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The atomic hydrogen flux to silicon growth flux ratio during microcrystalline silicon solar cell deposition

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The H flux to Si growth flux ratio is experimentally determined under state-of-the-art silicon thin-film deposition conditions by employing the recently introduced etch product detection technique. Under the technologically relevant high-pressure depletion conditions and for different process parameter settings such as pressure, SiH₄ concentration, rf power, and excitation frequency, it was demonstrated that the microcrystalline to amorphous silicon phase transition is uniquely and reactor independently determined by the flux ratio of H and Si growth species. © 2008 American Institute of Physics. [DOI: 10.1063/1.2987519]

The optimal phase composition of microcrystalline silicon (µc-Si:H) solar cell absorber layers is generally found in a narrow process window just before entering the amorphous growth regime.1–3 The presence of atomic hydrogen is recognized as a key parameter influencing the crystallinity of the silicon films.4,5 In the literature, it is often speculated that the hydrogen to Si growth precursor flux ratio should exceed a critical value for the nucleation of crystalline phase material to occur. Although the atomic hydrogen flux during deposition can in principle be determined by advanced techniques such as two-photon laser induced fluorescence or mass spectrometry,6,7 the technologically relevant data available concerning the abundance of atomic hydrogen during µc-Si:H deposition remain largely based on correlations with indirect optical emission spectroscopy measurements and modeling work.6,9–13

Preferential insertion of atomic hydrogen in strained Si–Si bonds and subsequent silicon etching lead to a higher etch rate of amorphous silicon (a-Si:H) relative to crystalline Si.14–16 In a recent Letter,17 we demonstrated that this difference in etch rate can be exploited to determine in situ the phase composition of silicon films in the µc-Si:H growth regime. In this letter we introduce a quantification of the etch rate of amorphous silicon with a substrate area of 10 cm² was used for most experiments.2,17,18

Figure 1 shows fₑ/ₑₓ as a function of f_SiH₄ for two process conditions in reactor A (Pₑₓ=80 and 120 W). Note that the SiH₄ emission at f_SiH₄=0 is that part of the emission that can be attributed to the dissociation of etch products. The good linearity between f_SiH₄ and fₑ/ₑₓ strongly suggests that the presence of small SiH₄ fractions can be treated as an impurity in the H₂ plasma. The amount of etch product generated and the result of exposing the Si thin films to a H flux,
expressed in an equivalent SiH₄ flow \( \Phi_{\text{SiH₄,etch}} \) can be determined by extrapolating the linear fit to the \( x \)-intercept at \( I_{\text{EH}} = 0 \). More information on the used linear dependence is given in Ref. 18. Note that this procedure should be repeated for every fixed plasma setting throughout a given in Ref. 18. Note that this procedure should be repeated for every fixed plasma setting throughout a given in Ref. 18. Note that this procedure should be repeated for every fixed plasma setting throughout.

Figure 2 shows \( \Phi_{\text{SiH₄,etch}} \) corresponding to films deposited with various SiH₄ flows for the conditions \( P_{\text{dep}} = 80 \) W and \( P_{\text{rf}} = 120 \) W in reactor A. Three SiH₄ flow regions can be identified in Fig. 2(a): an initial plateau region, a steep increase, and a second (sloping) plateau region. From solar cell analysis, as well as Raman spectroscopy, we deduced that the transition from the first plateau region to the steep increase coincides with the onset of the phase transition to mixed phase growth (at \( f_{\text{SiH₄}} = f_{\text{et}} \)).

We define the subsequent transition from the steep increase to the sloping plateau as the transition from mixed phase to amorphous silicon (at \( f_{\text{SiH₄}} = f_{\text{a}} \)). In Fig. 2(b) we illustrate the correlation of etch product detection with the deposited material quality by showing the solar energy conversion efficiency \( \eta \) of solar cells deposited for both the 80 and 120 W series. Highest efficiencies were obtained for films deposited at the onset of the phase transition, i.e., at \( f_{\text{SiH₄}} = 3.2 \) SCCM for \( P_{\text{rf}} = 80 \) W and \( f_{\text{SiH₄}} = 4.0 \) SCCM for \( P_{\text{rf}} = 120 \) W.

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Note that \( \Phi_{\text{<}} \), defined as the etch product generation rate for etching of highly crystalline \( \mu c \)-Si:H films in the plateau region of Fig. 2(a), is observed to increase from \( 0.7 \pm 0.05 \) to \( 0.95 \pm 0.05 \) SCCM when increasing \( P_{\text{rf}} \) from 80 to 120 W. As has been mentioned above, the linearity between \( f_{\text{SiH₄}} \) and \( I_{\text{EH}} \) (Fig. 1) and \( f_{\text{SiH₄}} \) and the deposition rate \( f_{\text{a}} \) indicates that the influence of \( f_{\text{SiH₄}} \) on the H flux can be neglected in a first approximation (for small SiH₄ concentrations, 0.2%–2%), and we can state that the H flux during deposition is equivalent to the H flux during H₂ plasma probing. We thus explain the higher \( \Phi_{\text{<}} \) for higher \( P_{\text{rf}} \) in terms of a larger atomic hydrogen flux toward the film surface under these conditions. To investigate the dependence of the H flux on process parameters, we consider \( \Phi_{\text{<}} \) in reactor A for various \( P_{\text{dep}} \) and \( P_{\text{dep}} \). As can be seen in Figs. 3, \( \Phi_{\text{<}} \) decreases with pressure and increases with power. These effects can be explained in terms of a lower electron temperature and smaller diffusion length for increasing pressure, and a rising electron density and dissociation rate of H₂ as a result of the increase in power.\(^{20}\)

The H flux toward the film surface \( \Gamma_{\text{H}} \) (cm\(^{-2}\) s\(^{-1}\)), can now be expressed in terms of \( \Phi_{\text{<}} \).

\[
\Gamma_{\text{H}} = \frac{\Phi_{\text{<}}}{A_{\text{surface}}} / \gamma_{\text{etch}},
\]

with \( \gamma_{\text{etch}} \) the etch yield of H atoms impinging on the film and \( A_{\text{surface}} \) the total surface area exposed to the H flux (lower and upper electrode). \( \Phi_{\text{<}} \) is given in particles per second (1 SCCM = \( 4.48 \times 10^{17} \) particles s\(^{-1}\)).

To determine the absolute value of the H flux from Eq. (1), an appropriate value for the etch yield should be substiti-
tated. Our results indicate that the etch yield is strongly dependent on the phase composition of the silicon film. In addition, factors such as substrate temperature, H-recombination probability, and ion bombardment should be taken into account for thorough analyses, as well as a possible difference in etch yield between the Si film on the upper electrode and on the lower electrode. For an order of magnitude estimate, however, an etch yield of 10^{-2} is assumed.\textsuperscript{8,21} Therewith, from Fig. 3, H flux values between 6 \times 10^{16} and 2 \times 10^{17} cm\textsuperscript{-2} s\textsuperscript{-1} can be derived. Note that the order of magnitude of the H flux is in agreement with modeling results of high-pressure conditions of Lyka et al.\textsuperscript{13}

To structure the discussion further, we introduce the dimensionless parameter \( \kappa \), which is the ratio between the H flux \( \Gamma_H \) and the Si growth flux \( \Gamma_{Si} \):

\[
\kappa = \frac{\Gamma_H}{\Gamma_{Si}} = \frac{\left( \Phi_c / A_{\text{surface}} \right) / \gamma_{\text{etch}}}{r_{\text{dep}} / \rho_{\text{Si}}} \tag{2}
\]

Next, we determined for the various power and pressure conditions of Fig. 3, the deposition rate for which the phase transition from \( \mu \)-c-Si:H to the mixed phase (\( a + \mu \)) and from \( a + \mu \) to \( a \)-Si:H occurred. From Fig. 3, we know \( \Phi_c \) for the corresponding deposition regimes and thus using Eq. (1), the appropriate \( \gamma_{\text{etch}} \Gamma_H \). By plotting \( \gamma_{\text{etch}} \Gamma_H \) versus \( \Gamma_{Si} \), we determined the slope \( \kappa \gamma_{\text{etch}} \) for the transition data points in reactors A, B, and C. Figure 4 displays this main result of this letter and illustrates that the change in the phase composition of the material can be well described and understood in terms of only two parameters, namely, \( \Gamma_H \) and \( \Gamma_{Si} \). A qualitative view on the data behind Fig. 4 is that in a \( f_{\text{SiH}} \) optimization series (at constant \( P_{\text{rf}}, P_{\text{dep}} \) excitation frequency or reactor geometry), the phase transition can be understood by variation in \( \Gamma_{Si} \) at constant \( \Gamma_H \). When changing any of the parameters (\( P_{\text{rf}}, P_{\text{dep}} \) excitation frequency, or reactor geometry), generally both \( \Gamma_H \) and \( \Gamma_{Si} \) change. However, the \( \Gamma_{Si} \) to \( \Gamma_H \) ratio \( \kappa \gamma_{\text{etch}} \), at which the phase transition occurs, remains constant under the various reactor geometries and deposition conditions applied. This strongly suggests that the phase transition is uniquely determined by the H to Si growth flux ratio. These results might therefore indicate that under the used high-pressure high depleting deposition conditions the phase transition is a surface induced process, as \( \kappa \gamma_{\text{etch}} \) reflects a ratio between the time constant related to the arrival rate of atomic H and the time constant related to the growth rate of 1 ML of silicon film.

Note that the absolute value for the H to Si growth flux ratio can be obtained by assuming again that \( \gamma_{\text{etch}} \) is in the order of 10^{-2}. We obtain \( \kappa \approx 40 \) for the \( \mu \rightarrow a + \mu \) phase transition. Conversely reasoned, to comply with the modeled estimates of Strahm et al.\textsuperscript{11} (\( \kappa \approx 12 \)) and Klein et al.\textsuperscript{3} (\( \kappa \approx 5 \)), slightly higher values for \( \gamma_{\text{etch}} \) between 0.03 and 0.05 seem more appropriate.

To summarize, the recently introduced technique of etch product detection was extended to determine the absolute H flux under \( \mu \)-c-Si:H deposition conditions. From the H flux the ratio between the H and Si growth flux was determined in the phase transition regime for three different reactors and various plasma settings. From the results, we infer that the H to Si growth flux ratio at which the phase transition occurs is a constant, which strongly suggests that the phase transition is governed kinetically by the arrival rate of atomic hydrogen relative to the arrival rate of the growth precursors. The insights obtained provide an outlook to achieve high growth rates for silicon thin films in or close to the mixed phase region.

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