Advanced diagnostics for exploring the growth mechanism of plasma deposited materials

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Introduction

Insight into the growth mechanism of plasma deposited materials is essential for full optimization of the deposition process and improvement of the material properties of the deposited films. The complexity of the deposition process requires knowledge on the different aspects of plasma deposition. This means that in addition to measurements of the gas phase densities of the plasma species, also experiments on the species’ surface reactivity are required as well as on the “nature” of the surface during film growth. In the following sections, some studies concerning these three different aspects will be shortly reviewed. It will be concentrated on the technologically very relevant deposition processes of a-Si:H and a-SiNₓ:H, which are both known to be dominated by radical species rather than by ions.

Radical density measurements

Threshold ionization mass spectrometry (TIMS) and cavity ring down spectroscopy (CRDS) are two powerful diagnostics for studying radical densities in deposition plasmas. TIMS uses electron energies higher than the ionization potential of the radical but lower than the dissociative ionization energy of the parent molecule to distinguish radicals from parent molecule cracking products in the mass spectrometer (Fig. 1) [1]. The advantages of this technique are that it measures radicals very close to the surface/substrate (where deposition takes place) and that it can easily be applied to a large variety of radicals. However, TIMS cannot easily and non-intrusively be applied at several positions in the plasma and the densities are relatively difficult to quantify. This is partially related to the loss of radicals during their extraction into the mass spectrometer. CRDS is a direct absorption technique that

![Figure 1](image1.png)

**Figure 1:** Electron energy scan at mass/charge ratio showing ionization of N radicals at low energies and mainly dissociative ionization of N₂ at high energies.

![Figure 2](image2.png)

**Figure 2:** Basics of CRDS. From the difference in decay time of the laser pulse between “plasma on” and “plasma off” the absorption by radicals and therefore their density can be determined.
is very sensitive due to the fact that decay times of a laser light pulse in an optical cavity are measured (Fig. 2) [2,3] rather than differences in absolute light intensity. Compared to TIMS and laser-induced fluorescence (LIF), radical densities are very easy to quantify with CRDS, while its poorer spatial resolution (compared to LIF) can be overcome by Abel inversion. Furthermore, the radicals probed need only to absorb and not necessarily to fluoresce. This enables also the detection of radicals with a very short “radiative lifetime” (due to predissociation) such as CH₃ and SiH₃. Both TIMS and CRDS have been applied in the Expanding Thermal Plasma (ETP) and their results on the radical densities have revealed interesting new insights in the growth mechanism of a-Si:H and a-Si₃N₉:H (Figs. 3 and 4).

![Figure 3: Contribution of SiH₃ to a-Si:H film growth in an ETP Ar-H₂-SiH₄ plasma [2,3]. Interesting is that the film quality also improves with increasing H₂ flow. At high H₂ flows, the contribution of SiH₂, SiH, Si, and Si₃H₄⁺ is <5%, 2%, 0.2%, ~7%, respectively [3].](image)

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**Figure 4:** SiH₃ and (relative) N density in an ETP Ar-H₂-N₂-SiH₄ plasma. Because the Si/N ratio in the films increases with increasing SiH₄ flow, this suggests “nitration” of an a-Si:H-like overlayer by N radicals as growth mechanism.

**Surface reactivity measurements**

To determine the relevancy of certain plasma radicals to film growth not only their density needs to be known, but also their surface reaction probability. As a matter of fact, a high gas phase density of a radical can be due to favored production of this radical but can also be due to a very low surface reactivity and therefore a relatively low significance of this radical for film growth. A prominent method to study the surface reactivity of radicals is the “Imaging of Radicals Interacting with Surfaces” (IRIS) technique (Fig. 5) [4]. In the IRIS method a molecular beam is effusively extracted from a plasma and the radical of interest is probed by LIF. The fluorescence, which is proportional to the radical’s density, is detected by a 2-D intensified CCD array. In a typical IRIS experiment, first an image is taken of the freely expanding molecular beam (Fig. 6a). Subsequently, a substrate is rotated into the path of the molecular beam and a new image is taken (Fig. 6b). In this image, not only the radicals in the forward molecular beam are detected but also radicals possibly scattered and/or produced on the surface. The difference in the two images shows these radicals (Fig. 6c).

![Figure 5: The IRIS experiment.](image)
Figure 6: CCD images of LIF signals produced by NH$_2$ molecules in a SiH$_4$/NH$_3$ plasma (a) in the molecular beam only and (b) with the substrate in the path of the molecular beam. Both images are corrected for spurious signals caused by plasma emission and laser light scattering. Figure (c) is the difference between images (a) and (b) showing the NH$_2$ radicals scattered from the substrate.

The reactivity of the radicals is determined from simulations relating the intensity of the scattered radicals to the intensity of the radicals in the incident beam in cross-sectional images along the laser axis (Fig. 7). A scatter coefficient $S=1$ means that all radicals are scattered at the surface, $S<1$ means surface loss and $S>1$ surface production. Although both NH$_2$ and SiH show surface loss in a NH$_3$/SiH$_4$ plasma [5,6], the reactivity of NH$_2$ is very small to the one of SiH. Depending on their density in the plasma, this might imply that SiH is more important than NH$_2$ in the deposition of a-SiN$_x$:H from a NH$_3$/SiH$_4$ plasma.

Figure 7: Cross-sectional images of the radicals in molecular beam and scattered from the surface for (a) NH$_2$ and (b) SiH in a SiH$_4$/NH$_3$ plasma. The surface reaction probability $\beta=1-S$ of NH$_2$ and SiH is 0.13$\pm$0.07[5] and 0.98$\pm$0.05 [6], respectively. The substrate temperature is 300 K.

**In situ** film growth measurements

The surface reactivity of radicals depends on the nature of the film’s surface. This nature itself depends on the reactions taking place at the surface. Therefore, by probing the chemical species and their bonds in the film and on the surface during film growth, information can be obtained about the atomistic reactions on the surface. Attenuated-total-reflection infrared spectroscopy (ATR-FTIR) (Fig. 8) is a very powerful tool in this respect. Due to multi-passing and/or multiple reflections at the crystal or film surface a very high sensitivity is obtained. Surface selectivity can be obtained by isotope experiments (e.g., D on a-Si:H) or by
ion-induced desorption of the surface species (Fig. 8) [7,8]. The latter method has been applied to study the surface hydrides on a-Si:H during growth (Fig. 9). It has been observed that the surface changes from dominantly SiH$_3$ at low substrate temperatures to SiH$_2$ and subsequently to SiH at high substrate temperatures. On the basis of this observation, a thermal decomposition set in which SiH$_3$ → SiH$_2$ → SiH has been proposed with crucial importance for H-elimination in SiH$_3$ dominated a-Si:H film growth [9].

Acknowledgments
F.J.H van Assche, A.A.E. Stevens, M.G.H. Boogaarts, D.C. Marra, and K.L. Williams are gratefully acknowledged for their contribution to this work. Prof. D.C. Schram is acknowledged for the fruitful discussions.

References