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Hot wire radicals and reactions

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Abstract

Threshold ionization mass spectroscopy is used to measure radical (and stable gas) densities at the substrate of a tungsten hot wire (HW) reactor. We report measurements of the silane reaction probability on the HW and the probability of Si and H release from the HW. We describe a model for the atomic H release, based on the H_2 dissociation model. We note major variations in silicon-release, with dependence on prior silane exposure. Measured radical densities versus silane pressure yield silicon-silane and H-silane reaction rate coefficients, and the dominant radical fluxes to the substrate.

Keywords: Solar cells; Amorphous silicon; Chemical vapor deposition; Radicals

1. Introduction

Neutral radicals induce the film growth in hot-wire (HW) chemical vapor deposition (CVD), so the fluxes of various radicals to the substrate are considered crucial to film and device properties. We measure several observables that yield radical fluxes to the substrate, and use this data to build models for the radical fluxes under device-production conditions.

There have been many radical measurements in silane discharges and HWCVD, and only a representative portion will be cited [1–10]. Threshold ionization mass spectroscopy has been used by the Atwater group and in the present measurements to detect radicals. This can detect all radical species, but only at a substrate surface. Optical detection of radicals in the central region of a reactor is more common and can provide details such as the translational temperature, but is difficult to apply to higher silanes. One might summarize current knowledge as providing many important insights regarding the dominant radicals, but we do not have a comprehensive model for the character and values of the dominant radical fluxes to the substrate versus conditions. Here we provide part of this model, and some of the data needed to make it quantitative.

The cause of radical fluxes to a HWCVD substrate can be separated into three parts; (1) the probability of SiH_4 and H_2 dissociation on the HW, (2) the probability of releasing various radical species from the HW, and (3) the radical-gas reactions that modify the fluxes and species reaching the substrate. The discussions below are thus arranged.

2. Experiment

The experimental arrangement is shown in Fig. 1. The (tungsten) HW to sampling-orifice gap is 3 cm, and the surfaces are only heated by the HW radiation. An 0.3 mm diameter sampling orifice to the mass spectrometer and a 1 μA ionizing electron-beam current provides $S/N \cong 30$ in 1 s for ionization 2 eV above threshold and typical radical density ($10^{11}/cm^3$). Turbomolecular pumps are used, and the HW is heated with a DC current to provide accurate resistance.

For all measurements the HW chamber contains 20 mTorr of argon in addition to the reported SiH_4 pressure, to ensure constant radical detection efficiency. A gate valve is typically adjusted to yield ~12 l/s evacuation of the ~3 l HW chamber, and a slight interaction between SiH_4 and H_2 (from SiH_4 decomposition) at the exit orifice is taken into

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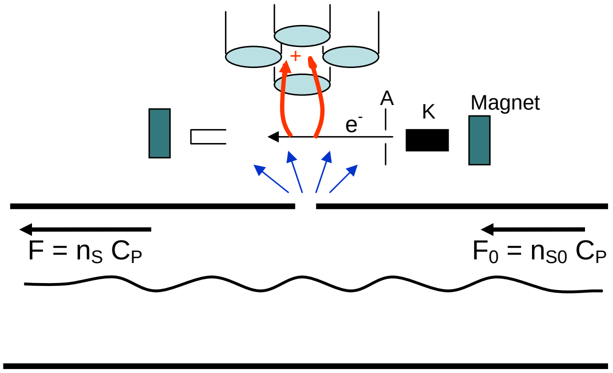

Fig. 1. Diagrammatic representation of the apparatus, with silane inlet and outlet flow.

account. Gas flow is obtained from the chamber filling rate. Measurement of the HW temperature (T) is often difficult, as the emissivity and resistance change as Si is incorporated into the W. We generally use resistance within the first 30 min exposure, and thereafter compare it to one- and two-wavelength optical pyrometry. T uncertainties of >100 °C still occur after long exposures.

We measure three observables to obtain radical fluxes to the substrate: (1) changes in SiH_4 flow, due to its decomposition by the HW and subsequent radical-SiH_4 reactions; (2) T changes due to power removed by SiH_4 and H_2 dissociation on the HW; (3) densities of radicals at the substrate. In principal, this yields radical fluxes from the HW and to the substrate, including required knowledge of the radical-film reaction probabilities (β_j for radical j). However, the HW changes as silicon is incorporated, and the β_j often change as the film-growth conditions vary. As a result, we are still acquiring data and here report work in process.

3. Silane and H_2 dissociation probability on a tungsten HW

To obtain the SiH_4 dissociation probability per collision with the HW (α_{HW}), as in Ref. [11] we measure the change in SiH_4 flow (ΔF_{Sil}) out of the HW chamber as the HW is heated, and divide this by the rate ($R_{Sil-HW} = n_{Sil} v_{Sil} A_{HW}/4$) of SiH_4 collisions with the HW, where n_{Sil} and v_{Sil} are the molecular density and thermal velocity and A_{HW} is the HW surface area. This yields $\alpha_{Tot} = \Delta F_{Sil}/R_{Sil-HW}$, shown in Fig. 2. ΔF_{Sil} results from loss on the HW plus subsequent radical-silane reactions, so $\alpha_{Tot} = \alpha_{HW}(1+N)$ where N is the number of radical-silane reactions per HW dissociation. To obtain N, we combine a result from section 5 with Si atom data shown on the left side of Fig. 2. In that section, we obtain the ratio of total Si flux from the HW to Si flux at the substrate (at the P_{Sil} used for the data in Fig. 2). This was done at one T, but should be almost independent of T. We also find there that almost all of the Si reacts with silane at this P_{Sil}. Thus, the total Si flux can be obtained from the

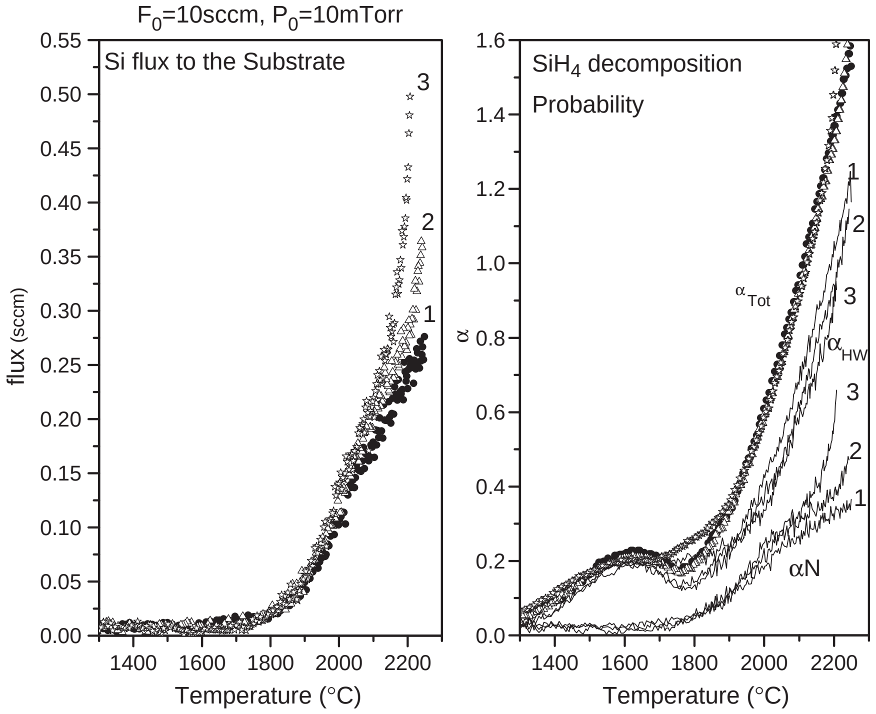

Fig. 2. Silicon flux to the substrate and SiH_4 decomposition probability (α_{Tot}) versus hot wire temperature. Three successive T scans, labeled in order, each yielded ~5 min SiH_4–HW reactions with an initially clean tungsten wire. The contribution to α from Si–SiH_4 reactions is labeled α_N, and α_{HW} is decomposition on the wire only. The cold-HW silane pressure and flow are indicated above the figure.