Wavelength-dependent Deposition of Thiol-terminated Films

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Abstract: Thiol-terminated films were prepared via photo-initiated chemical vapour deposition from gas mixtures of acetylene (C₂H₂) and hydrogen sulfide (H₂S) using four different vacuum-ultraviolet sources, namely KrL (λ_{peak} =123.6 nm), XeL (λ_{peak} =147.0 nm), XeE (λ_{peak} =172.0 nm), and Hg (λ =184.9 nm) lamps. Results demonstrated that photolytic reactions are governed by the gases' absorption coefficients, $k(\lambda)$. Highest thiol concentrations reported in the literature, up to 7.7 %, were obtained with the XeL source.

Keywords: Thiol-terminated films, wavelength-dependent deposition, film growth.

1. Introduction

The development of thiol (SH)-terminated surfaces has gained interest over the past years due to their wide field of applications, ranging from optics to biomedicine [1-5]. Especially in the biomedical field, SH-terminated surfaces can be used as platforms for covalent immobilization of biomolecules through selective and specific thiol-ene coupling reactions. This coupling reaction has been successfully used for the construction of immobilized antibodies, enzymes, and peptides [4, 6-10].

So far, SH-terminated surfaces have been mainly synthesized using lengthy, non-specific, multi-step wetchemical approaches, which often involve the use of toxic and expensive solvents [4, 9, 10]. During the last decade, SH-terminated surfaces have been also created using plasma-enhanced chemical vapour deposition (PECVD) [2, 3, 5, 11-14]. Plasma-based techniques offer several advantages over wet-chemical approaches as they are recognized to be cleaner, substrate independent, room-temperature, single-step, solvent-fee processes, producing reduced amounts of waste. Nevertheless, the reactions occurring in a plasma are difficult to predict and control due to the main initiators of chemical reactions in low-pressure plasmas, "hot" electrons, which possess a broad, Maxwell-Boltzmann-like energy distribution [15-17].

More recently, photo-initiated CVD (PICVD) techniques have been studied and used to create high quality, functional thin films, often comparable to traditional plasma CVD [18-22]. Since these techniques retain only one energy-source component of the plasma, the (VUV) photons, to carry out (photo-) chemistry, they allow for additional control of the overall process.

Thin films from specific precursors can only be created if the absorption of photons is significant, and photon energies are sufficient high to overcome bond dissociation energies, D_0 , to induce photo-dissociation. Therefore, photo-absorption by molecules as a function of wavelengths, $k(\lambda)$, must be considered for successful photo-induced deposition. Activation and photodissociation of acetylene (C₂H₂) and hydrogen sulfide (H₂S) are expected for all four sources on account on their relatively strong absorption, $k(\lambda)$ (Fig. 1), throughout the studied spectral range (123.6 $<\lambda<$ 184.9 nm). Nevertheless, the radiation from some lamps is more strongly absorbed by the two precursor gases than others, and these differences should be reflected in the deposition behaviour of the films at different λ .



Fig. 1. VUV-absorption spectrum of gaseous H_2S and C_2H_2 (adapted from [23] and [24]).

In this work, we present a wavelength-dependent study of photo-deposited SH-terminated coatings using variable gas mixture ratios, *R*, of C₂H₂ and H₂S, and four different λ values, namely, λ_{KrL} =123.6 nm, λ_{XeL} =147.0 nm, λ_{XeE} =172.0 nm, and λ_{Hg} =184.9 nm. This study aims to understand the film growth mechanisms of the synthesized SH-terminated films using PICVD, since only one kind of excitation (VUV photons) at a specific wavelength is active and available for reaction initiation. Besides determination of the chemical composition of the coatings, deposition kinetics, film growth and morphology are also studied. The dependence of these as a function of λ was of special interest. By exploring a wide range of photon energies, an "ideal" combination of *R* and λ , which gives highest thiol concentrations on the surface were to be found.

2. Experimental Methods

Boston, MA, USA).

VUV Photo-polymerization

The reactor used for VUV photo-chemical experiments was based on the design developed by Truica-Marasescu et al. [15, 16, 22, 25] and was similar to the one used in our earlier work [13]. Briefly, it consisted of a stainless steel six-way "cross" chamber, pumped down to high vacuum using a turbo-molecular pump supported by a two-stage rotary vane pump. The operating pressure during deposition was maintained at p = 400 Pa (3 Torr). The flow rate of the hydrocarbon source gas C₂H₂ (99.6%, MEGS Inc., Montreal, QC, Canada), FC2H2, was kept constant at 10 sccm using a mass flow controller (Brooks Instruments, Hatfield, PA), while that of H₂S (99.5 %, MEGS Inc., Montreal, QC, Canada), F_{H2S} , was varied between 0 and 10 sccm; this yielded values of the gas mixture ratio R $\left(\frac{F_{(H2S)}}{F_{(C2H2)}}\right)$ ranging from 0 to 1. The polymer-like [26] coatings resulting from the photo-chemical reactions, hereafter designated "UV-PA:S" (for "ultravioletpolymerized sulfurized acetylene", were deposited on 500 µm-thick (100) p-type silicon wafers (University Wafer,

Four different VUV sources were used in the present λ dependent study to deposit UV-PA:S films, namely a lowpressure mercury (Hg) lamp (STER-L-RAY[®], Hauppauge, NY, USA) and three non-coherent commercial resonant or excimer noble gas VUV lamp (Resonance Ltd., Barrie, ON, Canada), based on an electrodeless radio-frequency (r.f., 100 MHz)-powered discharge. Depending on the particular lamp, noble gases such as Krypton (Kr) or Xenon (Xe) is sealed into a high-grade Pyrex ampoule with a MgF₂ window (cut-off wavelength, λ =112 nm), as described elsewhere [16, 21, 22]. The spectral characteristics of the different VUV sources are summarized in Table 1.

Table 1. Characteristics of the VUV sources used, measured under high vacuum at the respective frontal distances, *d* (see text).

VUV Source	Peak Wavelength, $\lambda_{peak} (nm)$	Photon Flux, Φ (ph/cm ² /s) at given d
Hg	184.9	7.1.1015
XeE	172.0	6.3·10 ¹⁴
XeL	147.0	2.5.1015
KrL	123.6	1.4.1015

The c-Si substrates were mounted on a stainless-steel sample holder which could be moved axially within the VUV reactor chamber, to frontal distances of d_{KrL} =0.9 cm, d_{XeL} =0.9 cm, and d_{XeE} =0.7 cm. Varying *d* between the substrate and the VUV source allowed us to adjust the photon flux, Φ , impinging on the gas mixture in the gap. In the case of the Hg source, the lamp was moved to d_{Hg} =8.0 cm away from the fused silica window, behind which the c-Si substrate was placed. This allowed us to achieve comparable experimental Φ vales while guaranteeing deposit creation on the substrates. Coatings of comparable thicknesses (~50 nm) were obtained by varying the treatment duration between 1 and 5 h (depending on the VUV source and gas mixture ratio).

X-ray Photoelectron Spectroscopy

All deposits were characterized by X-ray photoelectron spectroscopy (XPS), performed in a Thermo Scientific K-AlphaTM instrument (Waltham, MA, USA) using a monochromatic Al K α radiation source (hv = 1486.6 eV). The samples were mounted onto a vacuum transfer module (VTM, Thermo Scientific K-AlphaTM) inside the glovebox and directly transferred to the instrument without exposure to air, allowing determination of the films' native chemical composition, without ageing.

The elemental composition in atomic %, (at. %) and chemical environment of the constituent elements in the deposits were obtained from XPS analyses. The constituent elements were quantified from the broad-scan spectra using 2.3.16 PR 1.6 Casa XPS software, by integrating the areas under relevant peaks after a Shirley-type background subtraction, and by using sensitivity factors from the Wagner table.

Chemical Derivatization with N-ethylmaleimide

Chemical derivatization with N-ethylmaleimide (98%, BioShop Canada Inc., Burlington, ON, Canada) was used to quantify thiol concentrations, [SH], as recently described by Thiry et al. [27].

Profilometry

The thickness of deposits was determined by profilometry, using a Dektak XTTM Stylus Profilomter (Bruker, Tucson, AZ, USA).

Atomic Force Microscopy

The morphology of deposits was investigated by atomic force microscopy (AFM) using a MFP-3D instrument (Asylum Research, Santa Barbara, CA, USA). All samples were measured in tapping mode using silicon cantilevers (ACTA model, AppNano) with a nominal spring constant of 37 N/m, nominal resonant frequency of 300 kHz, and nominal tip radius of 6 nm. Gwyddion 2.47 software was used to process the AFM images.

3. Results and Discussion

Deposition Kinetics Error! Reference source not found. Photo-dissociation and deposition is expected to be dependent on the absorption of the precursor gases in the gas mixtures. Based on different absorption coefficients of the gas mixtures, α , substantial differences in the photoinduced deposition kinetics at different λ were expected. This was indeed the case, where deposition rates normalized with respect to photon flux were seen to vary significantly for different λ and to follow the same trend as α , being the highest at λ =147.0 nm, followed by λ =123.6 nm, λ =172.0 nm, and λ =184.9 nm, respectively. Furthermore, normalized deposition rates were seen to decrease with rising *R*.

Chemical Composition Error! Reference source not found.Similar to the deposition rates, chemical compositions, more particularly [S] as a function of *R*, showed different trends among the four different UV-PA:S film families (Fig.2, black symbols).



Fig. 2. Sulfur concentrations (black, full symbols), [S] (in at.-%), and thiol concentrations (blue, open symbols), [SH] (in %), of UV-PA:S films deposited using (a) KrL, (b) XeL, (c) XeE, and (d) Hg VUV sources as a function of gas mixture ratio, R. The lines are to guide the reader's eye.

The most efficient S-incorporation was observed for the XeL source. This can be explained by the highest absorption of C₂H₂ at the given wavelength and the fact that a polymer-like backbone needs to be created first and foremost in order to incorporate S-containing groups into the films. For the case of the Hg source, the absorption of C₂H₂ and therefore the creation rate of C_xH_v• radicals was much smaller, even though the possibility of S incorporation was higher. This could help explaining why [S]~50 and ~40 at.% for the XeL and Hg lamps, respectively. Contrary to trends reported in the literature and our previous work [13, 14], the heteroatom concentration (here [S]) did not increase with rising R values but remained nearly constant. We attribute this to the higher pressure (p=400 Pa=3 Torr) used in the present study compares to much smaller vales (p << 133 Pa=1 Torr) reported in the literature.

Since [S] does not give any information about the desired thiol functionalities incorporated into the UV-PA:S films, the selective and quantitative derivatization based on *N*-ethylmaleimide was used to determine [SH], as shown in Fig. 2 (open, blue symbols). The plot of [SH] versus R

displays similar trends as that of [S] versus *R*. The highest thiol incorporation was observed for the case of XeL-based deposits, followed by Hg, KrL, and XeE ones. These films, especially in the case of XeL ([SH]~7.7 %), were much richer in SH groups than their plasma counterparts [14], and also for sulfur-rich films that were created using a single molecule precursor (i.e. propanethiol, [SH]~5 %) [11, 12, 27]. The observed higher photochemical [SH] values for UV-PA:S films compared to their plasma-chemical counterparts can be explained by the selective and specific VUV-photochemical reactions via the present gas mixtures. It is noteworthy that comparable [SH] was achieved using the Hg lamp, far more affordable and readily available than the other three VUV sources used here.

Surface Morphology

Since specific surface-chemical and -topographical features are critically important to cells' response, surface morphologies of the UV-PA:S films deposited using the four different VUV sources were examined at R=0.1 R=1, see Fig. 2.



Fig. 2. AFM images of UV-PA:S films deposited using the XeL and XeE VUV sources at R=0.1 and R=1.

Irrespective of the VUV lamp, similar UV-PA:S morphologies were observed, namely island-like features which are seen to increase with R. UV-PA:S films appear to present Volmer-Weber growth morphology, where incoming film-forming precursors have more affinity for one another than for the (c-Si) substrate surface [28]. As a result, they tend to form clusters which grow into 3D islands that can eventually coalesce and merge into a continuous film. Furthermore, deposits tend to form islands minimizing their surface energy, if it is significantly different from that of the underlying substrate. From this, we could inter that the surface energy of the UV-PA:S films deviated from the one of the substrate with rising R and thus with [S].

4. Conclusions

The present study aimed to understand λ -dependent

deposition of thiol-terminated films using four different VUV sources covering roughly 123 nm $\leq \lambda \leq 185$ nm. We have shown that UV-PA:S coatings could be successfully deposited by VUV irradiation of acetylene (C2H2) / hydrogen sulfide (H2S) mixtures, growth rates and properties of the resulting films being highly λ -dependent. The results showed that photolytic reactions of C_2H_2 and H₂S are governed by the gases' absorption coefficients, $k(\lambda)$, and by that that of the C₂H₂/H₂S gas mixtures, α . The latter was found to be highest for the XeL VUV source, and was found to yield the highest sulfur, [S], and thiol, [SH], concentrations. [SH] values reported here are the highest in the literature so far, a good choice if high [SH] are desired for further (biomedical) applications. Slightly lower [SH] (\sim 5%) were obtained with the more economic and readily accessible Hg lamp. Independent of λ , UV-PA:S deposits showed island-like growth morphology, more pronounced with increasing [S].

With this wavelength-dependent study, we have been able to show that thiol-terminated films with different properties can be obtained by selecting different photon energies (i.e. values of λ).

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