughness thickness $d_s(t)$, and the growth rate $r(t)$. The growth rate $r(t)$ is integrated over time in order to obtain the bulk layer thickness for each data point and to create a depth profile $x(d_b)$. Figure 5 depicts the bulk layer thickness evolution of (a) the flow ratio $G(d_b) = [\text{GeH}_4]/([\text{SiH}_4] + [\text{GeH}_4])$, designed in a stepwise fashion for a multilayer structure ($G = 0.042 \rightarrow 0.15 \rightarrow 0$), and (b) the surface roughness thickness, as well as depth profiles in (c) the Ge content and (d) band gap $E_g$ at the measurement temperature $T_s = 200$ °C. Here $d_b = 0$ Å corresponds to the instant when $G$ is increased above the substrate film value $G = 0.042$. Secondary ion mass spectroscopy (SIMS) depth profiling has been performed on this sample to obtain the Ge content $x$ as a function of bulk layer thickness also shown in Fig. 5c (solid squares). There is excellent correlation between the depth profiles in the
Dielectric function parameters versus a-Si$_{1-x}$Ge$_x$:H alloy composition $x$, obtained at $T_s = 200$ °C and deduced in fits such as those of Fig. 2 ($R = 10$, cathodic deposition, closed circles). The dielectric functions were deduced by inversion at bulk layer thicknesses of ~150–300 Å. The following parameters were fixed in the analysis: $\varepsilon_\infty = 1$ and $E_0 = 3.74$ eV.

Ge content determined by RTSE and SIMS analysis – essentially identical on the depicted scale.

4 Conclusion Real time spectroscopic ellipsometry has been applied to study the growth of structurally or compositionally graded Si$_{1-x}$Ge$_x$:H films. Virtual interface analysis (VIA) was used to deduce the dielectric function $\varepsilon$ of the fully microcrystalline phase of a Si$_{1-x}$Ge$_x$:H film, as well as to track the evolution of the microcrystallite volume fraction and surface roughness versus bulk layer thickness. The $a\rightarrow (a + \mu)c$ and $(a + \mu)c\rightarrow \mu c$ transition thicknesses obtained by RTSE have been confirmed by transmission electron microscopy. Study of a second a-Si$_{1-x}$Ge$_x$:H film prepared with graded Ge content $x$, has also required similarly advanced data analysis techniques. A newly developed parameterization of $\varepsilon$ has been applied to fit a series of spectra for a-Si$_{1-x}$Ge$_x$:H whereby each film is prepared to obtain a different fixed $x$. The dependence of the best fit parameters has been used to produce a database in $\varepsilon$ for a-Si$_{1-x}$Ge$_x$:H dependent only on $x$, over the range 0 ≤ $x$ ≤ 0.4. A VIA technique utilizing this database and model has been applied to extract a depth profile of the Ge content. Secondary ion mass spectroscopy was then used to confirm the results determined by RTSE.

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References