SIMS proceedings paper

SURFACE and INTERFACE ANALYSIS

Received: 14 October 2011 Revised: 8 March 2012 Accepted: 13 March 2012 Published online in Wiley Online Library: 25 April 2012

(wileyonlinelibrary.com) DOI 10.1002/sia.4966

A statistical interpretation of molecular delta layer depth profiles

A. Wucher,[a]* K. D. Krantzman,[b] C. Lu[c] and N. Winograd[c]

The delta layer depth response predicted by a simple statistical sputtering model is compared with molecular sputter depth profile data obtained on Langmuir–Blodgett delta layer systems. All input parameters of the statistical sputtering model 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 calculated and measured depth response functions can be parametrised by the semiempirical Dowsett expression. The resulting parameters (leading and trailing edge slope, full-width at half-maximum) agree surprisingly well with those determined from the measured depth profiles. Copyright © 2012 John Wiley & Sons, Ltd.

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

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 makes it possible to directly determine the response function. The technique has therefore been adopted as a standard method to characterise 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.[2–5] As a consequence, the measured depth resolution is characterised by the leading and trailing edge slope λ_g and λ_d along with the centre and width σ of the embedded 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 used 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,[6–10] we have recently coupled a statistical sputtering model (SSM) with multi-impact molecular dynamics (MD) simulations to describe the microscopic erosion characteristics during a sputter depth profile.[11] The model is based on parameters extracted exclusively from low-fluence MD simulation and allows an extrapolation towards larger primary ion fluencies, which are relevant in a real depth profile. The calculated data can be used to extract the delta layer depth response function, which can be compared with empirical descriptions published in the literature as well as to the results of recent experiments on sputter depth profiling of molecular delta layers. In this article, we attempt such a comparison using a Langmuir–Blodgett multilayer stack as a model system for molecular depth profiling under C_{60} cluster ion bombardment.

Experiment

The experimental data shown in the next section was acquired on a Langmuir–Blodgett molecular delta layer model system comprising of a double layer of dimyristoyl phosphatidate (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.[3,4] Sputter depth profiling was performed on a time of flight SIMS instrument equipped with a 40-kV C_{60}^+ ion source aimed at the target surface under a 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 data have been given elsewhere and need not be repeated in this study.[12–14]

Statistical sputtering model

A detailed description of the SSM used in this study has been given elsewhere.[11,15] 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 'virtual' layers above and unity for 'real' layers

* *Correspondence to: A. Wucher, Faculty of Physics, University Duisburg–Essen, Duisburg 47048, Germany. E-mail: andreas.wucher@uni-due.de*

a *Faculty of Physics, University Duisburg–Essen, Duisburg 47048, Germany*

b *Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424, USA*

c *Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA*

below the original surface. The primary ion fluence is parametrised 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 filled layer. Successive surface erosion manifests as a variation of the filling factors $\theta_i(x)$, which are calculated via a set of differential equations using depth-dependent sputtering probabilities.[11] The vertical relocation of particles (i.e. ion bombardment–induced interlayer mixing) is treated in terms of a diffusion-like approach with diffusivity constants, which also depend on the depth below the instantaneous surface. By calculating the contribution of particles originally located in a particular layer (i_0) to the sputtered flux as a function of x, the model can be used to extract the depth response function for a delta layer located at (i_0) as described in great detail elsewhere.[11,15]

The essential parameters entering the model calculation are the depth-dependent sputter emission probabilities c_j and diffusivity constants D_j, where the index (j) refers to the depth below the instantaneous surface. Because the surface is receding during the depth profile, each layer (i) becomes located at a certain depth (j) with a probability $p_i^{(j)}$ that is calculated from the values of all filling factors (θ) and changes as a function of removed monolayer equivalents (x). Conceptually, the parameters c_j and D_j can be determined from MD simulations. The coefficients c_j reflect the depth-of-origin distribution of the sputtered material, which can be extracted from static MD simulations with each projectile affecting an ideal, undisturbed surface. Although under low energy atomic ion bombardment, nearly all sputtered particles originate from the uppermost layer (rendering $c_1 = 1$ and $c_{j>1} = 0$), such simulations show that for the case of energetic cluster ion bombardment a significant fraction of the sputtered material is being emitted from deeper layers ranging down to several nanometres below the surface.

The diffusion coefficients D_j, on the other hand, must be determined from multi-impact simulations modelling the effects of accumulating projectile impacts onto the same surface area. For the case of energetic clusters bombarding inorganic targets, such simulations have recently been performed, and D_j values have been obtained by analysing the fluence dependence of the depth distribution of particles originally located in layer (j) throughout the early, low fluence stages of the simulation. Unfortunately, such *dynamic* calculations are not yet available for a molecular system under cluster ion bombardment. We therefore revert to simulations performed for silicon bombarded by 20-keV C_{60} projectiles and use the parameters determined from the first 50 successive impacts treated in these calculations as described in detail elsewhere.[11] The layer thickness used in this process corresponds to the monolayer thickness of Silicon (0.27 nm). It should be noted that practically the same values are obtained from similar simulations performed for a silver target,[16] suggesting the resulting set of c_j and D_j to be representative for cluster impact onto inorganic surfaces in general. From *static* MD simulations performed on a *molecular* system consisting of Langmuir–Blodgett multilayers on silver,[17] on the other hand, one can extract sputtering probabilities c_j, which are quite similar to the ones obtained for inorganic targets as long as the layer thickness d is redefined as the *molecular* monolayer thickness (2.6 nm in this case).[18]

Results and discussion

A molecular depth profile measured for a DMPA delta layer is shown in Fig. 1. The data were acquired using a 10-keV C_{60}^+ ion beam with the sample held at cryogenic temperature (~100 K) during the analysis. The measured depth response function can be compared with the empirical Dowsett function,[1] which was based on the analysis of a large set of experimental data on inorganic delta layer depth profiling. The red line depicts a fit of this expression to the data, 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 Fig. 2. Details of the calculation and the procedures used to extract this function from the calculated data can be found elsewhere.[15] Probably the most apparent observation is that the model predicts 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 (red line in Fig. 2), we find the parameters depicted in the upper panel of Fig. 2. It should be noted that the least square fit 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 as depicted in the lower panel of Fig. 2.

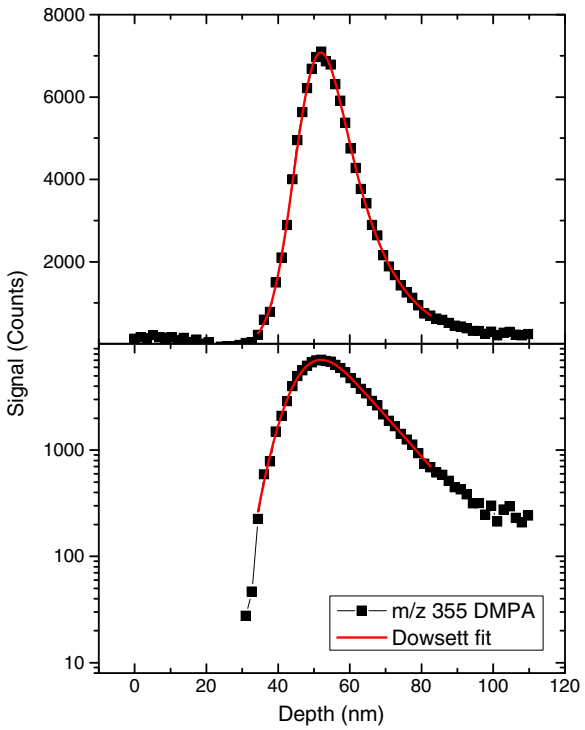

Figure 1. Molecular depth profile of DMPA delta layer embedded in an AA multilayer matrix measured at 100 K using a 10-keV C_{60}^+ ion beam impinging under 40° with respect to the surface normal. Solid line: fit of empirical Dowsett function (see text).

Table 1. Leading and trailing edge growth and decay lengths (λ_g and λ_d), Gaussian width (σ) and 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
Experiment	1.0 nm	11.2 nm	5.3 nm	19.5 nm

SURFACE and INTERFACE ANALYSIS

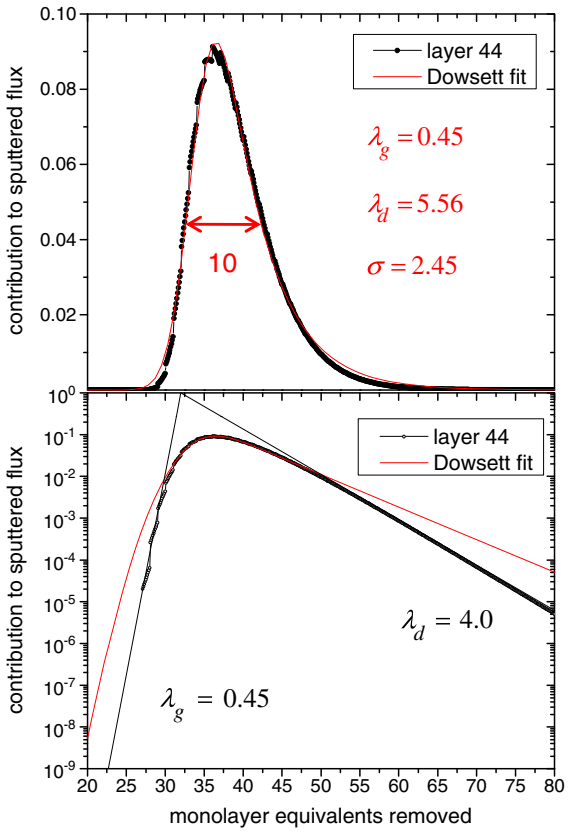

Figure 2. Delta layer response function calculated with the SSM model for $i_0 = 44$. Red line: lest square fit of Dowsett function (see text) yielding the parameters displayed in the upper panel; black lines: exponential fit of leading and trailing edge yielding the parameters displayed in the lower panel.

These values can now be compared with the experimental data. Note that the parameters depicted in Fig. 2 are given in layer 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 approximately 2 nm. Under these conditions, the depth response parameters predicted by the SSM translate to values which are also depicted in Table 1. 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 full-width at half-maximum (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.[15] As a limiting case, one might, for instance, switch the mixing completely off by setting all D_j to zero. Under these conditions, we obtain practically unchanged values of λ_g, σ and the FWHM with only the decay length λ_d being slightly reduced. Although such a reduction is qualitatively expected, it is surprising how small the influence of interlayer mixing appears to be. If we then assume another limiting case by restricting the information depth to the uppermost layer only, all parameters will undergo drastic changes. As intuitively expected, the leading edge slope decreases to values smaller than one layer thickness. However, also the decay length is predicted to decrease to about one layer thickness, illustrating that this parameter is largely influenced by the depth-of-origin distribution of the sputtered material as well.

Conclusions

We show that the SSM is capable of reproducing the characteristic features of a measured delta layer depth response function in a molecular sputter depth profile. Being based on input data extracted from low-fluence MD simulations, the model is *de facto* parameter free but reproduces experimental data measured under cluster ion bombardment of organic delta layers fairly well. The results suggest that the depth resolution obtained in molecular depth profiling experiments is to a large extent determined by the statistical nature of the sputtering process and the resulting depth-of-origin distribution of the sputtered material. One should note that this distribution can also be influenced by bombardment-induced surface microtopography, which could in principle be incorporated into the model using a corresponding variation of the c_j parameters. In this context, it will be of interest to determine those parameters from MD simulations at different projectile fluences and follow their evolution from static into steady-state sputtering conditions. Investigations of this kind will be the subject of a forthcoming article. In this context, it should be noted that a modified version of the model based on steady-state MD data has recently been used to investigate how the input parameters will change as a function of relevant experimental parameters such as the projectile impact energy and angle, the sample temperature, and so on.[19]

Acknowledgements

The authors thank R. Paruch and Z. Postawa for making their data available to us before publication. The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft in the frame of the SFB 616 'Energy dissipation at surfaces'. Partial financial support from the National Science Foundation (grant no. CHE-0908226) and the Department of Energy (grant no. DE-FG02-06ER15803) is also acknowledged.

References

[1] M. G. Dowsett, G. Rowlands, P. N. Allen, R. D. Barlow, *Surf. Interface Anal.* **1994**, *21*, 310.
[2] A. G. Shard, F. M. Green, P. J. Brewer, M. P. Seah, I. S. Gilmore, *J. Phys. Chem. B* **2008**, *112*, 2596.
[3] C. Lu, A. Wucher, N. Winograd, *Surf. Interface Anal.* **2011**, *43*, 81.
[4] C. Lu, A. Wucher, N. Winograd, *Anal. Chem.* **2011**, *83*, 351.
[5] A. G. Shard, R. Foster, I. S. Gilmore, J. L. S. Lee, S. Ray, L. Yang, *Surf. Interface Anal.* **2011**, *43*, 510.
[6] A. Benninghoven, *Z. Phys.* **1971**, *230*, 403.
[7] S. Hofmann, *Appl. Phys.* **1976**, *9*, 59.
[8] S. Hofmann, J. Erlewein, A. Zalar, *Thin Solid Films* **1977**, *43*, 275.
[9] S. Hofmann, *Appl. Phys.* **1977**, *13*, 205.
[10] M. P. Seah, J. M. Sanz, S. Hofmann, *Thin Solid Films* **1981**, *81*, 239.
[11] K. D. Krantzman, A. Wucher, *J. Phys. Chem. C* **2010**, *114*, 5480.
[12] J. Cheng, A. Wucher, N. Winograd, *J. Phys. Chem. B* **2006**, *110*, 8329.
[13] L. Zheng, A. Wucher, N. Winograd, *Appl. Surf. Sci.* **2011**, *43*, 41.
[14] A. Wucher, J. Cheng, L. Zheng, N. Winograd, *Anal. Bioanal. Chem.* **2009**, *393*, 1835.
[15] A. Wucher, K. D. Krantzman, *Surf. Interface Anal.* **2012**; DOI: 10.1002/sia.4931.
[16] R. Paruch, Z. Postawa, personal communication
[17] R. Paruch, L. Rzeznik, B. Czerwinski, B. J. Garrison, N. Winograd, Z. Postawa, *J. Phys. Chem. C* **2009**, *113*, 5641.
[18] Z. Postawa, personal communication
[19] R. Paruch, B. J. Garrison, Z. Postawa, *Anal. Chem.* **2012**, DOI: 10.1021/ac300363j.

