INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON MICROCHEMICAL TECHNIQUES
AND TRACE ANALYSIS*

DEPTH OF ORIGIN OF SPUTTERED ATOMS

(Technical Report)

Prepared for publication by
M. J. PELLIN and J. W. BURNETT
Argonne National Laboratory, Argonne, Illinois 60439, USA

Depth of origin of sputtered atoms (Technical Report)

Abstract

Sputtering, the ejection of target material following bombardment by energetic ions, is an extremely important technological process. Sputtering is a particularly important technique for the surface analyst, since it is used for both quantitative analysis of impurity concentrations and determination of depth distributions of impurities. Because of the complexity of sputtering, many of its fundamental parameters are difficult to ascertain. The depth of origin of sputtered atoms is a fundamental parameter of the sputtering process which, until recently, has been the subject of considerable controversy. Fortunately, both experiments and theory have improved greatly in this area, allowing a consensus to be reached on this important parameter. This report describes and evaluates these critical experiments and theories.

I. INTRODUCTION

Energetic ion bombardment of a target surface can, following a series of atomic collisions, lead to the ejection of target atoms and molecules. A fundamental understanding of this process, known as sputtering, is technologically important to a wide variety of industries. In the semiconductor industry, for instance, sputtering is used to create structured device surfaces by both deposition of sputtered atoms (sputter-deposition) and removal of surface atoms (plasma etching). Sputtering processes are destructive to materials in plasma environments. For example, in magnetic confinement fusion, the sputtering of the wall materials can lead to high-Z impurities in the plasma which could unfavorably alter the input energy required to reach the scientific breakeven temperature. Sputtering is also used for the reproducible deposition of thin films and is currently under intensive study for the manufacture of superconducting thin films.

For the analytical chemist, sputtering represents an important tool for the study of surfaces. Ion-beam-based techniques, such as Secondary Ion Mass Spectrometry (SIMS) and Secondary Neutral Mass Spectrometry (SNMS), utilize sputtering to gather chemical information from surfaces. In SIMS, secondary ions that are ejected from surfaces during the sputtering event are mass spectrometrically detected. SNMS, on the other hand, requires the ionization of sputtered neutral species, both atoms and clusters, which are subsequently detected mass spectrometrically. Utilization of appropriate standards and/or calibrations using these techniques represents one of the most sensitive and quantitative methods of determining surface concentrations. Ion bombardment of a target surface for extended periods of time can be used to remove material in a controlled manner, a technique called ion milling or depth profiling. Standard analytical surface techniques, including SIMS, SNMS, and Auger electron spectroscopy (AES), may be used in conjunction with depth profiling to measure target stoichiometries as a function of depth.

Despite the importance of sputtering, a fundamental understanding of many aspects of this process has remained lacking. This is due to both the complexity of a sputtering event and the experimental difficulties involved in its study. Because of its technological and fundamental importance, the depth of origin of sputtered atoms has received extensive attention from sputtering experimentalists and theorists. Recent advances in both experimental measurements and theoretical modeling of the sputtering process have lead to an increased understanding of the depth of origin. This paper will review and critically analyze the state of knowledge for this important fundamental aspect of the sputtering process.

Measurements of the depth of origin of sputtered atoms are experimentally difficult for several reasons. In order to determine the origin of a sputtered atom, individual target layers must be "labeled," that is, a well-characterized target with a monolayer variant-layered structure is needed. In addition, the sputtering yields of each target component must be measured without significant target damage or any change in the surface concentration. This requires that the primary ion dose be low enough that no primary ion strikes a previously impacted area of the surface. Such low-ion dose experiments are said to be done under "static mode" sputtering conditions. "Primary" is used to refer to the energetic ion beam that initiates the sputtering process. Recent experimental investigations have taken three separate approaches to solve this difficulty.

The most straightforward method utilized laser ionization SNMS to directly measure the partial sputtering yields of Cu and Ru ejected from a target with Cu overlayers on a single crystal Ru surface (0001) [1]. In these studies, nonresonant laser ionization of sputtered species allowed quantitative sputtering yield determinations to be accomplished under static mode sputtering conditions.

Several groups [2-7,10-14] have used the properties of surface segregation to overcome a relatively low-detection sensitivity in order to determine the second-layer contribution to the sputtering process. In one series of experiments [2,3], a fast segregant (In in Ga) was used to create a monolayer variant target which was unaffected by large primary ion doses. Catcher foils then were used to monitor the partial sputtering yield of each target component. One advantage of this method of investigation is that angularly resolved studies can be conducted. Another series of experiments [4-7] monitored the surface concentrations of slowly segregating alloys (e.g., Cu/Ni) in the high primary ion dose limit. These experiments then used a model to calculate the second-layer sputtering yield. In closely related experiments, self-sustaining carbon- [10,11] and alkali- [12-14] thin films were observed to reduce the sputtering yields of substrate materials.

A final series of experiments [8-9], pertinent to depth of origin studies, looked at the primary ion dose dependence of the removal rate of adsorbed gases (as measured by AES) on clean polycrystalline surfaces. These experiments often found that unusually large primary ion doses were required to remove the adsorbed gas. The explanation for this behavior involved the formation of a thermodynamically stable "underlayer structure" for the adsorbed gas species. In this picture, removal of substrate atomic layers was required to remove the second-layer gas atoms.

Theoretical efforts to understand the physics of sputtering, including the depth of origin of sputtered atoms, have taken two primary forms - analytical and computer simulations. The analytical theory is based on an isotropic binary collision approximation and has successfully calculated many experimentally measured parameters of the sputtering process. These parameters include the sputtering yield dependence upon primary ion mass, energy, and angle of incidence [15]. Very recently, the depth distribution of sputtered atoms has been studied within the framework of transport theory [16]. It was found that, in contrast to earlier work, the analytical theory and the computer simulation studies of the depth of origin agree quite well.

The computer simulation approach to the theoretical study of the sputtering process has been an extremely active area of study for the past ten years [9,17-41]. Several groups have produced computer codes with varying degrees of complexity, processing speed, and accuracy. A few generalizations concerning the different methods of simulating the sputtering event with respect to the depth of origin, as well as representative calculated depth of origin results, will be presented in this paper. An extensive round robin has been carried out to compare and contrast the ejection probabilities of energetic atoms from targets for the most common sputtering simulations [20]. A unique feature of this round robin was that all of the codes were used to simulate the same event.

II. EXPERIMENTAL STUDIES

Experimental studies of the depth of origin of sputtered atoms may be grouped into three categories: first, direct determination with high useful yield techniques; second, surface segregation techniques; and third, gas adsorption studies. A brief discussion of the results, along with the relative strengths and weaknesses of each of these experimental, approaches is presented in this paper.

II.1 Direct determination

Laser-based SNMS [42-46] has been used to investigate the depth of origin of sputtered atoms from solid surfaces [1,42]. The method of investigation was straightforward. A well-characterized Cu overlayer was deposited by evaporation onto a clean single crystal Ru(0001) surface. The Cu/Ru(0001) system was a good choice for this work since an extensive series of surface studies has been completed on this important bimetallic system [47-52]. Deposition of Cu on Ru (0001) surfaces has been demonstrated to result in layer-by-layer film growth for coverages of up to 2 monolayers [47-52]. Furthermore, this growth is essentially pinhole free [52] with the first layer being more strongly bound to the surface than is the second Cu layer [47-52]. The increased surface binding of the first Cu layer allows surface coverage to be easily calibrated by thermal desorption spectrometry [1,47-52]. LEED patterns, as a function of Cu

coverage, demonstrate pseudomorphic growth up to 2 monolayers of Cu coverage [47-52]. Especially important in the sputtering experiments is the fact that Cu is immiscible in Ru; therefore, a truly discrete Cu monolayer may be grown onto Ru(0001).

In Table 1, the Cu/Ru sputtering yield ratios, Y_{Cu}/Y_{Ru}, are shown for various Cu overlayer coverages as measured by Burnett et al. [1]. The ratio of the sputtering yields of bulk Cu and bulk Ru, $Y_{BULK,Cu}/Y_{BULK,Ru}$, is 1.67 [53], a value less than the experimentally determined ratios for any of the Cu coverages studied. This is indicative of a strong surface contribution to the sputtering yield. The table further shows that values of Y_{Cu}/Y_{Ru} rapidly increase with increasing Cu coverage. By the time 2.5 layers of Cu have been deposited, only one Ru atom is sputtered for every 38 Cu atoms.

Table 1. The Cu/Ru Sputtering Yield Ratio for Various Cu Coverages on a Ru (0001) single crystal surface.

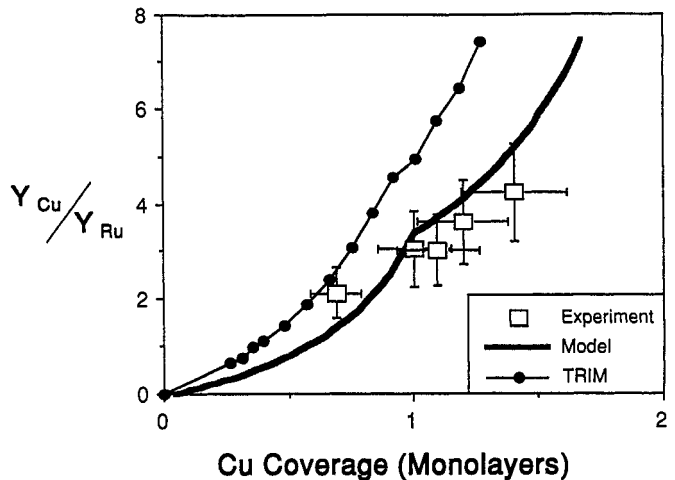| Cu Coverage (Monolayers)	Cu/Ru Sputtering Yield Ratio, S_{Cu}/S_{Ru}
0.69 ± 0.06	$2.1 \pm .4$
1.0 ± 0.1	$3.1 \pm .6$
$1.1 \pm .11$	$3.0 \pm .6$
$1.20 \pm .12$	$3.6 \pm .7$
$1.40 \pm .14$	$4.2 \pm .8$
$2.5 \pm .5$	38 ± 8

Fig. 1 - The Cu/Ru sputtering yield ratios, Y_{Cu}/Y_{Ru}, are plotted as a function of Cu coverage. The smooth gray curve is the plot of an exponential depth-of-origin sputtering model described in the text. For comparison, the results from TRIM calculations are also shown [1].

Under the assumption that Cu and Ru sputter as if from bulk Cu and Ru, respectively, and that the depth-of-origin distributions are similar for bulk Cu and bulk Ru, then, for a coverage of one Cu monolayer

$$\frac{Y_{Cu}}{Y_{Ru}} = \frac{X \, Y_{BULK,Cu}}{(1 - X) \, Y_{BULK,Ru}} \qquad (1)$$

Substituting the bulk sputtering yields for Cu and Ru, 4.5 and 2.7, respectively, X, the fraction of the sputtered atoms originating from the first atomic layer, can be calculated. Since at a Cu coverage of one monolayer Y_{Cu}/Y_{Ru} equals 3.1 ± 0.6, X is approximately 0.65; therefore, roughly two-thirds of the sputtered atoms originate in the first layer in this experiment.

A few words should be said regarding the assumption that Cu and Ru sputter as if from their respective bulk materials. Because the Cu overlayer on Ru(0001) has only a slightly larger surface binding energy, 3.64 eV, than Cu has from bulk Cu, 3.53 eV [48], very little change in the first-layer Cu sputtering yield, resulting from differences in surface binding energies, may be expected. The first-layer Cu yield may be higher from Ru than from pure Cu as energetic Cu atoms would be more likely to reflect off Ru than off Cu. This has been estimated to be a relatively small effect, resulting of an elevated Cu sputtering yield of ≤ 10% [54]. In the opposite direction, the first-layer Cu yield from Ru may be less than that from bulk Cu since the Cu surface atom density is 11% lower on Ru than on Cu [68] because of the pseudomorphic nature of thin Cu layers on Ru(0001) [47-52]. The Ru sputtering yield from beyond the first layer is expected to be larger from the Cu-covered target than from bulk Ru as the Cu overlayer is less effective in shielding the Ru substrate. The primary ion can deposit more energy in the second and third layers of the Ru if the first layer is Cu. Energetic Ru atoms can escape more easily from beneath Cu than from Ru. This assumption represents a good first approximation. More complete interpretation is required.

In Fig. 1, Y_{Cu}/Y_{Ru} is plotted as a function of Cu coverage. The results of computer calculations using the Transport of Ions in Matter (TRIM) sputtering code [31,32] are shown along with the results of a simple empirical model described below. The TRIM results are fully discussed in Ref. 1 but are shown here to compare with the empirical model and as an introduction to the theory section which follows. For the empirical model, an exponential depth dependence of the depth of origin was assumed; a mean free path, λ, is the depth giving rise to $(1 - 1/e)$ or approximately 63% of the sputtered atoms.

$$\frac{Y_{Cu}}{Y_{Ru}} = \frac{Y_{BULK,Cu}[X\,(1-e^{-(n+1)t/\lambda}) + (1 - X)\,(1-e^{-(n+1)t/\lambda})\,]}{Y_{BULK,Ru}[X\,e^{-(n+1)t/\lambda} + (1 - X)\,e^{-nt/\lambda}]} \qquad (2)$$

Here, n is the number of completed Cu monolayers, X is the fractional monolayer Cu coverage of layer $(n + 1)$, and t is the thickness of a Cu monolayer. A best fit of this model to the data yields a value of 2.2 Å or 0.9 lattice units for λ. Taking the mean free path, λ, to be the characteristic depth of origin of sputtered atoms, λ is the depth giving rise to the majority of the sputtered atoms and is roughly equal to one atomic layer in full agreement with Eq. (1). The model shows good agreement with the data.

These results suggest that two-thirds of the sputtered atoms originate in the first atomic layer. The first-layer yield, however, is less than that typically calculated in computer simulations for the sputtering of pure materials. The Cu/Ru(0001) system is expected to show a deeper depth of origin than that of a clean, single-element metal for several reasons. A Cu adatom is less effective in blocking the Ru substrate than a Ru adatom because of its lower mass, smaller size, and lower binding energy.

The TRIM calculation of a 70% suppression of the Ru sputtering yield by a single Cu overlayer is in agreement with the experimental results showing a suppression of 67 ± 15%. However, the TRIM calculation predicts a higher value for Y_{Cu}/Y_{Ru} than that observed experimentally.

II.2 Surface segregation studies

A second class of experimentally measured depths of origin utilize the properties of surface segregation to overcome problems associated with primary ion-induced damage during the experimental measurements. In these experiments, static mode sputtering conditions are not achieved. For the rapidly segregating targets, the segregation restores the surface concentration following bombardment. In effect, each primary ion strikes an undamaged surface. In targets with kinetics too slow to restore the surface stoichiometry, the surface concentration is monitored as a function of ion fluence. The results are then modeled to determine the kinetics of the various mechanisms of diffusion and segregation of the target atoms as well as the depth of origin of the sputtered atoms. These methods will be discussed in terms of the degree and rate of segregation occurring in the target materials.

II.2.1 Rapidly segregating (liquid) alloys

Tombrello and co-workers [2,3] used passive collection techniques [Rutherford backscattering (RBS) measurements of catcher foils] to investigate the depth of origin for atoms sputtered from a *liquid* Ga-In eutectic alloy. The surprisingly low vapor pressure of liquid Ga allows these experiments to be carried out in an ultrahigh vacuum environment. The alloy has a bulk composition of 16.5 at.% In; however, ion scattering spectroscopy (ISS) and AES measurements demonstrated that the surface composition was at least 94 at.% In. Moreover, as expected for thermodynamic surface segregation, deviations from bulk stoichiometry were assumed to be limited to the first 2 atomic layers. Analysis of the ISS and AES results within this context were used to determine the first- and second-layer target stoichiometries.

Experiments were conducted with a normal primary ion beam incident upon the Ga/In eutectic target. Carbon catcher foils were placed upon a cylinder whose radial axis was placed along the primary ion beam. Because of RBS sensitivity limitations, relatively high primary ion doses were required. The fundamental assumption in these experiments is that the high mobility of the In atoms in the liquid Ga matrix assures that the surface concentration remains constant and strongly enriched in In during the bombardment. While this is, no doubt, a logical assumption, as yet no unequivocal measurement of the target surface composition during primary ion bombardment has been made.

Table 2. Experimental measurements of the first and second layer
contribution to sputtering.

Alloy System	Primary Ion and Energy	Layer Contributions to Sputtering First Layer	Second Layer
Cu on Ru	3.5 keV Ar+	0.67 [1]	
Ga-16 at.% In	3 keV Ar+	0.94 [3]	
Ga-16 at.% In	25 keV Ar+	0.88 [3]	
Ga-16 at.% In	50 keV Ar+	0.87 [3]	
Ni-40 at.% Cu	3 keV Ne+		≥ 0.35 [4]
Ni-6 at.% Au	3 keV Ne+		0.35 - 0.50 [5]
Ni-10 at.% Ge	3 keV Ne+		0.45 [6]
Ni-9.5 at.% Si	3 keV Ne+		≤ 0.05 [7]

The results of these experiments have been compiled in Table 2. Clearly, these results demonstrate a strong surface component to the sputtered flux. For all bombarding conditions, more than 80% of the sputtered flux originated in the surface layer. A small dependence upon the primary ion energy illustrates a slight decrease in the surface contribution to sputtering for higher primary energies. These determinations of the surface contribution to the sputtering yield relied heavily upon the surface and subsurface concentrations of the target. If the surface layer was more enriched with In atoms than the ISS and AES analyses indicated, then the depth of origin of sputtered atoms is actually *overestimated* in this work [3]. As opposed to the Cu on Ru results, this system has a heavy first-layer atom, covering a relatively light bulk atom. From this point of view, the depth of origin of atoms sputtered from pure matrices may be underestimated in this experiment. An underestimate may also occur if the second-layer concentration of In rises during bombardment.

II.2.2 Slowly segregating (solid) alloys

While the experiments of Lam and his co-workers [4-7] were aimed primarily at measuring the compositional modification of binary alloys by ion beam bombardment, their work has yielded unique information regarding the depth of origin of sputtered atoms. In these experiments, alloy targets are ion bombarded at various temperatures, while the surface composition is constantly being monitored by ISS. Due to complicated and competing atomic processes during the ion bombardment of a surface, changes in the surface and near-surface stoichiometry occur. These processes include preferential sputtering, displacement mixing, Gibbsian segregation, radiation-induced segregation, and radiation-induced diffusion.

In order to study the relative roles of each of these processes, the surface composition of these targets was followed for varying lengths of sputtering time and for different target temperatures. At low-ion fluences, changes in the surface and subsurface target composition led to changes in the sputtered ion flux composition. Eventually, a steady-state sputtering flux is reached in which the composition of the sputtered flux is identical to that of the bulk alloy [55]. Lam asserts that this steady-state sputtering occurs when the surface concentration of the target, as observed by ISS, reaches a constant value. If the sputtered atoms arise solely from the topmost atomic layer, then the steady-state surface concentration of the alloy would be stoichiometric with that of the bulk alloy. In fact, a temperature-dependent steady-state surface composition is observed with no change in the bulk composition, implying that a fraction of the sputtered atoms originate from below the first layer. In order to fit the experimentally determined time evolution of the surface composition to a phenomenological model of the various diffusion and segregation processes, a second-layer contribution to the sputtering yield is required. The second-layer concentration of the steady-state sputtered alloy was determined by first rapidly cooling the target (to quench any thermally driven diffusion processes) and then depth profiling using ISS as the surface probe.

In Table 2, the second-layer contribution to the sputtering yield is shown for several binary alloys. The shallow depth of origin of sputtered atoms is demonstrated in all four experiments. In all cases, more than half of the sputtered atoms originate in the first atomic layer. It is also quite evident that significant differences in the first-layer contribution to sputtering occur in different alloy systems. The limitations of the sensitivity of this method are apparent in the Ni-6 at.% Au experiment in which 35-50% of the sputtered atoms are believed to originate from beyond the first atomic layer.

Several factors must be carefully considered in assessing the depth of origin results from these experiments. The first is the assumption that steady-state sputtering yields have been reached, that is, that the sputtered flux is truly representative of the bulk stoichiometry. This is probably an acceptable assumption as many monolayers have been removed before the steady-state surface composition has been reached and a relatively large ion flux was used. It is necessary to point out, however, that only the surface target composition was measured and not the composition of the sputtered flux. Taken to an extreme, as in the sputtering experiments on the liquid eutectic of In-Ga described above [2,3], Gibbsian surface segregation occurs so rapidly that the sputtered flux is never representative of the bulk alloy stoichiometry. Indeed, if any of the segregation and diffusion processes are fast relative to the rate of removal of material via sputtering, the bulk-stoichiometric sputtering flux would not be attained [56].

Another possible weakness in this determination of the depth of origin of sputtered atoms involves the contribution to sputtering from beneath the first atomic layer. In the interpretation of these experiments, it is assumed that any sputtering not originating in the first layer, originates in the second layer. Any appreciable sputtering from a third atomic layer, with a stoichiometry significantly different from that of the second layer, would lead to an inaccurate estimate of the first-layer contribution to the sputtering yield. Related to these questions is the actual measurement of the second-layer composition. The stoichiometry of the second layer is determined using ISS in conjunction with a depth profile as stated above. Any ion-beam-induced stoichiometry changes (radiation-enhanced diffusion, displacement mixing, and radiation-induced segregation) would result in an inaccurate compositional profile, which would be reflected in the sputtered atom depth of origin estimate. These experiments clearly indicate a substantial first-layer contribution to the sputtering yield but may not represent absolutely quantitative estimates of the depth of origin.

Morita et al.[10,11] vapor-deposited carbon films ($\approx$ 400 Å) onto nickel films ($\approx$ 6000 Å). Following an extensive anneal, RBS was used to determine that most of the carbon diffused to the back surface of the nickel, leaving a thin carbon film on the front surface of the target. The thickness of the front-surface carbon layer was estimated to be $\leq$ 2 Å from the RBS measurements. The front surface of the C/Ni target was bombarded by 5 keV Ar$^+$ with the target being held at several different temperatures and using varying current densities. At elevated target temperatures, RBS showed that a self-sustaining carbon overlayer formed at current densities below a critical current density. This was interpreted to mean that the thick carbon layer at the back surface of the nickel "fed" the front-surface overlayer via diffusion. Under the appropriate temperature and current densities, virtually all of the carbon could be sputtered from the target before any change in the thickness of the nickel layer was observed. Because the sensitivity of RBS is insufficient to determine quantitatively the thickness of the carbon overlayer, the only conclusion that may be drawn from these results is that ejection by sputtering is a near-surface process.

In similar types of experiments, Krauss et al. [12-14] have been studying self-sustaining thin films for application in fusion devices. Binary alloys of copper and lithium have been proposed as materials for plasma-interactive components for a variety of reasons. Li is a low-Z element. Plasma erosion and the subsequent sputtering of high-Z materials are unacceptable in confinement fusion devices, as even very low impurity levels are expected to quench the thermonuclear burn. Li is known to segregate in Cu and form 1 to 2 Li-rich layers at the Cu surface, even for dilute Cu/Li alloys. A large fraction, >50%, of the Li species sputter as ions rather than neutral atoms. The Li overlayer is expected to be conserved by two mechanisms. By applying a bias to the Cu/Li material, secondary Li ions will be returned to the surface. Gibbsian segregation is also expected to replenish the Li-rich surface layer. At elevated temperatures and sufficiently low ion fluxes, the sputtering yield of Cu from the Cu/Li alloy was measured and found to be reduced by $\geq$ 4 times that of pure Cu when bombarded by 100 eV He$^+$. These results are in good agreement with Monte Carlo simulations for 1 to 2 layers of Li on Cu [57]. Again, lack of knowledge of the actual stoichiometry of the Cu/Li targets in the near-surface region prevents any quantitative determination of the depth of origin. However, these experiments illustrate the practical application of the shallow depth of origin of sputtered atoms.

II.3   Gas adsorption studies

Pellin et al. investigated the sputtering of polycrystalline titanium with adsorbed oxygen using AES to monitor the surface composition and laser-induced fluorescence (LIF) to detect sputtered Ti atoms [8]. In these experiments, the sputtering yield of oxygen from O/Ti was determined by measuring the ion-induced desorption cross section from the relative O and Ti AES intensities. The sputtering yield of Ti was directly observable by LIF. An extremely low oxygen sputtering yield [9] led the investigators to conclude that oxygen formed an underlayer at O coverages of less than 2 monolayers. The dependence of the sputtering yield of Ti and O on O coverage was modeled using a Monte Carlo sputtering simulation, TRIM, and the subsequent results supported the formation of an oxygen underlayer.

Assuming that the sputtered atoms arise from only the first two atomic layers, at one monolayer of oxygen coverage, the sputtered fraction arising from the first atomic layer would be Ti atoms, and from the second layer, O atoms only. For 3 keV Ar^+ bombardment, the measured sputtering yield of Ti and O atoms from a Ti target with one monolayer of adsorbed oxygen was 0.8 and 0.2, respectively. This implies that 80% of the sputtered atoms arose from the first atomic layer. The corresponding sputtering yields for sputtering by 3 keV He^+ were 0.054 Ti atoms/He^+ and 0.0082 O atoms/He^+, suggesting that 86% of the sputtered atoms originated in the first atomic layer. Uncertainties regarding the actual compositional depth profile of the oxygen-dosed Ti target prevent any real quantitative conclusions with respect to the depth of origin. In addition, the assumption that only two atomic layers contribute significantly to the sputtered flux may not be true in cases of low-mass underlayer formation.

III.   THEORY

III.1   Analytical theory

In 1969, Peter Sigmund published his linear cascade theory of sputtering which accurately calculates many experimentally measured parameters associated with sputtering yields, including dependence upon bombarding ion mass, energy, and angle of incidence and the mass of the target atoms [17]. The general Boltzmann transport equation is solved for an ion slowing down in an infinite and amorphous single-element target under the assumption of binary collisions. A shallow depth of origin, approximately 500 ppm, or 2 atomic layers for Cu sputtering by Ar^+, is estimated as the average depth from which sputtered atoms originate. This estimate of the depth of origin was given by:

$$D_0 = (3/4) \, (2/\pi \, \lambda_0 \, N \, a^2) \qquad (3)$$

where a is the screening radius, a function of the atomic number of the primary ion and target atoms, and N is the number density of the target atoms. λ_0 is a dimensionless function dependent upon the hardness of collisions leading to sputtering and associated with the assumed form of the scattering cross section [58]. Interestingly, the depth of origin is independent of the primary ion energy, as well as the mass of both the target and primary ion. It should be pointed out that, in deriving this estimate of the depth of origin, it was necessary to assume that the depth of origin was relatively small and that nuclear and electronic collisional energy losses of the sputtered atoms could be ignored as they are ejected.

Sigmund and Falcone later expanded the theoretical treatment to yield a depth distribution of sputtered atoms [59]. In this work, unlike that based upon general transport theory, the model was simplified by assuming that recoil target atoms slow down continuously along a straight line. In other words, the scattering of recoil atoms was not explicitly considered; however, the resultant sputtering yield formula was found to be identical to that derived more rigorously in the transport theory treatment. This somewhat surprising result was interpreted by the authors to mean that any directional change in recoil particle distribution induced by scattering would be compensated for when considering an initially homogeneous and isotropic particle flux in an amorphous target.

The average depth from which sputtered atoms originated was consistent with that of the earlier work and included an explicit dependence upon ejection angle and energy of the sputtered atom. It was found that energetic sputtered atoms could originate from deep within the target. In fact, the average depth of origin as a function of sputtered atom energy was found to increase with increasing sputtered atom energy. The depth distribution of the sputtered atoms was determined

to be maximum at the target surface and was well represented by an exponential profile, accentuating the significant surface contribution to the sputtered atom flux. This exponential dependence suggests that a mean free path may be a more accurate description of the depth dependence of the sputtering yield than is the concept of an average depth of origin [60]. In this context, the mean free path of sputtering is approximately 3.7 atomic layers implying that roughly 30% of the sputtered atoms originate in the topmost layer [61].

In a review of experimental and theoretical estimates of the depth of origin, Kelly [61] pointed out that analytical theory indicated a significantly lower first-layer sputtering yield than did computer simulations and experiments. In that review, however, the comparison was made between a global average of computer simulation results and existing experimental work. The average value of the mean free path of sputtering was determined to be 0.8 ± 0.10 atomic layers. Of the six experimental results that were presented, only one (the In-Ga liquid eutectic experiment [2,3] discussed above) was carried out on a well-characterized surface. The remaining experiments either relied heavily on theory for the estimated sputtering depth [4-7] or were carried out on surfaces that were not well characterized [62,63]. Furthermore, the range of values presented in this review were quite broad. The values of the first-layer contribution to the sputtering yield varied from a low of 50% to a high of 93% while the mean free path for sputtering varied from a low of 0.35 to a high of 1.85 atomic layers (or lattice units). Average values of these results appear to be of questionable significance and the results of analytical theory, when compared with the individual experimental and computer simulation depth of origin estimates, do not look so bad.

Very recently, the depth dependence of the sputtering yield has again been studied within the framework of transport theory [16]. In this work, the results of the analytical calculations, using several different simplifications, are compared with those from a Monte Carlo simulation code, designed to match the same underlying physical model as closely as possible. The Monte Carlo simulation was found to agree quite well with several of the analytical calculations with respect to sputtering yield depth and angular distributions. In other words, very little discrepancy in the predictions of the <u>functional</u> depth of origin was found to exist between the analytical theory [16] and the Monte Carlo simulation. Further investigation of the earlier numerical discrepancy revealed that the constant (λ_0 from Eq. 3 above), used in fitting the approximate power [16] scattering cross section to the Born-Mayer scattering cross section, was not optimized. Utilization of an improved estimate of the constant (λ_0), and including small-angle scattering in the calculation, results in an average depth of origin of approximately one atomic layer [16, 54]. Assessment of the results of solutions of analytical calculations, based upon transport theory, indicates that practical and qualitative understanding of the sputtering depth distribution can be easily extracted but that quantitative solutions require critical knowledge of, and attention to, the details of the scattering process. In addition, estimates of the depth of origin by analytical theory are, so far, limited to single-element conductive amorphous targets. Severe deviations from these theoretical predictions can occur in the sputtering of crystalline [17] or multicomponent materials [9,55].

III.2 Computer simulations

In view of the many computer codes commonly used to simulate sputtering, this section will be limited to generalizations regarding the major types of codes. Complete discussions of the role of computer simulations in sputtering can be found in Refs. 17-19. In Ref. 20, an ambitious round robin of ejection probabilities for sputtering has been carried out comparing all of the most commonly used sputtering simulations. While the depth distribution of sputtered atoms is not explicitly compared in this round robin review, important and practical similarities and differences between various codes are presented. The calculated results presented in this round robin lend insight into the depth distribution determined by the various computer codes.

Basically, three different approaches to sputtering simulation have been taken: binary collision (BC) approximation lattice simulations [17,21-25], Monte Carlo (MC) simulations [18,26-33], and molecular dynamics (MD) simulations [19,34-39]. In MC computer simulations the target is amorphous; that is, target atoms are generated as they are required. Collisions are assumed to be binary. In both MC- and BC-type codes, the collision cascade develops through a series of many two-body collisions. Because the binary collision approximation breaks down at low energies, methods of approximating simultaneous collisions have been introduced in BC-type simulations [55]. BC codes generally calculate sputtering of monocrystalline targets but often can be altered to allow for polycrystalline targets [55]. MD codes do not utilize the binary collision approximation; rather, the position and velocity of each target atom is allowed to develop in time and, therefore, simultaneous collisions are calculated.

Table 3. Selected sputtering depth of origin estimates from computer simulations.

Computer Simulation Type (see text for details)	Target Material	Primary Ion and Energy	Estimated First Layer Contribution to Sputtering	Ref.
MD	Cu(111)	8 keV Ar$^+$	0.91	[40]
MD	Cu(111)	600 eV Ar$^+$	0.96	[41]
MD	Cu(100)	600 eV Ar$^+$	1.00	[41]
MD	Cu(110)	600 eV Ar$^+$	0.81	[41]
MD	Liquid Cu	5 keV Ar$^+$	0.83-0.94	[35]
MD	Solid Cu Average of (100),(110), (111) surfaces	5 keV Ar$^+$	0.88	[35]
BC	Au(001)	700 eV Xe$^+$	0.91	[55]
BC	Cu (poly)	90 keV Cu$^+$	0.73	[65]
BC	Cu-Ni (poly)	90 keV Cu$^+$	0.79	[66]
BC	U (poly)	2 keV U$^+$	0.96	[67]
BC	U (poly)	5 keV U$^+$	0.95	[67]
BC	U (poly)	9 keV U$^+$	0.92	[67]
MC	Ru (amorphous)	3.6 keV Ar$^+$	0.79	[1]
MC	Cu (amorphous)	3.6 keV Ar$^+$	0.79	[1]
MC	1 ML Cu/Ru (amorphous)	3.6 keV Ar$^+$	0.82	[1]
MC	Ni (amorphous)	1 keV Xe$^+$	0.91	[31]
MC	Ni (amorphous)	10 keV Xe$^+$	0.86	[31]
MC	Ni (amorphous)	100 keV Xe$^+$	0.82	[31]

In Table 3, various estimates of fractional first-layer sputtering yield measurements are presented for each of the different simulation approaches. The data in this table are by no means comprehensive but are intended to serve only as examples. All three types of codes predict that the first layer contributes a significant fraction of the sputtered flux. It is also quite clear that different ion-target combinations, as well as different crystal orientations, result in different first-layer contributions to sputtering. MD and BC codes generally find that nearly all of the sputtered atoms originate in the top four atomic layers, while MC simulations allow sputtering from greater depths in the target [20]. Reasonable agreement has been shown between one Monte Carlo code, TRIM, and a binary collision code, Marlowe [31]. As in the case of analytical theory, insight into the depth of origin of sputtered atoms may be obtained through simulation, but quantitative results are dependent upon the assumed model of the target (crystalline, polycrystalline, or amorphous) and the interatomic potential used [20]. It has further become apparent that different ion-target combinations and target compositions will lead to different sputtering depths of origin. The depth of origin is not a definable constant associated with the sputtering process; rather, it is a variable property of a particular ion and target interaction.

IV. CONCLUSIONS

The sputtering process is important for many aspects of surface analysis and materials science. Among the myriad of surface analysis tools, techniques, using an ion beam as a surface probe, provide the best combination of quantitativity and sensitivity. In addition, sputtering, as a method of controlled removal of target materials when combined with other surface techniques, has proven to be a powerful method of measuring concentration depth profiles [64]. The depth of origin of sputtered atoms is a fundamental property of the sputtering process with implications for the resolution of depth profiles. Recent advances, both in theoretical and experimental science, have shed considerable light on this important quantity.

It is clear that sputtered atoms arise predominantly from the first atomic layer. Experimental and theoretical results indicate that the depth of origin of sputtered atoms is not a constant associated with the sputtering process but is dependent upon a variety of factors, including the relative masses of the target and the primary ion species, the binding energy of target atoms, the surface morphology (crystalline or amorphous), and especially the concentration depth profiles of multicomponent materials. Theoretical results indicate that sputtered atoms can originate from deep within the target. A severe limitation of experiments involved in the study of the depth of origin is that only the first layer contribution to sputtered atoms has been measured. It is apparent that experimental measurements of depth of origin distributions of sputtered atoms would be useful in understanding the sputtering process. While much progress has been made, much work remains to be done. In particular, an understanding of the explicit dependence of the depth of origin upon the parameters described above must be developed on both a theoretical and an experimental footing.

REFERENCES

[1] J. W. Burnett, J. P. Biersack, D. M. Gruen, B. Jørgensen, A. R. Krauss, M. J. Pellin, E. L. Schweitzer, J. T. Yates, Jr., and C. E. Young, J. Vac. Sci. Technol. A6 (1988) 2064.

[2] M. F. Dumke, T. A. Tombrello, R. A. Weller, R. M. Housley, and E. H. Cirlin, Surf. Sci. 124 (1983) 407.

[3] K. M Hubbard, R. A. Weeler, D. L. Weathers, and T. A. Tombrello, accepted, Nuclr. Instrum. Methods Phys. Res. B.

[4] N. Q. Lam, H. A. Hoff, H. Wiedersich, and L. E. Rehn, Surf. Sci. 149 (1985) 517-536.

[5] N. Q. Lam, H. A. Hoff, and P. G. Régnier, J. Vac. Sci. Technol. A 3 (1985) 2152-2160.

[6] H. A. Hoff and N. Q. Lam, Surf. Sci. 204 (1988) 233-246.

[7] N. Q. Lam and H. A. Hoff, Surf. Sci. 193 (1988) 353-372.

[8] M. J. Pellin, C. E. Young, D. M. Gruen, Y. Aratano, and A. B. Dewald, Surf. Sci. 151 (1985) 477-502.

[9] H. F. Winters and P. Sigmund, J. Appl. Phys. 45 (1974) 4760-4766.

[10] K. Morita, T. Tsuchiya, M. Hayashibara, and N. Itoh, J. Nucl. Mater. 116 (1983) 63-68.

[11] K. Morita, H. Ohno, M. Hayashibara, N. Itoh, Nucl. Instrum. Methods Phys. Res. B2 (1984) 596-600.

[12] A. R. Krauss, D. M. Gruen, M. H. Mendelsohn, R. W. Conn, D. M. Goebel, Y. Hirooka, and W. K. Leung, J. Nucl. Mater. 145-147 (1987) 401-407, and references therein.

[13] A. R. Krauss, A. B. DeWald, D. M. Gruen, and N. Q. Lam, Radiat. Eff. 89 (1985) 129.

[14] A. R. Krauss and D. M. Gruen, J. Nucl. Mater. 93/94 (1980) 686.

[15] P. Sigmund, Phys. Rev. 184 (1969) 383;187 (1969) 768.

[16] M. Vicanek, J. J. Jimenez Rodriguez, and P. Sigmund, Nuclr. Instrum. Methods Phys. Res. B36 (1989) 124-136.

[17] Sputtering by Ion Bombardment I Physical Sputtering of Single Element Solids, Ed. by R. Behrisch, Springer-Verlag Berlin Heidelberg 1983, chapters 3 and 5 and references therein.

[18] H. H. Andersen, Nuclr. Instrum. Methods Phys. Res. B18 (1987) 73.

[19] D. E. Harrison, Jr., Radiat. Eff. 70 (1983) 1-64.

[20] P. Sigmund, M. T. Robinson, M. I. Baskes, M. Hautala, F. Z. Cui, W. Eckstein, Y. Yamamura, S. Hosaka, T. Ishitani, V. I. Shulga, D. E. Harrison, Jr., I. R. Chakarov, D. S. Karpuzov, E. Kawatoh, R. Shimizu, S. Valkealahti, R. M. Nieminen, G. Betz, W. Husinsky, M. H. Shapiro, M. Vicanek, and H. M. Urbassek, Nuclr. Instrum. Methods Phys. Res. B36 (1989) 110-123.

[21] M. T. Robinson and I. M. Torrens, Phys. Rev. B9 (1974) 5008.

[22] M. T. Robinson, J. Appl. Phys. 54 (1983) 2650.

[23] M. Hautula, Phys. Rev. B30 (1984) 5010.

[24] Y. Yamamura and W. Takeuchi, Nucl. Instrum. Methods Phys. Res. B29 (1987) 461.

[25] V. I. Shulga, Radiat. Eff. 70 (1983) 65.

[26] H. J. Kang, E. Kawatoh, and R. Shimizu, Jpn. J. Appl. Phys. 24 (1985) 1409

[27] H. J. Kang, E. Kawatoh, and R. Shimizu, Jpn. J. Appl. Phys. 23 (1984) L262.

[28] T. Ishitani, A. Shimase, and S. Hosaka, Jpn. J. Appl. Phys. 22 (1983) 329.

[29] M. Hautala, Radiat. Eff. 51 (1980) 35.

[30] M. Vicanek and H. M. Urbassek, Nucl. Instrum. Methods Phys. Res. B30 (1988) 507.

[31] J. P. Biersack, Nucl. Instrum. Methods Phys. Res. 174 (1980) 257; J. P. Biersack and W. Eckstein, Appl. Phys. A34 (1984) 73.

[32] W. Möller, W. Eckstein, and J. P. Biersack, Computer Physics Communications 51 (1988) 355-368.

[33] F. Z. Cui and H. D. Li, Nucl. Instrum. Methods Phys. Res. B7/8 (1988) 507.

[34] D. Y. Lo, T. A. Tombrello, M. H. Shapiro, B. J. Garrison, N. Winograd, and D. E. Harrison, Jr, J. Vac. Sci. Technol. A6 (1988) 708-711.

[35] D. Y. Lo, T. A. Tombrello, and M. H. Shapiro, Nucl. Instrum. Methods Phys. Res. B17 (1986) 207-212.

[36] M. H. Shapiro, D. Y. Lo, P. K. Haff, and T. A. Tombrello, Nucl. Instrum. Methods Phys. Res. B13 (1986) 348.

[37] M. H. Shapiro and T. A. Tombrello, Nucl. Instrum. Methods Phys. Res. B18 (1987) 355.

[38] M. H. Shapiro, P. K. Haff, T. A. Tombrello, D. E. Jarrison, Jr., and R. P. Webb, Radiat. Eff. 89 (1985) 243.

[39] V. I. Shulga, Radiat. Eff. 5 (1980) 1.

[40] D. E. Harrison, Jr., B. J. Garrison, and N. Winograd in Secondary Ion Mass Spectrometry, SIMS II, ed. by A. Benninghoven, et al., Springer-Verlag, 1979, p. 12.

[41] D. E. Harrison, Jr., P. W. Kelly, B. J. Garrison, and N. Winograd, Surf. Sci. 76 (1978) 311.

[42] B. Jorgensen, M.J. Pellin, C.E.Young, W.F. Calaway, E.L. Schweitzer, D.M. Gruen, J.W. Burnett and J.T. Yates, Proceedings of the Materials Modification by High-Fluence Ion Beams NATO Advanced Study Institute, Viano do Castelo, Portugal, Aug. 24-Sept. 4, 1987, in press.

[43] M.J. Pellin, C.E Young, and D.M.Gruen, Scanning Microscopy, Vol. 2, No. 3, 1988, pp.1353-1364.

[44] M.J. Pellin, C.E Young, W.F. Calaway, J. W. Burnett, B. Jorgensen, E.L. Schweitzer, and D.M.Gruen, Nucl. Instr. Meth. Phys. Res. B18, 446-451 (1987).

[45] C.E Young, M.J. Pellin, W.F. Calaway, B. Jørgensen, E.L. Schweitzer, and D.M.Gruen, Inst. Phys. Conf. Ser. No. 84: Section 4, pp. 163-168.

[46] C.E Young, M.J. Pellin, W.F. Calaway, B. Jørgensen, E.L. Schweitzer, and D.M.Gruen, Nucl. Instr. Meth. Phys. Res. B27, 119-129 (1987).

[47] K. Christmann, G. Ertl, and H. J. Shimizu, J. Catal. 61, 397 (1980).

[48] H. J. Shimizu, G. Ertl, and K. Christmann, J. Catal. 61, 412 (1980).

[49] J. C. Vickermann, K. Christmann and G. Ertl, Surf. Sci. 120, 1 (1982).

[50] J. C. Vickermann, K. Christmann, G. Ertl, P. Heimann, F. J. Himpsel, and D. E. Eastman, Surf. Sci. 134, 367 (1983).

[51] J. E. Houston, C. H. F. Peden, D. S. Blair and D. W. Goodman, Surf. Sci. 167, 367 (1986).

[52] J. T. Yates, Jr., C. H. F. Peden and D. W. Goodman, J. Catal. 94, 576 (1985).

[53] N. Matsunami, Y. Yamamura, Y. Itikawa, N. Itoh, and Y. Kazumata, Institute of Plasma Physics Report of Nagoya University, Japan, IPPJ-AM-14, Chikusa-Ku, Nagoya 464, Japan, (1980) .

[54] P. Sigmund, private communication.

[55] Sputtering by Ion Bombardment II Sputtering of Alloys and Compounds, Electron and Neutron Sputtering, Surface Topography, Ed. by R. Behrisch, Springer-Verlag Berlin Heidelberg 1983, chapter 1 and references therein.

[56] N. Q. Lam, Surface and Interface Analysis 12 (1988) 65-77.

[57] D. M. Gruen, A. R. Krauss, and M. J. Pellin, Radiat. Eff. 89 (1985) 113-127.

[58] J. Lindhard, V. Nielsen, and M. Scharff, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 36 (1968) No. 10.

[59] G. Falcone and P. Sigmund, Appl. Phys. 25 (1981) 307-310.

[60] G. Falcone, Radiat. Eff. Lett. 87 (1985) 101.

[61] R. Kelly and A. Oliva, Nuclr. Instrum. Methods Phys. Res. B13 (1986) 283-294.

[62] K. Morita, T. Tsuchiya, M. Hayashibara, and N. Itoh, J. Nuclr. Mater. 116 (1983) 63-68.

[63] K. Morita, H. Ohno, M. Hayashibara, and N. Itoh, Nuclr. Intrum. Methods Phys. Res. B2 (1984) 596-600.

[64] M. Grasserbauer, Yu. A. Zolotov, G. H. Morrison, GT. Stingeder, Yu. A. Karpov, F. A. Gimelfarb, Pure and Appl. Chem. 57 (1985) 1153.

[65] M. Rosen, G. P. Mueller, and W. A. Fraser, Nucl. Instrum. Methods Phys. Res. 209/210 (1983) 63-66.

[66] M. Rosen and R. H. Bassel, Nucl. Instrum. Methods Phys. Res. B2 (1984) 592.

[67] M. T. Robinson, J. Appl. Phys. 54 (1983) 2650.

[68] M. W. Roberts and C. S. McKee in Chemistry of the Metal-Gas Interface, Clarendon Press, Oxford, (1978) Chap. 2.