

Deposition of Amorphous Hydrogenated Silicon (*a*-Si:H): *in situ* Gas Analysis by Time-of-Flight Mass Spectrometry

Gudrun Andrä¹, Fritz Falk¹, Herbert Stafast^{1,2,*},
and Ewa Witkowicz¹

¹ Institut fuer Physikalische Hochtechnologie e.V., D-07743 Jena, Germany

² Friedrich Schiller University, Faculty of Physics and Astronomy, D-07743 Jena, Germany

Summary. Time-of-flight mass spectra generated by ArF laser photoionization have been obtained in a molecular beam effusing from an *a*-Si:H deposition system with a dc discharge in a gas mixture of SiH₄ and He. The XeF, KrF, and ArF laser wavelength dependence and the kinetics of the SiH₀₋₃⁺ and the Si₂H₀₋₂⁺ signals show that the ions predominantly originate from disilane.

Keywords. Silicon hydrides; Gas phase reactions; Mass spectra.

Abscheidung von amorphem, wasserstoffhaltigem Silicium (*a*-Si:H): *in situ*-Gasanalyse mit Flugzeitmassenspektrometrie

Zusammenfassung. Flugzeitmassenspektren nach Photoionisierung mit einem ArF-Excimerlaser wurden in einem effusiven Molekülstrahl aufgenommen, dessen Ursprung in der *a*-Si:H-Schichtbildungszone einer Gleichstromgasentladung in SiH₄ und He liegt. Die Wellenlängenabhängigkeit bei der Bestrahlung mit XeF-, KrF- und ArF-Lasern sowie die Kinetik der Signale von SiH₀₋₃⁺ und Si₂H₀₋₂⁺ zeigen, daß die Ionen hauptsächlich von Disilan stammen.

Introduction

Thin film deposition of amorphous hydrogenated silicon (*a*-Si:H) by various methods of chemical vapor deposition (CVD) has been known since a quarter of a century and applied to produce technical devices like photovoltaic cells, electrophotographic drums, and thin film transistors [1]. Nevertheless, there are still open questions like those regarding the identity and properties of the film forming species in the gas phase [2] and the origin of mechanical stress in *a*-Si:H thin films [3].

A variety of gas phase species like Si atoms, molecular intermediates SiH₃ and H₂SiSiH₂, as well as stable molecules like Si₂H₆ and Si₃H₈ have been reported to contribute to *a*-Si:H thin film formation. Depending on the details of the

* Corresponding author

deposition process, one or several film forming species appear *a priori* possible. They are, however, hard to identify experimentally, especially due to their very low concentration in comparison with that of the precursor molecules of similar chemical composition. A mass balance in the gas phase during CO₂ laser CVD, for instance, and comparison with the *a*-Si:H film growth led to the conclusion that the film forming species contribute to the silane processing gas in the order of 10⁻⁵ to 10⁻⁶ only [4]. To reveal Si_xH_y intermediates in (laser) CVD processes, a molecular beam apparatus was set up to provide sampling in the film forming region and collision free transfer into a time-of-flight (TOF) mass spectrometer with laser photoionization to achieve high selectivity and high efficiency. In the following, our first TOF mass spectra obtained during *a*-Si:H deposition by dc gas discharge are reported.

Results and Discussion

Figure 1 shows a TOF mass spectrum obtained by photoionization of the effusive molecular beam derived from the *a*-Si:H film deposition region. Photoionization was achieved by ArF excimer laser radiation (193 nm), affording the ions SiH₀₋₃⁺ (*i.e.* Si⁺, SiH⁺, SiH₂⁺, and SiH₃⁺) and Si₂H₀₋₂⁺ (*i.e.* Si₂⁺, Si₂H⁺, and Si₂H₂⁺). With KrF (248 nm) and XeF (351 nm) excimer laser radiation under comparable conditions (laser pulse energy), no ions Si_xH_y⁺ ($x = 1, 2; y = 0-3$) were obtained.

In a second series of experiments, the temporal evolution of the Si_xH_y⁺ signals generated by ArF laser radiation was observed while integrating the signals of ions with one ($x = 1$) and two ($x = 2$) Si atoms, respectively (Fig. 2). No ions are observed without gas discharge (SiH₄/He mixture). Both ion signals rise within a few seconds upon switching on the gas discharge, and after about 1 min they display a constant level (steady state). The steady state signal in both cases amounts to about 80% of the maximum value in the beginning. After switching off

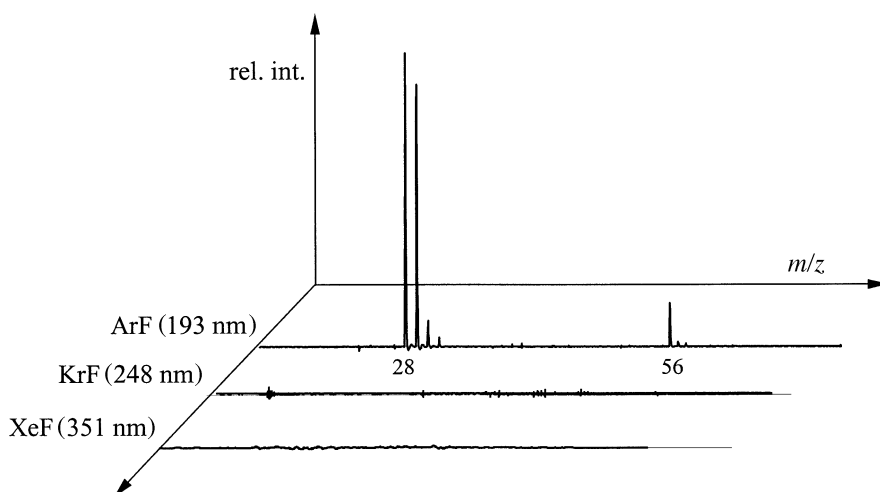


Fig. 1. TOF mass spectrum generated by ArF, KrF, and XeF laser photoionization in a molecular beam effusing from the *a*-Si:H deposition region (dc discharge in SiH₄/He)

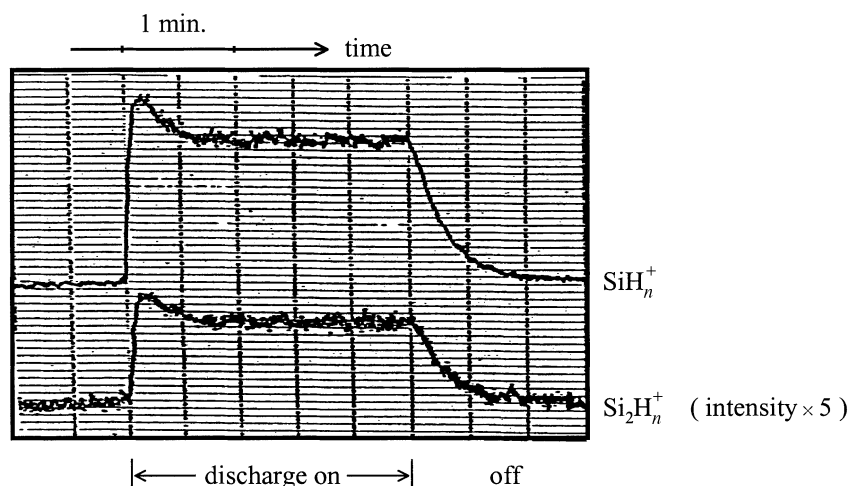


Fig. 2. Temporal evolution of the integrated SiH_{0-3}^+ and $\text{Si}_2\text{H}_{0-2}^+$ ion signals upon switching on and off the dc gas discharge in SiH_4/He

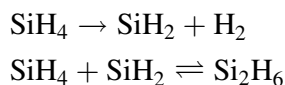
the discharge, both ion signals decrease with the same time constant of about 30 s, which corresponds to the time for gas exchange in the deposition reactor (flow system).

From the findings presented in Fig. 2 it is concluded that the ion signals, within the error limits, have the same source and originate from a stable species. Ions from short-lived intermediates like SiH_2 , SiH_3 , or Si_2H_4 should disappear immediately when switching off the discharge. The stable parent of the registered ions is assumed to be disilane (Si_2H_6) in agreement with the laser wavelength dependence of the ion yield. The adiabatic and vertical ionization energies of 10.0 eV and 10.53 eV, respectively, can be derived from the UV photoelectron spectrum of disilane [5, 6]. Consequently, vertical photoionization by XeF (3.53 eV) and KrF laser light (5.00 eV) requires the energy of three photons compared to that of two ArF laser photons (6.42 eV) only. Moreover, XeF or KrF laser radiation require (synchronous) three photon ionization (MPI). Each ArF laser photon, on the other hand, is in resonance with the long wavelength tail of the electronic $4s \leftarrow 2\sigma_{1g}$ transition of disilane ($\sigma = 2 \times 10^{-18} \text{ cm}^2$) [7, 8], leading to (sequential) resonance enhanced MPI (REMPI). Two ArF laser photons can ionize disilane and provide an excess energy of 2.84 eV (273 kJ/mol) in addition to the adiabatic ionization energy. This energy evidently is sufficient to generate the fragment ions observed in the TOF mass spectrum (Fig. 1).

The concentration of trisilane (Si_3H_8) in the deposition reactor is assumed to be negligible: The vacuum UV absorption cross section of trisilane at 193 nm is about five times larger than that of disilane [7], and high ion yields are expected. However, no Si_3H_y^+ ions were observed under ArF laser irradiation, possibly because the excess energy in addition to the adiabatic ionization of trisilane is high (3.54 eV, 341 kJ/mol) [5]. On the other hand, the amount of trisilane relative to that of disilane was found to be small under comparable gas discharge conditions [9]. This can be rationalized by the small concentration of Si_2H_6 relative to that of SiH_4

(1–10%, see below), resulting in a small probability for the SiH₂ biradicals to react with Si₂H₆ and to form Si₃H₈.

One can assume a relatively fast equilibration between SiH₄ and Si₂H₆ [10] following the simplified equations



on a second time scale (steep ion signal rise in Fig. 2). The signal decrease from the maximum to the stationary level then is a measure for the depletion of SiH₄ in the discharge (probe) volume. The small discharge volume of several cm³ is buffered over some 10 s by the large volume of about 3000 cm³ of the deposition chamber until stationary conditions are achieved. Hereafter, the stationary Si₂H₆ concentration is in the order of 1–10% of the initial SiH₄ concentration, *i.e.* 10⁻³–10⁻² mbar. This corresponds to 10⁻¹²–10⁻¹¹ mbar Si₂H₆ in the laser ionization region of the TOF mass spectrometer.

These results represent an important technical step towards detection, identification and characterization of metastable Si_xH_y intermediates of very low concentration in the thin film deposition system. Photoionization mass spectra of Si₂H_n (*n* = 2–5) transient species are known [12]. In our case, however, detection under *a*-Si:H deposition conditions in an effusive molecular beam imposes several experimental difficulties. Further experiments applying tunable narrow-band radiation from a pulsed dye laser are currently in progress.

Experimental

The basic concept of the experimental setup has been described previously [4, 10]. Briefly, the substrate for *a*-Si:H thin film deposition provides a small hole (100 μm diameter) being the source of an effusive molecular beam. This beam passes through a differential pumping stage into the ion source of a mass spectrometer. The gas transfer by the molecular beam is collision-free (no intermediate chemical reactions). Recently, the quadrupole mass spectrometer of the original setup for *in situ* gas analysis has been replaced by a TOF mass spectrometer (reflectron type, Kaesdorf RTF 10) with pulsed laser photoionization. In the above experiments, an excimer laser (Lambda Physik, EMG 201 MSC) was used for photoionization. The TOF spectra were registered on a digital oscilloscope (Tektronix TPS 644B), and the temporal evolution of the ions was recorded by a boxcar integrator (SRS model SR 250). For convenience of operation, *a*-Si:H deposition was performed by a dc gas discharge in SiH₄ (3%)/He (97%) gas mixture at 0.5 mbar total pressure.

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