Properties of secondary particles for the reactive ion beam sputtering of Ti and TiO₂ using oxygen ions

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ABSTRACT

The ion beam sputtering of a metallic Ti and a ceramic TiO₂ target by bombardment with oxygen ions was investigated systematically. Emphasis was put on the properties of the secondary particles emitted from the target, namely, the angular distribution of the sputtered Ti and the energy distribution of the secondary ions. Ion energies of 0.5, 1.0, and 1.5 keV and incidence angles of 0°, 30°, and 60° were used. The angular distribution of the flux of sputtered Ti particles was determined by measuring the thickness of TiO₂ films that were deposited under emission angles in the range between −40° and +80°. An empirical formula was used to describe the angular distribution as a superposition of an isotropic and an anisotropic cosinelike function. Increasing the ion energy or decreasing the ion incidence angle leads to a more isotropic emission of the sputtered Ti particles. The mass and energy distribution of the secondary ions were measured using an energy-selective mass spectrometer. The most prevalent ion species are O⁺, O₂⁺, Ti⁺, and TiO⁺. Ion energy and sputtering geometry, i.e., the combination of an ion incidence angle and an emission angle, were found to have a strong influence on the energy distribution of the secondary ions.

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I. INTRODUCTION

Ion beam sputter deposition (IBSD) is a physical vapor deposition (PVD) technique, in which ions are extracted from an ion source and accelerated toward a target. These primary ions transfer energy and momentum to the target particles, which lead to their emission and subsequent condensation on a substrate.

Compared to the more commonly used magnetron sputtering, where a plasma is formed in the vicinity of the target, the spatial separation of the ion source and the target in IBSD come at the cost of a lower deposition rate.¹ On the other hand, it leads to several advantages regarding the quality of the deposited films. Some of these advantages are lower working pressure,¹ i.e., less contamination from and collisions with the background gas, a wider range of sputtering parameters (incidence and emission angles), and a lower defect density, e.g., for the fabrication of multi-layer extreme ultraviolet mirrors.² A comprehensive tutorial on the benefits of IBSD is given in Ref. 3.

While the interdependencies between the properties of the film forming particles and the properties of the PVD deposited films are a rather complex matter,⁴ it is commonly agreed in the literature that one of the most important factors for the optimization of any PVD process is the energy that is available at the growing film.^{5,6}

We could confirm this fundamental correlation, among other things, in earlier works related to the reactive IBSD of TiO₂. These works cover either the properties of the secondary particles for the Ar and Xe ion bombardment of a Ti target and a TiO₂ target in an oxygen-rich atmosphere^{7,8} or the properties of the TiO₂ films deposited under the same conditions.^{9–11} An important aspect of these studies is the wide range in which the sputtering geometry is varied and the focus on sputtered and backscattered secondary ions.

Sputtering is a phenomenon that has been intensively studied for many decades, e.g., the review by Oechsner in 1975¹² or the comprehensive book by Behrisch and Eckstein on sputtering in 2007.¹³ Nevertheless, most studies related to the properties of secondary

particles during ion beam sputtering are either restricted to a fixed sputtering geometry or only focus on the properties of sputtered particles, e.g., the excellent research studies by Goehlich *et al.*^{14–19}

The aim of this work is to reveal the effect of substituting the noble gas primary ions by reactive oxygen ions on the properties of the secondary particles and to set these results into context with earlier works related to the properties of the TiO₂ films deposited under the same conditions.²⁰

II. EXPERIMENT

The setup consists of a broad-beam ion source, a target holder, and an energy-selective mass spectrometer (ESMS). A schematic sketch of the experimental setup is depicted in Fig. 1. All parts of the setup are grounded, and therefore, no potential differences are expected inside the vacuum chamber, which might have an influence on the energy of secondary ions. In an earlier study, the same setup was used to deposit TiO₂ thin films by simply replacing the ESMS with a semicircular substrate holder.²⁰

The ion source was developed in-house and uses inductively coupled radio frequency (RF) excitation to form a plasma inside its discharge chamber.²¹ The three-grid extraction system has an open diameter of 16 mm. O₂ was used as a sputter gas with a gas flow rate of 5.0 SCCM and an RF power of 100 or 110 W. The total ion beam current was measured with a Faraday probe and was found to be between 6 and 10 mA. In order to prevent excessive erosion of the commonly used graphite grids by oxygen plasma, Ti grids were used. The beam to target distance was 15 cm while the target to ESMS distance was 25 cm, which adds up to 40 cm for the measurement of the ion beam composition with the ESMS.

The sputtering target was a disk of either polycrystalline Ti or TiO₂ with a diameter of 100 mm, thickness of 3 mm, and purity of 99.99%. During sputtering from both targets, no additional O₂ was lead into the vacuum chamber since it was shown in earlier works²⁰ that the O₂ flow of 5.0 SCCM from the ion source already provided enough oxygen to ensure the formation of TiO₂ under the same

sputtering conditions. The base pressure was 2.0×10^{-6} mbar, while the working pressure was 4.0×10^{-5} mbar.

The mass and energy distributions of the secondary ions were measured with an ESMS Balzers Quadstar PPM 422 (mass range 1–512 u; energy range 0–500 eV). All energy distributions measured with the PPM 422 were normalized to their respective maximum intensity and then smoothed by the method of moving average with an average over 40 adjacent data points. Mass distributions were recorded at an ion energy of 10 eV. Due to the limitations in the energy range of the Balzers Quadstar PPM 422, the mass and energy distributions of the primary ions were measured with a second ESMS Hiden EQP300 (mass range 1–300 u; energy range 0–1100 eV). It should be noted that the used energy-selective mass spectrometers actually measure the mass-to-charge ratio and the energy-to-charge ratio. Since most measured ions are expected to be single-charged, these ratios will be considered as the ions mass and energy, respectively, if not stated otherwise. It is well known that energy-selective mass spectrometers have an influence on the measured energy distributions due to their transmission function.²² This effect is not corrected in the presented data, though it is clear that the observed variations in the data can be correlated to variations of the deposition parameters.

As an important site note regarding the presented energy distributions in this work, we would like to point out that only the energy distributions of ions were measured. We would like to give a rough estimate of the ionization rate. Taga *et al.* reported that during sputtering with 18.5 keV O₂⁺ ions of a clean Ti target at a working pressure of 10^{-7} mbar, about 0.013% of sputtered Ti atoms were ionized.²³ Benninghoven reported that during sputtering with 2.5 keV Ar⁺ ions, full oxygen coverage of a Ti target leads to an increase of the absolute values of measured Ti⁺ and TiO⁺ ions by three orders of magnitude compared to Ti⁺ from a clean Ti target.²⁴ Consequently, the number of Ti⁺ and TiO⁺ ions during sputtering from a Ti target with full oxygen coverage can be estimated to be of the order of roughly 10%. The influence of the 90% neutral particles is not discussed here.

The angular distribution of the sputtered Ti particles was determined by the collection method, i.e., TiO₂ films were deposited with the same process parameters.²⁰ The deposition rate and mass density of the films were used to calculate the differential sputtering yield of the sputtered Ti, i.e., the number of sputtered Ti atoms per solid angle and the primary ion impinging on the target, which are given by

$$\frac{\partial Y}{\partial \Omega} = \frac{D \cdot \rho \cdot r^2}{M \cdot I}, \quad (1)$$

where D is the deposition rate, ρ is the mass density of the deposited TiO₂ films, r is the distance between the target and the semicircular substrate holder, M is the mass of a TiO₂ molecule, and I is the ion current impinging on the target. Spectroscopic ellipsometry was used to determine the thickness of the TiO₂ films in order to calculate the deposition rate, and x-ray reflectivity was used to determine the mass density of the TiO₂ films.

All determined mass densities for the films deposited from the Ti and TiO₂ targets were used to calculate the respective average, which was found to be 3.53 g/cm³ for the Ti and 3.51 g/cm³ for the

FIG. 1. Sketch of the experimental setup. The sum of incidence, emission, and scattering angles is 180°.

TiO₂ target. The maximum film thickness for each deposition was set to roughly 100 nm. The highest deposition rates for oxygen ion bombardment of the Ti and TiO₂ targets were achieved for an ion energy of 1.0 keV, an ion incidence angle α of 60°, and an emission angle β of 40°. They were 0.31 and 0.23 nm/min, respectively.

Energy distributions were measured for four most prevalent secondary ion species, namely, O⁺, O₂⁺, Ti⁺, and TiO⁺, at emission angle β in steps of 10° for primary ion energy E_{ion} of 0.5, 1.0, and 1.5 keV and at ion incidence angle α of 0°, 30°, and 60°. The geometrical dimensions of the ion source and the ESMS result in a minimal detectable emission angle β for a given ion incidence angle α . An ion incidence angle α of 0°, 30°, and 60° results in a minimal emission angle β of 60°, 30°, and 0°, respectively. It should be noted that the sum of ion incidence angle α , emission angle β , and scattering angle γ is 180°, i.e., an increase in α or β leads to a decrease in γ . The primary ion energies of 0.5, 1.0, and 1.5 keV are realized by beam voltages of 0.5, 1.0, and 1.5 kV.

III. RESULTS AND DISCUSSION

A. Energy distribution of primary ions

In earlier works related to ion beam sputtering of Ti and TiO₂, we used the noble gases Ar and Xe as primary ions. When an ion source is operated with a noble gas like Ar, the emitted ions are mostly single-charged Ar⁺ atoms.^{21,25} With a reactive gas like N₂ or O₂, however, the composition of the ion beam becomes more complex.^{21,25}

In this work, O₂ was led into the discharge chamber of the ion source. The predominant ion species emitted from the ion source were molecular O₂⁺ and atomic O⁺ ions. Similar investigations on an ECR ion source operated with O₂, which had a discharge chamber made of graphite, revealed that most of the extracted ions were C or C containing molecules while only 13% were O₂⁺ ions and 22% were O⁺ ions.²⁵ Since the ion source used here was equipped with Ti grids, the number of C containing ions was negligible.

Molecular O₂⁺ ions can be formed by a single collision with an energetic electron,

which requires an ionization energy of 12.07 eV.²⁶ In order to form atomic O⁺ ions, O₂ needs to be dissociated first,

which requires a dissociation energy of 5.16 eV.²⁶ An atomic oxygen atom O can then be ionized by electron impact,

which requires an ionization energy of 13.60 eV.²⁶ It should be noted that the formation of an atomic O⁺ ion is also possible by the dissociation of a molecular O₂⁺ ion. Nevertheless, the formation of an atomic O⁺ ion from O₂ requires more energy than the formation of a molecular O₂⁺ ion.

Besides the threshold energy for ionization and dissociation, the corresponding cross sections constitute another important aspect. These are depicted in Fig. 2 for three aforementioned processes [see

FIG. 2. Cross sections for the ionization of O₂ (Ref. 27), O (Ref. 28), and the dissociation of O₂ (Ref. 29) as a function of electron energy.

Eqs. (2) and (3)]. Up to an electron energy of roughly 40 eV, all three processes have similar cross sections. The cross section for the dissociation decreases for electron energies >40 eV, while both ionization cross sections continue to increase with electron energy. For electron energies >60 eV, the cross section for the ionization of atomic O saturates, while the cross section for the ionization of molecular O₂ reaches its maximum at roughly 100 eV.

These considerations may lead to the assumption that the primary ions are mostly O₂⁺ ions, since they are more likely to form and at a lower energy cost. This is actually in good agreement with the measured energy distributions as presented in Fig. 3 (mind the different scales), but it should be noted that predicting the composition of a plasma is actually a much more challenging task.

Aside from the clear domination of the molecular O₂⁺ ions relative to the atomic O⁺ ions, Fig. 3 reveals that for a beam voltage of 0.5 kV, both energy distributions show a main peak close to an energy of 500 eV with a series of lower-intensity peaks at higher energies. For O₂⁺ ions, there is also a low-intensity structure, which stretches from 700 to 1000 eV and a low-energy structure around 10 eV. For a beam voltage of 1.0 kV, only a single peak is visible. Potentially existing higher-energy peaks could not be measured, since the energy range of the used ESMS is limited to 1100 eV.

The main peak for O₂⁺ ions in Fig. 3(a) is located at 526 eV for a beam voltage of 0.5 kV and at 1032 eV for a beam voltage of 1.0 kV. The corresponding positions of the main peak for O⁺ ions in Fig. 3(b) are 537 and 1024 eV. This leads to the conclusion that the mean plasma potential, by which the ions are accelerated during extraction from the plasma, is roughly 30 V.

The energy distribution of the O₂⁺ ions for a beam voltage of 0.5 kV shows three low-intensity peaks at energies above the main peak. The origin of these three peaks is not clear but is tentatively assigned to the dissociation of double-charged O₂ containing molecules.

When a double-charged molecule is extracted from the plasma and accelerated by the sum of plasma potential and beam

FIG. 3. Measured energy distribution of the primary molecular O_2^+ ions (a) and the primary atomic O^+ ions (b) for beam voltages of 0.5 and 1.0 kV. The dotted line in panels (a) and (b) is positioned at the same count rate to clarify the different scales.

voltage, it gains an energy of

$$E_{\text{mol}} = 2 \cdot e \cdot (U_{\text{plasma}} + U_{\text{beam}}), \quad (5)$$

with e being the elementary charge, U_{plasma} being the plasma potential, and U_{beam} being the beam voltage. Assuming that this molecule dissociates after leaving the ion source and that the velocity of the fragments is the same as that of the initial molecule lead to the conclusion that the kinetic energy of a fragment is given by

$$E_{\text{frag}} = E_{\text{mol}} \cdot \frac{M_{\text{frag}}}{M_{\text{mol}}}, \quad (6)$$

with M_{frag} being the mass of the fragment and M_{mol} being the mass of the molecule. From Eqs. (5) and (6), it becomes clear that the kinetic energy of a fragment of this double-charged molecule is

larger than $e \cdot (U_{\text{plasma}} + U_{\text{beam}})$ if $M_{\text{frag}} > 1/2 \cdot M_{\text{mol}}$ and smaller if $M_{\text{frag}} < 1/2 \cdot M_{\text{mol}}$.

Following Eqs. (5) and (6), the three low-intensity peaks in the energy distribution of the O_2^+ ions as shown in Fig. 3(a) for a beam voltage of 0.5 kV can be explained by the dissociation of double-charged $\text{N}_2\text{O}_2^{++}$ (60 u), $\text{C}_2\text{O}_2\text{H}_2^{++}$ (58 u), and $\text{C}_2\text{O}_2^{++}$ (56 u), leading to kinetic energies of 565, 585, and 606 eV, respectively. These three energies are marked with arrows in Fig. 3(a). The broad low-intensity structure between 700 and 1000 eV is mostly likely also caused by the dissociation of multiple-charged O_2 containing molecules. No such additional peaks are visible for a beam voltage of 1.0 kV, which is consistent, since they would appear at energies above 1100 eV, i.e., out of the measurement range. The low-energy structure around 10 eV is probably caused by charge exchange processes, which lead to ionization of the O_2 molecules in the background gas. Energies as high as 10 eV are rather unlikely for molecules from the thermalized residual gas. The excitation to such high energies is tentatively assigned to collisions with energetic particles in the gas phase.

The energy distribution of the O^+ ions for a beam voltage of 0.5 kV shows one low-intensity peak below and three peaks at energies above the main peak. The peak below the main peak might be due to the dissociation of a single-charged H_2O^+ ion, leading to an energy of 471 eV according to Eq. (6). Of the three peaks above the main peak, only the center peak can be reasonably related to the dissociation of CO^{++} , leading to an energy of 606 eV. In Fig. 3(b), the peaks at 471 and 606 eV are marked with arrows.

The energy distribution of the O^+ ions for a beam voltage of 1.0 kV shows a peak at about half of the energy expected due to the sum of plasma and beam potential at roughly 515 eV, which is marked with an arrow in Fig. 3(b). These O^+ ions most likely originate from the dissociation of single-charged O_2^+ ions.

From the measured energy distributions of the primary ion beam in Fig. 3, it is concluded that most of the primary ions are single-charged O_2^+ and O^+ ions, with a clear dominance of O_2^+ ions. Additional low-intensity structures can be related to the dissociation of larger double-charged molecules, which were formed in the plasma.

In the following, the term “oxygen ion bombardment” will be used to describe this combined bombardment by O^+ and O_2^+ ions.

B. Mass distribution of secondary ions

The mass distribution of secondary ions during bombardment with oxygen ions with an ion energy of 1.0 keV and an ion incidence and emission angle of 60° is depicted in Fig. 4(a) for the Ti target and in Fig. 4(b) for the TiO_2 target. In both spectra, the most prevalent ion species are atomic O (O^+ , 16 u), molecular O_2 (O_2^+ , 32 u), Ti (Ti^+ , 46–50 u), and a diatomic molecule consisting of Ti and O (TiO^+ , 62–66 u).

The features between 78 and 82 u can be related to a molecule consisting of one Ti atom and two O atoms (TiO_2^+). The signal intensity of these TiO_2^+ ions is about two orders of magnitude smaller than that of the TiO^+ ions and is therefore not discussed in the following considerations.

Ti-containing ions in Figs. 4(a) and 4(b) are identified by their characteristic fingerlike structure, which is reflecting the natural

FIG. 4. Measured mass distribution of the secondary ions during oxygen ion bombardment of the Ti (a) and TiO₂ (b) targets for an ion energy of 1.0 keV and an ion incidence and emission angle of 60°.

abundance of the Ti isotopes. The relative signal intensities of peaks between 46 and 50 u (Ti⁺) in Figs. 4(a) and 4(b) are in good agreement with the natural abundance.

On the contrary, the relative signal intensities of peaks between 62 and 66 u (TiO⁺) in Figs. 4(a) and 4(b) show a slight shift toward higher masses. This shift can be explained by the formation of a hydroxyl group (O-H), i.e., the ions here are not just TiO⁺ but also TiOH⁺. A rough estimate leads to the conclusion that about 4% of the TiO⁺ ions during Ti target sputtering and about 9% during the TiO₂ target sputtering form hydroxyl groups.

C. Angular distribution of sputtered Ti particles

The mass distributions of the secondary ions as shown in Fig. 4 revealed that the Ti ejected from the target reaches the substrate in different forms, Ti, TiO, TiOH, etc. Nevertheless, the deposition rate of the deposited TiO₂ films can be used to derive the differential sputtering yield of the sputtered Ti, assuming that the sticking rate of the Ti-containing species is close to unity and that the

resputtering rate is close to zero. These assumptions are considered a valid approximation, since the measured energy distributions of the secondary ions in Figs. 7–10 clearly demonstrate that the vast majority of secondary ions have energies below 100 eV. Deviations are expected to lie within the error bar of ±10%. Neutral species are not expected to be overall more energetic than their ionized counterparts.

The differential sputtering yield of Ti is depicted in Fig. 5 for an ion incidence angle of 30° and ion energies of 0.5, 1.0, and 1.5 keV for the Ti (a, c, e) and TiO₂ (b, d, f) targets. The maximum of the differential sputtering yield increases with an increasing ion energy and is higher for the bombardment of the Ti target than for the bombardment of the TiO₂ target. The maximum of the differential sputtering yield also increases with an increasing ion incidence angle (not shown here). The observed dependence of the maximum sputtering yield on the ion energy and ion incidence angle is in good agreement with sputtering laws mentioned in the literature.¹³

The differential sputtering yield is fitted by a superposition of two cosine functions, as already proposed in earlier studies,^{7,8,30}

$$\begin{aligned}\Phi(\beta) &= \Phi_{\text{iso}}(\beta) + \Phi_{\text{aniso}}(\beta) \\ &= \Phi_{\text{iso,max}} \cdot \cos(\beta) + \Phi_{\text{aniso,max}} \cdot \cos^m(\beta - \beta^*). \quad (7)\end{aligned}$$

The first cosine function $\Phi_{\text{iso}}(\beta)$ represents the isotropic part of the differential sputtering yield, while the second over-cosine function $\Phi_{\text{aniso}}(\beta)$ represents the anisotropic part, which is tilted by an angle β^* , with the exponent m describing its directionality. The maxima of the isotropic and anisotropic cosine functions are denoted as $\Phi_{\text{iso,max}}$ and $\Phi_{\text{aniso,max}}$, respectively.

The best-fit results of Eq. (7) to the data shown in Fig. 5 are plotted together with the corresponding isotropic and anisotropic functions $\Phi_{\text{iso}}(\beta)$ and $\Phi_{\text{aniso}}(\beta)$. From panels (a, c, e) and (b, d, f) in Fig. 5, it becomes clear that an increase in ion energy favors the isotropic part of the differential sputtering yield. This also holds for a decreasing ion incidence angle (not shown here). The best-fit parameters of Eq. (7) to the differential sputtering yield for all deposition parameters are summarized in Table I.

Figure 6 depicts the ratio between the maxima $\Phi_{\text{iso,max}}$ and $\Phi_{\text{aniso,max}}$ for oxygen, Ar, and Xe ion bombardment of the Ti and TiO₂ targets for a fixed ion incidence angle of 30° in panel (a) and for a fixed ion energy of 1.0 keV in panel (b). The ratio $\Phi_{\text{iso,max}}/\Phi_{\text{aniso,max}}$ is a measure of the emission behavior of the sputtered Ti particles and, hence, for the distribution of the initial energy of the impinging ions among the target atoms participating in the collision cascades, which eventually led to the emission of Ti particles. Increasing the ion energy or decreasing the ion incidence angle leads to a deposition of the ion energy deeper into the target and, consequently, longer collision cascades. Longer collision cascades lead to a distribution of the initial energy of the impinging ions among more target particles, resulting in a more isotropic differential sputtering yield. This behavior is clearly visible in Fig. 6. The ratio $\Phi_{\text{iso,max}}/\Phi_{\text{aniso,max}}$ is in most cases higher for the bombardment of the TiO₂ target compared to that of the Ti target. This is tentatively assigned to the higher atomic density in the TiO₂ target.

FIG. 5. Differential sputtering yield of Ti for oxygen ion bombardment of the Ti [(a), (c), and (e)] and TiO_2 [(b), (d), and (f)] targets for an ion incidence angle of 30° . Panels [(a), (c), and (e)] and [(b), (d), and (f)] illustrate the influence of the ion energy (0.5, 1.0, and 1.5 keV). The lines refer to the respective best-fit function $\Phi(\beta)$ and to the corresponding isotropic and anisotropic part. The error bars were estimated with $\pm 10\%$.

TABLE I. Best-fit parameters of Eq. (7) to the differential sputtering yield presented in Fig. 5.

Target	E_{ion} (keV)	α (deg)	$\Phi_{\text{iso,max}}$ (atoms/ion sr $^{-1}$)	$\Phi_{\text{aniso,max}}$ (atoms/ion sr $^{-1}$)	$\frac{\Phi_{\text{iso,max}}}{\Phi_{\text{aniso,max}}}$	m	β^* (deg)
Ti	0.5	30	0.011	0.025	0.44	4.0	55
Ti	1.0	30	0.015	0.026	0.58	3.2	56
Ti	1.5	30	0.026	0.034	0.76	2.9	58
Ti	0.5	60	0.015	0.031	0.48	3.9	39
Ti	1.0	60	0.026	0.043	0.60	2.7	46
Ti	1.5	60	0.041	0.055	0.75	2.3	47
Ti	1.0	0	0.011	0.007	1.57	4.4	63
Ti	1.0	30	0.015	0.026	0.58	3.2	56
Ti	1.0	60	0.026	0.043	0.60	2.7	46
TiO_2	0.5	30	0.010	0.017	0.59	4.0	56
TiO_2	1.0	30	0.014	0.018	0.78	3.2	59
TiO_2	1.5	30	0.026	0.026	1.00	3.4	56
TiO_2	1.0	0	0.011	0.008	1.38	4.8	64
TiO_2	1.0	30	0.014	0.018	0.78	3.2	59
TiO_2	1.0	60	0.024	0.030	0.8	3.4	46

FIG. 6. Ratio $\Phi_{\text{iso,max}}/\Phi_{\text{aniso,max}}$ for varying ion energies (a) and varying ion incidence angles (b) for oxygen, Ar, and Xe bombardment of the Ti and TiO_2 targets.

These findings are in good agreement with the anisotropy criterion for sputtered particles by Stepanova and Dew,³¹ who used the ratio between the average initial momentum of the impinging ion transferred to each recoil p_d and the average momentum of each recoil p_r as a measure of isotropy,³¹

$$\frac{p_d}{p_r} = \sqrt{\frac{M_1}{M_2} \cdot \frac{\hat{E} + E_{\text{sb}}}{E_{\text{ion}}}}, \quad (8)$$

where M_1 and M_2 are the mass of the impinging ion and the target atoms, respectively. The parameter $\hat{E}$ is the mean energy of the sputtered atoms and E_{sb} is the corresponding surface binding energy. According to Stepanova and Dew, the collision cascades are more thermalized, i.e., more isotropic, for a higher average momentum of each recoil p_r . This holds for an increasing ion energy E_{ion} and a decreasing mass of the impinging ion M_1 . When comparing

the differential sputtering yields for the bombardment of the Ti and TiO_2 targets, the surface binding energy is expected to be the same, because the Ti target's surface is assumed to be fully oxidized.

D. Energy distribution of secondary Ti ions

Figure 7 depicts representative energy distributions of the secondary Ti^+ ions (48 u) for the bombardment of the Ti (a, c, e) and TiO_2 (b, d, f) targets. Panels (a) and (b) show measured energy distributions for an ion energy of 1.0 keV, an ion incidence angle of 60° , and emission angles between 0° and 80° . Panels (c) and (d) show measured energy distributions for an ion energy of 1.0 keV and a scattering angle of 70° , which is realized by several combinations of ion incidence and emission angles ($30^\circ/80^\circ$, $35^\circ/75^\circ$, $40^\circ/70^\circ$, $45^\circ/65^\circ$, $50^\circ/60^\circ$, $55^\circ/55^\circ$, and $60^\circ/50^\circ$). Panels (e) and (f) show measured energy distributions for a scattering angle of 120° , which is realized by several combinations of ion incidence and emission angles ($0^\circ/60^\circ$, $30^\circ/30^\circ$, and $60^\circ/0^\circ$), and for each scattering angle for an ion energy of 0.5, 1.0, and 1.5 keV.

The maximum of each energy distribution in Fig. 7 is followed by a high-energy tail, which falls off proportional to

$$\exp(-n \cdot E), \quad (9)$$

with the parameter n indicating different slopes, represented by a straight line when plotted with the logarithmic scale. The maximum is located between 10 and 30 eV in each case.

The slope of the high-energy tail in panels (a) and (b) of Fig. 7 becomes less steep for an increasing emission angle, i.e., it expands to higher energies. This effect is a clear sign of anisotropy in the energy distribution of the emitted Ti^+ ions. Similar effects have been observed by Goehlich *et al.*¹⁴ Panels (c) and (d) clearly demonstrate that the shape of the energy distribution of the sputtered Ti^+ ions strongly depends on the scattering angle, rather independent of the ion incidence angle and the emission angle, which were used to obtain the particular scattering angle. This correlation is also visible in panels (e) and (f), which additionally also reveal the influence of the ion energy. For both targets, an increase in ion energy leads to a broadening of the energy distribution of the sputtered Ti^+ ions. Comparing panels (a) and (b) with panels (e) and (f) shows that the influence of the scattering angle (varying with incidence and emission angles) dominates over the influence of ion energy. The choice of the target material seems to have only a marginal effect on the energy distribution of the sputtered Ti^+ ions.

E. Energy distribution of secondary TiO ions

Figure 8 depicts representative energy distributions of the secondary TiO^+ (partly TiOH^+) ions (64 u) for the bombardment of the Ti (a, c, e) and TiO_2 (b, d, f) targets, with the same layout as in Fig. 7.

The secondary TiO^+ ions are here referred to as “sputtered,” although they might also form in the gas phase after emission of Ti particles from the target's surface.³² The high-energy tail of the energy distributions of the sputtered TiO^+ ions in Fig. 8 shows a steeper slope compared to the energy distributions of the Ti^+ ions

FIG. 7. Measured energy distribution of Ti^+ ions (48 u) sputtered from the Ti [(a), (c), and (e)] and TiO_2 [(b), (d), and (f)] targets under oxygen ion bombardment. Panels (a) and (b) show the energy distribution for an ion energy of 1.0 keV, an ion incidence angle of 60° , and emission angles between 0° and 80° . Panels (c) and (d) show the energy distribution for an ion energy of 1.0 keV and a scattering angle of 70° for seven different combinations of ion incidence and emission angles. Panels (e) and (f) show the energy distribution for a scattering angle of 120° for three different combinations of ion incidence and emission angle and ion energies of 0.5, 1.0, and 1.5 keV.

presented in Fig. 7, i.e., the sputtered TiO^+ ions have a lower mean kinetic energy than the sputtered Ti^+ ions. Additionally, the main peak is located at lower energies. Another striking difference is the less pronounced influence of the scattering angle and ion energy. The lower mean kinetic energy of the TiO^+ ions might be due to the fact that molecules can receive energy in the form of rotational and vibrational energies and that the probability of a molecule to dissociate increases with increasing kinetic energy of its constituents.^{32,33}

F. Energy distribution of secondary O and O_2 ions

Figure 9 depicts representative energy distributions of the secondary O^+ ions (16 u) for the bombardment of the Ti (a, c, e) and TiO_2 (b, d, f) targets, with the same layout as in Figs. 7 and 8.

These secondary O^+ ions are backscattered primary O^+ ions, sputtered O^+ ions, or O^+ ions that are formed by charge exchange collisions with the residual gas. The low-energy maximum of the energy distributions of the secondary O^+ ions is located between 5

FIG. 8. Measured energy distribution of TiO^+ (TiOH^+) ions (64 u) sputtered from the Ti [(a), (c), and (e)] and TiO_2 [(b), (d), and (f)] targets under oxygen ion bombardment. Panels (a) and (b) show the energy distribution for an ion energy of 1.0 keV, an ion incidence angle of 60° , and emission angles between 0° and 80° . Panels (c) and (d) show the energy distribution for an ion energy of 1.0 keV and a scattering angle of 70° for seven different combinations of ion incidence and emission angles. Panels (e) and (f) show the energy distribution for a scattering angle of 120° for three different combinations of ion incidence and emission angles and ion energies of 0.5, 1.0, and 1.5 keV.

and 20 eV and is followed by a high-energy shoulder. The high-energy shoulder extends to higher energies with an increasing emission angle, i.e., a decreasing scattering angle, and with an increasing ion energy. As already discussed in detail in earlier works,^{7,8} these high-energy shoulders can be related to directly backscattered and directly sputtered O^+ ions. Similar to the observations made for Fig. 7, the energy distributions of the O^+ ions also show a strong influence of the scattering angle. The influence of the scattering angle again dominates over the influence of ion energy and target species.

Figure 10 depicts representative energy distributions of the secondary O_2^+ ions (32 u) for the bombardment of the Ti (a) and TiO_2 (b) targets for an ion energy of 1.0 keV, an ion incidence angle of 60° , and emission angles between 0° and 80° .

The energy distributions as shown in Fig. 10 show no significant dependency on scattering angle or ion energy; the latter is not shown here. For these reasons, the secondary O_2^+ ions are assumed to originate from the residual gas in the vacuum chamber and to be ionized by charge exchange processes. The low-energy maximum

FIG. 9. Measured energy distribution of O^+ ions (16 u) during sputtering from the Ti [(a), (c), and (e)] and TiO_2 [(b), (d), and (f)] targets under oxygen ion bombardment. Panels (a) and (b) show the energy distribution for an ion energy of 1.0 keV, an ion incidence angle of 60° , and emission angles between 0° and 80° . Panels (c) and (d) show the energy distribution for an ion energy of 1.0 keV and a scattering angle of 70° for seven different combinations of ion incidence and emission angles. Panels (e) and (f) show the energy distribution for a scattering angle of 120° for three different combinations of ion incidence and emission angle and ion energies of 0.5, 1.0, and 1.5 keV.

of the secondary O_2^+ ions is located between 2 and 15 eV and is followed by a sudden signal drop. Energies as high as 15 eV are again rather unlikely for molecules from the thermalized residual gas. The excitation to such high energies is tentatively assigned to collisions with primary and secondary particles in the gas phase.

Although O_2^+ ions are the most prevalent primary ion species, there is a striking absence of high-energy structures in the energy distribution of the secondary O_2^+ ions. This leads to the conclusion that the primary O_2^+ ions dissociate during their collision with the target atoms. This conclusion is supported by the fact that the

energy distribution of the secondary O^+ ions in Fig. 9 does show such high-energy structures.

C. Influence on thin film properties

The properties of TiO_2 thin films, which were deposited under the same sputtering conditions, have been reported in an earlier work.²⁰ It was revealed that thin TiO_2 films deposited by ion beam sputtering with oxygen ions have lower growth rate, refractive index (due to a lower mass density), and lower surface roughness,

FIG. 10. Measured energy distribution of O_2^+ ions (32 u) during sputtering from the Ti (a) and TiO_2 (b) targets under oxygen ion bombardment for an ion energy of 1.0 keV, an ion incidence angle of 60° , and emission angles between 0° and 80° .

compared to thin TiO_2 films deposited by ion beam sputtering with Ar and Xe ions in an oxygen-rich atmosphere.

Panel (a) of Fig. 11 depicts representative energy distributions of the secondary Ti^+ ions (48 u) for the bombardment of the Ti target with oxygen, Ar, and Xe ions for an ion energy of 1.0 keV and an ion incidence and emission angle of 60° . In the case of Ar and Xe ion bombardment, sputtering took place in an oxygen-rich atmosphere. Panel (b) shows the corresponding energy distributions of the secondary O^+ ions (16 u). It is important to note that the presented energy distributions are each normalized to their own intensity maximum in order to be able to compare the shape of the energy distributions without the influence of absolute intensity differences. Data on the mass density of thin TiO_2 films, deposited under the same deposition parameters, with varying emission angles, are presented in panel (c).

Figure 11 reveals that the high-energy tail for the sputtered Ti^+ ions is least pronounced for oxygen ion bombardment and

FIG. 11. Measured energy distribution of Ti^+ ions (48 u) (a) and O^+ ions (16 u) (b) during sputtering from the Ti target under oxygen, Ar, and Xe ion bombardment for an ion energy of 1.0 keV and an ion incidence and emission angle of 60° . Ar and Xe ion bombardments were performed in a reactive oxygen atmosphere, data taken from Ref. 7. Additionally, the mass density of thin TiO_2 films (c) deposited under the same sputtering conditions with a varying emission angle is shown, data taken from Refs. 10 and 20.

most pronounced for Ar ion bombardment. For the O^+ ions, however, the energy distributions for oxygen and Ar ion bombardment are almost identical, whereas for Xe ion bombardment, the high-energy shoulder is less pronounced. This behavior can be easily explained by applying the conservation of energy to a binary elastic collision between an incoming particle of mass m_1 and a resting particle of mass m_2 . The maximum transferrable energy $E_{\max}$ in such a collision is given by

$$E_{\max} = \frac{4 \cdot m_1 \cdot m_2}{(m_1 + m_2)^2} \cdot E_0, \quad (10)$$

with E_0 being the energy of the incoming particle. According to Eq. (10), the transferrable energy increases with a decreasing difference between the masses m_1 and m_2 . Consequently, the energy transfer in a single collision with a resting Ti atom (48 u) is higher for an incoming Ar atom (40 u) compared to a Xe atom (132 u) or an O atom (16 u). Similarly, it is higher for a resting O atom (16 u) for an incoming O atom (16 u) or Ar atom (40 u) compared to a Xe atom (132 u). Most of the oxygen ions are actually molecular O_2^+ ions, which are likely to dissociate into two O atoms with half the kinetic energy. This would explain why the energy distribution for Ar ion bombardment in Fig. 11(b) is almost identical to that for oxygen ion bombardment. The high-energy shoulder should be more pronounced for O ion bombardment due to identical masses m_1 and m_2 , but this effect is weakened since the bombarding ions are atomic O and molecular O_2 ions and the O_2 ions dissociate, which results in lower primary particle energy of atomic O after dissociation.

The mass density of the deposited films for low emission angles is about 0.2 g/cm^3 higher for Ar and Xe ion bombardment compared to oxygen ion bombardment. For higher emission angles, the mass density decreases for all three ion species, but it decreases only slightly for Xe ion bombardment.

The overall lower level of mass density of the films deposited by oxygen ion bombardment is tentatively assigned to the lower energy of the sputtered Ti^+ ions. The energy of the Ti^+ ions increases with an increasing emission angle, but at the same time also the energy of the secondary O^+ ions, and in the case of Ar and Xe ion bombardment, the energy of the secondary Ar^+ and Xe^+ ions increases. These high-energy O^+ , Ar^+ , and Xe^+ ions lead to a degradation of the TiO_2 films, i.e., a lower mass density. In the case of Xe ion bombardment, this degradation with an increasing emission angle is attenuated due to the higher mass of the primary Xe ions, which results in a lower energy of the backscattered Xe^+ ions, since its collision partners at the target, Ti and O atoms, have a significantly lower atomic weight.

In summary, a higher energy of the film forming Ti^+ ions is necessary to deposit high density TiO_2 films, while high-energy secondary O^+ and/or Ar^+ and Xe^+ ions will weaken this densification effect.

IV. SUMMARY AND CONCLUSIONS

The ion beam sputtering of a Ti and a TiO_2 target with oxygen ions was investigated systematically regarding the properties

of the primary ions and secondary particles. The findings are summarized as follows:

1. The primary ion beam was found to consist mostly of single-charged O_2^+ ions, which are most likely to dissociate during their first collision with the target atoms.
2. The most prevalent secondary ion species were O^+ , O_2^+ , Ti^+ , TiO^+ , and TiO_2^+ .
3. The angular distribution of the sputtered Ti particles can be described as a superposition of an isotropic and an anisotropic part. Increasing ion energy, decreasing ion incidence angle, or changing the target from Ti to TiO_2 results in a more isotropic emission of the sputtered Ti particles. Comparing with Ar and Xe ion bombardment reveals that a decreasing mass of the impinging ions also leads to a more isotropic emission.
4. The energy distributions of the secondary ions strongly depend on the sputtering geometry, i.e., the scattering angle. Decreasing scattering angle and increasing ion energy lead to a broadening of the energy distributions, i.e., an increasing mean energy. Comparing with Ar and Xe ion bombardment reveals that the ratio between the mass of the primary ions and the target atoms also has a strong influence.
5. The presented data on secondary particles properties are correlated with the properties of TiO_2 thin films reported in earlier works.²⁰

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