Analysis of controlled mixed-phase (amorphous+microcrystalline) silicon thin films by real time spectroscopic ellipsometry

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Engineered thin films consisting of periodic arrays of silicon microcrystallites in a hydrogenated amorphous silicon host matrix have been prepared by plasma-enhanced chemical vapor deposition where the hydrogen dilution of silane is modulated in multiple cycles. These types of films have been guided by a phase evolution diagram, depicting the deposition conditions and film thickness at which the material exhibits amorphous, microcrystalline, or mixed-phase (amorphous + microcrystalline) characteristics, developed for intrinsic Si:H prepared with varying H2 dilution on unhydrogenated a-Si:H. Real-time spectroscopic ellipsometry (RTSE) has been used in situ to noninvasively determine the phase evolution of the resulting hydrogenated mixed-phase (amorphous+microcrystalline) silicon thin films and corroborated with dark-field transmission electron microscopy. Such tailored microstructures are of growing interest as components of thin film photovoltaic devices, and RTSE is shown to be a key technique for structure verification.

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I. INTRODUCTION

Thin-film hydrogenated silicon (Si:H) based n-i-p and p-i-n photovoltaic devices may incorporate amorphous silicon (α-Si:H), microcrystalline silicon (μc-Si:H), and even mixed-phase (amorphous+microcrystalline) silicon [(α + μc)-Si:H] intrinsic layer (i-layer) components. Optimum single-step α-Si:H i-layers, as assessed by the stabilized efficiency of the resulting photovoltaic devices, are produced by plasma-enhanced chemical vapor deposition (PECVD) from SiH4 at the maximum H2 dilution possible while avoiding the nucleation of crystallites from the amorphous phase throughout the i-layer thickness.1–3 The high H2 dilution ensures a well-ordered amorphous network that rapidly reaches its fully light-soaked state in less than 100 h at air mass 1.5. In contrast, the corresponding optimum single-step μc-Si:H i-layers are produced by PECVD at the minimum H2 dilution while maintaining continuous crystal growth on a microcrystalline surface.4,5 In this case, the low H2 dilution ensures that grain boundaries are well passivated with an amorphous phase.

Improvements in thin film Si:H solar cell efficiency have been achieved using these optimization principles facilitated by phase evolution diagrams, depicting the deposition conditions and film thickness at which the material exhibits amorphous, microcrystalline, or mixed-phase (amorphous + microcrystalline) characteristics, as determined in real time spectroscopic ellipsometry (RTSE) studies.2,5–7 Further improvements in the stability of α-Si:H based thin film solar cells have been reported by incorporating (α+μc)-Si:H i-layers into the device structure.8–10 However, optimization and reproducible control of (α+μc)-Si:H deposition are a challenge due to the rapid evolution of the microcrystallite content, the extreme substrate dependence, and thus the difficulty of controlling the volume fraction of crystallites at a constant average value throughout the thickness. Although continuous hydrogen dilution profiling has been widely adopted in order to optimize grain boundary passivation in μc-Si:H i-layer materials throughout the thickness,11 the more challenging problem of modulating hydrogen dilution to generate (α+μc)-Si:H with a controlled fraction of embedded microcrystallites has yet to be widely applied. The present work demonstrates that (α+μc)-Si:H i-layer films can be fabricated with periodic arrays of microcrystallites in

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an amorphous matrix, whereby the average crystallite size as well as the in-plane and out-of-plane crystallite spacings can be separately modified solely by deposition conditions established and verified by RTSE.

II. EXPERIMENTAL DETAILS

The \((\alpha+\mu\alpha)-\text{Si}:\text{H}\) i-layer films studied here were deposited on single-phase \(a\)-Si:H layers, which were prepared, in turn, on native oxide coated crystalline silicon (c-Si) substrates using a single-chamber rf (13.56 MHz) PECVD system. The deposition parameters included a modulated hydrogen dilution ratio, \(R=[\text{H}_2]/[\text{SiH}_4]\), with all other parameters fixed as follows: a low substrate temperature \(T_s=200\degree\text{C}\), the minimum rf power possible for a stable plasma (0.08 W/cm²), a low partial pressure of the SiH₄ source gas (~0.06 Torr), and a low total pressure (<1.0 Torr). The initial \(a\)-Si:H layer was prepared under the same conditions but with fixed \(R=0\). This layer serves to erasure the memory of the c-Si wafer substrate and also mimics the underlying \(p\)- or \(n\)-layer for \(i\)-layer deposition in \(p-i-n\) or \(n-i-p\) solar cell configurations, respectively. An initial series of Si:H films was prepared on these structures at hydrogen dilution ratios of \(0\leq R\leq 170\) for phase evolution diagram development, while multilayer mixed-phase \((\alpha+\mu\alpha)-\text{Si}:\text{H}\) films were prepared by modulating \(R\) during the deposition. The Si:H deposition process was investigated in situ and in real time using a rotating-compensator multichannel ellipsometer.¹²

Films prepared at low H₂ dilution, for example, \(R=0\), remain in the amorphous growth regime throughout the thickness. For such films, the time evolution of the bulk and surface roughness layer thicknesses, as well as the bulk layer dielectric functions \(\varepsilon_1, \varepsilon_2\), were extracted from the RTSE data using a global \(\Sigma\sigma\) minimization procedure, where \(\sigma\) is the unweighted error function.¹³ Films prepared with high H₂ dilution tend to develop in the amorphous (protocrystalline) phase for an initial period of growth but subsequently nucleate isolated microcrystallites from within the amorphous matrix at a well-defined thickness. These nuclei grow in the form of inverted cones, and eventually coalesce to single-phase \(\mu c\)-Si:H. Consequently, the final films exhibit an amorphous phase near the substrate interface and a microcrystalline phase at the top of the film, each with distinct dielectric functions. An intervening structurally graded \((\alpha+\mu\alpha)-\text{Si}:\text{H}\) phase exists, wherein the microcrystallite fraction increases with bulk layer thickness from zero (initial nucleation) to near unity (full coalescence).

RTSE data collected during the growth of such structurally graded \((\alpha+\mu\alpha)-\text{Si}:\text{H}\) are conveniently interpreted using virtual interface analysis (VIA).¹⁴,¹⁵ This analysis utilizes a four medium optical model consisting of (i) the ambient, (ii) a surface roughness layer, (iii) an outer layer that contains the most recently deposited material, and a virtual interface to (iv) the pseudosubstrate which contains the past history of the deposition. The surface 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.¹⁶ The VIA approach is based on least-squares regression with free parameters that include the volume fractions of Si:H crystallites \(f_{\mu c}\) and voids \(f_{\text{void}}\) in the outer layer, the outer-layer growth rate \(r\), and the surface roughness layer thickness \(d_s\). After this information is obtained, additional structural parameters such as the areal density of microcrystallites in the amorphous matrix \(N_d\) and the half-angle \(\theta\) of the inverted cones can be estimated using a geometric model.¹⁵

III. RESULTS

Figure 1 shows the evolution of the surface roughness thickness and microcrystallite volume fraction in the outer layer (top 3 Å) for an \(R=40\) Si:H film prepared on a native oxide/c-Si substrate coated with \(R=0\) \(a\)-Si:H. Microcrystallites first nucleate from the amorphous phase at a bulk layer thickness of \(d_b=160\) Å, which is denoted as the amorphous to mixed-phase (amorphous+microcrystalline) \([a\rightarrow(\alpha+\mu\alpha)]\) transition. At \(d_b=500\) Å, the microcrystallites coalesce to form single-phase \(\mu c\)-Si:H, which is referred to as the mixed-phase to single-phase microcrystalline \([(\alpha+\mu\alpha)\rightarrow\mu\alpha]\) transition. The microcrystallite nucleation density is estimated at \(N_d\sim 6.0\times 10^{10}\) cm⁻², which corresponds to an initial in-plane microcrystallite spacing of ~400 Å, and the cone half-angle is estimated at \(\theta\sim 35\degree\).

The inset in Fig. 1 shows the spectra in the imaginary part of the dielectric function, \(\varepsilon_2\), for the near-substrate amorphous and near-surface microcrystalline \(R=40\) Si:H materials. The dielectric function for the amorphous phase was determined by exact inversion assuming bulk and surface roughness thicknesses obtained by \(\Sigma\sigma\) minimization using.
The fixed deposition parameters include a relatively low substrate temperature, $T_s=200$ °C, the minimum power for a stable plasma, $P=0.08$ W/cm², and a low total pressure, $p<1$ Torr. The variable parameter, forming the abscissa of the diagram, is the H₂-dilution ratio $R=[H_2]/[SiH_4]$, which is varied from $R=0$ to 170. The ordinate axis represents the bulk layer thickness at which the amorphous to mixed-phase (amorphous + microcrystalline) $[a\rightarrow(a+\mu c)]$ (solid squares) and mixed-phase to single-phase microcrystalline $[(a+\mu c)\rightarrow\mu c]$ (open squares) transitions occur.

Figure 2 shows a phase evolution diagram produced for a series of Si:H films prepared with H₂ dilution ranging from $R=0$ to $R=170$ on undiluted R=0 coated native oxide/c-Si substrates. The $[a\rightarrow(a+\mu c)]$ and $[(a+\mu c)\rightarrow\mu c]$ transitions are observed and depicted as functions of $R$. Films prepared at $R<15$ do not exhibit these transitions but remain amorphous throughout ~4000 Å of growth. Films prepared at $15\leq R \leq 150$ initially nucleate in the amorphous phase but undergo the $[a\rightarrow(a+\mu c)]$ transition at a bulk layer thickness, dependent on the H₂ dilution $R$. The bulk layer thickness at which this transition occurs decreases with increasing $R$ throughout the series. As with the $[a\rightarrow(a+\mu c)]$ transition, the $[(a+\mu c)\rightarrow\mu c]$ transition occurs at a bulk layer thickness, dependent on the H₂ dilution $R$, and this thickness decreases with increasing $R$. It should be noted that for $R>170$, the film initially nucleates as $\mu c$-Si:H on the amorphous $R=0$ substrate.

A modulated Si:H structure was then deposited while measuring by RTSE with the intention of fabricating a film with a volume average microcrystalline fraction. The modulated film was designed to consist of alternating high-dilution ($R=40$) crystallite nucleation regions and low-dilution ($R=0$) crystallite suppression regions in order to produce a multilayer mixed-phase film with microcrystallites spaced approximately 400 Å apart both in the film plane and out of the plane. The particular film described here consists of three pairs of $R=0/R=40$ layers deposited onto a native oxide covered c-Si substrate. Figure 3 shows the surface roughness layer thickness and the microcrystalline and void volume fractions in the outer layer (3–20 Å thick for $R=40$ to 0, respectively) as functions of the bulk layer thickness, which is obtained as a time integral of the instantaneous growth rate $r(t)$ determined from the VIA. The $(e_1, e_2)$ spectra used in the analysis of Fig. 3 have been deduced from the previous $R=0$ and $R=40$ depositions. Figure 4 shows a cross-sectional transmission electron microscopy (TEM) dark-field image of the structure in Fig. 3.

IV. DISCUSSION

The microstructural evolution of Si:H materials, as shown in Fig. 1, has been used to produce a phase evolution diagram as a function of the hydrogen dilution ratio $R$, as shown in Fig. 2. This phase diagram evolution diagram, coupled with previous microcrystallite nucleation density studies, has been used to guide the modulation of $R$ during the course of a deposition to produce a $(a+\mu c)$-Si:H film shown in Figs. 3 and 4 with a controllable microcrystallite growth as a function of depth.

A comparison of Figs. 3 and 4 corroborates the thicknesses of the amorphous and mixed-phase regions of the $(a+\mu c)$-Si:H film as determined by the VIA. Both VIA and
TEM results demonstrate that it is possible for the low-dilution $R=0$ deposition to suppress further microcrystallite growth on the $R=40$ mixed-phase material and thereby produce alternating amorphous and mixed-phase regions, the latter with a defined size and average spacing for the crystalline inclusions. Subsequent $R=0/40$ cycles, however, have shown variations in the microcrystallite evolution depending on the underlying structure which provide additional insights into the well-known substrate dependence of phase evolution. The most obvious example of such variations is the additional voids that appear with microcrystallite nucleation for the second and third $R=40$ layers; however, the protocrystalline film structure in Fig. 3 prepared by alternating Si:H with high $R$=0 layers can be used to produce films with periodic arrays of microcrystallites, adjusting for substrate dependencies so as to achieve controllable separations in the plane of the film and out of the plane.

V. SUMMARY

In conclusion, RTSE with virtual interface analysis has been applied to study the growth of mixed-phase $(a + \mu c)$-Si:H films fabricated so as to maintain a constant volume average microcrystallite fraction with thickness. RTSE studies have been used to determine the thickness and substrate dependence of the structural evolution, and thereby identify the required $H_2$ dilution and bulk layer thicknesses of components in engineered Si:H films that can result in specific isotropic or anisotropic distributions of microcrystallites. It is found that microcrystallite nucleation can be stopped and restarted with well-defined conical crystallite decay and growth behaviors via the use of alternating low and high $H_2$-dilution layers; however, the protocrystalline layers decrease in thickness with increasing cycle number due to the increase in ordering of the substrate with thickness. As a result, to obtain periodic arrays of crystallites, the hydrogen dilution $R$ of the high-dilution layers must be decreased with increasing cycle number.

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