SIMS proceedings paper

SURFACE and INTERFACE ANALYSIS

Received: 2 October 2011 Revised: 26 January 2012 Accepted: 5 March 2012 Published online in Wiley Online Library: 27 March 2012

(wileyonlinelibrary.com) DOI 10.1002/sia.4940

Mixed MD simulation – analytical model analysis of Ag(111), C_{60} repetitive bombardment in the context of depth profiling for dynamic SIMS

Robert J. Paruch,[a]* Barbara J. Garrison[b] and Zbigniew Postawa[a]

In this study, an analytical model is utilised to extract depth profiles from molecular dynamics simulations of dynamic secondary ion mass spectrometry (SIMS). The depth profiles for dynamic SIMS calculations for a reference system of C_{60} bombardment of Ag(111) with a kinetic energy of 20 keV and a polar angle of 0° are compared to those for 5 keV bombardment with a polar angle of 0° and 20 keV bombardment with a polar angle of 70°. It is shown that both decreasing the impact energy and making the polar angle more off-normal improve the depth resolution of the SIMS depth profile. The former condition, however, reduces the total sputtering yield achievable in the dynamic conditions making it less favourable for the depth profiling. It is also shown that the depth resolution dependence upon RMS roughness is not obvious when changing the primary beam conditions. Copyright © 2012 John Wiley & Sons, Ltd.

Introduction

Application of cluster primary beam sources in secondary ion mass spectrometry (SIMS) made molecular depth profiling practicable and molecular dynamics (MD) simulations became the theoretical partner to the SIMS technique in order to understand the important factors for depth profiling.[1,2] A recently developed 'divide and conquer' scheme has made MD simulations of dynamic SIMS feasible.[3] Modelling of fluences up to 10^{14} impacts/cm^2 is now tractable within several months of computing time.[4–6] Although some characteristics such as RMS roughness and total sputtering yield are useful for understanding the factors limiting the depth resolution in depth profiling SIMS experiments and can be directly calculated from MD simulations, obtaining depth profiles is beyond the current MD simulation capabilities. Only a few monolayer equivalents (ML) can be removed from the sample with MD simulations, which is far from the amount of material typically removed in a depth profiling experiment. The issue is how to utilise the wealth of simulation data that contains the properties of the target material, the incident cluster and the initial beam conditions and is therefore expected to provide the appropriate depth profiles.

In this paper, previously described,[7] a steady-state statistical sputtering model (SS-SSM) is applied to interpret MD simulation results of repetitive bombardment (dynamic SIMS) of Ag(111) by C_{60} for representative impact energies and angles in the context of depth profiling quality. The SS-SSM is a revised form of the statistical sputtering model (SSM) originally presented by Krantzman and Wucher.[8,9] The SSM model investigated the evolution of a bombarded system towards the steady state using data from the initial few impacts, whereas the SS-SSM model utilises the simulation data, in a form of numerical sputtering and displacement parameters, which are obtained directly from the steady-state region, as the belief is that the microscopic details of the roughened surface are sufficiently different from those of the flat surface to influence the depth profiles.

Model

Details of the SS-SSM construction and prescription for deriving the sputtering and displacements parameters from the MD simulation are given elsewhere.[7] In this paper, only a brief description will be provided.

The model is expressed by a set of differential equations for filling factors of arbitrary thick system layers, as a function of amount of eroded material in ML units. The filling factor is defined as the fraction of atoms that are currently present in the layer, taking values from 0 to 1, where 1 denotes a completely filled layer. Each differential equation contains three terms: a sputtering term, describing the loss of atoms by sputtering, and two displacement terms, describing the loss or gain of atoms by atom relocations to or from other layers. Special care is undertaken with model formulation so as to prevent unphysical behaviour such as layer overfilling. The model employs sputtering and displacement parameters for integration as well as the average filling factors as the initial condition. These quantities are determined as averages relative to the average surface level over all the impacts within the steady-state region of the MD simulation, i.e. the range of fluence in which the RMS roughness is relatively constant and the average surface level recedes at a constant rate. The property of such an approach is that these values will not depend on the fluence. The sputtering parameter in its raw form Γ_j denotes the average number of atoms

* *Correspondence to: Robert J. Paruch, Smoluchowski Institute of Physics, Jagiellonian University, ul. Reymonta 4, 30–059 Krakow, Poland. E-mail: robert.paruch@uj.edu.pl*

a *Smoluchowski Institute of Physics, Jagiellonian University, ul. Reymonta 4, 30-059 Krakow, Poland*

b *Department of Chemistry, Penn State University, 104 Chemistry Building, University Park, PA 16802, USA*

SURFACE and INTERFACE ANALYSIS

sputtered from j-th system layer per impact, where $j=0$ represents the average surface level, $j<0$ and $j>0$ – the levels above and below the average surface level, respectively; and the displacement parameter $\Delta_{j\to j'}$ denotes the average number of atoms relocated from j-th to j'-th system layer per impact. Naturally, the sum of Γ_j over all j values yields the total sputtering yield in dynamic conditions. In the same manner, the average filling factors are calculated for all the system layers denoting the average fraction of a layer that remains in the layer, i.e. neither sputtered nor displaced. Incorporation of the sputtering and displacement parameters by the model is preceded by appropriate scaling (normalization) of these parameters which is required for the consistency of model results. The SS-SSM differential equations are defined for space fixed system layers. The sputtering and displacement parameters are, however, calculated relative to the average surface level. Therefore, at each step of integration, the average surface level is determined upon the current calculated layer fillings and the parameters are employed, respectively. This procedure results in discrete shifting of the parameters along the space fixed system layers each time the average surface level switches position because of sputter removal from the system.

Extracting depth profiles requires tracking the fate of atoms originating from the initial system layers independently. This task is accomplished by dividing the system into a proper number of subsystems where each subsystem tracks the evolution of the atoms from one initial layer. Finite thickness of system layers and discrete shifting of the sputtering and displacement parameters along the space fixed system layers generate jagged depth profiles. In order to obtain smooth depth profiles as well as for quantitative purposes of determining the numerical characteristics of the depth profiles, the depth profile is fitted to the Dowsett's analytical response function,[10,11] which is typically used in experimental data analysis. To perceive at this point is that the integral of both the jagged depth profile and the fitted function remains a value of unity as denoting removal of 1 ML from the system. This observation follows on the procedure of normalization of the sputtering and displacement parameters, mentioned above.

Results and discussion

The 'divide and conquer' scheme has been used to carry on MD simulations of repetitive bombardment of a Ag(111) sample by C_{60} projectiles.[3,4] Following primary beam conditions were applied: a kinetic energy of 5 keV at a polar angle of 0°, 20 keV at 0° and 20 keV at 70°. The main Ag sample measured 53 × 53 × 27 nm. The steady state was reached after about 2500, 1000 and 1500 impacts, respectively. In order to calculate the sputtering and displacement parameters, the sample was divided into 0.94 nm thick layers, which corresponded to four atomic layers of an intact Ag(111) surface. Such a layer thickness is approximately equal to 1 nm, thus the depth profiles which are shown as a function of ML equivalents removed can be approximately interpreted as a function of depth in 1 nm units. The sputtering and displacement parameters were then calculated as averages over subsequent 1000 impacts within the steady state for each system. To note is that no more than 2.5 ML of material was removed during the steady-state MD simulations for every system. Including the introductory period starting from a flat surface before the steady state was reached, each MD simulation took almost one year to complete employing the MD code and computing resources used. Applying the SS-SSM allowed to extrapolate the simulation results towards fluence ranges corresponding to removal of about 30 ML of material. Consequently, the depth profiles could be obtained in a couple of hours of computing time.

The average number of atoms sputtered from system layers Γ_j (the sputter distribution) and the average number of atoms relocated between pairs of system layers $\Delta_{j\to j'}$ (the displacement distribution) *versus* layer number j for the systems investigated are shown in Fig. 1. For all the systems, the width of the sputtering distribution is comparable to the average surface level ±2 × RMS roughness distance, which indicates that most of the sputtered atoms come from the exposed surface, and the maxima of the sputtering distributions occur at the depth which is close to the average surface level. In addition, for all systems, atom displacements for moving one layer upwards or downwards are dominant as a manifestation of the most probable atom relocations between the nearest neighbouring layers. On the other hand, the widths and the heights of the sputtering and displacement distributions vary depending upon the primary beam conditions. The sputtering distributions widths differ for different systems as determined by the RMS roughness. The displacement distribution is wider and deeper than the sputtering distribution for the 20 keV, 0° bombardment reference

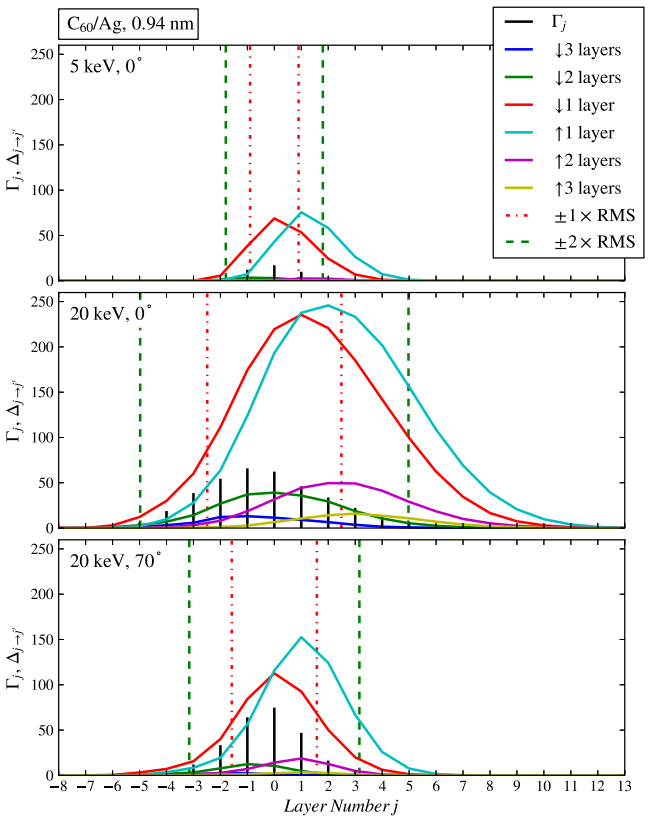

Figure 1. Average number of sputtered particles Γ_j (sputtering distribution) and average number of displaced atoms $\Delta_{j\to j'}$ (displacement distribution) *versus* layer number j for the systems investigated, calculated from the steady state of MD simulations. The sputtering yields are shown as vertical bars. The displacements are shown as solid lines for atom movement of the number of layers colour coded in the legend. The vertical dashed lines mark the positions of ±1 and ±2 × RMS roughness values relative to the average surface level $j=0$.

system than for the other systems. The height of the sputtering distribution is about three times lower than the atom displacements for ±1 layer and comparable to the atom displacements ±2 layers for the reference system. For the other systems, the atom movement of ±1 layer dominates over the sputtering for 5 keV, 0° but contributes comparably as the sputtering for 20 keV, 70°.

Depth profiles for a δ-layer from the SS-SSM *versus* ML equivalents removed are shown in Fig. 2. The layer chosen for the δ-layer is located approximately 14 nm below the original average surface level. The choice of the δ-layer location is arbitrary since the SS-SSM produces steady-state depth profiles that, in principle, are identical as well as representative for the MD simulation steady-state depth profiles. The depth profiles for all the systems show typical features such as a shift in the peak position to a higher position in the sample than the actual δ-layer position and an asymmetrical shape with the leading edge rising more quickly and the trailing edge decaying more slowly.[12,13] The FWHM of the depth profile for the 20 keV, 0° bombardment reference system is 6.1 nm, a value in a good agreement with experimental measurements of depth resolution of a Ni:Cr multilayer structure as determined from the first interface width, namely 5–8.7 nm over a 10–20 keV C_{60} energy range.[14,15] The depth profiles for 5 keV, 0° and 20 keV, 70° are almost identical in shape and distinctly different from the depth profile of the reference system. As the peak position of the profile is an apparent measure of the δ-layer location in the sample, the accuracy of δ-layer localisation in the sample during dynamic SIMS depth profiling should benefit from either reducing the primary beam energy or making the polar angle of incidence radically off-normal.

Total sputtering yields and RMS roughness values calculated from the steady state of MD simulations and depth resolutions in FWHM calculated from the SS-SSM are summarised in Table 1.[4,16] If the 20 keV, 0° system is considered as the reference system, then either lowering the incident kinetic energy or changing the incident angle to near grazing improves the depth profile as indicated by the smaller FWHM values. For the 5 keV, 0° system, the improvement results from a significantly reduced sputtering yield which has a narrow sputtering distribution Γ_j. Consequently, the RMS roughness is reduced.

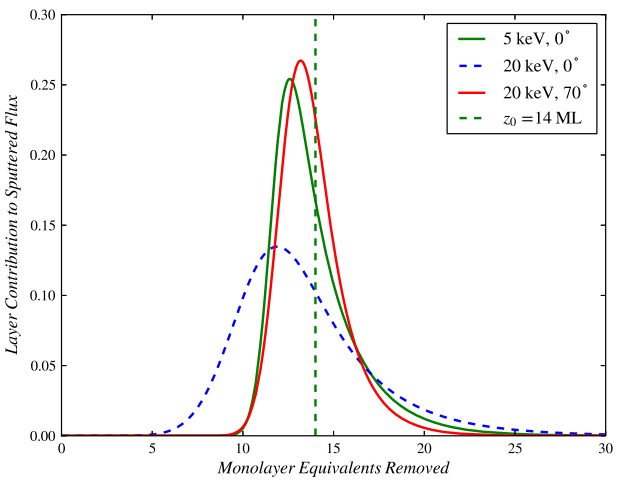

Figure 2. Depth profiles for a δ-layer from the SS-SSM for the systems investigated. The vertical green dashed line marks the actual position z_0 of the δ-layer.

Table 1. Total sputtering yields and RMS roughness values calculated from the steady state of MD simulations, and depth resolutions in FWHM calculated from the SS-SSM for the systems investigated

Energy (keV)	Angle (°)	Total sputtering yield (atoms)	RMS Roughness (nm)	FWHM (nm)
5	0	45	0.9	3.0
20	0	373	2.4	6.1
20	70	262	1.5	3.1

For the 20 keV, 70° system, the sputtering yield is only reduced ~30% from the reference system. The displacement distribution, however, is reduced in magnitude in width, thus yielding a smaller RMS roughness. Even though the calculated depth profiles are similar, the larger sputtering yield for the 20 keV, 70° system means that a lower total dose will be required to obtain the depth profile.

Interestingly, the depth resolution dependence upon the RMS roughness is not evident when changing the primary beam conditions. Namely, although the depth resolutions for the 5 keV, 0° and 20 keV, 70° systems are almost equal, the RMS roughness value for 20 keV, 70° is larger by a factor of about 1.7. This concludes that the basis of the dependence in question is complex, even though one would expect the larger RMS roughness to cause the worse depth resolution. An investigation into which factors such as RMS roughness, width of the displacement distribution, width of the sputtering distribution are most influential in controlling the depth profile is one of the objectives in further studies with the SS-SSM.

Conclusion

The SS-SSM has been used to interpret the results of MD dynamic SIMS simulations. It was shown that either lowering the impact kinetic energy or making the incidence radically off-normal improves the depth profiles when compared to a reference system of 20 keV, 0° C_{60} bombardment of Ag(111). Although the depth resolutions for the 5 keV, 0° and 20 keV, 70° systems are almost equal, the total sputtering yield achievable in the dynamic conditions reduces significantly for the low energy system. The larger sputtering yield for the near grazing incidence system means, on the other hand, that a lower total dose will be required to obtain the depth profile and so makes this choice of the primary beam conditions more favourable for the depth profiling. The results also show that systems which RMS roughness differs may produce the depth profiles of essentially equal depth resolutions.

Acknowledgement

The authors gratefully acknowledge financial support from the National Science Foundation Grant No. CHE-0910564 and the Polish Ministry of Science and Higher Education Program No. PB1839/B/H03/2011/40.

References

[1] N. Winograd, *Anal. Chem.* **2005**, *77*, 142A.
[2] N. Winograd, B. J. Garrison, *Annu. Rev. Phys. Chem.* **2010**, *61*, 305.
[3] M. F. Jr Russo, Z. Postawa, B. J. Garrison, *J. Phys. Chem. C* **2009**, *113*, 3270.

[4] R. Paruch, L. Rzeznik, M. F. Russo, B. J. Garrison, Z. Postawa, *J. Phys. Chem. C* **2010**, *114*, 5532.
[5] Z. Postawa, L. Rzeznik, R. Paruch, M. F. Russo, N. Winograd, B. J. Garrison, *Surf. Interface Anal.* **2011**, *43*, 12.
[6] L. Rzeznik, R. Paruch, B. J. Garrison, Z. Postawa, *Nucl. Instrum. Meth. B* **2011**, *269*, 1586.
[7] R. J. Paruch, Z. Postawa, A. Wucher, B. J. Garrison, *J. Phys. Chem. C* **2011**, *116*, 1042.
[8] K. D. Krantzman, A. Wucher, *J. Phys. Chem. C* **2010**, *114*, 5480.
[9] A. Wucher, K. Krantzman, C. Lu, N. Winograd, *Surf. Interface Anal.* (in press).
[10] M. G. Dowsett, G. Rowlands, P. N. Allen, R. D. Barlow, *Surf. Interface Anal.* **1994**, *21*, 310.
[11] C. Lu, A. Wucher, N. Winograd, *Anal. Chem.* **2011**, *83*, 351.
[12] Z. L. Liau, B. Y. Tsaur, J. W. Mauer, *J. Vac. Sci. Technol.* **1979**, *16*, 121.
[13] P. C. Zalm, *Mikrochim. Acta* **2000**, *132*, 243.
[14] S. Sun, A. Wucher, C. Szakal, N. Winograd, *Appl. Phys. Lett.* **2004**, *84*, 5177.
[15] S. Sun, C. Szakal, T. Roll, P. Mazarov, A. Wucher, N. Winograd, *Surf. Interface Anal.* **2004**, *36*, 1367.
[16] Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd, B. J. Garrison, *J. Phys. Chem. B* **2004**, *108*, 7831.