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Hot-wire CVD amorphous Si materials for solar cell application

Qi Wang

National Renewable Energy Laboratory, Golden, CO 80401, United States

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ABSTRACT

Hydrogenated amorphous silicon (a-Si:H) thin films and their application to solar cells fabricated using the hot-wire chemical vapor deposition (HWCVD) or (CAT)-CVD will be reviewed. This review will focus on the comparison to the standard plasma enhance (PE) CVD in the terms of deposition technique, film properties, and solar cell performance. The advantages of using HWCVD for a-Si:H solar cell research as well as the criteria for industry's adaptation of this technique for mass production will be addressed.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) fabricated by hot-wire chemical vapor deposition (HWCVD) or Catalytic (CAT) CVD has demonstrated its unique structural and electronic properties in the past [1–4]. Low H content a-Si:H that possesses low saturated defect density (N_d^{sat}) ($2\times10^{16}/cm^3$), high ambipolar diffusion length (~2000 Å), and high deposition rate (>10 Å/sec) was appealing to solar cells. This has encouraged many groups to work intensively to utilize this material for solar cells. Early work on superstrate cells having a structure of glass/TCO/*p*–*i*–*n*/Ag with hybrid PECVD doped layer and HWCVD intrinsic layer has achieved just over 10% conversion efficiency [5]. However, high temperature (about 400 °C) HWCVD intrinsic layer was detrimental to the *p*-layer that leads to a poor fill factor. Later work on substrate cell having a structure of SS/*n*–*i*–*p*/TCO represented an attempt to overcome this dilemma in the superstrate cell since *n*-layer, in general, is not critical as *p*-layer in forming junction and is compatible with the high temperature processing. However, the same issue occurs again in this structure. FF is lower when an intrinsic layer deposited over 400 °C is used. The best cell efficiency in this kind is also about 10% with an *i*-layer temperature around 350 °C [6,7]. Stability of HWCVD solar cells was in debate. High temperature cell has self-degradation about 5% and recoverable light induced degradation about 15%. Recently, hydrogen diluted a-Si:H solar cell fabricated by the Utrecht group showed relatively less degradation (about 10%) [8]. It was encouraging but it does not include a high temperature HW *i*-layer with low hydrogen content *i*-layer. In comparing to industrial standard radio-frequency (rf) PECVD process, HWCVD has shown its unique advantages in term of deposition rate and scale up. Will HWCVD replace PECVD for a-Si:H solar cell manufacturing? This paper will review the criteria and try to answer this question.

We find that the material grown at 300 °C can have a similar value of saturated defect density and ambipolar diffusion length as the one grown at 400 °C. We also study the effect of *i*-layer substrate temperatures ranging from 280 to 440 °C *n*–*i*–*p* solar cells. We now consistently grow devices with FF's over 0.66, with the best close to 0.70 at lower substrate temperature.

2. Experimental details

HWCVD is very similar to PECVD in term of vacuum system and substrate transport systems. Two deposition systems are often interchangeable. That makes it useful for research. The physics of HWCVD uses thermal energy to decompose process gas such as silane while PECVD uses electric energy to decompose silane. Fig. 1 shows the schematics of the chemical reaction for HWCVD. This sketch includes three regions: The hottest region is near the filament. Silane decomposes into Si and H when the molecule moves close to the hot-wire. The temperature gradient region is between the filament and the substrate. Here, atomic Si and H reacting with silane in the gas phase. The majority radials in this region are Si_2H_2 resulting of Si and SiH_4 reaction and some of SiH_3 from H and SiH_4 reaction [9]. The last region is at the substrate surface, where the temperature is constant. Temperature at the surface, to a large degree, determines the structure of the film. HWCVD is quite different from thermal CVD in that hot surface absorb the radicals and deposit the film. There is no film deposition on the hot-filament.

HWCVD also is called catalytic CVD. It is believed that hot-filament, normally a metal filament, acts as a catalytic to decompose the process gas. Does HWCVD is a thermal or catalytic process for silane? This is a difficult question to answer. Fig. 2 shows a plot of the deposition rate of a-Si:H with W and Ta filaments as a function of the filament temperature [10]. The filament and process configuration are identical for both types of filaments. At the same temperature, the deposition rate is the same as indicated by crosses for Ta filament and open circles for W. This experimental result suggests that the decompose rate of

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E-mail address: qi_wang@nrel.gov.

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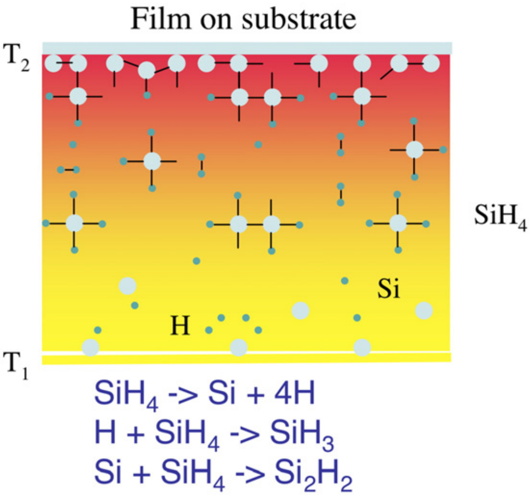

Fig. 1. Schematic of silane chemical reaction in HWCVD.

silane is independent of the filament materials and it is solely dependent on its temperature. HWCVD using silane is a thermally dominant process. However, we have not been able to exclude the possibility that both W and Ta have the same catalytic effect on silane decomposition.

One effect in HWCVD that we shall pay attention to is the emission of electrons from the hot-wire [11]. This can be detrimental to the film quality as shown in Fig. 3 a) and b). The conductivity of the a-Si:H film depends on the location on an isolated glass substrate. When a metal grid was applied to the glass substrate, the conductivity is uniform across the sample. This effect was explained by the so-called "charging effect" whereby the electrons charge the glass substrates. The filament is directly heated by passing a current. Without the presence of process gas, the HWCVD reactor is just like a vacuum tube. Based on the vacuum-tube theory, the emission current density J_c follows Richardson's law. For tungsten, A_c equals 60 A/cm^{2}K^2 and E_w equals 4.5 eV. At 2200 K, J_c equals 14.4 mA/cm^2, corresponding to 9×10^{16} electrons/s cm^2. Fig. 3c shows the voltage applied to the filament as a function of filament length. For a DC current with a positive voltage on the filament relative to ground, electrons are suppressed by the high potential at the filament and no electrons pass through the vacuum region. For a DC current with a negative voltage on the filament, electrons were accelerated in the vacuum region. The negative signal indicates it is negative charges be collected. The magnetic field also influences the emission of electrons from the filament and also the trajectory of the electrons entering the vacuum. An additional complication is that the electron distribution in the vacuum is not uniform because of the voltage drop across the filament.

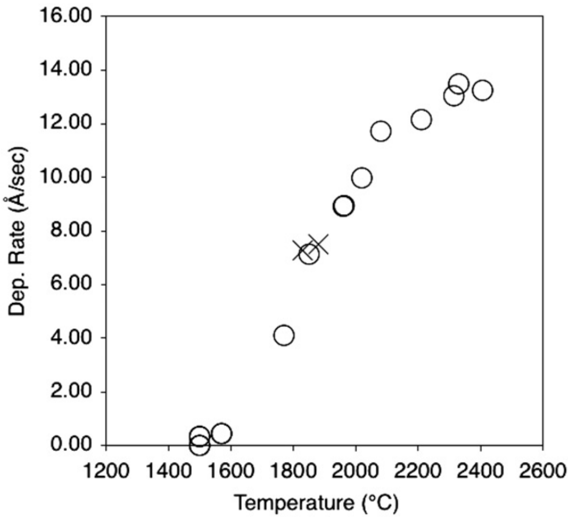

Fig. 2. Deposition rate of a-Si:H using W and Ta as a function of filament temperature. Cross symbols correspond to Ta filament and circles to W filament.

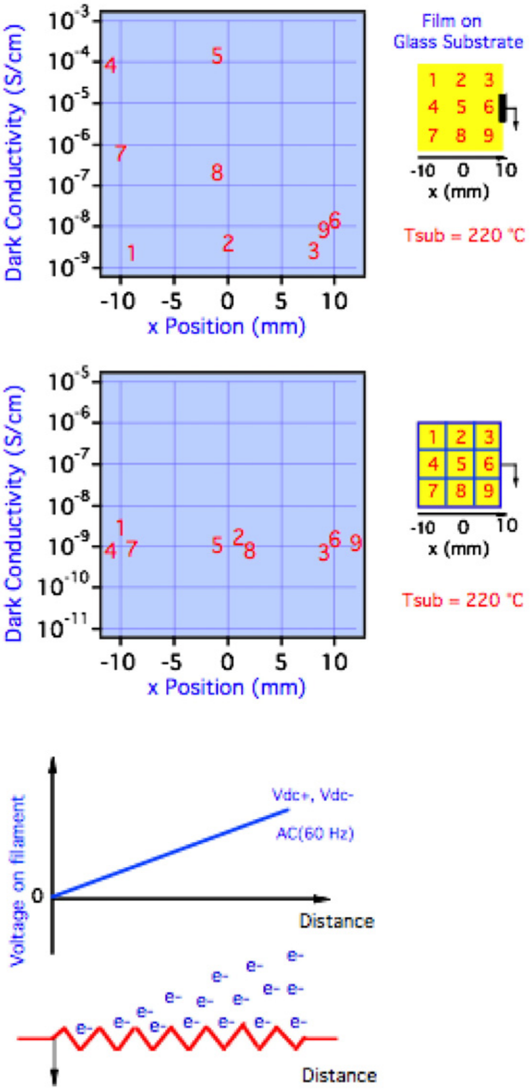

Fig. 3. Electron charging effect on an isolated substrate. a) distribution of dark conductivity on glass substrate; b) distribution of dark conductivity on metal grid glass substrate; c) electrons emission from hot-filament as a function of voltage bias.

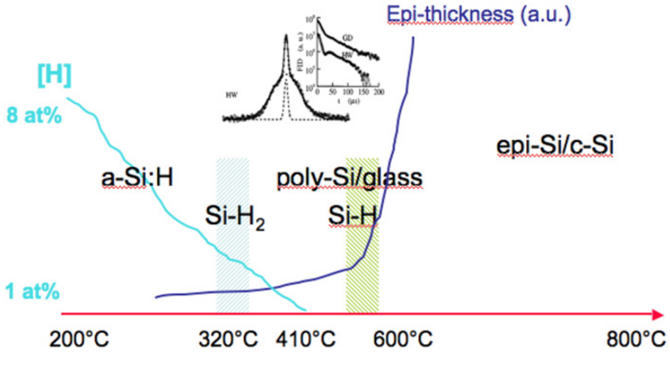

Fig. 4. Summary of substrate temperature effect on a-Si:H film structure and properties. H-content monotonically decreases with increasing T_{sub}. Epi-Si thickness rapid increases as T_{sub} greater than 600 °C.