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## A new nanomaterial synthesized from size-selected, ligand-free metal clusters

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Thin films are synthesized by deposition of size-selected  $\text{Mo}_n^-$  cluster anions on an inert substrate. Scanning tunneling microscopy pictures indicate that the deposited material consists of individual particles with diameters corresponding to the size of the preformed clusters from the gas phase. Previous attempts to manufacture cluster materials from metals failed since these clusters coalesced at room temperature. Our data suggest the possibility to synthesize new nanomaterials from clusters of high fusing metals. This may prove to be the key to harness size-dependent and tuneable properties of clusters for creating novel classes of functional tailor-made materials. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4868468>]

### INTRODUCTION

Clusters contain an ensemble of bound atoms whose size is intermediate between an individual atom and a bulk solid. As such, clusters are a unique class of materials which continue to attract intense scientific interest due to the fact that they often exhibit extraordinary electronic, optical, catalytic properties.<sup>1–3</sup> Metal clusters are of particular interest. Many of their features are strongly size-dependent, e.g., gold clusters catalyze CO oxidation at low temperatures, whereas bulk gold is chemically inert.<sup>4,5</sup> Synthesizing materials from highly functional metal clusters may open the gateway to the creation of novel classes of materials conveying completely new and oftentimes unexpected properties. Such materials can be used in a multitude of applications like catalysts, electrode materials (electrochemical) sensors or solar cells, etc., and therefore efforts have been undertaken to synthesize them.<sup>6</sup> However, for metal clusters there is a major obstacle. A sound synthesis route to materials made from metal clusters has to overcome the problem of coalescence resulting in an immediate loss of their original features. One way might be the use of ligand-stabilized metal clusters and in fact these condense into highly ordered crystals without the problem of coalescence.<sup>7</sup> Nevertheless, ligands isolate clusters and in consequence change their physical and chemical properties. In order to keep the attributes of bare clusters, an alternative and more promising method is the size-selected cluster formation in the gas phase and deposition under soft landing conditions.<sup>8,9</sup> So far this technique has been successfully used to investigate the properties of deposited clusters. In these studies, coalescence is circumvented by dramatically lowering the coverage and/or immobilizing clusters on the surface. The outcome is well-defined model systems with spatially separated clusters. Nevertheless, several attempts to synthesize cluster layers by increasing the coverage have failed since deposited clusters merged into larger particles.<sup>10–13</sup> Only in the case of large gold clusters, it seems that coalescence might have been

avoided.<sup>14–16</sup> In order to prevent coalescence, the mobility of the surface atoms of the cluster has to be decreased. Since these atoms have to be rearranged during coalescence, the displacement energy presents a barrier which prevents spontaneous reduction of surface free energy and stabilizes individual clusters in the material. The mobility of the surface atoms depends on the melting point. It is well-known that the melting point of small particles is drastically lowered with respect to the bulk.<sup>17,18</sup> This effect is even more pronounced for low-coordinated atoms at the “cluster-surface,” which leads to liquid-like behaviour (surface-premelting) and therefore facilitates merging of the individual particles. Previously, all attempts synthesizing such materials via the deposition of preformed metallic particles, apart from the aforementioned large Au clusters,<sup>14–16</sup> have failed.<sup>10–13,19–22</sup> In general, there are only few examples where actual cluster-assembled materials can be synthesized from any material beside metals. Fullerenes can be condensed into a bulk material called fullerite.<sup>22,23</sup> It represents a new allotrope of carbon besides well-known graphite and diamond. Apart from fullerite, there are only few known bulk materials containing clusters: Chevrel phases,<sup>24</sup> Zintl ion compounds,<sup>25</sup> and certain forms of sulphur, selenium, phosphorus,<sup>26</sup> and antimony.<sup>27</sup> Another example is silicon clusters. While clusters consisting of less than 50 atoms immediately coalesce,<sup>28,29</sup> larger silicon clusters (2–20 nm) form granular films and their fluorescence spectra exhibit a pronounced dependence on cluster size indicating that properties of individual clusters are at least partially preserved.<sup>30,31</sup> Using deposition of size-selected clusters, new materials made of small fullerenes<sup>32</sup> and metcars<sup>6</sup> have been synthesized. Therefore, ligand-free clusters forming a cluster material do indeed exist. However, for metals no such materials are known. Even binary clusters such as PbS show a strong tendency to coalescence.<sup>33</sup> Here, the synthesis of a novel granular material consisting of individual  $\text{Mo}_n$  clusters, grown on freshly peeled HOPG, is reported. This idea behind the experiments is quite simple: if the surface of a small cluster of a common metal such as silver is almost liquid at room temperature, it is not surprising that these clusters coalesce. For

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clusters of refractory metals such as molybdenum, the situation is different. Even if the melting point of the cluster surface is much lower than one of the bulk (Mo:  $\sim 2900$  K), it might still be very high compared to room temperature. Hence, clusters of these materials may be well suited as building blocks of a stable cluster-assembled material.

## EXPERIMENTAL

Clusters were produced via magnetron sputtering, mass-selected with a large sector magnet (mass-resolution  $m/\Delta m = 20$ ) and deposited within the soft-landing criterion at high-vacuum conditions ( $p < 1 \times 10^{-8}$  mbar). Subsequently, the topography of cluster structures was investigated by scanning tunneling microscopy (STM). To demonstrate the cleanliness of the grown material, samples were characterized by *ex-situ* X-Ray Photoelectron Spectroscopy (XPS). The cluster size was varied to exclude coalescence and also examines stability of granular materials in terms of particle size. For the experiments, two setups were used. In one, the transfer into the STM (Omicron 1) without breaking the vacuum is possible. Using the other setup, the sample has to be air exposed upon bringing it into the UHV-system for characterization by STM and XPS (magnesium  $K_{\alpha}$  with 1256 eV). The instrumentation is an Omicron VT-STM and a dual anode Al/Mg X-ray source from VG Microtech with an Omicron EA125 concentric hemispherical analyzer for XPS.

## RESULTS

Fig. 1 displays a comparison of STM scans of two samples of mid-sized  $\text{Mo}_n^-$  clusters deposited on HOPG. In both cases, the surface is rugged with deep notches and high spikes. The surfaces consist of spherical shapes, which can even be found in the deepest notches. The size of the granules is different for the two pictures. Even without an elaborate analysis, the larger size of the granular shapes in the left picture is obvious. In Fig. 1(a), clusters consisting of 275 atoms have been deposited, while in Fig. 1(b) smaller clusters with 150 atoms were used. However, the difference in size is not only due to the different mass of the deposited clusters but also caused by exposure to air. In the left picture, the clusters are oxidized and by this process the volume increases by a factor of three. There is one more important difference between the two pictures: The *in-situ* image (Fig. 1(b)) exhibits many streaks and is more blurred than the picture of the oxidized sample.

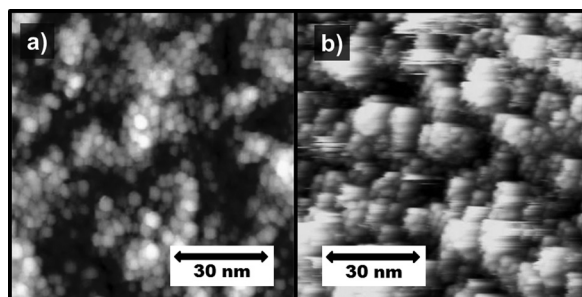


FIG. 1. (a) Overview STM image of air-exposed multiple monolayers of  $\text{Mo}_{275\pm 40}^-$  clusters deposited on HOPG. (b) Overview STM image of multiple monolayers of  $\text{Mo}_{150\pm 20}^-$  clusters deposited "*in-situ*" on HOPG.

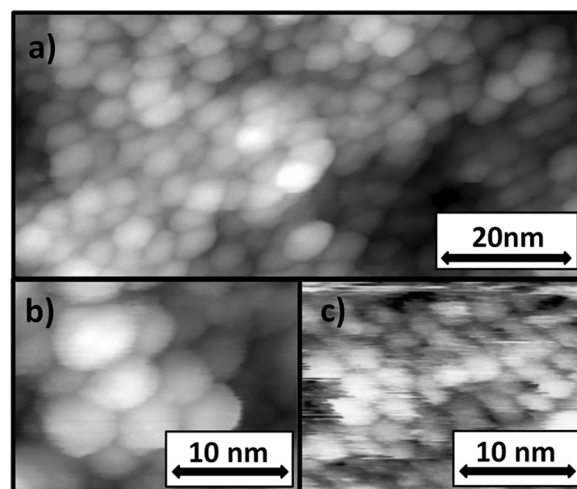


FIG. 2. (a) and (b) STM images  $U = 1.8$  V,  $I = 0.02$  nA of air-exposed multiple monolayers of  $\text{Mo}_{1500}^-$  deposited on HOPG. (a)  $90 \times 45 \text{ nm}^2$  overview and (b) detailed image  $25 \times 18 \text{ nm}^2$  (c) non air-exposed sample of  $\text{Mo}_{40}^-$  Cluster deposited on HOPG  $25 \times 18 \text{ nm}^2$ . The clusters completely cover the HOPG surface and can clearly be identified as spherical particles.

More details can be resolved for larger clusters. Figs. 2(a) and 2(b) show STM images of  $\text{Mo}_{1500\pm 100}$  deposited on HOPG after air exposure. Clearly, the surface consists of individual particles with an almost spherical shape. Fig. 2(c) displays an STM image recorded *in-situ* of a thin film made by deposition of small clusters consisting of 40 Mo atoms only. Although the picture is more blurred, small spherical shapes are still discernible. The chemical composition of the air-exposed sample displayed in Fig. 2(a) has been investigated by XPS. The survey scan (not shown) reveals the cleanliness of the sample. Besides oxidation of the molybdenum clusters due to air exposure, additional contaminants cannot be found. To further investigate the extent of oxidation, the XPS region scan of the molybdenum 3d signals is shown in Fig. 3. The broad feature indicates a mixture of different species. As shown by the fitting curves, the data can be explained by metallic and partially oxidized molybdenum  $\text{Mo}(0)$ ,  $\text{MoO}(+4)$ , and  $\text{MoO}(+6)$ . Since essential parts of the oxidation process take place during air exposure, they start at

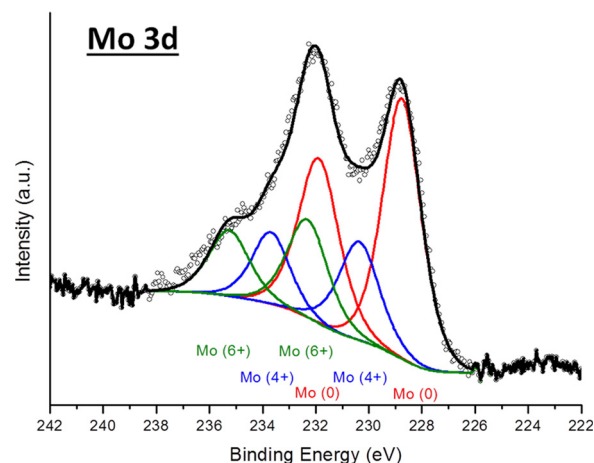


FIG. 3. X-ray photoelectron spectrum of the Mo 3d peak of deposited  $\text{Mo}_{1500\pm 100}$  on HOPG after air exposure. The broad features indicate various signals from  $\text{Mo}(0)$ ,  $\text{Mo}(4+)$ , and  $\text{Mo}(6+)$  which are interpreted by a core/shell structure. Positions of the fitting curves are taken from Ref. 35.

the outer shell of the cluster quickly forming a passivating oxide layer on the cluster shell. The inner atoms are therefore protected giving rise to a metallic core of the particle. Smaller particles are probably not able to form a protective oxide layer and therefore oxidise completely, as suggested by experiments on  $\text{Mo}_{100}^-$ .<sup>34</sup>

In order to gather further evidence that the films shown indeed consist of individual clusters preformed in the gas phase, a size-dependent deposition experiment was carried out. Deposited structures were investigated by STM without breaking vacuum conditions. Results are summarized in Fig. 4. The particle diameter is displayed versus cluster size. STM data show granular structures down to  $\text{Mo}_{25}^-$ . The evaluation of particle size from these data is difficult since more reliable information of particle height due to protrusions and lack of a plane background is not accessible. Lateral dimensions measured from STM pictures are less accurate because images are always a convolution of tip and surface structure. Therefore, the extracted values of particle diameters can be considered to be a rough estimate of the actual dimensions only. The data shown in Fig. 4 are obtained by fitting the size-distribution from STM data with a normal-distribution while the error corresponds to the width of the distribution for  $\text{Mo}_n$ ,  $n = 40, 100, 200,$  and  $400$ . For  $\text{Mo}_n$ ,  $n = 25$  and  $n = 150$ , the extracted values are arithmetic averaged, and errors correspond to scattering. The shapes of the clusters seem to be more elliptical, which might not be real and rather an effect of thermal STM drift. In these cases, both values the long and the short axis are taken and averaged.

## DISCUSSION

In Figs. 1 and 2, clusters can be identified as almost intact spherical particles with a narrow size distribution. They do not condense into planar layers with periodic structures, but due to cluster-cluster interaction rather randomly stick together and form a corrugated cluster surface. The size of the spherical objects visible in the STM pictures scales with the diameter of the deposited clusters. The dashed line in Fig. 4 represents the theoretical cluster diameter assuming a spherical shape calculated by  $d = \sqrt[3]{\frac{6 \times M_{\text{Mol}} \times N_{\text{cluster}}}{\pi \times \rho \times N_A}}$ , where  $N_{\text{cluster}}$  is

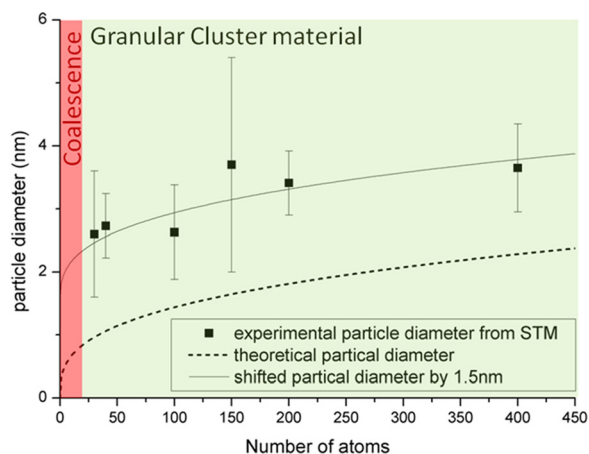


FIG. 4. Experimental cluster size measured from STM data is shown versus the number of atoms as chosen for mass-selection settings. Assuming a spherical shape, the data fit the theoretical expectation shifted by 1.5 nm, what is reasonable explained due to tip-structure broadening.

the number of atoms per cluster. The experimental data are in good agreement with an  $d^3$ -dependency but shifted by 1.5 nm to larger sizes, which can be explained by broadening due to the tip. Experimentally evaluated diameters match the sizes of preformed clusters obtained by mass-selection in the gas phase. This presents evidence that the surface of the granular film indeed consists of preselected particles. For cluster sizes below  $\text{Mo}_{25}^-$  cluster-assembled materials cannot be found as indicated by the red bar within the figure. Instead for  $\text{Mo}_{10}$  an amorphous bulk like material with no internal structure is observed. With an STM only information about the surface can be gained. Hence, at this point it is unclear, whether the bulk material below the surface consists of individual clusters or not. However, there are some additional indications supporting the hypothesis that the thin films studied here consist of weakly bound clusters:

- (i) It is possible to obtain some contrast in the deep notches visible in Figs. 1(a) and 1(b). Even there spherical shapes are observed. This suggests that in deeper layers there are granules, too.
- (ii) The ragged surface topography observed in Figs. 1(a) and 1(b) fit to our idea how these films form. We assume the clusters hit the surface as naked metal spheres. In the moment they touch the surface, a metal bond is formed and the particles are “spot-welded” in their respective position. This growth mode has a certain similarity to diffusion limited aggregation, which also results in the formation of ragged structures. If the atoms at the surface of the clusters would be able to move the bonds between neighboring clusters would be less rigid. The clusters would be able to migrate. Migration would result in smoothing, which is not observed. The connections between the clusters must be rather rigid.
- (iii) It is much more difficult to record STM images for the *in-situ* samples. In many cases, even with a fresh tip no picture could be recorded. Our explanation for this difficulty is that the tip immediately picks up pieces of material from the surface. This indicates that the material in the film is relatively weakly bond. In addition, the images show many streaks (Fig. 1(b)). It seems that even larger pieces of material are moved by the tip. This would probably not happen if the bulk material below the layer of granules would be solid metal. More likely, the whole film consists of loosely bound clusters. For the samples exposed to air, the bonding between the clusters might be stronger. Caused by the oxidation the particles expand and the contact areas between neighboring particles become larger making the cluster material more stable. In these pictures, there are no streaks (Fig. 1(a)).

For most materials, the creation of surface costs energy. Hence, two metal particles will always coalesce to minimize their surface. However, this process may be inhibited or slowed down. One possibility is the reduction of the surface energy by passivation. For example, in the case of Mo particles surface oxidation might reduce the tendency to coalesce. An oxide layer reduces surface tension (or surface free



energy) and in turn the thermodynamic driving force for cluster coalescence. In our experiment, oxidation during deposition cannot be completely ruled out. Work done on  $\text{Mo}_{100}^-$  clusters shows that this film was at least partially oxidized<sup>34</sup> due to insufficient vacuum conditions during deposition. However, the more important aspect in material stabilization might be blamed on kinetics rather than thermodynamics. Coalescence requires a substantial amount of atoms to be rearranged in a finite amount of time. The energy barrier (activation energy) for atom diffusion increases with the melting point (2896 K for bulk Mo). The other effect is cluster size since surface premelting is less drastic in larger than in smaller clusters. This means larger clusters have an ample advantage over smaller ones to serve as building blocks for a cluster-assembled material since their melting temperature and on top of that more atoms have to be rearranged to achieve coalescence. Large clusters of high-melting point metals might form a cluster material and our data support this hypothesis for molybdenum clusters consisting of more than 25 atom. Very small clusters such as trimers or tetramers are expected to coalesce immediately. While in the bulk metal the coordination number is 8 and in the surface it is 6, in small clusters the coordination number of most atoms is smaller making these species extremely unstable.

## CONCLUSION

In this paper, the deposition of metallic cluster thin films on freshly peeled HOPG is reported. The surface of the multilayer films is examined using scanning tunnelling microscopy. It consists of spherical objects. Size-dependent studies show that the diameter of these granules corresponds to the size of the clusters. Our data support the hypothesis that the molybdenum clusters form a new material consisting of metallic nanospheres bound together at the contact points. In contrast, clusters of common metals such as the coinage metals coalesce at room temperature. The critical parameter is the melting point. It seems that only clusters of high melting point metals are able to form cluster-assembled materials which are stable at room temperature. In addition, we found indications for the existence of a threshold size. Below that size, the clusters coalesce. Further studies are necessary to examine the various parameters influencing the structure and stability of such materials in more detail. The new nanomaterials made from clusters of refractory metals have a high internal surface and are thermally and chemically rather stable. This makes them interesting templates for applications in catalysis or as electrode materials.

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- <sup>1</sup>A. W. Castleman and K. H. Bowen, *J. Phys. Chem.* **100**, 12911 (1996).
- <sup>2</sup>M. D. Morse, M. E. Geusic, J. R. Heath, and R. E. Smalley, *J. Chem. Phys.* **83**, 2293 (1985).
- <sup>3</sup>W. A. de Heer, *Rev. Mod. Phys.* **65**, 611 (1993).
- <sup>4</sup>A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem., Int. Ed.* **45**, 7896 (2006).
- <sup>5</sup>A. A. Herzing, C. J. Kiely, A. F. Carley, P. Landon, and G. J. Hutchings, *Science* **321**, 1331–1335 (2008).
- <sup>6</sup>S. A. Claridge, A. W. Castleman, Jr., S. N. Khanna, C. B. Murray, A. Sen, and P. S. Weiss, *ACS Nano* **3**, 244–255 (2009).
- <sup>7</sup>H. Y. Yang, Y. Wang, H. Q. Huang, L. Gell, L. Lehtovaara, S. Malola, H. Häkkinen, and N. F. Zheng, *Nat. Commun.* **4**, 2422 (2013), and references therein.
- <sup>8</sup>P. Jensen, *Rev. Mod. Phys.* **71**, 1695 (1999).
- <sup>9</sup>V. N. Popok, I. Barke, E. E. B. Campbell, and K.-H. Meiwes-Broer, *Surf. Sci. Rep.* **66**, 347 (2011).
- <sup>10</sup>A. Lando, N. Kebaili, Ph. Cahuzac, A. Masson, and C. Brechignac, *Phys. Rev. Lett.* **97**, 133402 (2006).
- <sup>11</sup>A. Lando, N. Kebaili, Ph. Cahuzac, C. Colliex, M. Couillard, A. Masson, M. Schmidt, and C. Brechignac, *Eur. Phys. J. D* **43**, 151 (2007).
- <sup>12</sup>C. Brechignac, Ph. Cahuzac, F. Carlier, C. Colliex, J. Leroux, A. Masson, B. Yoon, and U. Landman, *Phys. Rev. Lett.* **88**, 196103 (2002).
- <sup>13</sup>R. Reichel, J. G. Partridge, F. Natali, T. Matthewson, S. A. Brown, A. Lassesson, D. M. A. Mackenzie, A. I. Ayesh, K. C. Tee, A. Awasthi, and S. C. Hendy, *Appl. Phys. Lett.* **89**, 213105 (2006).
- <sup>14</sup>A. Perez, P. Melinon, V. Dupuis, P. Jensen, B. Prevel, J. Tuillon, L. Bardotti, C. Martet, M. Treilleux, M. Broyer, M. Pellerin, J. L. Vaille, B. Palpant, and J. Lerme, *J. Phys. D: Appl. Phys.* **30**, 709 (1997).
- <sup>15</sup>L. Bardotti, B. Prevel, M. Treilleux, P. Melinon, and A. Perez, *Appl. Surf. Sci.* **164**, 52 (2000).
- <sup>16</sup>L. Bardotti, B. Prevel, P. Melinon, A. Perez, Q. Hou, and M. Hou, *Phys. Rev. B* **62**, 2835 (2000).
- <sup>17</sup>M. Schmidt, R. Kusche, B. v. Issendorff, and H. Haberland, *Nature* **393**, 238–240 (1998).
- <sup>18</sup>A. Aguado and M. F. Jarrold, *Annu. Rev. Phys. Chem.* **62**, 151–172 (2011).
- <sup>19</sup>G. Fuchs, P. Melinon, F. Santos Aires, M. Treilleux, B. Cabaud, and A. Hoareau, *Phys. Rev. B* **44**, 3926 (1991).
- <sup>20</sup>C. Brechignac, Ph. Cahuzac, F. Carlier, M. de Frutos, A. Masson, C. Mory, C. Colliex, and B. Yoon, *Phys. Rev. B* **57**, R2084 (1998).
- <sup>21</sup>I. M. Goldby, L. Kuipers, B. von Issendorff, and R. E. Palmer, *Appl. Phys. Lett.* **69**, 2819 (1996).
- <sup>22</sup>B. Wang, B. Yoon, M. König, Y. Fukamori, F. Esch, U. Heiz, and U. Landman, *Nano Lett.* **12**, 5907 (2012).
- <sup>23</sup>*Science of Fullerenes and Carbon Nanotubes: Their Properties and Applications*, edited by M. S. Dresselhaus, P. C. Eklund, and G. Dresselhaus (Academic Press, San Diego, 1996).
- <sup>24</sup>R. Chevrel, M. Hirrien, and M. Sergent, *Polyhedron* **5**, 87–94 (1986).
- <sup>25</sup>S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, and T. F. Fässler, *Angew. Chem.* **123**, 3712 (2011).
- <sup>26</sup>A. F. Holleman, E. Wieberg, and N. Wieberg, *Lehrbuch der Anorganischen Chemie*, 102 ed. (Walter de Gruyter, Berlin, 2007).
- <sup>27</sup>T. M. Bernhardt, B. Stegemann, B. Kaiser, and K. Rademann, *Angew. Chem., Int. Ed.* **42**, 199 (2003).
- <sup>28</sup>J. E. Bower and M. F. Jarrold, *J. Chem. Phys.* **97**, 8312 (1992).
- <sup>29</sup>S. Messerli, S. Schintke, K. Morgenstern, A. Sanchez, U. Heiz, and W.-D. Schneider, *Surf. Sci.* **465**, 331 (2000).
- <sup>30</sup>M. Ehbrecht, B. Kohn, F. Huisken, M. A. Laguna, and V. Paillard, *Phys. Rev. B* **56**, 6958 (1997).
- <sup>31</sup>F. Huisken, G. Ledoux, O. Guillois, and C. Reynaud, *Adv. Mater.* **14**, 1861 (2002).
- <sup>32</sup>A. Böttcher, P. Weis, S.-S. Jester, D. Löffler, A. Bihlmeier, W. Klopfer, and M. M. Kappes, *Phys. Chem. Chem. Phys.* **2005**(7), 2816–2820.
- <sup>33</sup>B. Kiran, A. K. Kandalam, R. Rallabandi, P. Koirala, Xiang Li, Xin Tang, Yi Wang, H. Fairbrother, G. Gantefoer, and K. Bowen, *J. Chem. Phys.* **136**, 024317 (2012).
- <sup>34</sup>K. 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).
- <sup>35</sup>D. S. Zingg, L. E. Makovsky, R. E. Tischer, F. R. Brown, and D. M. Hercules, *J. Phys. Chem.* **84**, 2898 (1980).