

Ion induced modification of size-selected MoO₃ and WO₃ clusters deposited on HOPG

Xiang Li, Kevin A. Wepasnick, Xin Tang, Yi Wang, Kit H. Bowen,^{a)}
and D. Howard Fairbrother^{b)}

Departments of Chemistry and Materials Science, Johns Hopkins University, Baltimore, Maryland 21218

Gerd Gantefoer

Department of Physics, University of Konstanz, Universitätsstr. 10, 78457 Konstanz, Germany

(Received 29 August 2011; accepted 2 April 2012; published 8 May 2012)

The effect of 4 keV Ar⁺ ions on size-selected (MoO₃)_n and (WO₃)_n clusters, where $n = 30 \pm 1$, deposited on highly ordered pyrolytic graphite was studied by x-ray photoelectron spectroscopy and atomic force microscopy. During deposition, both metal oxide clusters collected preferentially at step edges at low coverages, with larger cluster aggregates nucleating on the terraces at higher coverages. Under the influence of 4 keV Ar⁺ ion bombardment, both clusters initially experienced oxygen loss and corresponding reduction of the transition metal before the remaining species were sputtered from the surface. However, MoO₃ was only partially reduced to MoO₂, while WO₃ was fully reduced to metallic tungsten. As a consequence of these variations in ion induced chemistry, changes in the surface morphology of MoO₃ and WO₃ following prolonged Ar⁺ exposure differed significantly. For (MoO₃)_{30±1}, the size of the clusters decreased, due to removal of MoO₂ fragments. In contrast, for (WO₃)_{30±1}, the formation of smaller sized clusters was also accompanied by the appearance of clusters that were much larger in size than the original “as deposited” clusters. The creation of these larger structures is ascribed to the mobility and coalescence of metallic tungsten species produced during the sputtering process. The contrast in the behavior of the molybdenum and tungsten oxide clusters illustrates the interplay that can exist between ion induced changes in speciation and morphology of deposited clusters. © 2012 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4711134>]

I. INTRODUCTION

Transition metal oxide nanostructures have both technological and scientific significance due to their applications in the semiconductor industry and catalysis.¹ Nanosized clusters of transition metal oxides are especially interesting since they often exhibit novel electronic and magnetic properties compared to the corresponding bulk materials.^{2,3} In addition to size, the properties of clusters are influenced by their shape and composition.^{4,5} In most practical applications, clusters must be adsorbed onto solid surfaces.⁶ However, although the properties of many clusters have been well studied in the gas phase, much less is known about the behavior of the corresponding surface bound clusters and how their composition and structure is modified by external stimuli, such as heat, light, and charged particles.^{7,8}

Ion bombardment is a widely used means to fabricate,⁹ modify,¹⁰ clean, and analyze nanostructures.^{11–13} For metal oxides, ion bombardment can directly remove material (physical sputtering) but also has the potential to change the chemical composition, metal oxidation state, and valence band structure.^{14–17} All of these transformations will affect both the chemical and physical properties of the nanostructures, independently or collectively. The effect of ion sputtering on thin films or bulk transition metal oxides has been extensively studied using a variety of different surface analytical techniques, e.g., x-ray photoelectron spectroscopy (XPS), Auger

electron spectroscopy, electron energy loss spectroscopy, and ultraviolet photoelectron spectroscopy. Many metal oxides (e.g., Nb₂O₅, MoO₃, Ta₂O₅) undergo reduction caused by preferential oxygen loss upon high-energy (~1–5 keV) ion bombardment, decreasing the metal’s formal oxidation state and in some instances leading to the formation of metallic species.^{18–21} In addition to better understanding the extent to which ion induced chemical transformations observed in bulk materials and thin films can be extrapolated to chemically analogous nanosized clusters, there is also a need to understand how the structure of deposited clusters (e.g., size, shape, aggregation state) changes under the influence of ion bombardment. In this regard, structural transformations may arise as a result of the energy imparted to the surface during ion bombardment or as a consequence of differences in intrinsic reactivity and surface mobility of new species created as a consequence of ion bombardment. The study of such transformations is unique for deposited clusters since there is no analog for isolated gas phase clusters.

In a previous study,²² we have demonstrated our ability to soft-land size-selected metal and metal oxide clusters on highly ordered pyrolytic graphite (HOPG) surfaces, and to control the coverage of deposited clusters by varying deposition time or beam current. In this paper, we have studied the effect of ion bombardment on size-selected molybdenum and tungsten trioxide (MoO₃ and WO₃) clusters. These two transition metal oxide clusters were chosen as prototypical examples of transition metal oxides due to their chemical similarity (being in the same periodic group) and also their importance in surface science and catalytic applications.^{23–25} Previous

^{a)}Electronic mail: kbowen@jhu.edu

^{b)}Electronic mail: howardf@jhu.edu

experiments on bulk samples and thin films of these transition metal oxides have shown that ion bombardment of molybdenum trioxides and tungsten trioxides leads to the formation of substoichiometric oxides and a reduction of the metal's oxidation state. For molybdenum trioxides, ion induced effects are restricted to the reduction of MoO₃ to MoO₂, with no evidence of metallic species being formed by Ar⁺ ions in the energy regime from 400 eV to 5 keV.^{18,20,26} However, for tungsten trioxides, metallic tungsten has been observed after sputtering with 3 and 5 keV Ar⁺ ions.^{18,26}

In the present study, soft-landed, size-selected metal oxide clusters were prepared on HOPG prior to ion bombardment. The use of size-selected clusters deposited on an atomically smooth surface (HOPG) meant that changes in the structure and morphology of deposited clusters could be accurately probed by atomic force microscopy (AFM). Furthermore, the size of the deposited clusters was smaller than the inelastic mean free path of the photoelectrons created in XPS, which allowed XPS data to be used to quantify changes in both the speciation and concentration of the surface bound clusters. The focus of our study was to compare and contrast the effects of ion bombardment on the two different metal oxide clusters, with a particular emphasis on the relationship between changes in speciation and surface morphology. It should be noted that although the transformations we observe are caused by ion bombardment, they may also include contributions from the backscattered ions/neutrals produced by the interactions of the primary beam with the HOPG substrate.

II. EXPERIMENT

Molybdenum oxide and tungsten oxide cluster anions were produced using a magnetron sputter ion source that has been described in detail previously.²² Once produced, the molybdenum oxide cluster anions were extracted from the source chamber and then accelerated to 1000 V, while tungsten oxide clusters were accelerated to 500 V (based on our experience, using smaller voltages makes it easier to mass select heavier clusters). Mass selected (MoO₃)_{30±1}⁻, (WO₃)_{30±1}⁻, or (WO₃)_{19±1}⁻ cluster anions were produced by passing the ion beam through a magnetic sector mass spectrometer and then refocused and collimated by a series of ion optics, before reaching the deposition chamber where they were decelerated to kinetic energies of less than 0.1 eV per cluster and soft-landed onto a freshly cleaved HOPG substrate. The target was at room temperature and the pressure during cluster deposition was typically ~10⁻⁸ mbar.

Following cluster deposition, samples were removed from the deposition chamber and the coverage and chemical composition of the deposited clusters were determined using XPS in a PHI 5400 XPS system. Peak positions in the spectra were referenced to the C(1s) graphite peak (284.5 eV) of the HOPG substrate, and metal oxidation states were fit using mixed Gaussian(30%)/Lorentzian(70%) envelopes. Deposited clusters were also modified in the PHI 5400 XPS system by ion bombardment using a PHI 04-303 sputtering ion gun operated at 4 keV beam voltage, 25 mA emission, and 25 mPa pressure of Ar. Ion bombardment was alternated

with *in situ* XPS acquisitions at 30 s intervals. The ion flux [6.16×10^{17} ions/(s cm²)] was calculated from the target current (converted to number of ions) measured on the sample during ion bombardment divided by the sample's surface area (the sample surface is fully covered by the ion beam). The ion dose was determined by simply multiplying the ion flux by the exposure time.

To characterize the surface structure of clusters, *ex situ* AFM images [PicoSPM LE AFM (Agilent Technologies)] were acquired both as a function of increasing cluster coverage and as a function of argon ion dose. Samples were removed from the vacuum chamber after deposition and/or argon ion bombardment and adhered to an AFM sample plate using double-sided carbon tape. All image rendering and height measurements were performed with commercially available software from Agilent Technologies. Analysis by AFM revealed that the coverage of clusters on the edge of the HOPG sample was smaller than in the middle. Consequently, we used the optical microscope attached to the AFM to help position the tip in the middle of each sample prior to imaging. In principle, the AFM tips can also pick up or move loosely bound clusters. We verified that this effect was not playing a role in our studies by checking that the AFM images we acquired were identical when the same region of the sample was repeatedly imaged. In some instances this required us to adjust the scan speed.

III. RESULTS AND DISCUSSION

A. Cluster deposition

Figure 1 shows AFM images of (MoO₃)_{30±1} and (WO₃)_{30±1} clusters soft-landed onto HOPG substrates as a function of increasing cluster coverage (controlled by varying the ion dose). Both (MoO₃)_{30±1} and (WO₃)_{30±1} clusters behave similarly. At relatively low coverages, both (MoO₃)_{30±1} [Figs. 1(a)–1(c)] and (WO₃)_{30±1} [Figs. 1(d)–1(f)] clusters preferentially attach to step edges. Such a phenomenon has been observed in other systems (especially metal clusters,²⁷ but also for metal oxide nanoparticles^{28–30}) and is an indication of high cluster mobility and a lower nucleation barrier at step edges. This greater ease of nucleation at step edges is because the step edges consist of carbon atoms with fewer coordination numbers, free radicals, alcohols, carbonyls, or carboxylic acids and are more likely to trap clusters than the carbon atoms on the terraces.³⁰ As the cluster coverage increases, the clusters saturate the step-edge adsorption sites and larger structures composed of cluster aggregates appear on the HOPG terraces, presumably as a result of favorable cluster–cluster interactions. As the coverage increases, further cluster aggregates continue to populate the terrace and Figs. 1(c) and 1(f) show that the HOPG surface becomes saturated with adsorbed clusters in a loosely packed arrangement at high coverage.

B. Effect of ion bombardment on deposited clusters

As an initial step, XPS was used to establish the effect of ion dose on the chemical composition, bonding, and

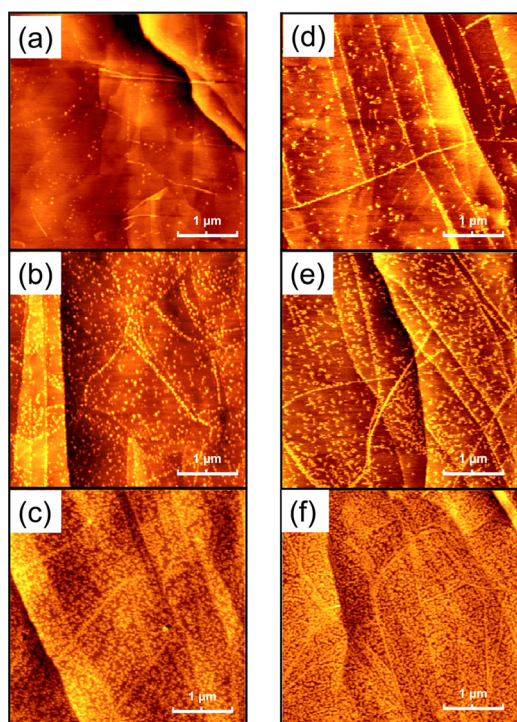


FIG. 1. (Color online) AFM images of (MoO₃)_{30±1} [(a)–(c)] and (WO₃)_{30±1} [(d)–(f)] clusters soft-landed on HOPG, shown as a function of increasing cluster coverage on moving from (a) to (c) and from (d) to (f), respectively.

concentration of adsorbed (MoO₃)_{30±1} and (WO₃)_{30±1} clusters. In summary, the XPS data shown in Fig. 2 reveal that ion bombardment transforms the oxide clusters in two largely sequential steps; ion induced reduction of the transition metal due to oxygen loss, followed by sputtering of the reduced species. The principle difference between molybdenum and tungsten oxide clusters is the extent of ion induced reduction that occurs prior to the onset of sputtering.

The initial coverage of (MoO₃)_{30±1} and (WO₃)_{30±1} clusters shown in the bottom x-ray photoelectron (XP) spectra of Figs. 2(a) and 2(b) correspond to the same cluster coverages as the AFM images of Figs. 1(c) and 1(f), respectively. For (MoO₃)_{30±1} clusters, the evolution of the Mo(3d) region under the influence of Ar⁺ ion bombardment is shown in Fig. 2(a). Prior to ion bombardment (ion dose = 0), the spectral envelope contains two peaks, centered at 232.5 and 235.6 eV, with an intensity ratio of 3:2 due to Mo(3d_{5/2}) and Mo(3d_{3/2}) transitions ($\Delta = 3.1$ eV); the Mo(3d_{5/2}) peak position is indicative of Mo atoms in a highly oxidized state, consistent with the formal +6 oxidation state of Mo in MoO₃. For comparatively small ion doses ($< 1.0 \times 10^{21}$ ions/cm²), changes to the Mo(3d) envelope are dominated by a broadening in the absence of any significant change in the integrated peak area. In this region, the spectral envelope can be reasonably well fit by a combination of fully oxidized MoO₃ clusters and two new Mo(3d_{5/2}, 3d_{3/2}) doublets associated with the production of Mo(V) and Mo(IV) species. To optimize the reliability of our spectral deconvolution, all of the Mo peak positions were based on literature XPS studies where single component molybdenum species (Mo, MoO₂, or MoO₃) were prepared and

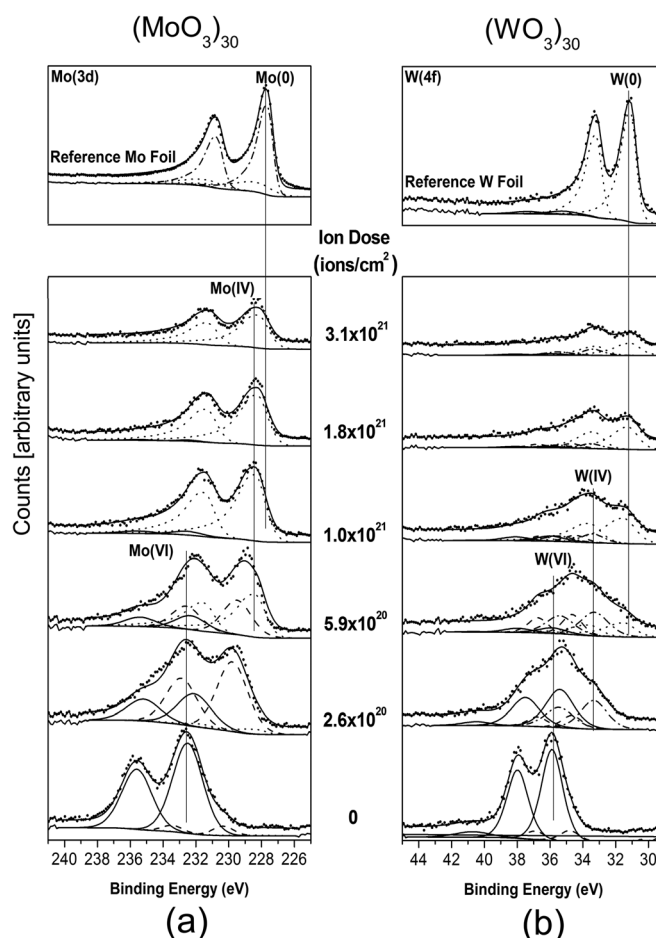


FIG. 2. Effect of Ar⁺ ion dose on (a) the Mo(3d) region of (MoO₃)_{30±1} clusters and (b) the W(4f) region of (WO₃)_{30±1} clusters, as shown by XPS. Reference XP spectra of sputter cleaned molybdenum and tungsten foils are also shown for comparison.

the Mo(3d_{5/2}, 3d_{3/2}) peak positions identified.³¹ For an ion dose of 1.0×10^{21} ions/cm², Fig. 2 shows that reduction of the parent MoO₃ cluster species to MoO₂ is essentially complete. For larger ion doses, a steady decrease in spectral intensity within the Mo(3d) region is observed while the shape of the spectral envelope itself remains unchanged. A comparison with the reference spectrum of a metallic Mo sample (shown in the uppermost left-hand spectrum of Fig. 2) confirms that ion induced reduction of (MoO₃)_{30±1} is restricted to the conversion of Mo(VI) to Mo(IV).

The corresponding XP spectra showing the changes in the W(4f) region of (WO₃)_{30±1} clusters adsorbed on HOPG as a function of Ar⁺ ion dose are presented in Fig. 2(b). Upon deposition (ion dose = 0) the W(4f) spectral envelope can be well fit with two dominant peaks, centered at 35.9 and 38.0 eV and an intensity ratio of 4:3. The binding energy separation (2.1 eV) is consistent with the spin-orbit splitting between W(4f_{7/2}) and W(4f_{5/2}) transitions, while the W(4f_{7/2}) peak position (35.9 eV) is indicative of tungsten atoms in a formal +6 oxidation state associated with the “as deposited” WO₃ clusters. A small contribution ($\sim 10.0\%$) to the W(4f) envelope is ascribed the W(4f_{7/2,5/2}) doublet associated with W(+5) species, with a W(4f_{7/2}) peak position at 34.9 eV.

During the initial stages of argon ion bombardment (ion dose $\leq 2.6 \times 10^{20}$ ions/cm²), the W(4f) peak broadens to lower binding energies, analogous to the behavior of the Mo(3d) region for (MoO₃)_{30±1} clusters. In this regime, the W(4f) spectral envelope can be fit to a combination of the W(4f_{7/2,5/2}) doublet associated with the native W(VI) species along with two additional W(4f_{7/2,5/2}) doublets with W(4f_{7/2}) peak positions at 34.7 and 33.3 eV that can be ascribed to W(V) and W(IV) species, respectively. However, for larger ion doses ($> 5.9 \times 10^{20}$ ions/cm²), and in contrast to the behavior of the Mo(3d) region for MoO₃ clusters, the W(4f) spectral envelope continues to broaden to lower binding energies. Spectral deconvolution of the W(4f) envelope in this regime reveals the appearance of a new W(4f_{7/2, 4f_{5/2}) doublet with a W(4f_{7/2}) peak position at 31.2 eV, whose presence indicates the formation of metallic tungsten. At even higher argon ion doses ($> 1.0 \times 10^{21}$ ions/cm²), the metallic W peaks become the dominant features while the overall intensity in the W(4f) region decreases. A reference XP spectrum of a sputter cleaned metallic tungsten sample [shown in Fig. 2(b)] confirms that ion induced reduction of WO₃ clusters produces metallic W(0). It should be noted that the effect of Ar⁺ ion bombardment was also examined on smaller size (WO₃)_{19±1} clusters (molecular weight = 4404), which have a nearly equal mass to (MoO₃)_{30±1} (molecular weight = 4318). The XPS results, shown in the supplementary information (Fig. S1),³² indicate a very similar trend in behavior between the (WO₃)_{19±1} and (WO₃)_{30±1} clusters.}

The XP spectra in Fig. 2 reveal that MoO₃ clusters were only partially reduced to MoO₂, while WO₃ clusters were reduced to metallic tungsten. This difference is consistent with previous studies on bulk and thin films of MoO₃ and WO₃,^{18,20,26} indicating that the effects of ion bombardment are similar for deposited clusters. The different phenomena observed for MoO₃ versus WO₃ upon sputtering is at least in part a reflection of the significant difference in the mass of argon (40 amu) and either oxygen (16 amu) or molybdenum (96 amu) atoms compared to the mass difference between argon (40 amu) and tungsten (184 amu).¹⁵ These mass differences mean that the effective momentum transfer between incident argon ions and tungsten atoms will be much less efficient than that to either oxygen or molybdenum, facilitating WO₃ reduction. These effects and other phenomena that contribute to different ion induced effects on metal oxides can be found in previous papers.³³ Further ion bombardment caused MoO₂ and W to be sputtered from the surface. The sputtering process, which occurs for ion doses in excess of approximately 1.0×10^{21} ions/cm², is evidenced by a systematic decrease in the signal intensities within the Mo(3d) and W(4f) regions (see Fig. 2), while the spectral envelopes remain unchanged.

To complement XPS data, AFM images were used to determine how argon ion dose affected the structure, size, and concentration of adsorbed clusters. By acquiring AFM images on samples that had been analyzed by XPS after ion bombardment we could investigate how the structure of the adsorbed clusters responds to the chemical transformations induced by ion bombardment.

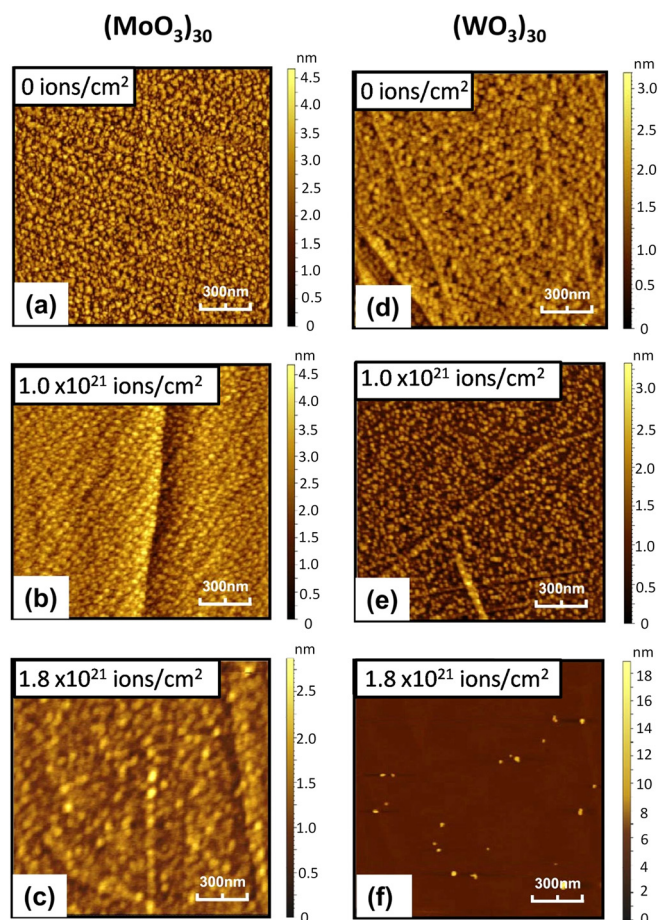


Fig. 3. (Color online) Effect of Ar⁺ ion dose on the surface structure of deposited (MoO₃)_{30±1} [(a)–(c)] and (WO₃)_{30±1} [(d)–(f)] clusters, as shown by AFM.

Figure 3 shows AFM images illustrating the effect of Ar⁺ ion bombardment on deposited (MoO₃)_{30±1} [Figs. 3(a)–3(c)] and (WO₃)_{30±1} [Figs. 3(d)–3(f)] clusters. For the as deposited (MoO₃)_{30±1} clusters, Fig. 3(a) shows that they are relatively uniformly deposited on the HOPG surface. After an ion dose of 1.0×10^{21} ion/cm² [Fig. 3(b)], there is little obvious change in the shape of the adsorbed clusters, except perhaps for a slight reduction in the cluster coverage and size. Based on the corresponding XPS data this image corresponds to the ion dose required to induce complete reduction of MoO₃ to MoO₂, in the absence of any significant MoO₂ sputtering. Since any MoO₂ clusters produced in vacuum will reoxidize upon air exposure²² prior to AFM imaging, we would not expect to see any significant change in the structure of the clusters. This is consistent with the similarity in structure and cluster size observed between the as deposited and ion exposed MoO₃ clusters in Figs. 3(a) and 3(b), respectively. After an ion dose of 1.8×10^{21} ion/cm² [Fig. 3(c)], however, a significant decrease in the size of the remaining clusters occurred [note the difference in size of height scale for Fig. 3(c)]. This is consistent with the onset of MoO₂ sputtering as observed for the same ion dose by XPS (Fig. 2). For even larger ion doses AFM results showed that the vast majority of the clusters were removed from the surface, leaving behind a

comparatively flat HOPG substrate (data shown in supplementary information, Fig. S2).³²

For the (WO₃)_{30±1} clusters, the initial structure prior to sputtering [Fig. 3(d)] is similar to that observed for the (MoO₃)_{30±1} clusters [Fig. 3(a)]. After an argon ion dose of 1.0×10^{21} ion/cm² [Fig. 3(e)] the two-dimensional coverage of tungsten clusters decreased and the underlying HOPG substrate is now clearly visible in places consistent with the XPS data for the same ion dose, which reveals that a large fraction of the WO₃ clusters has been fully reduced to metallic tungsten and the coverage of tungsten atoms has begun to decrease. However, as the ion dose was increased further to 1.8×10^{21} ion/cm² [Fig. 3(f)], at a point where the XPS data in Fig. 2 indicate that the prevalent change involves a loss of metallic tungsten atoms, a dramatic change in the structure of the tungsten clusters was observed by AFM. Specifically, a small number of extremely large structures had formed. This is perhaps most apparent in Figs. 3(e) and 3(f) by noting the change in height scale for Fig. 3(f). To check the validity of this phenomenon we conducted separate ion bombardment experiments on a different (WO₃)_{30±1} sample and observed the same changes in the AFM images. It is also worth noting that numerous smaller clusters are also present after an ion dose of 1.8×10^{21} ion/cm², although they are not observed in the image because their presence is obscured by the increase in height scale needed to capture the large structures that had formed. A representative AFM image highlighting the presence of these smaller clusters is shown in Fig. 4.

Figure 5 shows more quantitative information on the effect that Ar⁺ ion bombardment has on cluster heights, obtained by (top) comparing AFM line scans taken through the clusters observed after an ion dose of 1.8×10^{21} ion/cm² and (bottom) comparing between the height distributions of the as deposited (MoO₃)_{30±1} and (WO₃)_{30±1} clusters to the height of the clusters observed after an argon ion dose of 1.8×10^{21} ion/cm². For the as deposited clusters, the average height and height distribution of both (MoO₃)_{30±1} and (WO₃)_{30±1} clusters was very similar; 1.9 ± 0.4 nm for (MoO₃)_{30±1} and 1.9 ± 0.3 nm for (WO₃)_{30±1} clusters. For the (MoO₃)_{30±1} clusters exposed to an ion dose of 1.8×10^{21} ion/cm² the size of the remaining clusters decreased to 0.7 ± 0.2 nm. This decrease in cluster size compared to the as deposited clusters can be ascribed to

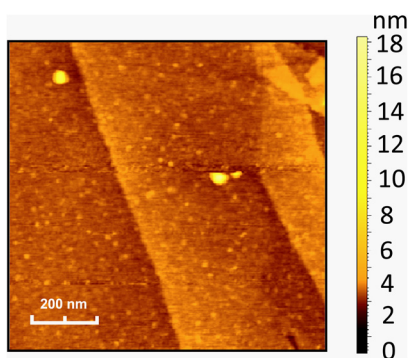


Fig. 4. (Color online) AFM image of sputtered (WO₃)₃₀ clusters (ion dose of 1.8×10^{21} ions/cm²). It should be noted that to acquire these images the scan speed was decreased to reduce tip induced displacement of adsorbed clusters and help identify the presence of small clusters on the surface.

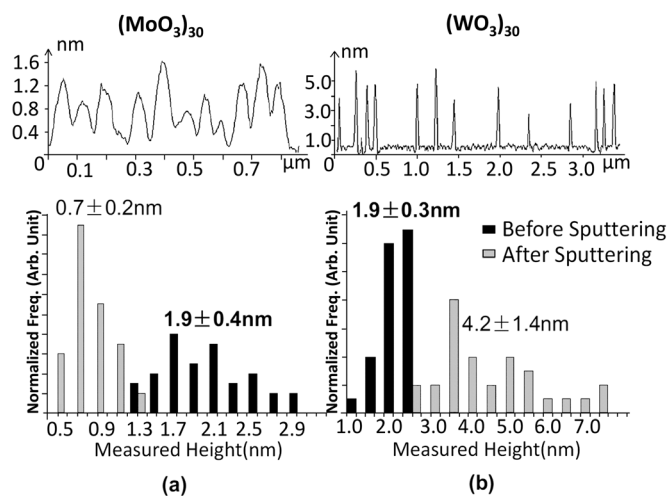


Fig. 5. (Top) AFM line scans showing cluster heights after (a) (MoO₃)₃₀ and (b) (WO₃)₃₀ clusters were exposed to an argon ion dose of 1.8×10^{21} ions/cm². (Bottom) Comparison of the height distribution of as deposited (a) (MoO₃)_{30±1} and (b) (WO₃)_{30±1} clusters to those observed after an argon ion dose of 1.8×10^{21} ions/cm². For (MoO₃)_{30±1} clusters, height distributions were based on measurements of 40 individual clusters before and after ion bombardment. For (WO₃)_{30±1} clusters, 30 individual clusters were analyzed before and after ion bombardment.

the onset of MoO₂ sputtering, in accord with the XPS data shown in Fig. 3. In contrast, for the (WO₃)_{30±1} clusters exposed to the same ion dose the size of the remaining clusters increased to 4.2 ± 1.4 nm.

We hypothesize that the appearance of a small number of much larger clusters compared to the as deposited oxide clusters is a consequence of the mobility and subsequent coalescence of small metallic tungsten clusters produced during WO₃ bombardment. This assertion is consistent with previous observations on the increased mobility of smaller clusters and metal versus metal oxide clusters.²² Ion bombardment could also help to initiate metal cluster coalescence by providing additional energy to the surface, which would facilitate the diffusion and coalescence process. For metallic tungsten, evidence of such an effect has been observed in a previous study where ion bombardment transformed small bunches of tungsten nanowires into tungsten cones.³⁴ It should also be noted that we also observed many small (~ 0.7 nm in height) tungsten clusters after this ion dose (see Fig. 4). These clusters could be pinned by defects created by the sputtering process, or be too large for cluster mobility. The idea that cluster size may be influencing the mobility and/or coalescence properties of the metallic tungsten clusters is also supported by the absence of large aggregates at lower ion doses, where XPS data revealed that metallic tungsten had already formed. The absence of significant coalescence phenomena during ion irradiation of MoO₃ is entirely consistent with the reduced mobility and propensity to coalesce expected for metal oxide clusters compared to metal clusters.

IV. SUMMARY AND CONCLUSIONS

During the initial stages of bombardment, the ion induced reduction of MoO₃ clusters to MoO₂ produces little change in the structure or size of the adsorbed clusters. However,

larger ion doses induce sputtering of MoO₂ and a decrease in the cluster size. For (WO₃)_{30±1} clusters, the W(VI) atoms in WO₃ are completely reduced to W(0) by ion bombardment. We hypothesize that the mobility and coalescence of sufficiently small metallic tungsten clusters formed during ion bombardment leads to the appearance of a small concentration of new larger sized clusters. Thus, although molybdenum and tungsten are in the same group in the periodic table, ion bombardment produces very different changes in their composition and surface morphology. In a broader sense, this study also demonstrates the important interplay that can exist between the ion induced chemical modification and structure of adsorbed clusters.

ACKNOWLEDGMENTS

This work was supported by the Division of Materials Science and Engineering, Basic Energy Sciences, U.S. Department of Energy, under Grant No. DE-FG02-09ER46558. The authors also thank the Materials Sciences Surface Analysis Laboratory of Johns Hopkins University (JHU). K.A.W. also acknowledges the JHU Department of Chemistry for the award of a Rudolf Sonneborn Fellowship.

¹C. N. R. Rao and B. Raveau, *Transition Metal Oxides: Structure, Properties, and Synthesis of Ceramic Oxides*, 2nd ed. (Wiley-VCH, New York, 1998).

²X. Huang, H. J. Zhai, B. Kiran, and L. S. Wang, *Angew. Chem., Int. Ed.* **44**, 7251 (2005).

³N. O. Jones, S. N. Khanna, T. Baruah, M. R. Pederson, W. J. Zheng, J. M. Nilles, and K. H. Bowen, *Phys. Rev. B* **70**, 134422 (2004).

⁴C. C. Jarrold, D. W. Rothgeb, E. Hossain, and J. E. Mann, *J. Chem. Phys.* **132**, 064302 (2010).

⁵D. W. Rothgeb, S. E. Waller, and C. C. Jarrold, *J. Phys. Chem. A* **114**, 11312 (2010).

⁶A. W. Castleman, S. A. Claridge, S. N. Khanna, C. B. Murray, A. Sen, and P. S. Weiss, *ACS Nano* **3**, 244 (2009).

⁷P. Jensen, *Rev. Mod. Phys.* **71**, 1695 (1999).

⁸V. N. Popok, I. Barke, E. E. B. Campbell, and K.-H. Meiwes-Broer, *Surf. Sci. Rep.* **66**, 347 (2011).

⁹I. P. Jain and G. Agarwal, *Surf. Sci. Rep.* **66**, 77 (2011).

¹⁰E. Taglauer, *Appl. Surf. Sci.* **13**, 80 (1982).

¹¹J. P. Coad and J. G. Cunningham, *J. Electron Spectrosc. Relat. Phenom.* **3**, 435 (1974).

¹²D. J. Ball, T. M. Buck, G. H. Wheatley, and D. Macnair, *Surf. Sci.* **30**, 69 (1972).

¹³A. Benninghoven, *Surf. Sci.* **35**, 427 (1973).

¹⁴S. Storp and R. Holm, *J. Electron Spectrosc. Relat. Phenom.* **16**, 183 (1979).

¹⁵R. Kelly, *Mater. Sci. Eng., A* **115**, 11 (1989).

¹⁶R. Kelly, *Nucl. Instrum. Methods* **182**, 351 (1981).

¹⁷V. S. Smentkowski, *Prog. Surf. Sci.* **64**, 1 (2000).

¹⁸T. J. Driscoll, L. D. McCormick, and W. C. Lederer, *Surf. Sci.* **187**, 539 (1987).

¹⁹D. R. Baer *et al.*, *J. Vac. Sci. Technol. A* **28**, 1060 (2010).

²⁰K. S. Kim, W. E. Baitinger, J. W. Amy, and N. Winograd, *J. Electron Spectrosc. Relat. Phenom.* **5**, 351 (1974).

²¹M. A. Langell, *Surf. Sci. Rep.* **186**, 323 (1987).

²²K. A. Wepasnick, X. Li, T. Mangler, S. Noessner, C. Wolke, M. Grossmann, G. Gantefoer, D. H. Fairbrother, and K. H. Bowen, *J. Phys. Chem. C* **115**, 12299 (2011).

²³A. Katrib, P. Leflaive, L. Hilaire, and G. Maire, *Catal. Lett.* **38**, 95 (1996).

²⁴C. Martin, G. Solana, P. Malet, and V. Rives, *Catal. Today* **78**, 365 (2003).

²⁵D. G. Barton, M. Shtein, R. D. Wilson, S. L. Soled, and E. Iglesia, *J. Phys. Chem. B* **103**, 630 (1999).

²⁶N. V. Alov, D. M. Kutsko, and K. V. Bordo, *J. Surf. Investig. X-Ray Synchro.* **2**, 184 (2008).

²⁷G. M. Francis, L. Kuipers, J. R. A. Cleaver, and R. E. Palmer, *J. Appl. Phys.* **79**, 2942 (1996).

²⁸M. P. Zach, K. H. Ng, and R. M. Penner, *Science* **290**, 2120 (2000).

²⁹B. J. Murray, Q. Li, J. T. Newberg, J. C. Hemminger, and R. M. Penner, *Chem. Mater.* **17**, 6611 (2005).

³⁰J. Taing, M. H. Cheng, and J. C. Hemminger, *ACS Nano* **5**, 6325 (2011).

³¹F. Werfel and E. Minni, *J. Phys. C: Solid State Phys.* **16**, 6091 (1983).

³²See supplementary material at <http://dx.doi.org/10.1116/1.4711134> for the corresponding XP spectra of (WO₃)₁₉ clusters as a function of ion doses and AFM image of (MoO₃)₃₀ clusters after ion dose of 3.1E+21 ions/cm².

³³D. F. Mitchell, G. I. Sproule, and M. J. Graham, *Surf. Interface Anal.* **15**, 487 (1990).

³⁴F. Y. Xie, L. Gong, X. Liu, J. Chen, W. G. Xie, and W. H. Zhang, *Appl. Surf. Sci.* **256**, 693 (2009).