Determination of the Surface Diffusion Coefficient and the Residence Time of Adsorbates via Local Focused Electron Beam Induced Chemical Vapour Deposition

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In this paper we present a model for local gas assisted focused electron beam induced deposition which allows estimating the surface diffusion coefficient and the residence time of volatile precursor adsorbates. Elaborating the existing continuum model for one adsorbate species¹ and using a novel set of parameters we simplified the differential equation describing the dynamics of this process. We will show that stationary exposure experiments do not allow for a unique determination of the parameters residence time, surface diffusion coefficient, and net cross-section. Rather an estimation of parameter windows is possible by assuming meaningful values for the electron dissociation cross section. The model was applied to the experimental results for Cu(hfac)₂ as a gas precursor.

Keywords: Electron Beam Induced Deposition, Surface Diffusion Coefficient, Residence Time.

1. INTRODUCTION

Focused-electron-beam-induced-deposition (FEBID) also referred to as focused electron beam induced CVD, is a process in which continuously supplied, physisorbed gas molecules are decomposed upon electronic excitation by the impinging electron beam and the emitted secondary electron flux. This process can be described by an adsorption rate model, where four key processes determine the local surface concentration of adsorbates: adsorption, desorption, surface diffusion, and electron stimulated decomposition.^{1,2} By varying the electron beam diameter and the electron beam current in a local deposition experiment, the contributions of diffusion and decomposition can be controlled, leading to distinctly different deposit shapes; in contrast to thin film CVD. As a result a local deposit with nanoscale dimensions is formed. Figure 1(a) shows a schematic of FEBID process.

The technique is widely used for fabrication of many functional nanostructures, such as strain sensors,³ Hall sensors,⁴ optical elements,⁵ and functional magnetic structures.⁶

Although the principle of FEBID is simple, the deposition process is complex and includes three types of interactions: substrate-electrons (emitted secondary electron flux), substrate-precursor adsorbate (adsorption

residence time, surface diffusion, desorption), and adsorbate-electrons (adsorbate dissociation). Therefore many different approaches are presented in literature to study the shape and the composition of fabricated deposits.^{7–10}

Here we develop a continuum model, which allows to estimate the residence time and the surface diffusion coefficient for adsorbates from a given precursor gas.

2. MODEL

We start from the adsorption rate model, which is based on the local surface concentration of adsorbates. The four key processes are taken into account: adsorption, desorption, surface diffusion, and electron induced decomposition. Assuming the rotational symmetry of the system, the number of adsorbates $n(r, t)$ is changing according to the equation:

$$\frac{\partial n(r, t)}{\partial t} = \underbrace{sJ \left(1 - \frac{n(r, t)}{n_0}\right)}_{\text{adsorption}} - \underbrace{\frac{n(r, t)}{\tau}}_{\text{desorption}} - \underbrace{\sigma f(r)n(r, t)}_{\text{decomposition}} + \underbrace{D \left(\frac{\partial^2 n(r, t)}{\partial r^2} + \frac{1}{r} \frac{\partial n(r, t)}{\partial r} \right)}_{\text{diffusion}} \quad (1)$$

with the six parameters: s —sticking probability ($s = 1$), J —molecular flux, n_0 —number of molecules in a complete

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Fig. 1. (a) Fundamentals of FEBID: molecule of gas precursor are injected into SEM chamber, where they are adsorbed and selectively dissociated upon electron irradiation. Non-volatile fragments stick to the surface, whereas the rest is pumped-out of the system (b) Model parameters: $\tilde{\varphi}$ —the resolution parameter, $\tilde{\tau}$ —the depletion parameter, $\tilde{\rho}_{\text{out}}$ —the diffusion parameter.

monolayer, τ —average residence time of molecules, σ —net cross-section, D —surface diffusion coefficient.

Here we will assume a Gaussian distribution of the electron beam $f(r) = f_0 \exp(-r^2/(2a^2))$, with the maximum value of f_0 at the beam centre $r = 0$. The net cross-section is an effective cross-section over the whole electron energy spectrum. We also use the stationary approach considering the system in a steady state ($\partial n/\partial t = 0$). The deposition rate is proportional to the number of adsorbates

$$R(r) = Vn(r)f(r)\sigma \quad (2)$$

where the V is the atomic volume of the deposited molecule fragment. In a stationary state the final deposit profile (shape) is the product of this deposition rate and the total exposure time. For the problem generalization it is convenient to use the parameters introduced before by Utke et al.¹ (Fig. 1(b)): the residence time in the centre of electron beam $\tau_{\text{in}} = (sJ/n_0 + 1/\tau + f_0\sigma)^{-1}$, and the residence time far away from the irradiated area $\tau_{\text{out}} = (sJ/n_0 + 1/\tau)^{-1}$. The dimensionless depletion parameter, defined as

$$\tilde{\tau} := \frac{\tau_{\text{out}}}{\tau_{\text{in}}} = 1 + \sigma\tau_{\text{out}}f_0 \quad (3)$$

is a measure of the amount of adsorbates dissociated at the beam centre ($r = 0$), with respect to adsorbates being far away from the irradiated area ($r \rightarrow \infty$). The second dimensionless parameter describes the diffusion length of adsorbates without being irradiated:

$$\tilde{\rho}_{\text{out}} := \frac{2\rho_{\text{out}}}{FWHM_B} = \frac{2\sqrt{D\tau_{\text{out}}}}{FWHM_B} \quad (4)$$

where $FWHM_B$ is the full width at half maximum of $f(r)$. Using the following set of dimensionless variables $\tilde{r} := r/\rho_{\text{out}}$, $\tilde{n}(\tilde{r}) = n(\tilde{r})/n_{\text{out}}$, $\tilde{f}(\tilde{r}) = f(\tilde{r})/f_0$ Eq. (1) takes the simple form:

$$0 = 1 - (\tilde{\tau} - 1)2^{-(\tilde{r}\tilde{\rho}_{\text{out}})^2}\tilde{n}(\tilde{r}) + \frac{\partial^2 \tilde{n}(\tilde{r})}{\partial \tilde{r}^2} + \frac{1}{\tilde{r}} \frac{\partial \tilde{n}(\tilde{r})}{\partial \tilde{r}} \quad (5)$$

with two unknown process parameters: $\tilde{\tau}$, $\tilde{\rho}_{\text{out}}$. The deposit shape is time-proportional to the dimensionless growth rate function

$$\tilde{R}(\tilde{r}) := \frac{R(\tilde{r})}{sJV} = \tilde{n}(\tilde{r})\tilde{f}(\tilde{r})(\tilde{\tau} - 1) \quad (6)$$

independent of the impinging molecule flux— J (can be calculated via Monte Carlo simulations¹¹), atomic volume of the deposited molecule fragment— V , and the sticking probability— s . At this point two things become obvious: (a) according to Eqs. (3), (4) we can find different sets of parameters (D , σ , and τ) giving the same $\tilde{\tau}$, $\tilde{\rho}_{\text{out}}$ values, and (b) according to Eq. (6) these different sets will result in identical deposit shapes (in the case of exposures fulfilling the stationary state conditions $\partial n/\partial t = 0$, i.e. exposure dwell times of larger than a few microseconds per pixel). This means that performing a series of stationary state experiments is not sufficient to determine a unique set of σ , τ_{out} , D . However, the choice of σ , τ_{out} , D is neither unrestricted; due to the physical meaning of these parameters some criteria must be fulfilled: the net cross-section is often found to be smaller than the planar size of a molecule $\sigma \leq \sigma^{\text{max}}$ (condition 1); also the relation $1/\tau = (1/\tau_{\text{out}} - sJ/n_0) > 0$ (condition 2) proves true. These conditions make significant constraints on the acceptable values of parameters.

From the deposition rate (Eq. (6)) we can calculate the full width at half maximum of the deposit profile— $FWHM_D$. Thus we can define the dimensionless resolution parameter— $\tilde{\varphi} = FWHM_D/FWHM_B$. Depending on the shape of deposit, the following three regimes are distinctive: adsorbate-limited, diffusion-enhanced and electron-limited, (Fig. 2). For the adsorbate-limited regime, ($\tilde{\rho}_{\text{out}} < 0.1$) the first scaling law¹ is fulfilled and we observe the flat-top deposit shape with the resolution given by $\tilde{\varphi} = \sqrt{\log_2(\tilde{\tau} + 1)}$ (Fig. 3(a)). When surface diffusion starts to play a role the indent shape (Fig. 3(b)) is observed. When it dominates over irradiative depletion the Gaussian-like shape (Fig. 3(c)) is observed. In addition to the resolution parameter $\tilde{\varphi}$, we define additional dimensionless parameters, characterizing the deposit

Fig. 2. Map of the resolution parameter $\tilde{\varphi}$ and the process regimes: I—adsorbate-limited, II—diffusion-enhanced, III—electron-limited. In regime-I the diffusion of adsorbed molecules does not influence the deposit shape and the first scaling law¹ is valid. In regime-II the contribution of diffusion is observed in a form of an indent shape. In the regime-III the diffusive replenishment is strong enough to transfer the molecules to the beam centre (the resolution parameter is equal to one).

shape: (a) the location of the maximum of the deposition rate with respect to the full width at half maximum of the beam— $\tilde{r}_{\text{max}} := 2r_{\text{max}}/FWHM_B$, (b) the indent value $\tilde{R}_{\text{ind}} = (\tilde{R}(0) - \tilde{R}(r_{\text{max}}))/\tilde{R}(r_{\text{max}})$ and (c) the value of the dimensionless deposition rate at $r = 0$ $\tilde{R}_0 = \tilde{n}(0)\tilde{f}(0)(\tilde{\tau} - 1)$ (see Fig. 3(b)). As the product of $\tilde{n}(0)\tilde{f}(0) \leq 1$, the straightforward conclusion from Eq. (6) is that $(\tilde{\tau} - 1) \geq \tilde{R}(r_{\text{max}})$.

Fig. 3. Different deposit shapes (a) flat-top—typical for regime-I, (b) indent—typical for regime-II (the additional parameters characterizing the deposit profile are marked at the scheme, see also Fig. 4), (c) Gaussian-like—typical for regime-III.

3. RESULTS AND DISCUSSION

The Eq. (3) has been solved numerically via Matlab solver *bvp4c* for a wide range of $\tilde{\tau}$, $\tilde{\rho}_{out}$ parameters including many orders of magnitude of the r variable by applying the logarithmic transformation $l = \ln(2r/FWHM_B)$, as suggested by Ref. [12]. The parameters describing the deposit profile are shown in Figure 2 and in Figures 4(a–c). The estimation of the residence time and the diffusion coefficient was done to the FEBID deposit obtained from a $\text{Cu}(\text{hfac})_2$ precursor, an example given in article.¹ The remaining values were also taken from this article: local molecule flux $sJ/n_0 = 10 \text{ ML/s}$, atomic volume of a deposited molecule fragment $V = 0.46 \text{ nm}^3$, $f_0 = 9 \cdot 10^4 \text{ nm}^{-2}/\text{s}$, $FWHM_B = 110 \text{ nm}$. The dimensionless deposition growth rate function $\tilde{R}(r)$ extracted from the experimental results after the exposures of the beam lasting 2s; 3s; 4s are plotted in Figure 5. The curves corresponding to different times are overlapping, which means that we can apply the stationary approach. The numerical solution was fitted to the experimental curves with an accuracy of about 10%, obtaining the $\tilde{\tau} - 1 = \sigma\tau_{out}f_0 = 140$, $\tilde{\rho}_{out} = 2\sqrt{D\tau_{out}}/FWHM_B = 27$. According to condition 1 the maximum value of cross-section cannot be

Fig. 4. Additional dimensionless shape parameters; (a) location of the maximum $-\tilde{r}_{max}$, (b) indent value $-\tilde{R}_{ind}$, (c) dimensionless deposition rate at the radius equal to zero $-\tilde{R}_0$, (logarithmic scale).

Fig. 5. AFM profiles of FEB-deposits from $\text{Cu}(\text{hfac})_2$ adsorbates (taken from Ref. [1]). The fit was performed using $\tilde{\tau} = 140$, $\tilde{\rho}_{out} = 27$ in Eq. (5).

larger than the planar size of a molecule $\sigma^{max} = 0.6 \text{ nm}^2$, thus the residence time outside the irradiated area must be at least equal to $\tau_{out}^{min} = 140/(0.6 \cdot 9 \cdot 10^4) = 0.003 \text{ s}$, and therefore the average residence time of a molecule on the surface $\tau^{min} = 0.0025 \text{ s}$. On the other hand, condition 2 says that $(1/\tau_{out} > sJ/n_0)$, therefore τ_{out} must be smaller than 0.1 s, which implies the net cross-section value to be greater than 0.015 nm^2 . For this range of values the surface diffusion coefficient was calculated using the formula $D = (\tilde{\rho}_{out} FWHM_B/2)^2 \tau_{out}^{-1}$. The maximum value $8.4 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was calculated for $\tau_{out} = 0.003 \text{ s}$ and the minimum value $2.2 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for $\tau_{out} = 0.1 \text{ s}$.

The range of D -values reported in Ref. [1] ($3 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1} - 4 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) overlaps with our present results, however, is about an order of magnitude lower; firstly because the depletion parameter was underestimated, secondly because the assumption about the typical residence time to be equal to 10^{-3} s may be small.

4. CONCLUSIONS

In this work we presented a way to estimate the surface diffusion coefficient and the residence time of adsorbates from deposit shapes obtained by local focused electron beam induced CVD. We showed that stationary exposure experiments are not self-sufficient to determine uniquely all parameters of the process. Instead, using further assumptions, it is possible to estimate the range of above parameters. This was demonstrated for the molecule $\text{Cu}(\text{hfa})_2$. A time-dependent model, which could account for electron beam pulses, is necessary to be developed in order to give an answer if the surface diffusion coefficient and the residence time of adsorbed gas precursor molecules could be determined with a better accuracy.

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Received: 3 May 2011. Accepted: 2 June 2011.