Sputtering and nitridation of transition metal surfaces under low energy, steady state nitrogen ion bombardment

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Abstract
Transition metal surfaces exposed to low-energy reactive ions undergo dynamic changes in composition and density due to implantation and compound formation. We report measurements of nitrogen ion induced sputter yields for transition metals relevant to fusion and optics applications. Thin films of molybdenum, ruthenium, palladium and tungsten are bombarded by nitrogen ions of kinetic energies in the range of 50–500 eV at steady state fluxes $(1 \times 10^{18} \text{ions/cm}^2)$. Measured sputter yields are explained through energy and momentum transfer under the binary collision approximation using the Monte Carlo code TRIDYN. X-ray Photoelectron spectroscopy (XPS) studies showed the nitrogen content in the films at the end of ion exposure is independent of incoming ion energy. This occurs due to competing implantation and preferential surface nitrogen sputtering processes within the XPS probing depth. All metals investigated showed evidence of a nitride formed due to energetic nitrogen impact. The combination of XPS and TRIDYN simulations were applied to extract effective reaction cross-sections for each metal.

1. Introduction

The interaction of a plasma with a metal surface is a common phenomenon in a multitude of scenarios: solar winds interact with satellite shielding [1]; particles in accelerators collide with electrostatic optics [2]; divertors in fusion reactors face high ion fluxes [3]; diffuse plasmas in extreme ultraviolet (XUV) lithography may interact with reflective optics [4–6]; magnetically confined plasmas in sputter deposition systems bombard metallic targets [7]. In nearly all cases, with the exception of sputter deposition, the interaction is unwanted and possibly damaging to the metal surface. Damage can manifest in many forms, some of which as: a loss of material; modification of surface topography; change of surface or sub-surface composition compromising functionality. Understanding the mechanisms of damage is therefore necessary to limit aforementioned changes and extend operational time.

The interaction of low energy nitrogen plasmas with transition metal surfaces is of academic and practical interest. Sputter damage [3] and ion retention [8] studies in plasma facing materials (PFM) such as tungsten (W) have proven helpful in assessing the viability of using nitrogen as a coolant in fusion plasmas. Liquid lithium is proposed as a PFM with molybdenum (Mo) as a substrate which would potentially be exposed to fusion plasmas as well [9]. Ruthenium (Ru) coatings in XUV applications may face plasmas and while sputtering has been investigated [10,11], retention is poorly understood. Palladium has been studied as well for PFM applications concerning hydrogen and tritium recycling through recombination and desorption [12,13]. The use of a nitrogen seed gas would require studies of palladium under nitrogen ion bombardment.

Currently available data on low energy nitrogen sputtering and retention is limited to energies above 0.5 keV. We aim to extend this datasets to more operationally relevant energies near the sputter threshold. In this paper, sputter yields for Mo, W, Pd and Ru atoms are measured down to 50 eV. The lower limit is dictated by experimental limitations of a low flux below 50 eV which extends experimental times to unreasonable durations. Below 50 eV, where sputtering does not dominate, deposition of adsorbent species and grid material from the ion source places further restrictions on lowest energy.

Near the sputter threshold, where sticking coefficients dominate over scattering coefficients, chemical effects begin to play a role in the evolution of collision cascades. Evidence of a chemical component involving nitride formation during the sputtering process is presented through X-ray photoelectron spectroscopy (XPS) analysis of ion irradiated thin films. The amount of retained nitrogen is compared among elements through corroboration of experimental measurements to Monte Carlo simulations. The retained nitrogen from XPS measurements is then used to determine effective reaction cross-sections for each element.

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2. Experimental methods

Experiments studying composition changes and measuring sputter efficiency place strict constraints on: the vacuum system, demanding ultra-high vacuum with bake-out; ion generation, demanding energy, composition and flux calibration; and metrology, requiring depth sensitivity comparable to the ion affected region. We describe in the following subsections, the tools available, restrictions imposed and countermeasures applied.

2.1. Ion exposure facility

The exposure facility has been described in previous publications [10, 11]. In short, a thin film deposition system equipped with magnetrons for sputter deposition and a 15 cm DC Kaufman ion source (Veeco Instruments) was used for the experiments. The base pressure was \(1 \times 10^{-6}\) mbar after bake-out dominated by water vapor. Samples of 4 mm \(^2\) before nitrogen exposure to remove \(+\) from the resonant ne-...mbar as measured by an ion gauge. XPS spectra, except where explicitly mentioned, are reported for a take-off angle of 34.25° with respect to the surface normal (which corresponds to the highest probing depth for the conditions of these experiments).

Nitrides of Group VI-VIII transition metals occur with nitrogen oc-...metal core intensities were obtained. This allowed comparisons of relative nitrogen content between target metals without spectral decon-...ation in the following manner:

Core level spectra were obtained for the metal 3d or 4f (Me) and nitrogen 1s (N1s) regions. In this way, N1s/Me ratios involving total metal core intensities were obtained. This allowed comparisons of relative nitrogen content between target metals without spectral decon-...nometry this implies that the structure of the metal core level spectra can at times be difficult to uniquely de-convolve into metal and metal nitride components [18]. The resulting lack of uniqueness of XPS spectral deconvolution was remedied in the following manner:

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3. Model and simulations

Simulations of ballistic transport with dynamic composition changes were performed using TRIDYN (version 2017) [19]. The resulting depth profiles of implanted nitrogen are fed into a two-compo-nent multi-layer model for calculating N1s/Me XPS intensity ratios.

We briefly discuss the TRIDYN code and parameters involved in the simulations as well as the XPS intensity calculations:

3.1. Simulating sputtering and implantation depth with TRIDYN

TRIDYN tracks asymptotic trajectories of atomic collisions under the binary collision approximation. The collision interactions are modelled using a Kr-C interaction potential [20] with the screening length approximated by the Firsov formulation [21].

The simulations were performed on a 80 nm thick target divided into 400 lamellae for a fluence of \(2 \times 10^{28}\) ions/cm\(^2\) (where \(f_i\) is the experimentally determined fluence), where the factor 2 comes from the assumption that all the incoming molecular nitrogen ions dissociate upon collision with the target surface. In order to account for the energy reorganization within the molecule, an incident molecular ion with energy \(E_{0}\) is simulated as impact of two atomic ions, each with an energy of \(E_{0}/2\). For comparing experimental and simulated results, all text and graphs in this work always refer to the incident energy \(E_{0}\). The beam was modelled as a combination of \(N^+\) and \(N_2^+\), with the \(N^+\) yields. A similar procedure was applied for the metal films grown on silicon substrates with a difference that only a single ion energy was used for a single sample of the metal film.

2.2. X-ray photoelectron spectroscopy

After exposure, metal films exposed to nitrogen ions were trans-...ated ambient oxidation after ion exposure, the samples were maintained under vacuum after exposure, until the moment of transfer. Reference samples were measured immediately after deposition without additional sputter cleaning and were also transferred through atmosphere exposure. A maximum of 20 min of ambient pressure exposure is estimated for all samples reported here. The oxide formed on the samples due to this ambient exposure was <1 nm.

Samples were transferred into a Thermo-Fisher Theta probe Angle Resolved X-ray photoelectron spectrometer which uses monochromatic Al-K\(\alpha\) radiation (1486 eV) with a spot size of 400 \(\mu\)m. Measurements were carried out at a pressure in the order of \(1 \times 10^{-9}\) mbar as measured by an ion gauge. XPS spectra, except where explicitly mentioned, are reported for a take-off angle of 34.25° with respect to the surface normal (which corresponds to the highest probing depth for the conditions of these experiments).

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concentration set to 20% of the total beam content. N⁺ ions retain their initial energy $E_0$. Increase in N⁺ concentrations in the ion beam leads to a higher metal sputter yield below 100 eV and shallower implantation depth. It also extends the sputter threshold to lower energies in comparison to a purely molecular ion beam. Setting the concentration to 20% gives us an upper limit to the increase in sputter yield due to N⁺ impurities.

Reactions between ion and target are not simulated in the present code. However, atomic fractions from incorporation by ballistic particle deposition in the target can be recorded. This can be used either to suppress over-stoichiometry or limit the incorporation of projectiles through the parameter, $f_{\text{res}}$ [22]. It is handled in two major ways: In the first case, we employ a method of local saturation. Here, each lamellum can saturate discretely in nitrogen concentration ($N_{\text{sat}}$) up to a predefined saturation fraction $N_{\text{sat}}$. Any nitrogen subsequently implanted in the lamella is transferred to the neighbouring lamella where the concentration is less than $N_{\text{sat}}$. If the nearest lamella is the surface, the nitrogen is re-emitted out to vacuum. This mimics a model involving short range (lateral) diffusion and allows for out-diffusion of implanted nitrogen. When an incoming nitrogen adsorbs (implants) on a site (either on a surface or implanted in a lamella in depth), it does so on both metal and nitrogen sites unless the surface (lamella) is fully saturated [23]. We shall refer to this type of incorporation as Mode 1. In the second case, the incoming nitrogen only adsorbs (implants) on a metal site (nitrogen sites are considered non-reactive for further nitrogen uptake). We shall refer to this as Mode 2. Mode 2 allows for a slow incorporation of ions in the target and can mimic either low concentrations of ion implantation or a target which forms clusters of stoichiometric compound in an otherwise metallic matrix. Here, metal sites become less available with increasing nitrogen incorporation, which leads to higher out diffusion of additional incoming nitrogen.

The concentration profile asymptotically reaches $N_{\text{sat}}$ as a function of fluence. Both modes can be controlled by the choice of $N_{\text{sat}}$, which we fix to the atomic fraction of stoichiometric nitrides as an upper limit. Allowing nitrogen to be freely incorporated leads to the atomic fractions to tend quickly to an unrealistic ‘pure nitrogen’ surface. The difference in the generated concentration depth profiles is shown in Fig. 1a for Mo irradiated by 300 eV N⁺ ions. The two modes show features of a saturation behavior controlled by $N_{\text{sat}}$ (Mode 1) and gradual uptake of nitrogen leading to an overall under-stoichiometric nitride (Mode 2). Applying Mode 1 and Mode 2, it is possible to generate collision cascades within a simulated target with a high or low reactivity, respectively. Chemical effects and diffusion can be sensitive to temperature which TRIDYN cannot simulate. The simulations thus agree best at low sample temperatures, as in our case, where external heating is not applied and radiative heating from the plasma increases sample temperature at most up to 50 °C.

TRIDYN requires a surface binding energy (SBE) matrix to evaluate sputtering events for cascades in a metal and metal nitride. The matrix elements are $SBE_{\text{Me-Me}}$, $SBE_{\text{M-N}}$, and $SBE_{\text{M-M}}$, representing interactions between metal atoms, between nitrogen atoms and metal atom with nitrogen atoms, respectively. The SBE matrix element values are approximated as [19,24]:

\[
SBE_{\text{Me-Me}} = U_S
\]

\[
SBE_{\text{M-N}} = \frac{1}{2} U_S + \frac{n + m}{2n m} \Delta H_r + \frac{n + m}{4n} \Delta H_{\text{dis}}
\]

\[
SBE_{\text{M-M}} = 0.1 eV
\]

where $U_S$ is the sublimation energy of the metal, $\Delta H_r$ is the formation energy of the nitride and $\Delta H_{\text{dis}}$ is the dissociation energy of molecular nitrogen gas (9.8 eV). $SBE_{\text{M-N}}$ represents the interaction of nitrogen atoms with other nitrogen atoms in the metal. It can usually be neglected [24]. Nitrogen in nitrides can recombine and diffuse to the surface, and the interaction can be of the order of the physisorption energy. $SBE_{\text{M-M}}$ is chosen to be in the order of adsorption energy of $N_2$ on metal surfaces to account for some interaction of gas species with the metal. Reported adsorption energies vary from 0.1 eV for W [25] up to 0.4 eV for Pd [26] and 0.8 eV for Mo [27]. Ruthenium was reported to allow negligible adsorption of nitrogen [28]. Our simulations however did not show significant changes in the yield and implantation results upon varying $SBE_{\text{M-M}}$ from 0.8 eV to 0.1 eV. Their low values do not influence the yields since $SBE_{\text{M-M}}$ values are at least an order of magnitude larger. However, we include them here for completeness. $n$ and $m$ are the stoichiometric coefficients of the formed metal nitride $M_nN_m$ ($n = 1$, $m = 1$ for $W$; $n = 2$, $m = 1$ for Mo). Formation energies of nitrides of Pd are not readily available and we set them to $+1$ eV (endothermic). The exact value is of little consequence as we shall see in Section 4.1. The parameters and values used for the simulations are summarized in Table 1. In the case of Mode 2, where fractional incorporation of nitrogen occurs, we assume $SBE_{\text{M-M}}$, is not significantly affected by compound formation and set $SBE_{\text{Me-N}} = SBE_{\text{Me-Me}} = U_S$.

3.2. Reconstructing XPS intensities

In order to compare results of TRIDYN depth profiles to experimentally observed nitrogen content, a reconstruction of the XPS N1s/Me intensity ratios is necessary. XPS intensity ratio reconstruction is possible for arbitrary concentration profiles. A multi-lamellar model was successfully demonstrated by Meisl et al. [31] for estimating the validity of simulated depth profiles of nitrogen in tungsten generated by the monte carlo code SD.TRIM.SP [32] by comparing it to sputter depth profiling by XPS. We apply a similar theoretical procedure to reconstruct energy dependent intensity ratios for Mo, Ru, Pd and W.

In general, the intensity of a photoelectron emission line from a thin film of material X can be written as [31,33]:

\[
I_X = \sigma_X \beta_X \Phi_{\text{ph}} \int_0^\infty \rho(z) \exp\left(-\int_0^z \frac{1}{\lambda(z) \cos(\alpha)} dz\right) dz
\]

where $\sigma_X$ is the elements subshell photoelectric cross-section [34], $\beta_X$ is the asymmetry parameter [35] and $\Phi_{\text{ph}}$ is the X-ray photon flux. $\rho$ is the atomic density, $\lambda$ is the inelastic mean free path (IMFP) [36] and $\alpha$ is the angle of detector with respect to the surface normal. $\Phi_{\text{ph}}$ vanishes upon comparison of intensity ratios assuming a stable X-ray source operation during spectrum acquisition. Considering a thin film to be
The experimentally obtained intensity, $I_{\text{expt}}$, is the detector (%)

being larger than for Sco of the pure metal (refer to Table 1). Pd does not readily form

sample and knowing the incident photon

mutilatively sums the intensities originating from each lamella within the

where intensity as normalized intensity (area) according to:

$$I_I = \sum_{i=1}^{N} \rho_i \left(1 - \exp \left(-\frac{\Delta Z}{\lambda \cos(\alpha)}\right)\right) \exp \left(-\sum_{j=1}^{k-1} \frac{\Delta Z_j}{\lambda \cos(\alpha)}\right)$$

or $k \geq 2$

A graphical representation of the model setup leading to Eq. (5) is shown in Fig. 1b. The term in the first parenthesis describes the photoelectron intensity from a lamella. The outgoing intensity will be

attenuated on its path to the detector while passing through k-1 layers and is factored in through the latter exponential function. Eq. (5) cumulatively sums the intensities originating from each lamella within the sample and knowing the incident photon flux, predicts the XPS intensity of an atomic specie in the thin film.

For comparison with experimental data, we report our measured intensity as normalized intensity (area) according to:

$$I_{\text{norm}} = \frac{I_{\text{expt}}}{I(E) ECF}$$

where $I_{\text{expt}}$ is the experimentally obtained intensity, $I(E)$ is the detector transmission function dependent on photoelectron kinetic energy and ECF is the energy correction factor, set to $E^{0.6}$ for Scofield sensitivity factors [34] and E is the photoelectron energy.

4. Results

We begin by evaluating experimental results in the following manner: First, the measured sputter yields are compared to TRIDYN simulations. It is observed that a chemical reactions can influence the magnitude of the yield. Next, the nature of the chemical interactions are studied through XPS spectra and evidence of nitride formation on inert metals is discussed. The TRIDYN simulations of ballisitic implantation are used to explain the nitrogen content in each metal film.

4.1. Sputter yields

Thick films grown on the QCM allowed for measurements of sputter yields of the metals. Using SBEs obtained from thermodynamic considerations as opposed to its use as a fitting parameter is insightful in assessing nitrogen sputtering and retention. It facilitates a more physically constrained comparison between elemental and compound sputtering while separating effects due to modification of SBE and altered collision cascades caused by N retention. It is expected for metals with known stable nitrides (W, Mo) to behave according to Mode 1 while relatively inert materials would behave according to Mode 2.

**Table 1** Parameters used for TRIDYN simulations.

| Element | Enthalpy of Formation (eV) | Nitride density (g/cm$^3$) | Saturation Atomic Fraction ($N_{\text{sat}}$) | SBE (Me-Me) (eV) | SBE (Me-N) (eV) | N$_{\text{sat}}^+$ N$_{\text{sat}}^+$ (%) |
|---------|---------------------------|--------------------------|---------------------------------|-----------------|-----------------|-------------------------------|
| Mo      | −0.72                     | 9.4                      | 0.33                            | 6.82            | 7.63            | 80:20                         |
| Ru      | +0.925                    | 9.48$^a$                | 0.5                             | 6.74            | 9.20            | 80:20                         |
| Pd      | −                        | 11$^b$                   | 0.1                             | 3.89            | 9.52            | 80:20                         |
| W       | −0.82                     | 16                      | 0.5                             | 8.90            | 10.1            | 80:20                         |

$^a$ Reference: [29].

$^b$ Reference: [30].

composed of k discrete lamellae, Eq. (4) can be expressed as:

$$I_K = \sigma_k \rho_k \Phi_{ph} \sum_{k=1}^{N} \rho_i \left(1 - \exp \left(-\frac{\Delta Z}{\lambda \cos(\alpha)}\right)\right) \exp \left(-\sum_{j=1}^{k-1} \frac{\Delta Z_j}{\lambda \cos(\alpha)}\right)$$

For metals which readily form nitrides, the mass loss is considered mainly due to metal removal. It is clear from the simulations shown in Fig. 2 that the formation of a compound, which is simulated according to Mode 1 (dashed lines in Fig. 2), results in a lowering of the sputter yield, compared to simulations using Mode 2, which only accounts for implantation. This is a direct result of the SBE$_{\text{Me-Me}}$ being larger than SBE$_{\text{Me-Me}}$. Ru forms a stable nitride [29,37], despite a positive enthalpy of formation. However, the sputtering is dominated by N retention causing cascade modifications (Mode 2) and a direct effect of a change to the surface binding energy is not observed. Mo readily forms nitride compounds, and this is evident in the simulated sputter yield which follows simulations accounting for both effects of cascade modification due to nitrogen retention and an increased SBE$_{\text{Me-Me}}$ (Mode 1). Tungsten is also known to form nitrides, however, the behavior of sputter yields is unlike that of Mo. This could potentially be due to a higher roughness of the tungsten film (See Section 5.1). Summarizing, we found that the binary collision approximation is capable of predicting sputter yields down to near-threshold regions for reactive ion bombardment. Yields for metals which do not readily form nitrides (Ru and Pd) can be explained by accounting for implantation only without modifying the compound surface binding energy (Mode 2). Yields for metals which readily form nitrides can be explained by a combination of implantation and binding energy change (Mode 1). Tungsten shows a higher sputter yield than predicted by Mode 1 due to dominant roughness variations. Investigation of compound formation for metals to better understand validity of the modes follows.

4.2. Nitrogen incorporation

To investigate compound formation, films grown on silicon wafers were exposed to fluences equal to those for the QCM experiments. The high fluence allowed for a steady state in sputtering and incorporation and the XPS spectra from the metal components for samples irradiated with selected ion energies are shown in Fig. 3. Mo and W show marked differences in core level spectra before and after nitrogen ion bombardment. The Mo3d region in Fig. 3a shows peaks at 229.1 eV and 232.4 eV, consistent with reported binding energies of an oversaturated Mo$_2$N [38]. The W4f region exhibits nitride peaks at 32.6 eV and 34.8 eV corresponding to the spin–orbit states of W 4f$_{5/2}$ and W 4f$_{7/2}$ respectively, comparable with reactively deposited WN sputtered by Ar$^+$ ions [39]. Both metals show traces of oxide due to exposure to ambient conditions. Ru and Pd XPS spectra demand closer inspection. The Ru3d$_{5/2}$ peaks in Fig. 3c do not show any observable shift in binding energy within the instrument resolution. The oxide content within the sample due to the sample transfer is not uniquely quantifiable and possibly overlaps with any nitride present. Contamination from carbon on ruthenium adds to errors in quantification due to overlap of the C1s peak with the Ru 3d$_{5/2}$ peak. Carbonaceous impurities were estimated to be similar between exposed samples by comparing the Ru3d$_{5/2}$ and Ru3d$_{3/2}$ peak ratios. A nitride component is assigned for deconvolution of core lines accounting for broadening of the metal spectrum. Exact binding energies for a thin nitride/nitrogen implanted layer could not be determined. Core level spectra of Pd show a marked broadening of 3d peaks with a change in asymmetry. Broadening of core spectra is indicative of either changes in the local order (amorphisation) within the crystal or electron screening variations due to bonding. Amorphisation due to ballistic impact was ruled out by etching the reference surface with 500 eV Ar$^+$ and measuring the broadening of the peak at the end of the etch step [see Supplementary Info] which was found to be negligible. Broadening could also be attributed to the presence of oxygen attached to surface atoms and its resolution is difficult due to the overlap of the Pd3p orbital with O1s. However, the absence of an oxygen KLL Auger line intensity in the survey spectra rules out oxide formation during the sample transfer [see Supplementary Info]. Observing peak intensity changes at various take-off angles, a binding energy of 335.9 eV is
assigned to a nitrogen implanted palladium. This is comparable to the value of 335.5 eV assigned to a palladium with a fractional positive charge (Pd$^{\delta+}$) after interaction with N atoms [40]. In order to confirm any nitridation, we analyse the positions of any N1s peaks present.

The N1s spectra in Fig. 4 illustrate the extent of nitrogen incorporation within the analysed sample volume. Metal-nitrogen bonds typically occur at binding energies of $\sim 397$–$398$ eV in the N1s region [41], clearly evidencing nitride formation. Mo and W show clear peaks at energies of 397.2 ± 0.1 and 397.1 ± 0.2 eV respectively, which are attributed to a metal nitride. Ruthenium is interesting as the N1s line developed upon irradiation with N$_2$ ions represents the nitrogen content within the film, even though the metal peak shows no discernable shift. A peak with a binding energy at 397.7 ± 0.2 eV is assigned for nitrogen implanted in ruthenium. Pd shows a broad nitrogen peak in the reference measurement at $\sim 399$–$400$ eV which is related to adsorbed nitrogen atoms and nitrogen containing species (such as NO) on the surface [34]. The structure of this broad Gaussian changes upon nitrogen ion bombardment with the adsorbed nitrogen peak separating out into neutral N at 399 eV and implanted nitrogen possibly forming a nitride at 398 eV. The contribution of oxynitride species to the signal at higher binding energy (399 eV) can be discounted due to the lack of a clear oxygen signal in the O KLL Auger region of the spectrum for N$_2$ exposed samples.

The N1s peaks indicate formation of nitride, but stoichiometry cannot be determined in all cases due to complexity of deconvolution. Mo and W metal peaks are well separated from the nitride peaks while Ru and Pd metal spectra are more complicated. Intensity ratios of measured nitrogen to the total metal however, do not suffer from problems of de-convolution and uniqueness of fits. Contamination by oxygen due to atmospheric exposure will lower intensity ratios and we expect this to not exceed a factor 2. We thus rely on the intensity ratios and TRIDYN simulations for understanding nitrogen transport and retention.

In order to compare experimental intensity ratios, we first look at depth profiles generated by TRIDYN which were used to model intensity ratios according to Eq. (5). TRIDYN simulations were performed according to the procedure in Section 3.1. Fig. 5 shows the depth profiles of the implanted nitrogen for each target element for selected modes at the end of fluence. Within Mode 1 (Fig. 5a -b), the nitrogen content reaches stoichiometric values. The depth of implanted nitrogen increases with increasing ion energy as expected from the energy dependence of the range of incident ions. Furthermore, increasing ion energy creates a nitrogen deficient nitride surface due to preferential sputtering of surface nitrogen by incident ions. Simulations with Mode 2 (Fig. 5c-d) for Ru and Pd show similar behavior in terms of nitrogen implantation depth increasing with ion energy with the notable difference that the implantation profile never reaches stoichiometric values. The depth of implanted nitrogen increases with increasing ion energy as expected from the energy dependence of the range of incident ions. Furthermore, increasing ion energy creates a nitrogen deficient nitride surface due to preferential sputtering of surface nitrogen by incident ions. Simulations with Mode 2 (Fig. 5c-d) for Ru and Pd show similar behavior in terms of nitrogen implantation depth increasing with ion energy with the notable difference that the implantation profile never reaches stoichiometry within the probed fluence.

Integration of the TRIDYN depth profiles to obtain N/Me ratios was performed by applying Eq. (5) to the depth profiles as in [31]. This involved integrating the entirety of the simulated depth (80 nm) and setting the metal concentration to (1 - $N_{\text{con}}$). The depth range contributing to the simulated signal is much smaller though, as accounted for through the IMFP of the outgoing photoelectrons (Eq. (4)).
comparison of the theoretical N/Me ratios to experimental XPS intensity ratios for the target materials is shown in Fig. 6. The experimental datasets exhibit two distinct features: First, the N/Me ratio remains relatively constant within 20% as a function of ion energy. Second, the intensity ratios vary by an order of magnitude upon changing target material. Intensity reconstruction from TRIDYN profiles shows differences in the nitrogen incorporation for different modes. Reconstruction depends on N concentration in the following manner as suggested by Eq. (5): Surface N contributes the most to the N1s intensity; Subsurface N contribution decays exponentially with depth, but having a higher N content in a particular lamella adds to the intensity contribution. Mode 2 shows a much lower intensity ratio of N/Me due to fractional incorporation of N. Pd and Ru data shows a better agreement with Mode 2, similar to the sputter yields in Fig. 2. Reconstruction with Mode 2 suggests that the N/Me ratio decreases with incident ion energy. This is because, as the energy is increased, N is transported deeper (lowering the N intensity contribution) and surface nitrogen is removed by sputtering (lowering N intensity). Similarly,

Fig. 3. Photoelectron emission spectra for a) Molybdenum 3d, b) Ruthenium 3d, and c) Palladium and d) Tungsten 4f, core levels, for selected ion energies. The spectra show oxide (substoichiometric and stoichiometric) peaks due to atmospheric exposure (light and dark blue). Points indicate measured data, solid lines fitted components. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Photoelectron emission spectra of the N1s region for a) Molybdenum showing overlap of the N1s peak with the Mo 3p3/2 peak, and d) Tungsten: for take-off angles of 34.25°; and angle averaged peaks showing the nitride and oxy-nitride, nitride and adsorbed N peaks respectively for b) Ruthenium and c) Palladium: Gray dots are measured data, solid lines are de-convolution fits to the data.
Fig. 5. Nitrogen atomic fractions as estimated by TRIDYN for a, a') Mo; b, b') W; c) Ru; and d) Pd. Mode 1 describes a process of lateral local diffusion with nitrogen incorporated in both metal and nitride sites until \( N_{\text{sat}} \). Mode 2 describes implantation of nitrogen into the target on metal sites only leading to an overall sub-stoichiometric levels of nitrogen.

Fig. 6. Intensity ratios of nitrogen 1s to entirety of Metal 3d/4f spectrum from XPS measurements for a) Pd; b) Ru; c) Mo and d) W. The lines are calculated intensity ratios for the ion-target combinations from the depth profile resulting from TRIDYN simulations for a nitrogen incorporation up to nitride stoichiometry (mode 1: dashed) and metal sputtering with nitrogen implantation (mode 2: solid). Filled areas depict error margins of the calculations.
decreasing the incident energy leads to accumulation of N closer to the surface (increasing N intensity). Mode 1 shows a higher N/Me intensity ratio in all cases due to a higher (saturated) N content in the measurable depth. The energy dependence here is markedly different from Mode 2: Increasing energy causes only a small increase in N/Me ratio because a saturation of N is present for all energies and transport of nitrogen deeper (increase in N intensity) is compensated by a deficiency in surface N content (decrease in N intensity). The behavior of Mo and W match well with Mode 1 incorporation indicative of a higher reactivity of these metals with N, which is also consistent with the observation of clearly separated XPS peaks of metal nitride in the Mo 3d and W 4f core levels. As pointed out before, the sputter yields for W observed experimentally are an outlier in the sense that they match Mode 2 simulations better than predictions by Mode 1, possibly due to surface roughness which we shall discuss in the following section.

5. Discussion

5.1. Sputtering and compound formation

TRIDYN simulations are in good agreement for the sputtering and possible implantation for three of the four metals studied. Mo and Ru data of yields and N/Me XPS intensity ratios are well corroborated by the simulations under the assumptions applied for the binding energy, implantation mode and atomic ion impurities. Molybdenum exhibits a stoichiometric nitride, Mo$_3$N$_2$, formed upon ion bombardment as is evidenced from the N1s peak position. This is well described within Mode 1 where transport of nitrogen within the Mo film is largely due to ballistic collisions and subsequent stopping and reaction. Ruthenium shows a lower N/Me intensity ratio, which is explained by its relative chemical inertness and a higher amount of reflected nitrogen. The transport of nitrogen in this case is also explained by ballistic collisions. The presence of the nitride N1s signal indicates the implanted nitrogen reacts with the Ru upon stopping. This amount of implanted nitrogen however, does not contribute to changing the overall surface binding energy of the target, rather, the modifications of the collision cascades due to different energy transferred by backscattered or recoiled atoms upon collision of an incident ion with a target Ru or implanted N atom is responsible for the observed sputter yields.

Sputtering of Pd by N$_2^+$/N$_2^-$ showed results which were successfully reconstructed in simulations (using Mode 2). Simulations at various N implantation fractions were carried out and an atomic fraction of N$_{\text{surf}}$=10% showed the best results. The XPS peaks of N1s point towards the formation of ballistically transported and subsequent stopping and reaction. Molybdenum exhibits a stoichiometric nitride, Mo$_3$N$_2$, formed upon ion bombardment as is evidenced from the N1s peak position. This is well described within Mode 1 where transport of nitrogen within the Mo film is largely due to ballistic collisions and subsequent stopping and reaction. Ruthenium shows a lower N/Me intensity ratio, which is explained by its relative chemical inertness and a higher amount of reflected nitrogen. The transport of nitrogen in this case is also explained by ballistic collisions. The presence of the nitride N1s signal indicates the implanted nitrogen reacts with the Ru upon stopping. This amount of implanted nitrogen however, does not contribute to changing the overall surface binding energy of the target, rather, the modifications of the collision cascades due to different energy transferred by backscattered or recoiled atoms upon collision of an incident ion with a target Ru or implanted N atom is responsible for the observed sputter yields.

Ion neutralization occurs with a 99% probability in a region of 0.5–0.6 Å from the metal surface [44,45]. Crudely approximating the ion beam to consist of molecular nitrogen ions in a single electronic excited state (1$^2$Σ$^+$) and no rotational or vibrational excitations, the threshold energy for dissociation of N$_2$ is 9.76 eV. Bombarding energies in the present study are at least a factor 5 higher than this threshold and nearly every incident N$_2$ can be considered to be dissociated upon collision and available for reaction. Rotational and vibrational states may lower this threshold of dissociation, which enforces the assumption [46]. Further, assuming neutralization and collision induced dissociation to be constant over the energy range, reaction and sputtering of nitrogen are then competing processes involved in the retention of nitrogen in the target. The amount of nitride product P$_N$ formed is approximated by [47]:

$$P_N = M_0 \left( \frac{q_N}{n_{\text{surf}} + m_{\text{surf}}} \right) \left( 1 - \exp \left( \frac{n_{\text{surf}} + m_{\text{surf}}}{A} R_0 \right) \right)$$

(12)

where $M_0$ is the amount of metal, $q_N$ is the reaction cross-section and $q_T$ is the sputtering cross-section. $q_T$ is directly proportional to the sputter yield $Y$ when the beam interacts with a certain areal density of atoms $n_{\text{surf}}$ within the projected range. In principle, both cross-sections vary as a function of the ion kinetic energy which evolves as the collision cascade progresses, and the dependence is not easily known. We shall limit the discussion to the dependence of the ratios of the cross-sections as a function of incident energy only. $n$ and $m$ are the stoichiometric coefficients for the metal nitride (Mo$_3$N$_2$) and $R_0$ is the number of ions incident on the surface with an area A. In the limit of saturation $R_0 \to \infty$ as the case of current experiments, the product to metal ratio is expressed as:

$$\frac{P_N}{M_0} = \frac{1}{n + m (q_T/q_N)}$$

(13)
The term on the left hand side of Eq. (13) describes the XPS intensity ratios. The right hand side determines the retention of nitrogen through the ratio of sputtering to reaction cross-section. Upon rearranging the terms it is clear that above the sputter threshold, $\sigma_s$ is proportional to $\sigma_r$. Determining the absolute value of $\sigma_s$ experimentally would require fluence dependent measurements below saturation fluence. However, knowing the intensity ratios and sputter yields, Eq. (13) can be evaluated to estimate $\sigma_r$. $\sigma_r$ here represents an apparent reaction cross-section involving a combination of pathways for reaction as well as implantation. Fig. 6 shows that the intensity ratio for each element varies fractionally with increase in energy. As the sputter yield (and $\sigma_s$) increases, $\sigma_r$ would have to increase as well in order to maintain the same XPS intensity ratio.

Relative ratios of sputtering and retention are extracted from experiments based on Eq. (13) and shown in Fig. 7a as function of incident ion energy. Over the energy range probed, the ratio of the cross-sections remains nearly constant. We know from the QCM experiments that the sputtering cross-section (proportional to sputter yield) of the metal increases non-linearly with increasing energy. Experimental measurements of N sputtering were not available in the current scheme of the setup. TRIDYN supplies as an output partial yields of the metal and N. The reasonable agreement of the experimental and predicted metal sputter yields gives confidence in the cascades and partial yields simulated by TRIDYN. Setting $\sigma_s$ to be equal to the partial yield of N, the behavior of $\sigma_r$ over the energy range can be understood. Fig. 7b shows trends in $\sigma_r$ over the energy range probed. Pd and Ru show a similar range of $\sigma_r$ in comparison to Mo and W whose reaction cross-sections are about $10^3$ times larger. Ru demonstrates a larger intensity ratio than ballistic predictions (Fig. 6b) which can be attributed to a larger compensation of $\sigma_s$ by $\sigma_F$ (Fig. 7a), hinting towards larger retention channels. Additionally, the magnitude of $\sigma_F$ being lower than $\sigma_s$ for a given element, is consistent with previous reports at higher energies [18,47].

6. Conclusions

We report the interaction of N$_2$/N$^+$ ions with transition metal surfaces. Ballistic interactions were observed through sputter yields and data was obtained down to 50 eV. Measured sputter yields were consistent within the binary collision approximation down to 50 eV as evidenced from TRIDYN simulations. Estimation of retained nitrogen at the end of a fluence of $1 \times 10^{18}$ ion/cm$^2$ from TRIDYN were performed assuming a low (Mode 1) and high (Mode 2) reflection coefficient, leading to nitrogen retention up to a stoichiometric nitride and sub-stoichiometric nitride level, respectively. Using simulated depth profiles, XPS intensity ratios were calculated, which were in accord with experimental values. The nitrogen content simulated by TRIDYN was corroborated by XPS measurements by comparing nitrogen/metal intensity ratios. Chemical interactions inferred from metal 3d/4f core levels indicated that Mo and W formed stoichiometric nitrides of Mo$_2$N and WN respectively; while Ru and Pd showed sub-stoichiometric levels of nitrogen. The metal core lines for Ru and Pd did not significantly change and unique deconvolution to estimate stoichiometry could not be performed. However, in all cases, experimental N1s core spectral lines indicated that the implanted nitrogen formed a metal nitride. Most importantly, it was shown that nitrogen retention in transition metals is nearly constant within the energy range of 50–500 eV. This was explained using reaction cross-sections, $\sigma_r$ that increase with increasing sputter yield as a function of energy. The increase in reaction cross-sections can be explained by a longer projected range of ions with higher energy. Reaction cross-sections were found to vary between elements as: $\sigma_r$(Ru) ~ $\sigma_r$(Pd) < $\sigma_r$(Mo) < $\sigma_r$(W). The combination of sputter yields + XPS + TRIDYN simulations serves as a useful tool to assess nitrogen content and metal reactivity where deconvolution of spectra is not unique and detailed fluence dependent data is unavailable.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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