Applied Surface Science Advances 32 (2026) 100953

Contents lists available at ScienceDirect

Applied Surface Science Advances

journal homepage: www.sciencedirect.com/journal/applied-surface-science-advances

Full Length Article

Reactive high-energy-per-molecule oxygen clusters for reliable ToF-SIMS depth profiling of hybrid nanomaterials

Giuseppe Ragusano [a], Marcus Rohnke [b], Alessandro Auditore [a,*], Nunzio Tuccitto [a], Alberto Bossi [c], Marta Penconi [c], Antonino Licciardello [a], Valentina Spampinato [a]

[a] Department of Chemical Sciences, University of Catania, Viale A. Doria 6 95125, Catania, Italy
[b] Institute of Physical Chemistry and Center for Materials Research, Justus Liebig University Giessen, Heinrich-Buff-Ring 17 35392, Giessen, Germany
[c] Istituto di Scienze e Tecnologie Chimiche "Giulio Natta" del Consiglio Nazionale delle Ricerche, CNR-SCITEC, via Fantoli 16/15 20138, and SmartMatLab Centre, via Golgi 19 20133, Milano, Italy

ARTICLE INFO

Keywords:
Time-of-flight secondary ion mass spectrometry
Oxygen cluster depth profile
Molybdenum oxide
Optoelectronics
Hybrid nanomaterials
Temperature-assisted depth profile

ABSTRACT

Hybrid materials that integrate organic and inorganic components within a single architecture pose significant challenges for depth profiling due to their compositional complexity. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) offers spatially resolved chemical information coupled with high sensitivity, but conventional sputtering conditions typically fail to simultaneously preserve organic molecular information while efficiently eroding inorganic materials. Here, we report a previously unexplored approach for the characterization of such complex hybrid systems. By employing a reactive oxygen gas cluster ion beam (O_2-GCIB) operated at high-energy-per-molecule, we achieve, for the first time, consistent and reliable depth profiling of both layered and blended hybrid structures comprising molybdenum oxide (MoO_3) and N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPD). High-energy per molecule oxygen clusters enhance the sputtering yield of the inorganic phase, also mitigating chemical degradation in the organic component, helping to preserve molecular information. This dual functionality effectively overcomes the limitations observed with argon-based clusters establishing a new paradigm for the molecular analysis of hybrid interfaces.

1. Introduction

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful and versatile technique for surface and interface analysis, offering high chemical specificity and spatial resolution at the nano- and microscale. Its intrinsic capability for three-dimensional profiling makes it especially suited for investigating layered or heterogeneous materials. However, the advent of hybrid nanomaterials comprising both layered and blended architectures of organic and inorganic components, [1] introduces a substantial challenge in defining optimal sputtering conditions for accurate depth profiling. Inorganic domains typically require high-energy per atom conditions to achieve sufficient erosion rates, favoring the use of monoatomic primary ion sources [2]. Depth profiling of organic materials with monoatomic ion sources, however, leads to significant damage accumulation and loss of molecular information [3–6]. In contrast, organic constituents are best preserved under low-energy per atom bombardment, such as that provided by argon gas cluster ion beams (Ar-GCIB), where the average energy per incident atom ranges from 2 to 5 eV [7–10]. This energy window aligns with the bond dissociation energies of common organic structures, effectively minimizing chemical degradation and preserving molecular information [11]. Conversely, under such low energy per atom conditions, the sputtering yields of inorganic materials are typically 2 to 3 orders of magnitude lower than those of their organic counterparts [10]. This pronounced yield mismatch can introduce significant instrumental artifacts, including interfacial broadening and topographical evolution, which severely compromise the accuracy and reliability of depth profiling in hybrid systems [10,12].

Several strategies have been explored to overcome these instrumental limitations while sampling hybrid systems, ranging from the use of low-energy monoatomic cesium beams [13] to fullerene (C_{60}^+) cluster sources [14]. However, these approaches have often resulted in data of difficult interpretation, highlighting the need for sputtering conditions capable of producing more consistent and reproducible outcomes. Recently [12] we investigated the use of argon gas cluster ion beams (Ar-GCIB) operated at high energy-per-atom regimes as a viable

* Corresponding author.
E-mail address: alessandro.auditore@unict.it (A. Auditore).

https://doi.org/10.1016/j.apsadv.2026.100953
Received 30 October 2025; Received in revised form 29 January 2026; Accepted 11 February 2026
Available online 17 February 2026

alternative. By reducing the cluster size, thereby increasing the energy delivered per constituent atom, we observed a significant reduction in the sputtering yield disparity between the organic and inorganic phases. This approach significantly enhanced the overall quality of the depth profiles, yielding sharper interface delineation and improved reliability in both the physico-chemical characterization and structural analysis of the hybrid systems under investigation. Nevertheless, the results also confirm that the presence of an inorganic layer atop an organic substrate leads to additional damage to the underlying organic material [12,14,15]. This includes the penetration of inorganic species into the organic layer, which influences the interface integrity and may distort the true compositional profile. Furthermore, it results in an additional contribution to the degradation of molecular information from the organic phase, highlighting the critical need for further optimization of sputtering conditions to preserve analytical fidelity in such complex multilayered systems.

Damage of the organic component can be partially avoided by lowering the temperature during the high-energy-per-atom GCIB depth profiling [12]. This finding underscores the critical role of chemical modification processes during ion beam-sample interaction, triggered by the formation of highly reactive species. Lowering temperature can effectively modulate the kinetics of crosslinking, recombination and rearrangement reactions responsible for the loss of the pristine molecular signal and highlights the potential of using reactive primary ion species capable of quenching the radical intermediates that are proposed to mediate chemical degradation [16–18].

Oxygen gas cluster ion beams (O_2-GCIB) have recently been introduced as a novel class of reactive sputtering sources capable of delivering clusters of variable size and acceleration energy [19]. While biatomic oxygen (O_2^+) has long been employed in SIMS depth profiling, primarily due to its ability to enhance the positive secondary ion yield, [20] the behavior of oxygen clusters remains comparatively underexplored. One might expect similar reactivity from O_2-based clusters; however, only limited literature is currently available on this topic [21]. A notable study by Holzer et al [19] investigated the use of oxygen clusters as a sputtering species for depth profiling alkali metals in thin SiO_2 films. In that work, the authors demonstrated that O_2-GCIB sources achieve erosion rates comparable to those obtained with conventional O_2^+ ion beams when applied to inorganic samples.

Mahoney et al [22] investigated the application of O_2-GCIB sources to parylene C films, demonstrating that such sputtering beams are capable of both efficiently eroding and preserving molecular information in organic species that are highly susceptible to cross-linking reaction when profiled using Ar-GCIB sources. The authors proposed two possible mechanisms to explain this behavior: (i) oxygen clusters may act as radical scavengers, reacting with and neutralizing reactive intermediates generated during sputtering; or (ii) they may initiate oxidative degradation pathways in the organic species under investigation.

Building upon these findings, the present study explores the application of reactive high-energy-per-molecule O_2-GCIB as a viable alternative for depth profiling of hybrid materials in dual-beam mode. This approach combines the exploitation of the hypothesized radical scavenging ability of oxygen clusters to quench transient reactive species generated during the sputtering of organic moieties, with the selection of small clusters at high energy per incident molecule, which simultaneously assures sufficient sputtering efficiency for the inorganic components. For this study, two materials commonly used in optoelectronics were chosen: molybdenum trioxide (MoO_3), largely employed as an electron acceptor and buffer layer, and N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPD), an arylamine widely used as a hole-transport and donor material. We investigated two representative model architectures: a layered hybrid structure with the inorganic part on top of the organic layer, analogous to that studied in our previous work [12] with Ar-GCIB sputter profiling, and a bulk heterojunction blended structure. The resulting hybrid interfaces exhibit sub-bandgap light absorption features in the near-infrared region, a property absent in the individual constituent materials, which offers novel promising applications in optoelectronics [23–25]. By employing an $(O_2)_{500}^+$ gas cluster ion beam accelerated at 20 keV as the sputter source, it was possible to achieve effective erosion and obtain consistent, reproducible results across both model systems, thereby paving the way for the comprehensive characterization of more complex hybrid architectures. Temperature-controlled experiments at low temperatures were also conducted to assess the potential to further suppress the reactivity of transient radical species. The results highlight a promising strategy to mitigate chemical damage during depth profiling, offering a groundbreaking avenue for the reliable characterization of hybrid material systems.

2. Materials and methods

2.1. Sample preparation

A commercially available arylamine, N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPD, Fig. 1a), was purchased from TCI Co. Ltd. Taipei, Taiwan (purified by sublimation, >99.00 %) and used as received as the organic component of the hybrid systems. Molybdenum trioxide (MoO_3, Merck, Darmstadt, Germany, purity 99.97 %) was selected as the inorganic counterpart. All thin films were deposited on silicon substrates (Test CZ-Si wafer 2 inch, thickness = 279 ± 25 μm, (100), 1-side polished, p-type (Boron), MicroChemical GmbH, Ulm, Germany), which were pre-cleaned by sequential sonication in deionized water, acetone, and isopropanol for 10 min each.

Film deposition was performed by physical vapor deposition (PVD) under a base pressure of 2×10^{-6} mbar in a KE-500 chamber (Kenosistec Srl. Milan, Italy). NPD was evaporated using a Knudsen cell, while MoO_3 was deposited using a resistively heated thermal source. The substrate holder was positioned 300 mm from the evaporation sources and maintained at room temperature throughout the process. A quartz crystal microbalance (INFICON, Bad Ragaz, Switzerland) equipped with a gold-coated sensor was placed near the substrate to monitor deposition rates, which were set between 0.15 and 0.40 Å/s.

The quartz crystal sensor was calibrated for each material by measuring at least the thickness of three evaporated films by means of a DektakXT contact profilometer (Bruker, Billerica, Massachusetts, U.S. A). Four distinct sample types were prepared on silicon substrates (Fig. 1b-e): a neat organic film of 50 nm-thick NPD, a pure inorganic film of 50 nm-thick MoO_3, a hybrid layered film consisting of 10 nm MoO_3 on top of 50 nm NPD, and a blended 50 nm MoO_3-NPD film, obtained by co-evaporation of the two materials. The first three samples were prepared according to [12], in order to ensure comparability among the dataset of both studies.

2.2. ToF-SIMS measurements

ToF-SIMS depth profiling was carried out using a ToF-SIMS M6 Plus instrument (IONTOF GmbH, Münster, Germany), equipped with a GCIB sputter source, a temperature-controlled sample holder for low-temperature measurements, and an *in-situ* atomic force microscope (AFM). Bi_3^+ clusters at 30 keV ("spectrometry mode", beam defining aperture 700 μm, cycle time 200 μs) were employed as analysis beam, with a primary ion current of 0.2 pA measured using the internal Faraday cup. The analysis beam was rastered over an area of 200 × 200 μm^2 for the NPD and the hybrid layered films and an area of 150 × 150 μm^2 for the MoO_3 and the hybrid blended films. The achieved mass resolution in the present experimental conditions was about 7000 at *m/z* 29.

Sputtering was performed by the GCIB source configured to deliver 20 keV oxygen clusters with a distribution peaked at 500 O_2 molecules. The sputter beam current, measured via a Faraday cup integrated into the sample holder, was 0.2 nA. Raster areas were 500 × 500 μm^2 for the

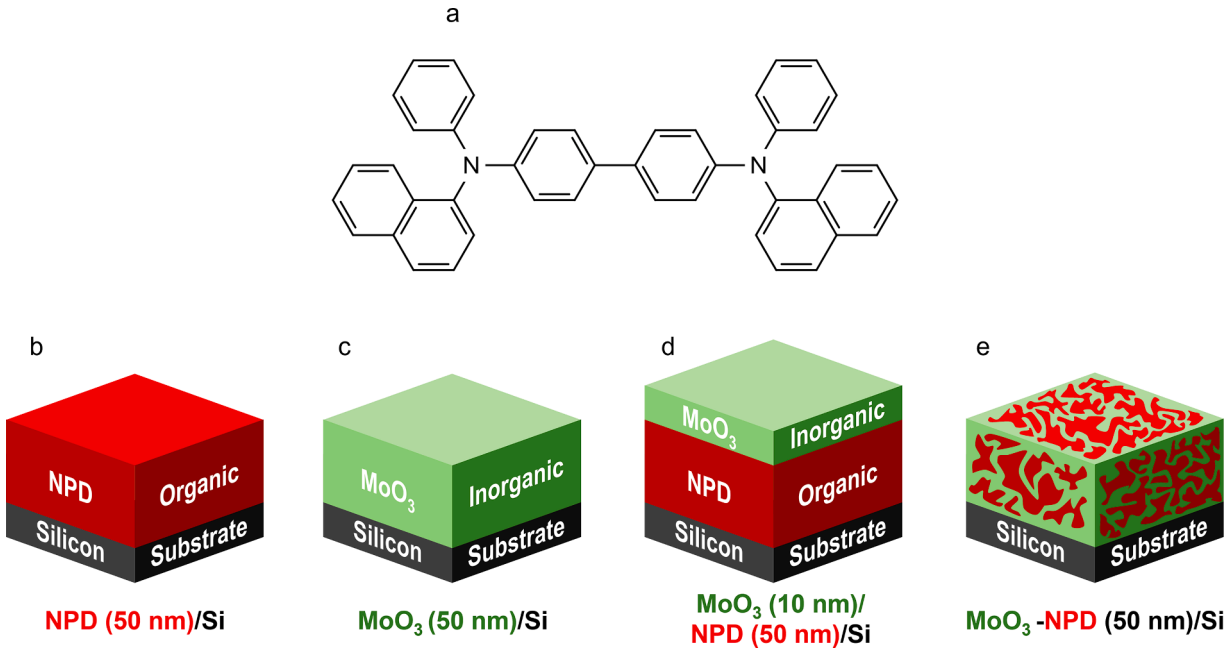

Fig. 1. Pictorial representation of the samples under investigation for illustrative purposes only. (a) Molecular structure of the organic donor material NPD, (b) 50 nm-thick NPD film, (c) 50 nm-thick MoO_3 film, (d) 10 nm-thick MoO_3/50 nm-thick NPD layered film, (e) 50 nm thick MoO_3-NPD blended film. All the films were deposited on silicon substrates.

NPD and the hybrid layered films and 300 × 300 μm^2 for the MoO_3 and the hybrid blended films. In addition, a 20 keV argon cluster beam, produced with the same GCIB source and having a cluster distribution peaked at 500 atoms, was utilized for depth profiling of the hybrid blended film. In this case, a raster area of 300 × 300 μm^2 was selected, with a measured current of 0.35 nA.

Depth profiling was performed in dual beam non-interlaced mode, with each cycle consisting of one analysis frame followed by one sputter frame and a 0.5-second pause. Spectra were acquired in positive polarity mode and calibrated using CH^+, $C_2H_5^+$, $C_3H_7^+$, and $C_6H_6^+$ ions. Each measurement was conducted in three replicates to ensure reproducibility.

2.3. AFM measurements

Long-range AFM line scans, with lengths ranging from 700 to 850 μm, were acquired before and after SIMS depth profiling using an *in-situ* AFM module integrated into the ToF-SIMS M6 Plus UHV analysis chamber. Measurements were performed with a NANOSENSORS PPP-NCLR (PointProbe® Plus Non-Contact/Tapping Mode - Long Cantilever - Reflex Coating) AFM probe (NANOSENSORS, Neuchatel, Switzerland) operated in tapping mode. The resulting profiles were employed to determine the sputtering yield of the pure MoO_3 and NPD films, as previously reported [12].

3. Results and discussion

To assess the sputtering efficiency of the $(O_2)^{+}_{500}$ clusters at 20 keV on the materials under investigation, preliminary tests were conducted on two distinct samples: a 50 nm NPD film deposited on silicon (Fig. 1b) and a 50 nm MoO_3 film deposited on silicon (Fig. 1c). Dual-beam depth profiles were acquired (Fig. 2), and the corresponding sputtering yields were determined for each case.

Fig. 2a shows the NPD depth profile acquired using $(O_2)_{500}^+$ at 20 keV. The organic layer is monitored via the molecular ion $[M]^+$ ($C_{44}H_{32}N_2^+$, *m/z* 588) and the characteristic fragment ion $C_{16}H_{11}N^+$ (*m/z* 217), while the silicon substrate is tracked via the $^{30}Si^+$ signal. This ion was chosen instead of the more abundant $^{28}Si^+$ to avoid signal saturation problems under the experimental conditions involving O_2-GCIB sputter beam. The persistence of the $[M]^+$ signal (red line) down to the NPD-

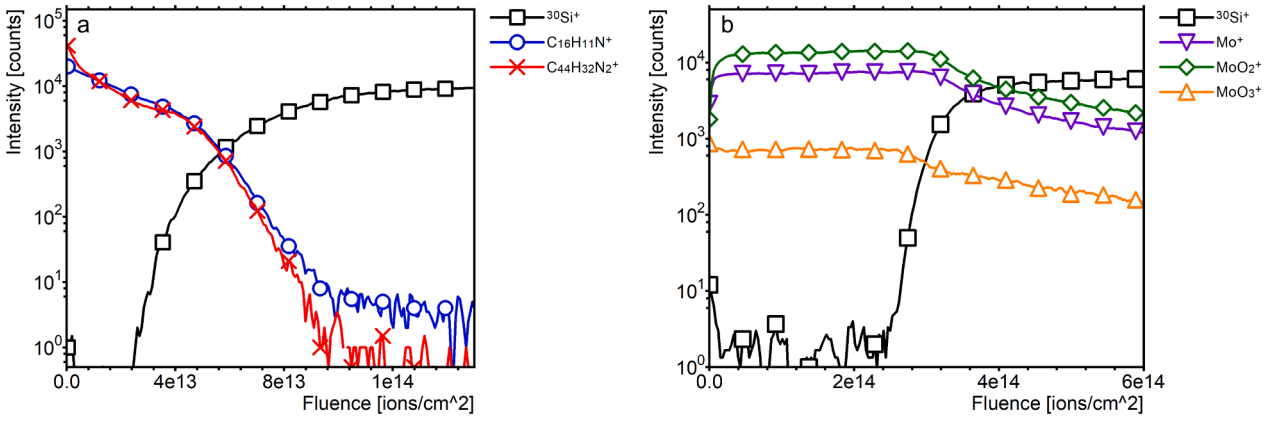

Fig. 2. Dual beam ToF-SIMS depth profiles of (a) NPD and (b) MoO_3 films, both obtained using 20 keV $(O_2)^{+}_{500}$ as sputtering beam.

silicon interface underlines that, despite the use of high-energy-per-incident-molecule clusters, which are not optimal for sputtering organic materials, the molecular information is effectively retained along the entire film thickness. It should be emphasized that an actual steady state is not achieved, indicating that a certain degree of damage accumulation occurs. Both the depth profile evolution and the sputtering yield of pure NPD under the present O_2-GCIB sputtering conditions (see Table 1) are comparable to those previously reported [12] for the same material using Ar-GCIB. Fig. 2b presents the depth profile of the MoO_3 film under the same sputtering conditions. Mo^+, MoO_2^+, and MoO_3^+ ions are tracked to characterize the MoO_3 layer, and $^{30}Si^+$ is used to monitor the silicon substrate. All MoO_x^+ ions ($0 \leq x \leq 2$) show a similar trend, with a well-defined steady state along the oxide film and a drop at the interface with silicon. This contrasts with profiles obtained using Ar-GCIB sputtering beams, where ions with lower oxygen-content show slower decay rate compared with the higher oxygen-content ones [12]. Such behavior can be attributed to the oxidizing effect of the oxygen gas cluster ions, which inhibits the ion beam-induced reduction of molybdenum oxide, observed under Ar-GCIB [12] irradiation and under monoatomic Kr ions [26,27]. This enables more reliable sputtering yield measurements and representative depth profiling results. The apparent persistence of Mo-related signals beyond the interface with silicon is attributed to the increased ionization probability of recoiled, diffused or redeposited molybdenum atoms, due to the oxidizing effect of oxygen cluster beam, analogously to what is well known in the case of O_2 beams [21].

Table 1 summarizes the sputtering yield values obtained for the two materials. For NPD, the measured value (85 ± 13 nm^3/PI) closely matches that observed using high-energy-per-atom argon clusters (74 ± 9 nm^3/PI). In contrast, the value found for MoO_3 (20 ± 2 nm^3/PI) is significantly higher than the average sputtering yield reported in the case of argon clusters (5.8 ± 1 nm^3/PI). In order to explain such a significant difference, we must consider that the reported yields are average values obtained from the fluence needed for removing about 25 nm of the film. In the case of Ar_{500} clusters such fluence is sufficient for total reduction to metallic molybdenum [12], so that the measured value is a trade-off between the initial sputtering yield of undamaged MoO_3 and the final one of Mo, with the contribution of intermediate oxidation states in between. Since, at our knowledge, no data are available for metallic molybdenum under cluster beam irradiation, we measured the sputtering yield of a Mo plate under 20 keV Ar_{500} ion irradiation, obtaining a value of 0.58 ± 0.03 nm^3/PI, which is compatible with the yield of other inorganic targets in similar experimental conditions [10], but about ten times lower than the average valued we obtain for MoO_3. So, it is reasonable to hypothesize that the "true" sputtering yield of MoO_3, i.e. the one that one would obtain in the absence of reduction, must be higher than the measured (average) value. Also, this is consistent with the higher values found in the case of sputtering of MoO_3 with O_2-clusters. Indeed, the use of an oxygen-based beam helps preserve the oxidation state of MoO_3 by providing, unlike argon clusters, reactive oxygen species that counterbalance the preferential loss of oxygen. An analogous effect of inhibition of the preferential loss of oxygen has been observed by XPS, [28] although in rather different experimental conditions, by comparing the effect of O_2^+ and Ar^+ ion beams at the keV range. As a consequence of the increased sputtering ratio of MoO_3 under O_2-cluster, the sputtering yield ratio between NPD and MoO_3 is lowered to approximately 4. This represents a noteworthy outcome, given that achieving comparable sputtering yields for both the organic and inorganic components is crucial for accurate depth profiling of hybrid organic/inorganic systems. Indeed, the use of high-energy-per-molecule O_2-GCIB meaningfully reduces the disparity of sputtering yields between the organic and inorganic component, compared to the case of 20 keV Ar_{500}^+ (NPD-to-MoO_3 sputtering ratio close to 12) that, in turn represents itself a substantial improvement (approximately one order of magnitude decrease of sputtering yield ratio) in comparison with the low-energy-per-atom argon clusters commonly used for depth profiling of organic systems [12].

Building on these promising results, ToF-SIMS depth profiling of the model hybrid layered film was performed at room temperature (R.T.) using 20 keV $(O_2)_{500}^+$ cluster ions. The resulting depth profiles are shown in Fig. 3a, where the MoO_2^+, $C_{44}H_{32}N_2^+$ and $^{30}Si^+$ secondary ions are chosen for monitoring, respectively, the MoO_3 layer, the NPD layer and the silicon substrate.

The maximum intensity of MoO_2^+ ion is observed in the initial part of the profile, as expected based on the presence of the 10 nm-thick MoO_3 layer. The MoO_3/NPD interface is marked, at a fluence of approximately 2.6×10^{13} ions/cm^2, by the drop of MoO_2^+ signal and by the simultaneous sharp intensity rise of the NPD molecular ion $C_{44}H_{32}N_2^+$. The latter persists until $\sim 2.0 \times 10^{14}$ ions/cm^2, where the interface with silicon is reached, as revealed by the rise of the $^{30}Si^+$ ion. Although the $[M]^+$ signal is clearly observed along the whole thickness of the organic layer, it decays by nearly one order of magnitude from its initial maximum at the MoO_3/NPD interface to the NPD/Si interface, clearly indicating that chemical damage is occurring and accumulating within the buried organic layer. The increase of the MoO_2^+ signal beyond the NPD/Si interface could be explained, as discussed in the case of Fig. 2b, with the enhancement of ionization probability in the silicon matrix oxidized by the O_2-GCIB, combined with some transport of molybdenum species through the organic layer down to the silicon interface, as discussed later.

Despite the presence of damage accumulation in the organic layer, if we compare the depth profile of Fig. 3a with the result obtained using Ar-GCIB, reported in a previous paper, [12], it is rather evident that the present experimental conditions, involving the use of high energy per molecule O_2 clusters, provide a more reliable representation of the sample structure. This confirms the hypothesis that the reactive oxygen cluster beam provides a mechanism for mitigating damage accumulation. Considering that, in the case of Ar-GCIB depth profiling, sample cooling allows to partly reduce damage, we investigated the sample cooling effect also during high energy per molecule O_2-GCIB depth profiling of the same layered structure of Fig. 3a. The depth profile, obtained at a sample temperature of 148 K and keeping unaltered all other experimental conditions, is reported in Fig. 3b. Such profile clearly describes more accurately the layered structure of the system under investigation. In particular, the NPD molecular ion, after the rise at the first interface, reaches a steady state until its drop at the silicon interface. In other words, the molecular information from the organic layer is preserved throughout the whole film thickness. In contrast with the evident positive effect of sample cooling in the reduction of damage accumulation and preservation of characteristic ions of the organic component (including the molecular ion), lowering the temperature has virtually no effect on the MoO_2^+ signal. A similar finding was reported in our earlier work with Ar-GCIB [12] where the shape of MoO_3-related signals wasn't influenced by sample cooling. This was attributed to the fact that the "injection" of metal containing species from the inorganic overlayer, already described also for other systems [14,15] can be regarded essentially as a somewhat ballistic phenomenon which is not influenced by temperature changes. On the other hand, the rate of chemical reactions, involving the active species generated during the cluster-sample interactions and contributing to damage of the organic layer, is expected to be influenced by temperature as well as by the

Table 1
Sputtering yields of NPD and MoO_3 obtained with 20 keV Ar_{4000}^+, 20 KeV Ar_{500}^+, [12] and 20 keV $(O_2)_{500}^+$. The last column shows the ratio between sputtering yields of the two pure materials for each sputter beam.

	Y_{NPD}	Y_{MoO_3}	$\frac{Y_{NPD}}{Y_{MoO_3}}$
20 keV Ar_{4000}^+	162 ± 7 nm^3/PI	1.3 ± 0.1 nm^3/PI	124.6
20 keV Ar_{500}^+	74 ± 9 nm^3/PI	5.8 ± 1 nm^3/PI	12.7
20 keV $(O_2)_{500}^+$	85 ± 13 nm^3/PI	20 ± 2 nm^3/PI	4.2

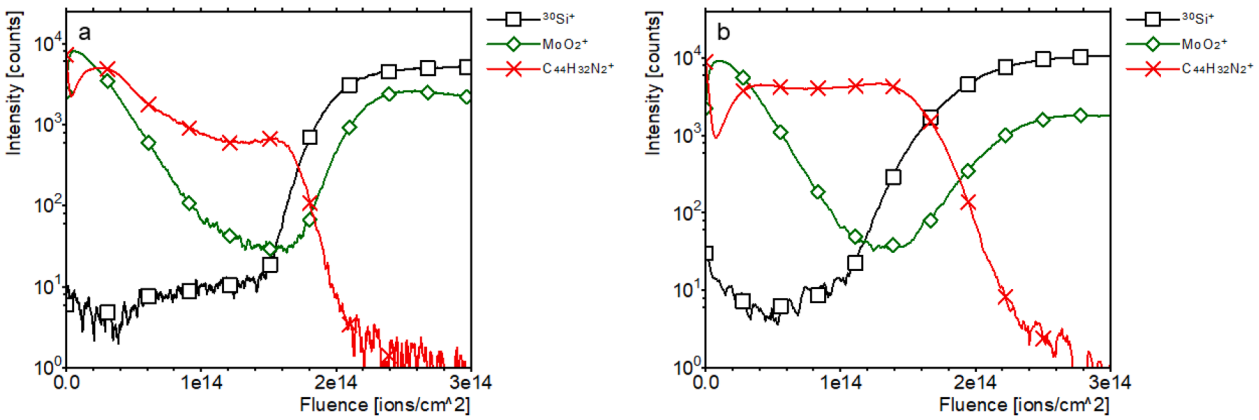

Fig. 3. Dual beam ToF-SIMS depth profiles of MoO_3/NPD layered film both obtained using 20 keV $(O_2)^+_{500}$ as sputtering beam (a) at room temperature and (b) at 148 K.

concentration of the reactive species involved in the reactions. This can explain why the better results in profiling the MoO_3/NPD/Si layered samples are obtained by combining sample cooling with the use of high-energy-per-atom O_2-GCIB: the former depresses the kinetic constant of the damaging reactions, the latter decreases, through its scavenger properties, the concentration of active species (such as radicals) produced by the interaction with the ion beam or promoted by atoms and clusters of the inorganic overlayer that are "pushed" into the organic layer. Indeed, the "injection" of inorganic species into the organic layer has been proposed to be responsible for the damage of such layer that, in the absence of the inorganic overlayer, would suffer much less damage accumulation under GCIB irradiation [14,15]. In other words, we hypothesize that the damage of NPD below MoO_3 is the result of least two different contributions: i) a "primary" contribution due both to the direct interaction with the high-energy-per-molecule beam itself or to the injection of atoms and clusters from the inorganic layer, which produce molecular fragmentation and formation of transient reactive species through energetic collisions and ii) the evolution of such transient reactive species (that we hypothesize to be, at least partly, radical species), [12,16–18] which undergo secondary reactions with their local chemical environment (e.g. cross-linking), ultimately leading to a loss of molecular specificity and information.

As discussed above, the improved depth profiling performance observed with O_2-GCIB involves the potential radical scavenging effect of the O_2-GCIB beam, already hypothesized by Mahoney et al [22] Here we propose a possible mechanism for this effect: upon impact with sample surface, oxygen clusters, in which only weak intermolecular forces are at play, dissociate into their constituent O_2 molecules. These molecules, in their triplet ground state, due to the presence of two unpaired electrons in antibonding molecular orbitals π*, can interact with reactive alkyl-type, allyl-type and aryl-type radicals bearing unpaired electrons to form more stable peroxyl radicals (ROO·), thus acting as an effective radical scavenger that limits the propagation of radical-induced damage, [29]. This process may also be accompanied by oxidation reactions occurring within the interaction volume, leading to the formation of volatile oxidized carbonaceous species, such as CO_x, so contributing to prevent the formation of an amorphous carbonaceous layer. Such layer, characterized by lower sputter yield than the pristine organic material, would in turn promote damage accumulation, leading to the loss of the molecular signals. It is also plausible that both proposed mechanisms - enhanced sputtering efficiency and radical scavenging action - act synergistically to reduce chemical damage and improve the reliability of molecular depth profiling. Moreover, we cannot exclude that similar effects are produced also by atomic oxygen produced during the impact of the cluster with the sample surface. A more detailed understanding would benefit from theoretical simulations of the oxygen cluster's impact. However, we are not aware of any literature data on that effect for O_2-GCIB.

Whatever the detailed mechanism involved, the results presented in Fig. 3 clearly show that high energy per molecule O_2-GCIB is a promising candidate for depth profiling of hybrid organic/inorganic systems. Hence, we extended the investigation to a more complex system, a 50 nm-thick nanostructured blend film, containing both NPD and MoO_3. In this case, the two materials were co-deposited, resulting in an intimate mixture, at the nanoscale level, of the two components. Figs. 4a-4d compare the results obtained on this system using Ar-GCIB and O_2-GCIB (first and second row, respectively), both performed at room temperature and at 148 K (first and second column, respectively).

Looking at the first row of Fig. 4, showing the profiles obtained with argon clusters at room temperature (a) and at 148 K (b), we observe that, independently of the sample temperature, heavy damage of the organic layer is present, as shown by the exponential intensity decay of the NPD molecular ion. By contrast, the non-specific C^+ fragment displays a box-shaped profile in the region where molecular information from the organic component would be expected. These results indicate that, although the organic material is present throughout the film thickness, the highly energetic sputtering conditions lead to a loss of molecular information due to progressive chemical damage accumulation.

Fig. 4c shows the depth profile obtained using the 20 keV $(O_2)^+_{500}$ beam at room temperature. Already at first glance, a significant improvement in profile quality is observed. Indeed, the mixed hybrid layer is clearly identified, with the characteristic signals from both the organic and inorganic components detected till the interface with the silicon substrate. In the very initial part of the profile, the molecular ion $C_{44}H_{32}N_2^+$ ($[M]^+$) associated with NPD, shows an initial decay while the MoO_2^+ ion, representative of the molybdenum oxide, displays a concurrent intensity increase. This behavior can be interpreted as a surface segregation of the organic component. However, the initial drop of the molecular signal could also reflect a transient situation in which ion beam-induced damage builds up until a steady state between damage accumulation and removal is reached [30].

In any case, beyond the transient region, steady-state signal levels are observed for both the organic and inorganic components, a notable result that could not be achieved using Ar-GCIB, which confirms the ability of oxygen clusters to inhibit damage in NPD/MoO_3 hybrid structures. Notably, the depth profile acquired with $(O_2)^+_{500}$ at 20 keV and 148 K (Fig. 4d) does not exhibit significant differences compared to the corresponding profile at room temperature (Fig. 4c), at variance of the behavior observed on the layered hybrid system where the decrease of temperature causes an additional suppression of damage in the organic layer. This indicates that, in the blended architecture, already at room temperature the scavenging effect of oxygen clusters is sufficient to inhibit the most part of beam-induced chemical damage by efficiently suppressing the active species responsible for the secondary

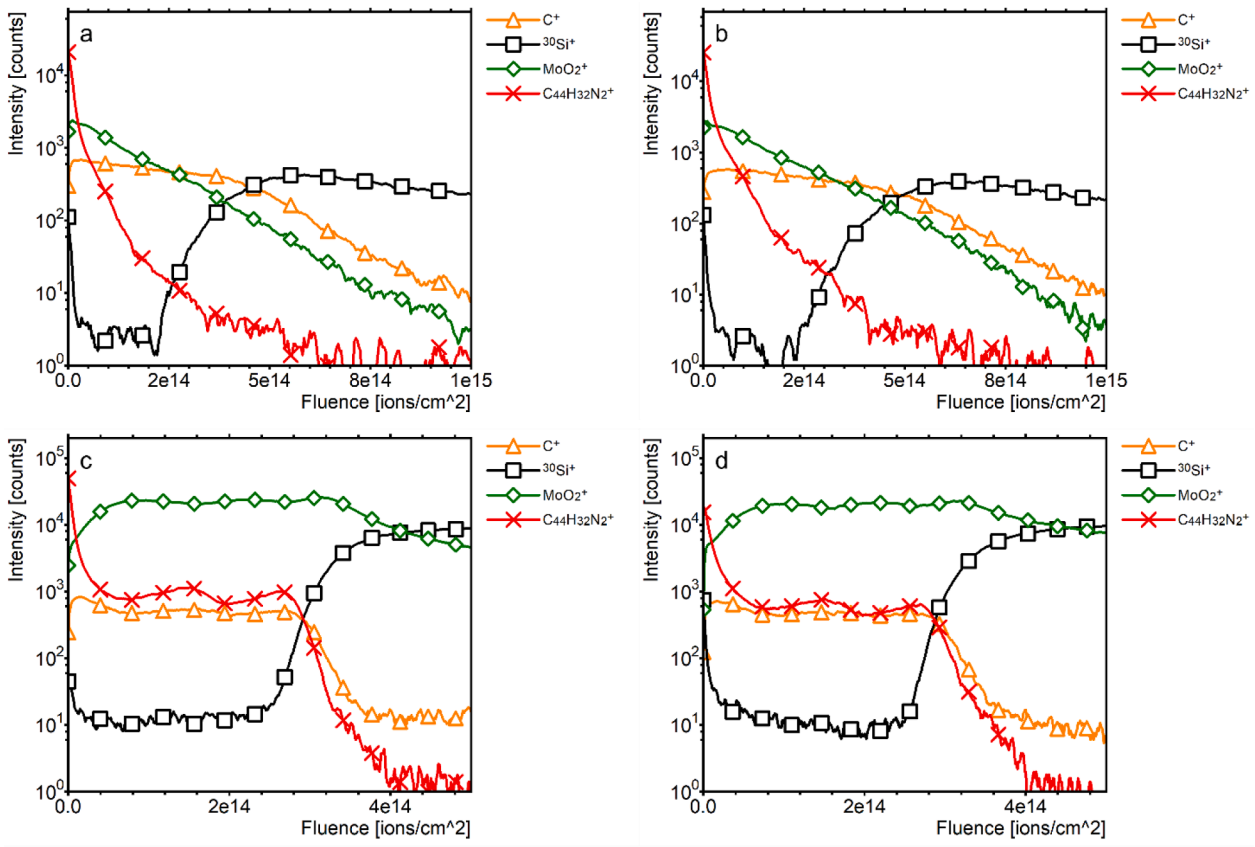

Fig. 4. Dual beam ToF-SIMS depth profiles of MoO_3—NPD blended film obtained using 20 keV Ar^+_{500} as sputtering beam (a) at room temperature and (b) at 148 K and with 20 keV $(O_2)^+_{500}$as sputter beam (c) at room temperature and (d) at 148 K.

crosslinking/rearrangement reactions, so that the decrease of sample temperature has no additional effect.

Considering that all the investigated hybrid systems are fabricated with the same components (NPD and MoO_3), we hypothesize that the different amount of damage accumulation observed in Figs. 3a and 4c, as well as the differences in damage relief by temperature decrease (Figs. 3b and 4d), are connected with the different architecture of the samples: a layered system the former, an intimately mixed structure the latter. In the bilayer, the presence of a continuous MoO_3 overlayer allows inorganic atoms and clusters generated during sputtering of the inorganic overlayer to penetrate the underlying organic film, thereby promoting fragmentation and generation of reactive species, although in less extent than in the case of argon clusters; in this context, temperature reduction helps to preserve molecular information by reducing the reaction rate of the active species. In contrast, the intimately mixed MoO_3/NPD blend is thought to be composed of nanometer-sized domains, which dimensions act as a physical constraint for damage accumulation, consenting the sole use of a reactive sputter beam as O_2-GCIB to prevent the damage mechanisms from extending further. As expected, this does not happen in the case of Ar-GCIB, which is unable to provide a radical scavenging action. An additional positive effect is also expected to arise from the reduced sputtering yield disparity between the organic and inorganic components (see Table 1) when using oxygen clusters instead of argon clusters.

Finally, it is worth noting that some indication regarding the structure of the blended architecture arises from the profiles in Figs. 4c-d. In both cases, a closer inspection of the profiles shows that the NPD $[M]^+$ and MoO_2^+ signals exhibit oscillations around the steady state value (see Figure S1 where signals are plotted in linear scale). Such alternating intensities suggest the presence of regions with varying local composition and may indicate an architecture of the co-deposited layer where the organization of nanometer-sized domains gives rise to a structure with alternating regions that, along the z-axis, are relatively enriched in one component and depleted in the other. Specifically, the NPD $[M]^+$ signal (Figs. 4c-d) shows two maxima (not considering the surface peak) corresponding to about 1.5×10^{14} ions/cm^2 and 2.7×10^{14} ions/cm^2, while the MoO_2^+ signal displays maxima approximately in correspondence of the NPD signal local minima, i.e. at about 0.9×10^{14} ions/cm^2, 2.1×10^{14} and 3.1×10^{14} ions/cm^2 respectively (see Figure S1). Considering that the total thickness of the hybrid layer is 50 nm, the peak-to-peak distances correspond to about 15 nm, which gives an indication of the average spacing of the domains and can be also considered as an upper limit for their dimension along the z-axis. Such reasoning is prompted by the similarity of the profile shapes of Figs. 4c-d with the profile shapes observed in the case of block copolymer films forming regularly arranged domains, which presence and spacing is detected along the z-axis as oscillations of the pertinent ToF-SIMS signals [31]. While these considerations remain hypothetical and require further validation, such preliminary insights were uniquely enabled by the reactive O_2 cluster beam approach. This method paves the way for efficient physico-chemical characterization of complex hybrid devices.

4. Conclusion

This work demonstrates, for the first time, the potential of employing a high-energy-per-molecule O_2-GCIB sputter source to perform reliable dual-beam SIMS depth profiling on both layered and blended hybrid films composed of molybdenum oxide (MoO_3) and N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPD). Oxygen clusters are proven to offer the dual advantage of mitigating the degradation of the organic component's molecular signals and reducing the disparity in sputtering yields of the two components. A proposed radical scavenging

mechanism accounts for the positive effect of the oxygen clusters in preserving molecular information along the whole sample thickness. In addition, the observed reduction of the gap between the sputtering yield of the organic and inorganic constituents is very promising in the quest for minimizing artifacts that would otherwise complicate data interpretation. Sample cooling during O_2-GCIB sputtering is found to be effective in improving the quality of molecular depth profiles in those instances where some damage accumulation persists at room temperature, such as the MoO_3/NPD layered sample, while it has negligible effect when the scavenging effect of the reactive oxygen cluster beam is enough, as in the case of the blended system, for efficiently suppress damage accumulation. Moreover, the SIMS depth profiles obtained using the high-energy-per-molecule O_2-GCIB provided valuable insights into the nanoscale structure of the blended hybrid system. The proposed methodology for the characterization of technologically relevant organic-inorganic hybrid materials addresses long-standing limitations of SIMS-based depth profiling and offers a new, effective approach for the accurate characterization of such complex systems.

CRediT authorship contribution statement

Giuseppe Ragusano: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marcus Rohnke:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Alessandro Auditore:** Writing – review & editing, Supervision, Methodology, Data curation. **Nunzio Tuccitto:** Writing – review & editing, Methodology. **Alberto Bossi:** Writing – review & editing, Resources. **Marta Penconi:** Writing – review & editing, Resources. **Antonino Licciardello:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Valentina Spampinato:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

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.

Acknowledgements

G.R. gratefully acknowledge Pascal Dippell and David Schäfer for their helpful discussions and technical support during this work. M.R. thanks the BMFTR for funding the AFM-SIMS within the ProGrAL project (FKZ 03XP0427). G.R., V.S., A.B. and A.L. would like to acknowledge PRIN 2022 project “MEET” (project code 20225P4EJC, CUP E53D23008350006), funded under the National Recovery and Resilience Plan (NRRP), Mission 4, Component 2, Investment 1.1, call tender number 104.. of 2.2.2022 of Italian Ministry of University and Research (MUR), funded by the European Union - NextGenerationEU.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.apsadv.2026.100953.

Data availability

Data will be made available on request.

References

[1] P. Gomez-Romero, A. Pokhriyal, D. Rueda-García, L.N. Bengoa, R.M. González-Gil, Hybrid materials: a metareview, Chem. Mater. 36 (2024) 8–27, https://doi.org/10.1021/acs.chemmater.3c01878.
[2] P.K. Chu, SIMS and microelectronics, Mater. Chem. Phys. 38 (1994) 203–223, https://doi.org/10.1016/0254-0584(94)90195-3.
[3] S. Netcheva, P. Bertrand, Ion-beam-induced morphology on the surface of thin polymer films at low current density and high ion fluence, J. Polym. Sci. B Polym. Phys. 39 (2001) 314–325, https://doi.org/10.1002/1099-0488(20010201)39:3<314::AID−OLB1003>3.0.CO;2-6.
[4] A. Chilkoti, G.P. Lopez, B.D. Ratner, M.J. Hearn, D. Briggs, Analysis of polymer surfaces by SIMS. 16. Investigation of surface crosslinking in polymer gels of 2-hydroxyethyl methacrylate, Macromolecules 26 (1993) 4825–4832.
[5] A. Benninghoven, D. Jaspers, W. Sichtermann, Secondary-ion emission of amino acids, Appl. Phys. 11 (1976) 35–39, https://doi.org/10.1007/BF00895013.
[6] D. Stapel, O. Brox, A. Benninghoven, Secondary ion emission from arachidic acid LB-layers under Ar+, Xe+, Ga+ and SF5+ primary ion bombardment, Appl. Surf. Sci. 140 (1999) 156–167, https://doi.org/10.1016/S0169-4332(98)00584-4.
[7] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, Precise and fast secondary ion mass spectrometry depth profiling of polymer materials with large Ar cluster ion beams, Rapid. Commun. Mass Spectrom. 23 (2009) 1601–1606, https://doi.org/10.1002/rcm.4046.
[8] D. Rading, R. Moellers, H.G. Cramer, E. Niehuis, Dual beam depth profiling of polymer materials: comparison of C_{60} and Ar cluster ion beams for sputtering, Surf. Interface Anal. 45 (2013) 171–174, https://doi.org/10.1002/sia.5122.
[9] C.M. Mahoney, Cluster Secondary Ion Mass spectrometry: Principles and Applications, John Wiley & Sons, 2013.
[10] M.P. Seah, Universal equation for argon gas cluster sputtering yields, J. Phys. Chem. C 117 (2013) 12622–12632, https://doi.org/10.1021/jp402684c.
[11] K. Moritani, G. Mukai, M. Hashinokuchi, K. Mochiji, Site-specific fragmentation of polystyrene molecule using size-selected Ar gas cluster ion beam, Appl. Phys. Express. 2 (2009) 046001, https://doi.org/10.1143/APEX.2.046001.
[12] G. Ragusano, V. Spampinato, A. Auditore, N. Tuccitto, M. Penconi, A. Bossi, A. Franquet, T. Conard, A. Licciardello, Temperature-assisted high-energy-per-atom argon cluster SIMS of layered hybrid nanomaterials, Appl. Surf. Sci. (2025) 164456, https://doi.org/10.1016/j.apsusc.2025.164456.
[13] C. Noël, L. Houssiau, Hybrid organic/inorganic materials depth profiling using low energy cesium ions, J. Am. Soc. Mass Spectrom. 27 (2016) 908–916, https://doi.org/10.1007/s13361-016-1353-9.
[14] K. Shen, D. Mao, B.J. Garrison, A. Wucher, N. Winograd, Depth profiling of metal overlayers on organic substrates with cluster SIMS, Anal. Chem. 85 (2013) 10565–10572, https://doi.org/10.1021/ac402658r.
[15] P.E. Kennedy, Z. Postawa, B.J. Garrison, Dynamics displayed by energetic C_{60} bombardment of metal overlayers on an organic substrate, Anal. Chem. 85 (2013) 2348–2355, https://doi.org/10.1021/ac303348y.
[16] R. Möllers, N. Tuccitto, V. Torrisi, E. Niehuis, A. Licciardello, Chemical effects in C60 irradiation of polymers, Appl. Surf. Sci. 252 (2006) 6509–6512, https://doi.org/10.1016/j.apsusc.2006.02.083.
[17] G. Zappalà, V. Motta, N. Tuccitto, S. Vitale, A. Torrisi, A. Licciardello, Nitric oxide assisted C_{60} secondary ion mass spectrometry for molecular depth profiling of polyelectrolyte multilayers, Rapid. Commun. Mass Spectrom. 29 (2015) 2204–2210, https://doi.org/10.1002/rcm.7383.
[18] N. Tuccitto, D. Maciazek, Z. Postawa, A. Licciardello, MD-based transport and reaction model for the simulation of SIMS depth profiles of molecular targets, J. Phys. Chem. C 123 (2019) 20188–20194, https://doi.org/10.1021/acs.jpcc.9b01653.
[19] S. Holzer, S. Krivec, S. Kayser, J. Zakel, H. Hutter, Large O_2 cluster ions as sputter beam for ToF-SIMS depth profiling of Alkali metals in thin SiO_2 films, Anal. Chem. 89 (2017) 2377–2382, https://doi.org/10.1021/acs.analchem.6b04222.
[20] J.C. Lee, H.J. Kang, K.J. Kim, Y.S. Kim, D.W. Moon, Oxygen enhanced secondary ion emission of Fe and Co by TOF-SIMS and ISS/DR, Surf. Sci. 324 (1995) 338–344, https://doi.org/10.1016/0039-6028(94)00696-2.
[21] S. Ninomiya, T. Aoki, T. Seki, J. Matsuo, Secondary ion measurements for oxygen cluster ion SIMS, Appl. Surf. Sci. 252 (2006) 7290–7292, https://doi.org/10.1016/j.apsusc.2006.02.138.
[22] C.M. Mahoney, K. Adib, R. Yongsunthon, Cluster ion bombardment and depth profiling of parylene C using Ar vs O2 gas cluster ion beams, Appl. Surf. Sci. 687 (2025) 162282, https://doi.org/10.1016/j.apsusc.2024.162282.
[23] S.H. Wu, M.F. Lo, Z.Y. Chen, T.W. Ng, X. Hu, H.W. Mo, C. Wu, W.L. Li, C.S. Lee, Simple near-infrared photodetector based on charge transfer complexes formed in molybdenum oxide doped N,N′-di(naphthalene-1-yl)-N,N′-diphenyl-benzidine, Phys. Status Solidi (RRL) - Rapid Res. Lett. 6 (2012) 129–131, https://doi.org/10.1002/pssr.201105596.
[24] H. Wang, S. Liu, Y. Li, X. Yue, Y. Shen, H. Xu, H. Xu, Y. Tan, L. Zeng, B. Yao, Z. Fang, Near-infrared-II photodetection realized by introducing organic-inorganic charge-transfer-complex photosensitive material into pentacene phototransistor, Org. Electron. 77 (2020) 105500, https://doi.org/10.1016/j.orgel.2019.105500.
[25] A. Calloni, M. Cornago, F. Goto, S. Arnaboldi, C. Graiff, C. Riccucci, G. Di Carlo, G. Bussetti, S. Cauteruccio, M. Penconi, A. Bossi, Efficient near infrared absorbers made easy: benzodithiophene-based donors in tailored organic-inorganic hybrid architectures for near infrared photodetectors, Opt. Mater. 169 (2026) 117640, https://doi.org/10.1016/j.optmat.2025.117640.
[26] H.M. Naguib, R. Kelly, On the increase in the electrical conductivity of MoO3 and V2O5 following ion bombardment. Studies on bombardment-enhanced conductivity-I, J. Phys. Chem. Solids. 33 (1972) 1751, https://doi.org/10.1016/S0022-3697(72)80469-4. -IN5.
[27] R. Kelly, N.Q. Lam, The sputtering of oxides part i: a survey of the experimental results, Radiat. Eff. 19 (1973) 39–48, https://doi.org/10.1080/00337577308232213.

[28] N.V. Alov, D.M. Kutsko, K.V. Bordo, Ion-beam reduction of the surface of higher oxides of molybdenum and tungsten, J. Surf. Investig., X-Ray Synchrotron. Neutron. Tech. 2 (2008) 184–188, https://doi.org/10.1134/S1027451008020043.
[29] C.A. Taatjes, Uncovering the fundamental chemistry of alkyl + O_2 reactions via measurements of product formation, J. Phys. Chem. A 110 (2006) 4299–4312, https://doi.org/10.1021/jp056997f.
[30] A. Wucher, A simple erosion dynamics model of molecular sputter depth profiling, Surf. Interface Anal. 40 (2008) 1545–1551, https://doi.org/10.1002/sia.2933.
[31] T. Terlier, G. Zappalà, C. Marie, D. Leonard, J.P. Barnes, A. Licciardello, ToF-SIMS depth profiling of PS- b -PMMA block copolymers using Ar_n^+, C_{60}^{++}, and Cs^+ sputtering ions, Anal. Chem. 89 (2017) 6984–6991, https://doi.org/10.1021/acs.analchem.7b00279.