A Statistical Approach to Molecular Delta Layer Depth Profiling

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Abstract

The delta layer depth response predicted by a simple statistical sputtering model (SSM) is compared with molecular sputter depth profile data obtained on Langmuir-Blodgett delta layer systems. All input parameters of the SSM are determined from low-fluence molecular dynamics simulations performed for 20-keV C_{60} cluster bombardment of silicon, making the model de facto parameter-free. It is found that both the calculated and measured depth response functions can be parametrized by the semi-empirical Dowsett expression. The resulting parameters (leading and trailing edge slope, full width half maximum) agree surprisingly well with those determined from the measured depth profiles.

Keywords: Molecular depth profiling; delta layers; depth resolution; response function; statistical sputtering model

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1. Introduction

The analysis of delta layers represents an elegant way to assess the depth resolution in sputter depth profiling. Following the SIMS signal representative for a thin, buried layer embedded in a matrix allows to directly determine the response function. The technique has therefore been adopted as a standard method to characterize the performance of SIMS for inorganic depth profiling using, for instance, delta dopant layers in semiconductors as a standard material. More recently, similar experiments have been carried out for molecular films as well, using cluster ion beams for sputter depth profiling. The measured delta layer profile can generally be fitted to an empirical expression published by Dowsett et al.[1], which comprises exponential leading and trailing edges connected by a Gaussian function. As a consequence, the measured depth resolution is characterized by the leading and trailing edge slope λ_g and λ_d along with the center and width σ of the intermittant Gaussian. The physical interpretation of these parameters, however, is not entirely clear.

In principle, the depth resolution obtained in a sputter depth profiling experiment is influenced by many phenomena, including the information depth of the employed surface analytical method, ion bombardment induced interlayer mixing, surface segregation, preferential sputtering and surface topography which may develop under ion bombardment. Many of these contributions are coupled with the statistical nature of the sputtering process, which needs to be taken into account in a model description of a depth profiling experiment. Following ideas outlined many years ago[2-6], we have recently coupled a statistical sputtering model (SSM) with multi-impact molecular dynamics (MD) simulations in order to describe the microscopic erosion characteristics during a sputter depth profile. The model is based on parameters extracted exclusively from low-fluence MD simulation and allows an extrapolation towards larger primary ion fluences which are relevant in a real depth profile. The calculated data allow to extract the delta layer depth response function, which can be compared to empirical descriptions published in the literature as well as to the results of recent experiments on sputter depth profiling of molecular delta layers. In the present paper, we attempt such a comparison using Langmuir-Blodgett multilayers as a model system for molecular depth profiling under C_{60} cluster ion bombardment.

2. Experiment

The experimental data shown below was acquired on a Langmuir-Blodgett molecular delta layer model system comprising of a double layer of dimethoyl-xxx (DMPA) of ~ 4 nm thickness embedded between two Barium-arachidate (AA) multilayer stacks of 50 and 54 nm thickness, respectively. The fabrication of this system has been described in great detail elsewhere. Sputter depth profiling was performed on a ToF-SIMS instrument equipped with a 40-kV C_{60}^+ ion source aiming at the target surface under 40° impact angle with respect to the surface normal. Details of the experimental setup and the applied procedures to extract depth profiles from 3D imaging profiles have been given elsewhere and need not be repeated here.

3. The statistical sputtering model

A detailed description of the statistical sputtering model employed here has been given elsewhere[7,8]. Briefly, the ion bombarded solid is divided into layers of freely selectable thickness *d*, and the filling of each layer (*i*) is described in terms of a dimensionless filling factor θ_i which is initially set to zero for all "virtual" layers above and unity for all "real" layers below the original surface. The primary ion fluence is parametrized in terms of the amount of sputter removed material, which in turn is described in units of "monolayer equivalents" *x*, where $x = 1$ corresponds to the removal of the number of particles (atoms or molecules) present in a completely filled layer. Successive surface erosion manifests as a variation of the filling factors $\theta_i(x)$, which is calculated via a set of differential equations using depth dependent sputtering probabilities. [7] The vertical relocation of particles is treated in terms of a diffusion-like approach with diffusivity constants D_i which also depend on depth below the momentary surface. By calculating the contribution of particles originally located in a particular layer (i_0) as a function of x, the model allows to extract the depth response function for a delta layer located at (i_0) as described in great detail elsewhere.

The parameters entering the model calculation were determined from low-fluence multi-impact MD simulations performed for silicon bombarded by 20-keV C_{60} projectiles.

4. Results and discussion

The molecular depth profile measured for a DMPA delta layer is shown in Figure 1. The data were acquired using a 10-keV C_{60}^+ ion beam with the sample at cryogenic temperature (~100 K). The measured depth response can be compared to the empirical function introduced by Dowsett et al., [1] which was based on the analysis of a large set of experimental data on inorganic delta layer depth profiling. The solid line depicts a fit of this function yielding the fitting parameters λ_g , λ_d and σ depicted in Table 1.

The response function for a delta layer located at an arbitrary depth (here at $i_0 = 44$) as calculated using the SSM is plotted in Figure 2. Probably the most apparent observation is that the model prediction exhibits the same general features as the measured data, namely an asymmetric shape with exponential leading and trailing edges. Fitting the Dowsett function to the SSM calculation (solid line in Figure 2), we find the parameters depicted in Figure 2. It should be noted that the least square fit (red line) describes the central part of the predicted response function quite well, but does not accurately reproduce the calculated leading and trailing edges. Fitting these slopes independently (black lines), we find an unchanged value of λ_g but a slightly lower decay length λ_d.

These values can now be compared to the experimental data. Note that the parameters depicted in Figure 2 are given in monolayer equivalents. For the case of LB multilayers studied here, a layer in the SSM must be defined by the thickness of a molecular layer, which for the present case amounts to about 2 nm. Under these conditions, the depth response parameters predicted by the SSM translate to values which are also depicted in Table 2. It is seen that the parameters predicted by the SSM model agree astonishingly well with the experimental data. Not only is the observed depth resolution (FWHM) correctly reproduced, but also its asymmetry and trailing edge slope is predicted rather accurately.

Given the observed agreement, one can try to use the SSM to unravel the different mechanisms that contribute to the observed depth resolution. For that purpose, we artificially vary either the depth distribution of sputtered particles ("information depth") or the beam induced particle relocation ("mixing") via the respective SSM model parameters. [8] Switching, for instance, the ion beam induced particle relocation (mixing) completely off, we obtain practically unchanged values of λ_g, σ and the FWHM, only the decay length λ_d is slightly reduced by 25%. While this reduction is qualitatively expected, it is surprising how small the influence of interlayer mixing appears to be. If we then restrict the information depth to the uppermost layer only, all parameters undergo drastic changes. As intuitively expected, the leading edge slope decreases to values smaller than one layer thickness. However, also the decay length is observed to decrease to about one layer thickness, illustrating that also this parameter is largely influenced by the depth-of-origin distribution of the sputtered material rather than by interlayer mixing.

5. Conclusions

We show that the statistical sputtering model (SSM) is capable to reproduce the characteristic features of measured depth response functions in molecular sputter depth profiling. Being based on input data extracted from low-fluence molecular dynamics simulations, the model is de facto parameter free, but reproduces experimental data measured under cluster ion bombardment of organic delta layers fairly well. Based on that assessment, the model appears to provide a useful tool to model real depth profiles by extrapolation of the extremely time consuming multi-impact MD simulations to large projectile fluences.

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Table 1

Leading and trailing edge growth and decay lengths (λ_g and λ_d), Gaussian width (σ) and full width half maximum (FWHM) of depth response function predicted by the SSM and measured for a molecular delta layer system under bombardment with 10-keV C_{60}^+ ions.

	λ_g	λ_d	σ	**FWHM**
SSM	~ 1 nm	~ 8 nm	~ 5 nm	~ 20 nm
10-keV C_{60}^+	1.0 nm	11.2 nm	5.3 nm	19.5 nm

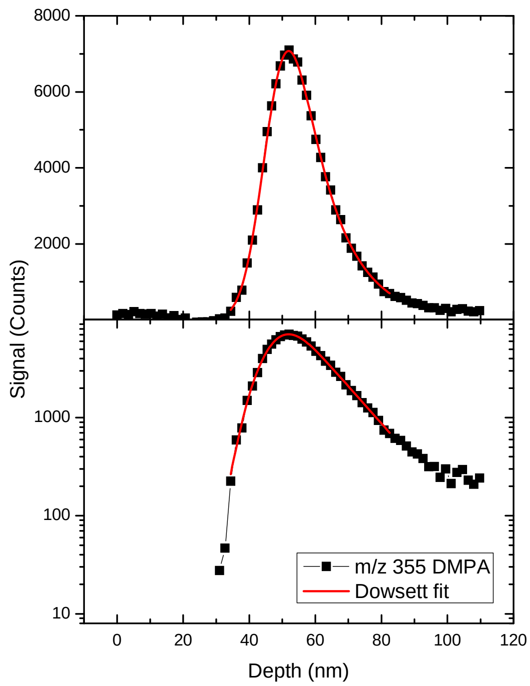

Figure 1 Molecular depth profile of DMPA delta layer embedded in an AA multilayer matrix measured at 100 K using a 10-keV C_{60}^{+} ion beam impinging under 40° with respect to the surface normal. Solid line: Fit of empirical Dowsett function.

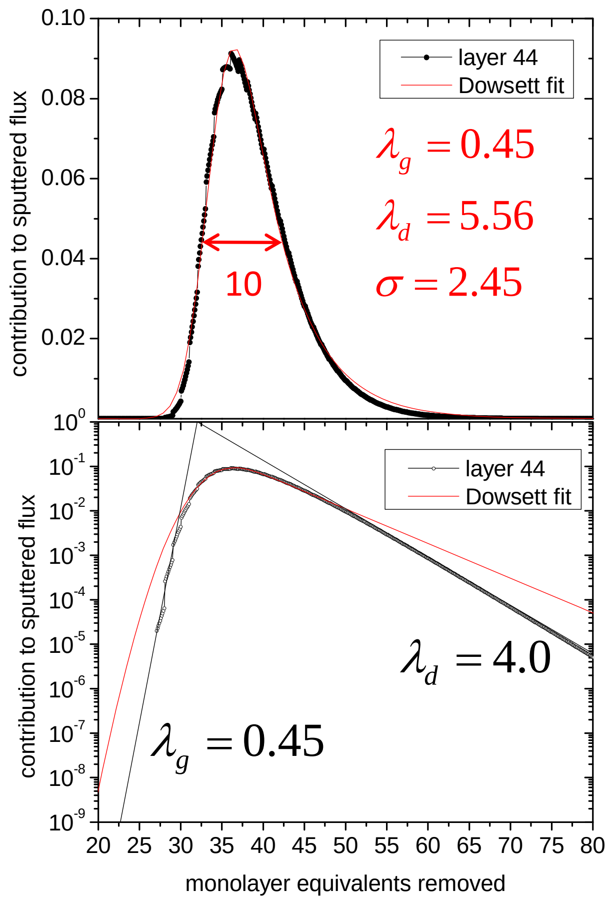

Figure 2 Delta layer response function calculated with the SSM model for i = 44. Red line: lest square fit of Dowsett function (see text) yielding the parameters displayed in the upper panel; black lines: exponential fit of leading and trailing edge yielding the parameters displayed in the lower panel.