The atomic hydrogen flux during microcrystalline silicon solar cell deposition

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ABSTRACT

Etch product detection by in situ optical emission spectroscopy is used to detect the phase transition from amorphous to microcrystalline silicon. In this contribution it is demonstrated that a calibrated version of this technique can be used to determine the absolute hydrogen flux under state-of-the-art silicon thin film deposition conditions.

INTRODUCTION

The phase transition from amorphous- to microcrystalline silicon and associated growth and nucleation processes are key issues of research in the field of microcrystalline silicon. In the past a range of diagnostic techniques has been applied to study the microstructure of microcrystalline silicon as it evolves as a function of process parameters and film thickness. Nonetheless, a straightforward, easily applicable diagnostic for in-situ studies is still lacking.

A widely used, non-invasive, easy-to-apply and in situ plasma diagnostic is optical emission spectroscopy. In this contribution we present a novel approach to optical emission spectroscopy, by which the phase composition of $\mu\text{c-Si:H}$ can be studied in-situ.

The etch product detection method is based on the difference in etch probability between disordered (a-Si) and ordered (c-Si) material. The method was successfully correlated with in-situ absorption spectroscopy and Raman spectroscopy and has been cross-checked on various reactors operating in a wide range of process settings [1].

Employing a calibrated version of the technique the atomic hydrogen flux is experimentally determined under state-of-the-art silicon thin film for different process parameter settings in the high pressure depletion regime, such as pressure, silane concentration, RF power and excitation frequency.

Fig. 1: (a) SiH* emission intensity as obtained by H₂ plasma etching of silicon films deposited under various SiH₄ flows. The inset is a schematic of the experimental procedure employed. (b) Raman crystallinity I_c^{RS} of the silicon films as measured in the center and corner of the substrate. The laser wavelength was 680 nm yielding a Raman penetration depth exceeding the film thickness. (c) Solar energy conversion efficiency η and open circuit voltage V_{oc} for the corresponding thin film silicon *p-i-n* solar cells. No ZnO back reflector was applied.

ETCH PRODUCT DETECTION DURING RF-PECVD OF MICROCRYSTALLINE SILICON

The phase composition of microcrystalline silicon ($\mu\text{-Si:H}$) varies with process settings such as SiH_4 concentration, RF power and deposition pressure. The optimal phase composition of the $\mu\text{-Si:H}$ silicon solar cell absorber layer is found in a narrow process window just before entering the amorphous growth regime (cf. Fig. 1).¹⁻³ The presence of atomic hydrogen is recognized as a key parameter influencing the crystallinity of films³⁻⁶, and 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. The atomic hydrogen flux during deposition can in principle be determined by advanced techniques such as two-photon laser induced fluorescence or mass spectrometry^{7,8}, but no easy-to-implement diagnostic has been available. Consequently technologically relevant data concerning the abundance of atomic hydrogen during $\mu\text{-Si:H}$ deposition remain largely based on correlations with optical emission spectroscopy (OES) signals and modeling work.^{6,9-13}

Preferential insertion of atomic hydrogen in strained Si-Si bonds and subsequent silicon etching leads to a higher etch rate of amorphous silicon (a-Si:H) relative to crystalline Si.¹⁴⁻¹⁶ In a recent letter this difference in etch rate was exploited to determine *in-situ* the phase composition of silicon films in the $\mu\text{-Si:H}$ growth regime. Both optical emission spectroscopy (OES) and infrared absorption spectroscopy in the gas exhaust were employed for the detection of (SiH_4) etch products during H_2 plasma probing of the film surface, and a correlation between the etch product density and the amorphous silicon fraction of a silicon film was established (cf. Fig. 1).¹⁷

THE ATOMIC HYDROGEN FLUX DURING MICROCRYSTALLINE SILICON SOLAR CELL DEPOSITION

In this contribution a quantification of the etch product density in terms of the absolute atomic hydrogen flux is introduced and tested under various plasma conditions and on different reactors. The atomic hydrogen flux is given by

$$\Gamma_H = (\Phi_{\text{etch}} / A_{\text{surface}}) / \gamma_{\text{etch}} \quad (1)$$

with Φ_{etch} the etch product flow at low SiH_4 dilutions (cf. Fig. 1), A_{surface} the total exposed film surface area, γ_{etch} the atomic hydrogen etch probability. The right hand side of Eq. (1), except for γ_{etch} , can be determined experimentally employing the technique of etch product detection. Under different pressure and power condition we have determined the silicon etch flow Φ_{etch} through a calibration of Φ_{etch} by studying the phase transformation

as function of the silane flow. The result is given in Figs. 2. Using typical values for the etch yield and the surface area of the electrodes the absolute hydrogen flux can be determined. Since the absolute hydrogen flux is thus directly proportional to the silicon etch flow Φ_{etch} it can be concluded that the hydrogen flux increases with applied plasma power and decreases with increasing pressure.

Figure 2: The silicon etch flow Φ_{etch} as function of power and pressure. The atomic hydrogen flux can be determined if the hydrogen etch yield is known (cf. Eq. (2)).

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