Near-threshold, steady state interaction of oxygen ions with transition metals: Sputtering and radiation enhanced diffusion

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1. Introduction

Metal oxides are of interest to a wide range of applications, from semiconductor manufacturing, to extreme ultraviolet (XUV) lithography optics and fusion research. Oxygen ion and plasma interactions with metals have been particularly relevant in these fields [1–4]. On one hand, controlled interactions, in semiconductor manufacturing and thin film deposition applications, can assist in selective, anisotropic oxidation of metal films or deposition of oxide layers. On the other hand, uncontrolled ion–target surface interactions, in photo-lithography and fusion applications, can lead to material loss [5,6] and undesirable oxidation of plasma facing components [4,7–11]. In either case, insights into the interaction processes, namely, sputtering and oxide formation, help offer better control over the evolution of surface (and sub-surface) composition.

Low energy (<500 eV) oxygen ions are of particular interest as sputter processes can depend on ion–surface interaction times [12]. Further, oxidation can be influenced by an increased sticking probability at low energies in which case an extrapolation from high energy data cannot be made. In this regard, studies on low kinetic energy oxygen ion induced sputtering and oxidation of metals are few and scattered. Initial reports by Hechtl and Bohdansky [13] study the sputter yields for molybdenum under O⁺ ion bombardment down to 100 eV. This was complemented also by Hechtl et al. [14] for tungsten. While sputter yields were reported, they mention neither the depth of ion distribution nor a sputter threshold. The oxidation states for molybdenum and tungsten [15], nickel [16] and chromium [17] were studied as a function of ion fluence using 1 keV O²⁻ ions. However, the depth of oxygen penetration and energy dependence was not discussed in detail. Given the disparities in metals, energy ranges, ion species and transport processes studied so far, a complete map of information regarding sputtering and oxidation of transition metals at low ion energies is difficult to construct for any particular metal.

We aim to provide a more complete dataset in the energy region of 50–500 eV, and discuss the processes involved in low energy oxygen ion induced sputtering and oxidation of transition metals relevant for the applications outlined above. Sputter yields were measured for molybdenum, tungsten, ruthenium and palladium at steady state, where implantation of oxygen (and compound formation) is balanced by sputtering of metal and implanted oxygen. In the case of ruthenium and
palladium, yields are reported for the first time using oxygen ions. Sputter yields are then compared to the predictions by the dynamic Monte Carlo code TRIDYN and discrepancies between experiments and simulations are briefly discussed. Oxygen transport within the metal targets is then studied in the same energy range by measuring oxide thickness. Additionally, the influence of particle kinetic energy on oxide thickness is investigated by comparing results of ion exposed samples to samples exposed to atomic oxygen species at thermal energies. For ion exposed samples, in most cases the depth of oxygen penetration was seen to be under-estimated by TRIDYN, which only accounts for ballistic transport. This indicates existence of diffusion mechanisms, which were then externally modelled using existing TRIDYN outputs. Thus, radiation enhanced diffusion mechanisms are hypothesized to act in transport of oxygen deeper into the target.

2. Experimental methods

The ion exposure facility used in this work has been described in detail in previous publications [6,18]. The setup is comprised of a vacuum chamber and ion source assembly baked out to a base pressure of $1 \times 10^{-6}$ mbar. A 15 cm DC Kaufman ion source (Veeco Instruments) was supplied with pure oxygen feed gas to generate oxygen ions. The source was retrofitted with a Faraday cup which also served as a retarding field energy analyser (FC+RFEA). The FC+RFEA and metal film samples were mounted at a distance of 7 cm from the source exit. Ion energies were calibrated using the FC+RFEA operating in energy analyser mode. The beam of oxygen ions created at a discharge voltage of 80 V was mono-energetic with a FWHM of ~10 eV over the energy range of 50–500 eV used in this work. The composition of the beam in terms of atomic and molecular ion species was not explicitly measured. However, comparing reported composition from similar Kaufman-type sources, the beam is expected to comprise of 80–90% O and 10–20% O$^+$ ions with <1% of O$^{3+}$ impurities.

Ion exposures were carried out on metal films. Two kinds of samples were produced using magnetron sputter deposition: 400 nm (thick) films grown on a quartz crystal microbalance (QCM) which we shall refer to as M-QCM to differentiate them from the mass measuring crystal itself; and 80 nm (thin) films grown on silicon substrates (MSi). Both M-QCM and MSi samples were mounted at the same radial distance from the center of the source radial axis as the FC+RFEA. This allowed simultaneous ion exposure and flux monitoring. QCM and MSi experiments were carried out separately due to the nature of the experiments, where M-QCM samples allowed for multiple variations in ion energy in a single experiment while M-Si samples were exposed to a single energy for a fixed fluence.

For QCM irradiation to O$^+_2$/O$^+$ ions, the experiments comprised of alternating steps of 300 eV Ar$^+$ exposure to clean the layer, followed by O$^+_2$/O$^+$ exposure steps to determine the sputter yield. The Ar$^+$ exposure step was introduced to remove adsorbed impurities, native oxides and oxides formed by the O$^+_2$/O$^+$ ion bombardment on the M-QCM film surface from a previous exposure. The energies of the O$^+_2$/O$^+$ exposure steps were varied randomly to avoid systematic errors. The frequency response from the QCM was constantly monitored and converted to a thickness value through the Z-match method [6,18]. The QCM signal in the initial stage of O$^+_2$/O$^+$ exposure showed a non-linear response due to incorporation of oxygen and thermal loads on the QCM oscillator from the ion and thermal flux from the ion source. After this initial stage (~1 $\times 10^{16}$ ions/cm$^2$), the QCM shows a linear response consistent with material removal, and ion exposures were carried out up to a fluence of 1 $\times 10^{18}$ ions/cm$^2$, where the high fluence was chosen to obtain good statistics at lower energies while ensuring the impingement processes reached a steady state. Exposure of Pd, Mo and W to ~60 eV ions resulted in an increase of the measured thickness value during ion exposure due to oxidation of the metal dominating sputtering and/or deposition of source grid material on the QCM. The source grids, made of molybdenum, sputter at low ion energies due to the inefficient lensing of the ion beam and sputtered grid material can redeposit onto the MSi and M-QCM samples as evidenced from post exposure XPS measurements. This deposition is negligible at energies ≥~60 eV as no Mo peaks were found in post-exposure XPS. MSi samples were exposed to a single Ar$^+$ cleaning step followed by an O$^+_2$/O$^+$ exposure at a single energy to fluence of the order of 1 $\times 10^{18}$ ions/cm$^2$.

Errors in estimated sputter yields from M-QCM samples arise from drifts in ion current (<2%) and calculation of the etch rates (~10%–20%, decreasing with increasing ion energy) from the frequency response. Corrections to the frequency response due to density changes from compound formation were not performed. Finally, charge exchange neutralization of O$^+$ ions leads to errors of ~5% assuming cross-sections in the order of those of N$_2^+$ [19]. In total, an error of up to 40% is expected, which decreases with increasing ion energy.

To compare reactivity of oxygen ions and the role of energy in the oxidation process, MSi samples were exposed to neutral atomic oxygen (at-O) in a separate facility. The direct use of at-O eliminates the dissociation step of O$_2$ (which occurs upon impact with the surface for molecular oxygen ions) and maintains a high concentration of strong electron acceptors at the surface [20,21]. With this, a strong electric field $E_M$, generated by the oxygen and metal interactions, promotes positive metal ion diffusion to react with the adsorbed oxygen, forming an oxide layer at the surface. $E_M$ is determined as $E_M = -V_M/L(t)$. $V_M$ is the Mott potential and L(t) is the formed oxide thickness. The oxide growth will only cease when the field generated by the Mott-potential is insufficient to act as driving force for ionic diffusion through the oxide. This also results in a laterally uniform oxide, as defects and irregularities at atomic and nanoscales (responsible for molecular dissociation) will not play an important role in the oxidation process [22,23]. Neutral at-O were generated by a Spect MPS-ECR mini plasma source, at an atomic oxygen flow in the order of 1 $\times 10^{16}$ atoms/cm$^2$/s (partial pressure of 1 $\times 10^{-3}$ mbar – background O$_2$). The samples were exposed at room temperature for 240 min, which was sufficient to saturate the oxide thickness [21].

MSi samples exposed to O$^+_2$/O$^+$ ions and at-O were stored under a high vacuum of 1 $\times 10^{-7}$ mbar before being transferred through ambient pressures for AR-XPS analysis. MSi samples were exposed to a maximum of 20 min in ambient pressures prior to analysis. AR-XPS measurements were acquired using a Thermo-Fisher Theta probe angle resolved spectrometer with monochromatic Al-K$\alpha$ (1486 eV) radiation and 400 µm spot size. Angle resolved measurements were obtained for all MSi samples, however, for brevity AR-XPS spectra reported in the present work are limited to a take-off angle of 34.25° (corresponding to the highest probing depth available).

3. Model and simulations

3.1. TRIDYN simulations of sputter yields and depth profiles

Sputter yields obtained from frequency changes of the QCM were compared to theoretical predictions of the Monte Carlo code TRIDYN [24]. TRIDYN tracks asymptotic trajectories of atomic collisions under the binary collision approximation. TRIDYN accounts for dynamic changes in surface composition during the sputtering process and has been successfully applied to study effects of target poisoning [25], reactive sputtering [26] and ion implantation [27].

Simulations were performed on an 80 nm metal target divided into 400 lamellae, for a fluence of 2 $\times 10^{18}$ ions/cm$^2$. The simulated beam comprised of O$_2^+$ ions with 20% O$^+$ impurity. Molecular O$_2^+$ species having an energy E$_B$ are assumed to neutralize near the metal surface and dissociate under collision, resulting in 20 particles, each having energy 0.5 E$_B$, interacting with the target. For comparing simulations and experiments, all text and graphs in this work always refer to the initial kinetic energy E$_B$. The surface binding energy (SBE) is defined by a uniform surface potential which determines whether an atom from a cascade induced by incoming ions, whose momentum vector points in
the direction of the surface-vacuum interface, leaves the surface and is consequently sputtered. The choice of SBE is important in determining the sputter yield and SBE values required by TRIDYN are chosen to be equal to the sublimation energy for the pure metal (U₀). The binding energy of the compound (SBE_{MeO}) was chosen through thermodynamic considerations as [24,26,28]:

\[
\text{SBE}_{\text{MeO}} = \frac{1}{2} U_0 + \frac{n + m}{2n \pi} \Delta H_f + \frac{n + m}{4 \pi} \Delta H_d \tag{1}
\]

where \( n \) and \( m \) are the stoichiometries of the formed oxide of type MeₙOₘ, \( \Delta H_f \) is the enthalpy of formation of the compound and \( \Delta H_d \) is the dissociation energy of the oxygen molecule (~5.15 eV). To mimic compound formation, an oxygen saturation limit (O_sat) was set corresponding to the O atomic fraction in the most abundant bulk metal oxide. Oxygen accumulating above O_sat is considered to be reflected and is removed from the simulation. A summary of parameters used is listed in Table 1.

We carry out simulations under two conditions: (i) a saturable oxygen uptake accounting for only collision cascades modified by implanted oxygen; and (ii) a saturable oxygen uptake accounting for modified collision cascades with an additional surface binding energy dependent on oxygen concentration according to Eq. 1. All simulations were carried out using the dynamic mode. The density of oxygen implanted in the material was allowed to a maximum of the fraction in the bulk value.

3.2. Multi-overlayer model

AR-XPS measurements were deconvolved to separate metal core level peaks from the metal oxide components. Subsequently, the peaks were used to determine thickness of the oxide layer formed after ion bombardment using the multi-overlayer model. This model relates the XPS peak intensity ratios from substrate and thin films to a thickness via [29]:

\[
d = \frac{\lambda \cos(\theta) \log (1 + \frac{R}{R_a})}{\frac{\lambda}{\lambda_a}} \tag{2}
\]

where \( \lambda_\text{i} \) is the effective attenuation length of the photoelectrons calculated using the approach of Cumpson and Seah [30]. A list of attenuation lengths used is provided in Table 2. \( \theta \) is the photo-electron take-off angle with respect to the surface normal, \( R \) is the ratio of the measured film XPS peak intensity to the XPS peak from the substrate layer underneath. \( R_a \) is the (hypothetical) ratio for bulk film and substrate intensities, which accounts for sensitivity factors. The thin film thickness, \( d \), can be obtained by a least square fitting of Eq. 2 to intensity ratios as a function of \( \theta \). This is particularly useful for low energy implantation studies where the depth of data acquisition is comparable to the region of ion influence. We rely on the multi-overlayer calculator in the commercially available Thermo-Advantage software (v.5.952, © 1999–2014 Thermo Fisher Scientific) for AR-XPS data processing.

### Table 1 Parameters used for TRIDYN simulations. Negative values of \( \Delta H_f^\circ \) indicate exothermic reactions for oxide formation.

| Element | Saturated Oxide | \( \Delta H_f^\circ \) (eV) | Oxide density (g/cm³) | Saturation Atomic Fraction (O_sat) | U₀ (eV) | SBE (Me-O) (eV) |
|---------|----------------|--------------------------|----------------------|-----------------------------------|--------|-----------------|
| Mo      | MoO₃           | -7.82                    | 4.69                 | 0.75                              | 6.82   | 13.8            |
| Ru      | RuO₂           | -3.25                    | 6.97                 | 0.66                              | 6.74   | 9.67            |
| Pd      | PdO            | -1.18                    | 8.30                 | 0.5                               | 3.89   | 5.71            |
| W       | WO₃            | -8.71                    | 7.16                 | 0.75                              | 8.90   | 15.3            |

### Table 2 Attenuation lengths of metal (\( \lambda_M \)) and metal-oxide (\( \lambda_{M-O} \)) used in estimating oxide thickness using the multi-overlayer model in Eq. 2 using the Cumpson-Seah equation [30].

| Element | \( \lambda_M \) (nm) | \( \lambda_{M-O} \) (nm) |
|---------|----------------------|--------------------------|
| Mo      | 1.50                 | 1.99                     |
| Ru      | 1.35                 | 1.62                     |
| Pd      | 1.32                 | 1.49                     |
| W       | 1.35                 | 1.95                     |

### 4. Results and discussion

#### 4.1. Sputter yields from QCM measurements

The sputter yields measured from M-QCM films at steady state correspond to the (partial) yield of the metal, since at steady state the mass loss due to sputtering of O atoms from the formed oxide film is compensated by implantation of new oxygen atoms in the film. Measured yields are shown in Fig. 1 along with sputter yields from TRIDYN simulations performed according to Section 3.1. Reference data for O⁺ ion irradiation were available for molybdenum [13] and tungsten [14] and are also included.

As mentioned in Section 2, below 60 eV a net negative yield is obtained for Pd, Mo and W, due to deposition of material on the QCM and these data are discarded in the present report. Sputter yields from palladium (Fig. 1a) are well described by TRIDYN's binary collision approximation. A change in surface binding energy due to compound formation does not deviate significantly from implantation induced modification of collision cascades. The calculated SBE_{Mo-O} = 5.6 eV, which is ~45% larger than the pure metal, which leads to a reduction in the predicted sputter yield by as much as a factor 2 at 70 eV. Given the error in the data, both models provide reasonable estimates of the sputter yields although at energies below 100 eV the model without modifications to the SBE seems to describe the data better. Sputtering by energies below 70 eV was not measurable, however, a threshold energy (E₀) of 22 ± 3 eV is predicted from simulations.

Ruthenium demonstrates a unique behaviour with respect to oxygen ion bombardment (Fig. 1b) compared to the other transition metals studied here. The measured sputter yields do not behave according to predictions by standard binary collision approximations and energy transfer models of TRIDYN. The sputter yields remain as high as 0.02 atoms per ion even down to 30 eV, even in the presence of grid material deposition that led to negative sputter yields for the other materials. The results suggest a mechanism other than ballistic energy transfer through binary collisions. Sublimation or production of volatile species can enhance sputter yields through ‘chemical’ processes. Ruthenium is known to have a single volatile oxide: RuO₃, which, if produced under ion bombardment would explain the behaviour observed here. We shall discuss this possibility, along with other pertinent factors in the following section.

Molybdenum sputter yields (Fig. 1c) were measured successfully down to 70 eV. Comparison to literature reports on sputtering of molybdenum by O⁺ ions [13] shows that reported yields are consistent with values measured in the present work. Yao et al. [12] have shown that molecular and atomic ion species vary in sputter efficiency due to differences in energy transferred to the metal lattice. However, these differences appear at energies <100 eV/atom for oxygen. Available literature is limited to energies above 100 eV/atom, and a comparable yield is expected and subsequently observed. Simulations from TRIDYN qualitatively mimic the sputter process with better agreement at higher energies and a steady divergence from predictions upon approaching the sputter threshold. Measured yields being higher than theoretical predictions could be due to changes in roughness of the bombarded
film, structure, thickness and stress of the formed oxide film. The experimentally observed sputter threshold of 70 eV lies at the edge of the threshold of 60 ± 10 eV obtained from averaging the two simulation results.

Available data for tungsten \[14\] from O\(^+\) ion sputtering is consistent within error to yields obtained by QCM measurements (Fig. 1d). The comparison between O\(^+\) and \(\text{O}_2\)\(^+\) is possible as mentioned previously. Experiments below 90 eV resulted in a frequency response indicating thermal drift; and mass gain below 60 eV. Although errors in low energy yield values are large due to influence of thermal drift of the QCM and more generally a low sputter rate, the experimental values are significantly larger than simulations. Both experimental datasets in Fig. 1d for tungsten begin to deviate from TRIDYN predictions at energies <250 eV. The sputter yields show a near linear trend on a log-log scale. Such a behavior is akin to chemical sputtering of targets like carbon under oxygen or hydrogen ion bombardment \[31\].

Given that certain materials (palladium) behave consistently with simulations while others show discrepancies at low energies, we shall consider the experimental factors that can potentially skew measurements of yields in the following section.

### 4.1.1. Factors influencing sputter yields

Experimental measurements of sputter yields can be affected by uncertainties in beam diagnostics or experimental design. We have previously considered factors that play a role in the uncertainty of measured values, but there exist factors that can linearly or non-linearly skew measurements such as: sample charging, presence of atomic impurities, molecular effects dictated by ion−target interaction times, and chemical effects. Here, we shall briefly discuss each effect and consider the impact on the measured sputter yields.

Effects of charging of the formed oxide films can be ruled out in the present sputter yield measurements as the samples and QCMs were grounded and the formed oxide is relatively shallow (Section 4.3).

Sputter yields can increase due to the presence of atomic impurities. As O\(^+\) ions do not dissociate, they maintain an energy larger by a factor 2 than \(\text{O}_2\)\(^+\) ion species. Their effect on sputter yields would then be larger near the sputter threshold where \(\text{O}_2\)\(^+\) ions dissociate and possess energies below \(E_{\text{th}}\) while O\(^+\) ions can still have an energy larger than \(E_{\text{th}}\) and sputter target material. The source was not directly characterized for beam composition, nor was the beam mass-filtered due to geometric constraints, therefore, the presence of higher concentrations (>20%) of O\(^+\) ions cannot be excluded. However, due to the ballistic nature of the process involved, we expect TRIDYN to predict the yield under higher O\(^+\) ion concentrations. Subsequently, TRIDYN simulations were performed for all materials by defining ion beams with a 40% O\(^+\) ion fraction. For an O\(^+\) fraction of 40% under conditions of only incorporation of oxygen without binding energy variation, the yields were larger by a factor 2 at 70 eV in comparison to simulations with 20% O\(^+\) content. As the experiments were carried out for all elements under the same conditions, this impurity concentration would encompass all metals studied. This over-estimates the sputtering for palladium (by a factor 2), and still underestimates the sputtering for the remaining targets (by at least a factor 2). Given the larger errors at the lower energies, it can be posited that O\(^+\) impurities may be larger than the estimate of 20% (by at most a factor 2) for all experiments and influence the sputter yields. However, the enhancement observed in simulations by a larger impurity concentration does not fully explain the yields at low energies which remain as high as 3× and 8× for Mo and W, respectively in comparison to simulations.

It was shown by Yao \[12\] that molecular effects can play a role for \(\text{O}_2\)\(^+\) below 100 eV, where the interaction time of an ion-atom collision is larger than the vibrational frequencies of the O-O bond. In such cases,
the incoming O$_3^+$ ions can behave as a rigid body with 2× the mass of O and thus show an increased sputter yield in comparison to O$^+$. This behavior is not modelled in our present simulations and would be an active phenomenon in the experiments for all metals studied. We can assess the magnitude of this effect as per Yao’s considerations. From a ballistic standpoint, the yield enhancement is dictated by the effective energy transferred by the molecule to the target. The bounds can lie between the energy transfer of a single atom mass (as TRIDYN assumes) and a rigid molecule colliding with the mass of 2 atoms (the unified atom limit). It is described as [12]:

$$\frac{\Delta E_{\text{molecule}}}{\Delta E_{\text{atom}}} = \frac{(m_{\text{ion}} + M_{\text{target}})^2}{(2m_{\text{ion}} + M_{\text{target}})^2}$$

(3)

For our targets studied, this approximation leads to an enhancement in sputtering by ~1.5× for Mo, Ru and Pd, and 1.7× for W when bombarded by O$_3^+$ over O$^+$. The enhancement factor is responsible for effectively rescaling the energy axis by the appropriate ratio. While this may not necessarily describe the exact process, it describes the limits to which an incoming molecular ion species can enhance the sputter yield. Thus, under the limits of a unified atom and a rigid bond, the experimental data may deviate (on the abscissa) by as much as the enhancement factor for energies below 100 eV.

Volatile oxide formation can result in chemical etching and thus a higher sputter yield. Volatile oxides of molybdenum and tungsten exist, however, literature reports are confined to studies at elevated temperatures [32–34]. Palladium does not form volatile oxides which is consistent with findings in the present study. As mentioned in the previous section, volatile species of ruthenium may form, leading to a chemically enhanced sputter yield. In some detail, ruthenium exhibits a tendency for volatile RuO$_3$ formation under thermal O$_3$ interactions [35]. Generation of ozone occurs in oxygen plasmas from 3 body collisions between excited at-O and oxygen or ozone molecules [36–37]. While dedicated corona discharges can efficiently generate ozone, in most industrial ion sources, ozone concentration is low. It is expected that a fraction of <1% of the gas species in this experiment consist of O$_3$ [38]. The etching of ruthenium by ozone proceeds as [39]:Ru + 2O$_3$ → RuO$_3$ (gas) + O$_3$. The volatile RuO$_3$ readily decomposes to RuO$_2$ and is difficult to detect without dedicated experiments [35]. Crudely, assuming the O$_3$ etching proceeds in a similar manner and is independent on energy due to its chemical nature for a fixed temperature (300 K) of experiments, we can assign a yield value of 0.5 atoms/O$_3$ molecule. A weighted average of the ozone yield with the yield predicted by TRIDYN for slight variations in O$_3^+$ impurity fraction is shown in Fig. 2.

It is evident from the calculated yields that the effect of adding a chemical component to sputter yield simulations is important at energies below a few hundred eV and becomes negligible at higher energies. At energies below 100 eV the chemical sputtering dominates and a saturation of the yield occurs which is proportional to the concentration of the ozone impurity. The presence of ozone up to ~3% of the incident ion flux could partially explain the high sputter yields at low energies for ruthenium, with the remainder of deviations attributed to variations of the extracted ion flux or ion impact enhanced chemical kinetics [40]. For the above assumptions to be valid, ozone must form within the plasma, which is not un-realistic [36], and reach the target as neutral molecules at near thermal energies to prevent dissociation upon impact. The flux of ozone should thus result from background gas of the plasma and would therefore remain constant at all ion energies. In the calculations above, however, a weighted average of O$_3$ and O$_2$/O$^+$ etching is calculated under the assumption that O$_3$ species form a specific fraction of the ion beam flux (without consideration of background gas species). To compare with the estimate of 0.1% of background gas generated by DC Kaufman type ion sources [38], let us assume the flux generated by an ion source is constant at all energies and equal to 1 × 10$^{12}$ ions/cm$^2$.s. Operating at a background pressure of 1×10$^{-4}$ mbar, of which 0.1% partial pressure is O$_3$, the flux of O$_3$ molecules neutral particles is then 2.2 × 10$^{13}$ molecules/cm$^2$.s. A flux of thermal O$_3$ equal to 3% of the ion flux (as assumed in Fig. 2), would correspond to 3 × 10$^{13}$ ozone/cm$^2$.s. Thus, a 0.1% of O$_3$ in the background during experiments, consistent with the estimate in literature [38], can explain the observed contribution of O$_3$ etching for the typical ion flux and background pressure in our experiment. This comparison gives qualitative agreement between the experimental observations and calculated predictions. Sources of deviations at high energies can arise from either an under-estimate of the TRIDYN ballistic model to physical sputter yields of O$_3^+$/O$^+$ on ruthenium, or a possible ion enhanced etching of ruthenium by ozone under simultaneous ion bombardment.

Mass analyzing and filtering the ion beam is therefore an important aspect for studying sputter yields by reactive ion species near the sputter threshold. While impurities (atomic ions and ozone) may be present in several percent in ion exposures for all materials studied, they do not significantly affect the physical sputter yields in most cases. However, the presence of a chemical etching component as demonstrated by ruthenium-ozone sputtering can greatly dominate physical sputter yields. Impurity (ozone) concentrations of even a few percent of the incident ion flux will create deviations of orders of magnitude and a physical sputter threshold cannot be reliably determined. Atomic O does not contribute to a chemical etching mechanism for Ru as no mass loss was observed in the experiments of metal target exposure to at-O.

4.2. Chemical modifications: oxygen ions vs. atomic oxygen

The sputtering process also dynamically changes chemical composition of the target materials and usually a self-terminating oxide is formed due to a balance of sputtering and transport processes at steady state. In this section, we shall assess the oxidation states of the metal after ion irradiation.

In order to characterize the oxides formed at the end of the sputtering process as a function of ion energy, MSI samples exposed to O$_2$ or O$_3^+$ were analyzed by AR-XPS according to Section 3.2. MSI samples were also exposed to at-O in order to compare the chemical states formed for similar oxygen species under two different oxidation mechanisms. On one hand, the kinetics for oxidation by oxygen ions are
expected to be governed by the ion energy. Oxide formation occurs by athermal activation of chemical and diffusion pathways [41]. On the other hand, MSi samples exposed to atomic oxygen at room temperature are expected to oxidise following the Cabrera-Mott (CM) mechanism [20]. According to this theory, a strong electric field—generated by the oxygen and metal interaction—promotes positive metal ion diffusion towards the surface to react with the adsorbed oxygen, forming a new metal oxide layer at the outer surface. This electric field reduces in magnitude as the oxide thickness grows and a limiting oxide is formed when the electric field no longer reduces the diffusion barrier.

Fig. 3 shows a compendium of XPS measurements of 3d levels of molybdenum, ruthenium, palladium and tungsten. Reference measurements with unexposed, as-deposited samples are shown along with spectra from the lowest and highest ion energy used in the experiments. Results from oxidation by atomic oxygen are also shown. Fig. 4 additionally shows the O1s peaks for the samples in the same order.

Fits to XPS data were performed by first evaluating the as-deposited metal spectra to assess metal peak position and asymmetry. Oxide peaks in the metal core levels of oxygen exposed samples were then fit with a symmetric peak for molybdenum [42,43] and tungsten [43] oxides and an asymmetric peak for ruthenium [44] and palladium [45]. The metal peak positions were fixed to the reference measurements for comparison of oxide components between ion and at-O exposed samples. Metals like molybdenum and tungsten exhibit multiple oxides within a small BE range. For simplicity, the oxide components were fit with a single peak while the full-width half maximum (FWHM) was allowed to vary. A larger FWHM was interpreted as a metal containing stoichiometric and non-stoichiometric states. The peak positions and FWHMs for the metal reference and various oxide samples are compiled in Table 3.

Magnetron sputter deposited films of molybdenum exhibit a Mo 3d$_{5/2}$ ground state peak at a binding energy (BE) of 228.0 eV consistent with reports of metallic molybdenum [46]. Peaks at higher binding
energy develop upon exposure of metallic films either to neutral at-O or O\(^2^-\)/O\(^+\) ions. Mo is known to form multiple stoichiometries [42], including upon oxygen ion bombardment at steady state [15] with Mo\(^{6+}\) (229 eV) being the most abundant at 1 keV O\(^2^-\) ion energies followed by Mo\(^{5+}\) (231.2 eV) and Mo\(^{4+}\) (232.4 eV). A comparison to our experimental ARXPS spectra rules out the formation of Mo\(^{6+}\) species during ion bombardment or at-O exposures. The Mo\(^{6+}\) oxidation state dominates in the MSI samples with Mo\(^{5+}\) making up a minority in the oxide at higher O\(^2^-\) ion energies which is encompassed in the larger FWHM. An increase in FWHM would then, in our case, indicate the presence of sub-stoichiometric oxide of Mo\(^{6+}\) present at lower BE. The metal oxide peak positions of Mo 3d\(_{5/2}\) were found to be invariant to the method of oxidation. This implies the most abundant stoichiometry (leading to the most intense XPS intensity) remains the same for all oxygen exposed films. The FWHMs indicate a more stoichiometric oxide formed at low ion energies which reduces as the FWHM broadens to include sub-stoichiometric oxides at high ion energy. The high ion energy oxide peaks are comparable to the peaks developed after at-O exposure. The O1s peaks positions and FWHMs do not vary with oxidation technique.

Ruthenium surfaces present quite slow oxidation at ambient conditions [47]. Upon exposure to at-O, the development of a sharp RuO\(_2\) peak does not occur due to the small separation of the peaks (0.8 eV) conflated by the shallow depth of oxidation. A broadening of the Ru3d peak along with a clear O1s peak however indicate the formation of an oxide. For at-O exposed samples, a binding energy of 280.6 eV is assigned to the Ru3d\(_{5/2}\) peak, based on the fact that at more surface sensitive angles, this RuO\(_2\) peak is distinct from its metallic counterpart. Energetic O\(^2^-\)/O\(^+\) shifts the oxide binding energy by as much as 0.6 eV towards higher binding energies. The O1s peak varies between the two methods by 0.2 eV, but more importantly, the O1s peak for O\(^2^-\)/O\(^+\) ion exposures is much sharper relating to a more ordered and well defined oxide. The additional component in the O1s region arising from atmospheric exposure and adsorption of water or formation of hydroxides is difficult to constrain for the two oxidation techniques. This is in part to slight variations in atmospheric exposures and varying surface structures which could not be measured in the present experiments.

Palladium is inert to oxidation under ambient conditions. Interactions with highly reactive and energetic species however, lead to formation of an oxide with the most stable and consequently most studied being PdO [45,48,49]. No difference in peak positions and valency were observed for palladium for either kinds of oxidizing species. The Pd 3d\(_{5/2}\) peak positions are consistent with PdO [45] with Pd 3d\(_{5/2}\) and Pd 3d\(_{3/2}\) present at 336.6 ± 0.1 eV and 341.9 ± 0.1 eV respectively.

Tungsten behaves similar to molybdenum in that it contains multiple oxidation states within a BE region of 3–5 eV. The metal peak for unexposed tungsten is consistent with literature at a binding energy of 31.2 eV [46]. We fit the entirety of the oxide signal with a single peak while varying the FWHM. Reports on 1 keV O\(^2^-\) ion bombardment [15] of tungsten shows formation of W\(^{6+}\) (32.7 eV), W\(^{5+}\) (34.4 eV) and W\(^{5+}\) (35.6 eV) oxide species at steady state. Upon oxidation with 60 eV O ions, a W 4f\(_{7/2}\) peak develops at a BE of 35.1 eV. The BE moves to lower values (lower oxidation states) of 34.8 eV at an ion energy of 480 eV. Ion exposed W thus forms W\(^{5+}\) with small quantities of W\(^{6+}\) oxidation states at low ion energies. With increasing energy, the abundance of W\(^{5+}\) increases and the oxide formed is sub-stoichiometric. At-O oxidation leads to a much higher BE peak at 35.6 eV corresponding to W\(^{6+}\). The energetics involved in ion bombardment leads to preferential spattering of oxygen from the oxide, thus generating a lower stoichiometry. The O1s peak also shifts to higher BE by 0.4–0.6 eV when comparing ion irradiation to at-O exposure.

Thus, we find that every target studied undergoes oxidation with the oxidation generally being similar for oxygen ions and atomic oxygen. The marked difference between them is the intensity of the elemental (ground state) peak, meaning the depth of oxygen transport being more shallow for at-O. In the following section, we shall assess the depth of oxygen transport by employing the AR-XPS results.

| Orbital Binding Energies (eV) | 3d\(_{5/2}\) | 3d\(_{3/2}\) | O1s | 4f\(_{7/2}\) | 4f\(_{5/2}\) |
|-----------------------------|-----------|-----------|-----|-----------|-----------|
| Mo (as deposited) | 228.0 (0.7) | 231.1 (0.9) | 530.7 (1.8) | - | - |
| Mo oxide (60 eV) | 223.2 (1.5) | 235.3 (1.5) | 530.3 (1.3) | - | - |
| Mo oxide (480 eV) | 232.2 (1.7) | 235.2 (1.8) | 530.2 (1.3) | - | - |
| Ru (as deposited) | 280.1 (0.8) | 284.3 (1.3) | 529.9 (1.1) | - | - |
| Ru oxide (60 eV) | 280.9 (0.9) | 285.2 (2.1) | 529.4 (1.2) | - | - |
| Ru oxide (480 eV) | 280.9 (0.8) | 285.1 (1.5) | 529.3 (1.1) | - | - |
| Pd (as deposited) | 335.1 (1.1) | 340.4 (1.3) | 529.8 (1.5) | - | - |
| Pd oxide (at-O) | 336.5 (1.2) | 341.8 (1.5) | 529.8 (1.1) | - | - |
| Pd oxide (60 eV) | 336.7 (1.2) | 342.0 (1.5) | 529.9 (1.1) | - | - |
| Pd oxide (280 eV) | 336.1 (1.2) | 342.0 (1.5) | 529.9 (1.1) | - | - |
| W (as deposited) | 530.6 (1.7) | 31.2 (0.7) | 33.3 (0.7) | 33.7 (1.2) | 37.2 (1.0) |
| W oxide (at-O) | 530.6 (1.4) | 35.6 (1.2) | 37.2 (1.0) | 37.2 (1.0) | 37.2 (1.0) |
| W oxide (60 eV) | 530.2 (1.2) | 35.1 (1.0) | 37.2 (1.0) | 37.2 (1.0) | 37.2 (1.0) |
| W oxide (480 eV) | 530.0 (1.2) | 34.8 (1.1) | 36.9 (1.1) | 36.9 (1.1) | 36.9 (1.1) |
compared to the experimental results. TRIDYN simulations were carried out assuming an oxygen atomic fraction up to saturation of a stoichiometric oxide and bulk oxide density. The ion transport mean free path is inversely proportional to the atomic density of the target material. For the purely implantation driven simulations (without SBE changes) that consider ion transport and a stoichiometric oxide formation (near bulk oxide density), the simulations present the maximum oxide thickness that can be formed due to ballistic collisions only. The results in Fig. 5 show ballistic transport correctly predicts the oxide thickness only for Ru and Pd while Mo and W show significant deviations.

The deviations signify the presence of diffusional components, possibly natural or enhanced by the ion irradiation process. We shall consider this possibility in the following section.

4.3.1. Oxygen transport: radiation enhanced diffusion

Ion implantation processes can usually be described as a competition between sputtering and implantation where a higher energy leads to a higher penetration range but also increased sputtering, forming a limited implantation thickness. Relocations can further enhance the depth to which ion species can be transported. At high energies (>1 keV), this is generally the case, however, for certain material combinations, effects of diffusion of implanted atoms cannot be ignored. This was demonstrated by Vancauwenberge [50] and Todorov [51] for oxidation of silicon by low energy oxygen ions. We can describe the transport of oxygen into the metal as a partial differential equation (PDE) of the form:

\[
\frac{\partial O(x)}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{therm}} \frac{\partial O(x)}{\partial x} \right) + S(x) - Z(x) + g(x)
\]  

(4)

where \(O(x)\) represents the concentration of oxygen, \(S(x)\) is the deposition function, which is correlated to the incoming ion flux \((j_0)\) and the reflection coefficient \(R\) dependent on incident energy [52]. In principle, \(S\) is a representation of the four moments of ion incorporation: range, straggle, skewness and kurtosis [52,53]. \(Z(x)\) is the etching function for removal of oxygen from the target. \(g(x)\) is a generation term bringing in interstitials into a slab x in the target. The diffusion coefficient is described as:

\[
D_i = D_{\text{therm}} + D_{\text{rad}} \left( \frac{n_{\text{LO}}}{n_{\text{max}}} \right)
\]

(5)

where \(D_{\text{therm}}\) is the thermal diffusivity (cm²/s) of oxygen which scales with the concentration of oxygen in a lamella to account for different diffusion coefficients in the metal and the oxide. Here we use the oxygen diffusivity in the metal only as data on oxide diffusion for current transition metals is scarce. \(D_{\text{rad}}\) is the radiation enhanced diffusivity which is limited to the region of ballistic collision induced damage and proportional to the concentration \(n_{\text{LO}}\) of oxygen atoms that are displaced by impacting ions. \(n_{\text{max}}\) is a normalization factor representing the total concentration of vacancies/interstitials generated.

Fig. 5. Experimental oxide thicknesses calculated using Eq. 2 after deconvolution of AR-XPS peaks for (a) molybdenum (b) ruthenium (c) palladium and (d) tungsten. Implantation depth from TRIDYN simulations are shown for a pure implantation case (solid line) and an implantation with a surface binding energy change (dashed). Experimental thickness was calculated using bulk metal oxide densities. The thickness obtained from at-O exposures (gray dashed line) is also plotted for comparison.
Here, impact onto an oxide can generate oxygen from the target, where the
oxide is considered to be decomposed into free oxygen and the
metal. The oxygen is then available to diffuse either further into the
target, or outwards to the surface where it is lost. Beyond the damaged
region, \( D_{\text{rad}} \) is 0. In the absence of any type of diffusion, the oxygen
profile generated at each depth interval is determined by the deposition
and etching components only and the results would match TRIDYN
outputs.

TRIDYN already accounts for \( S(x), Z(x) \) and \( g(x) \) on the right hand
side of Eq. 4. In order to address the diffusion of oxygen, an algorithm
is used as follows: TRIDYN outputs a number of \( O \) concentration depth
profiles and damage profiles corresponding to a partial fluence for a
certain time step. After each time step, the concentration profile is al-
lowed to diffuse for a time corresponding to the ratio of partial fluence
to experimental flux (~87 s). The resulting profile serves as initial
condition for the next partial fluence as simulated by TRIDYN. The
damage profile generated at a previous time step is used to assign a
scaling for \( D_{\text{rad}} \) under the assumption that the diffusion does not alter the
damage profile in the target for the next time step. Any excess oxygen
resulting from addition of partial fluences to the system, leading to
over-stoichiometry is assumed to out-diffuse and a stoichiometric
oxide is maintained. The PDE is discretized by a finite difference
scheme as a central difference in space and a forward difference in time
[54]. Integration is performed numerically and in order to fulfill the
stability criterion for the PDE, smaller time steps were used such that
\( \Delta t < \Delta x^2/D_{\text{ff}} \) where \( \Delta t \) is the time step and \( \Delta x \) is the spatial step
(0.2 nm). This implementation is necessary as the built-in option in
TRIDYN to simulate diffusive transport of oxygen results in unrealistically large oxygen penetration depths and lacks tunability.

We perform the above procedure for metals that show the largest
discrepancy in oxide thickness from TRIDYN predictions: molybdenum
and tungsten. The resulting oxide thicknesses are plotted in Fig. 6. The
thermal diffusivity of oxygen in tungsten has a value of \( 4.3 \times 10^{-16} \) cm²/s
(at 380 K) from [55]. A criterion for the choice of magnitude for \( D_{\text{rad}} \) is
that a single value (and not a functional form) should be able to de-
scribe the observations over a wide range of incident energies [41,50].
A \( D_{\text{rad}} \) of \( 4.8 \times 10^{-16} \) cm²/s provides the best match to the experimental
results which is ~1000x greater than the thermal diffusivity.

The nature of \( D_{\text{therm}} \) deserves some comment as previous reports
[50,56] describe it as a thermal diffusivity. \( D_{\text{therm}} \) would then be influ-
enced by temperature, as well as structure of the film unless \( D_{\text{therm}} \) is
a bulk diffusivity. For an a-thermal process such as ion beam oxidation,
the ion energies cannot be directly translated to a macroscopic tem-
perature to scale the diffusion coefficient given an Arrhenius form. The
choice of temperature (here 380 K) can influence \( D_{\text{therm}} \) and affect the
choice of \( D_{\text{rad}} \). We attempt to remedy this by performing a crude sen-
sitivity analysis on \( D_{\text{therm}} \) which provides bounds for regions where \( D_{\text{rad}} \) and
\( D_{\text{therm}} \) exist. The sensitivity of \( D_{\text{rad}} \) to changes in \( D_{\text{therm}} \) can be
understood by varying \( D_{\text{therm}} \) to \( 3.2 \times 10^{-15} \) cm²/s (corresponding to
400 K). A value of \( D_{\text{rad}} \) of \( 2.2 \times 10^{-17} \) cm²/s provides a reasonable
agreement with the oxide thickness which is over-estimated (by 20% of
experimental value) at 60 eV and under-estimated (by 5%) for 500 eV.
We posit that \( D_{\text{therm}} \) in the case of metals exposed to oxygen ions could
be functionally dependent on the field produced between the free
oxygen created by ion bombardment at the interface of the metal oxide
and the metal underneath. The oxidation process would then be driven
in a CM-like mechanism [57]. This interpretation of \( D_{\text{therm}} \) does not
directly negate the analysis presented so far. It does imply that the
assignment of a particular temperature is erroneous, however, the
magnitude of diffusivity is necessary for oxygen transport and can stem
from a CM-like mechanism. Assigning a diffusivity to a CM driven oxide
for comparison to present values is not trivial and requires further
study.

\( D_{\text{therm}} \) values for Mo were not readily available, however, assuming
it to be in the same order of magnitude as W, the oxide thickness is
predicted with \( D_{\text{therm}} = 4 \times 10^{-18} \) cm²/s and \( D_{\text{rad}} = 4.8 \times 10^{-18} \) cm²/s.
The comparable magnitudes of both diffusivities lead to a near-constant
‘saturable’ thickness as a function of energy. According to
Vancauwenbergh [50], we find that both \( D_{\text{rad}} \) and \( D_{\text{therm}} \) are
responsible for diffusion, with \( D_{\text{rad}} \) limited to the region where ions
generate damage (vacancies/interstitials), and \( D_{\text{therm}} \) pervasive
throughout the target. The surface acts as a sink to outward diffusing
oxygen and prevents \( D_{\text{therm}} \) from continually diffusing oxygen deeper
into the target. In both cases, for molybdenum and tungsten, a single
value of \( D_{\text{rad}} \) explains the results, over a wide range of energies.

Ruthenium and palladium show oxide thicknesses that are well
predicted by TRIDYN simulations. In the case of ruthenium, the
anomalous sputtering of the metal can be posited to reduce deeper
oxygen transport. \( D_{\text{ff}} \) may still play a role in ruthenium oxidation by ion
bombardment, which will require elimination of the species involved in
chemical sputtering. Sputter yields as well as the depth of oxide pene-
tration in palladium are well described by ballistic transport without
having to account for additional oxygen diffusivity. Thermal diffusivity
of oxygen in palladium is low [58] with oxygen penetration limited to 0.5
ML. For \( D_{\text{therm}} \) in palladium to be comparable to that of tungsten and
molybdenum, requires temperatures >1000 K and pressures in the
order of \( 10^3 \) – \( 10^5 \) Pa [59]. It can be posited that a \( D_{\text{rad}} \) component
can exist in palladium, however, in cases where \( D_{\text{rad}} \) is the primary driver,
the transport of oxygen is not significantly greater than the prediction
by TRIDYN and similar models [50]. This would explain the agreement

![Graph of oxide thickness vs ion energy for Mo and W](image)
between experiment and TRIDYN simulations without \(D_0\).

Oxygen ion exposures, studied in this work, can be compared to our recent report on transport and retention of nitrogen in the same metals upon nitrogen ion incidence [60]. It was implicitly shown in [60] that nitrogen incorporation is mediated by ballistic processes. The nitrogen content in the target materials can be accounted by TRIDYN without influence of additional diffusion processes. This is in contrast to our studies of oxygen where diffusion clearly plays a role. We hypothesize the reason for such behavior to be due to longer (shorter) diffusion time scales of nitrogen (oxygen) within the nitride (oxide) formed at steady state. In the case of tungsten, for instance, time scales for nitrogen incorporation is mediated by ballistic processes. The nitrogen content in the target materials can be accounted by TRIDYN without nitrogen incorporation of oxygen within the nitride (oxide) formed at elevated temperatures (970 K) [61]. In contrast, the time scales for oxygen transport in tungsten, from this work can be obtained from a consideration: \(\Delta t - \Delta x^2 / D_0\) using \(\Delta x = 0.2 \text{ nm}\) as the jump distance in tungsten [62], lie between 9 ms and 9 s. The exact nature of diffusional processes within the two ion exposed samples warrants investigation as one is a desorative process directed outwards, and the other is directed inwards.

5. Conclusions

In this work, we have reported the interaction of low energy oxygen ions with transition metals relevant for semiconductor, photolithography and fusion applications in the energy range of 50–500 eV. Ballistic damage was studied by measuring sputter yields for molybdenum, ruthenium, palladium and tungsten near the sputter threshold. Comparison of experiments with TRIDYN simulations showed agreement for palladium and deviations for the rest of the metals studied. Factors such as volatile compound formation and molecular ion effects were discussed and found to affect ruthenium significantly. Ozone (<1% of background gas) produced in the plasma is hypothesized to cause chemical etching of ruthenium. Molybdenum and tungsten are also potentially affected by volatile oxide formation, but the precise nature of the interaction is yet unknown. All metals form oxides which are not necessarily governed by ballistic transport only. Thermal and radiation enhanced diffusion of oxygen was hypothesized for oxygen transport, where ion damage creates free oxygen which diffuses further into the bulk. A diffusion algorithm was implemented using TRIDYN simulations of depth profiles in order to assess the effect of radiation enhanced diffusion on oxygen transport. Transport of oxygen within the film (via oxide thickness measurements) was found to be governed by ballistic (collisions for palladium and ruthenium). Molybdenum and tungsten exhibited oxygen transport depth which is under-estimated by ballistic models and was explained by radiation enhanced diffusion. Ruthenium can be susceptible to radiation enhanced diffusion of oxygen, however, due to the high sputter rate (from ozone etching), a conclusion could not be made.

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CRediT authorship contribution statement

Parikshit Phadke: Conceptualization, Methodology, Investigation, Software, Formal analysis, Data curation, Writing - original draft. Cristiane R. Stilhano Vilas Boas: Investigation, Validation, Writing - original draft. Jacobus M. Sturm: Conceptualization, Supervision, Writing - review & editing. Robbert W.E. van de Kruijf: Supervision, Writing - review & editing. Fred Bijkerk: Writing - review & editing, Project administration, Funding acquisition.

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