

Adlayer formation on C-plane (0001) and R-plane ($1\bar{1}02$) Al_2O_3 surfaces

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Abstract

Adlayers on C-plane (0001) and R-plane ($1\bar{1}02$) terminated surfaces of corundum phase aluminum oxide were synthesized by annealing mixtures of two oxide powders, aluminum oxide with an additive. Using high-angle annular dark field scanning transmission electron microscopy, the adsorbed layers were characterized, and image simulations aided interpretation of the results. The adlayers were pseudomorphic, one atomic layer thick and with a fractional site occupancy. Atomic positions of the adlayer atoms relaxed and changed relative to the bulk structure, where there is evidence that the magnitude of the relaxation is sensitive to the ionic radius of the adsorbate. The pseudomorphic adlayer structure formed for different elements including, but not limited to, the lanthanides (i.e., Ge, Ba and Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm).

Keywords

adsorption; aluminum oxide; pseudomorphic; scanning transmission electron microscopy

Introduction

Reports on aluminum oxide exemplify how solute segregation (or adsorption) to interfaces (solid-solid or solid-vapor) can affect the properties of a ceramic. For example, grain boundary segregation of different dopants, including Ca, Nd, Si and Y, in corundum phase aluminum oxide ($\alpha\text{-Al}_2\text{O}_3$) has been correlated to changes in grain boundary mobility.(1-3) A model has been proposed where the thickness of the segregant layer (classified as interfacial complexions) has a distinct grain boundary transport rate. (4) Functional properties of $\alpha\text{-Al}_2\text{O}_3$ also change in response to interfacial segregation, such as an improvement in creep resistance when doped with Nd, Zr, Lu, La, or Y(5-10) and an increase in the occurrence of intergranular fracture when doped with Y, Gd, or La.(11) To explain this observation, it has been hypothesized that segregants alter the electronic band structure of $\alpha\text{-Al}_2\text{O}_3$ near interfaces, thereby affecting the charge compensation mechanisms and resulting point defect composition.(12) Examples are not limited to bulk ceramics and grain boundaries, adsorption of La to the surfaces of gamma phase aluminum oxide ($\gamma\text{-Al}_2\text{O}_3$) powders reportedly stabilizes $\gamma\text{-Al}_2\text{O}_3$ at elevated temperatures against coarsening and transformation to the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ phase.(13)

Complementary to correlating interfacial segregation with property relationships, is the practice of characterizing the structure of interfacial layers and identifying the processing conditions under which interfacial layers form. Studies on Ca- and Mg-doped sapphire substrates identified interfacial layers which formed as the solute segregated to the surface from the bulk of the material.(14-16) It was observed that the interfacial layer was sensitive to annealing temperature and surface termination. On (0001) surfaces no segregation of Ca was detected when annealed between 800 °C and 1500 °C. While on (10 $\bar{1}$ 0) surfaces, significant Ca segregation was measured on samples annealed above 1300 °C with less Ca segregation on samples annealed below 1300 °C.(14) Low energy electron diffraction (LEED) identified a $\sqrt{31}\times\sqrt{31}$ R9° surface reconstruction on the (0001) surface of a crystal doped with Mg when annealed at temperatures between 1200 °C and 1500 °C.(15) While LEED patterns recorded from (10 $\bar{1}$ 0)

surfaces annealed at 1200 °C and 1300 °C of crystals doped with Ca were indexed as (1x1) and (2x1) surface structures, respectively.

Only a brief mention will be made because the focus of this work is on the α -Al₂O₃ phase; a large body of work from the catalysis community studied the adsorption of different elements to the surfaces of γ -Al₂O₃ and a broad swath of the periodic table has been interrogated, including rare earths and transition metals such as V, Mo, and W.(13, 17-22) Because this work was conducted using powders it made atomic-level structure characterization and determination difficult and the structures were often inferred and described in general terms like “monolayer”.(17, 22) For example, x-ray diffraction acquired from samples after annealing suggested the formation of monolayers due to the disappearance of reflections associated with the bulk phase of the additive.(17, 23) When used, high resolution electron microscopy (HREM) was able to provide additional information on the structure of the adsorbates on γ -Al₂O₃. Amorphous and ordered bi-layer MoO₃ films were observed,(24) and by comparison, La was reported to adsorb as isolated atoms, rather than as clusters or monolayers.(13) In general, HREM has proven useful in characterizing the surface structure of oxide particles.(25, 26)

To further explore the formation of adlayers on aluminum oxide surfaces we combined α -Al₂O₃, in the form of a powder, with a series of different additives, with a particular focus on the lanthanide series; lanthanide interfacial layers have been reported to affect the properties of aluminum oxide.(3, 5, 6, 8, 9, 13) Further, the lanthanide series exhibit systematic variations in properties, e.g., ionic radius or bulk lattice parameter, which monotonically decreases with increasing atomic number.(27) This helps to identify changes in adlayer formation as a function of a specific property. Additional elements were screened to provide a comparison to elements that are distinctly different from the lanthanides. After heat treating the powders, the C-plane (0001) and R-plane ($1\bar{1}02$) terminated surfaces were characterized using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Pseudomorphic adlayers one atomic layer thick were observed to form for a range of processing

conditions (i.e., annealing temperature and time, cooling rate, and additive concentration) as well as for different additives (i.e., Ge, Ba and Ln = La, Ce Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er or Tm).

Experimental Procedure

Sample Preparation

Aluminum oxide powder (corundum, Alfa Aesar¹, 99.9985 % metals basis) was combined with the additive oxide at a concentration of 2 atomic percent, except in the case of Dy₂O₃ oxide where 5 atomic percent was used. These oxides were 99.9 % pure or greater (metals basis or rare earth oxide) except for BaO (99.5 %) and Tm₂O₃ (unspecified) and were sourced from various vendors, although, most were from Alfa Aesar. The powders were added to high density polyethylene jars with a radius of 3.78 cm along with isopropanol and 3 mm and 8 mm diameter aluminum oxide milling balls. The powders were milled at a rate of 3.14 rad s⁻¹ (30 rpm) in a planetary ball mill with a radius of approximately 10 cm for a period of (50 to 70) minutes. The isopropanol was evaporated, and the resultant powder collected and stored until heat treatment.

Samples were placed in a platinum crucible and hung in a vertical tube furnace. Heat treatments were conducted in air at a temperature of 1100 °C for 2 hours, unless indicated otherwise, and quenched in air to room temperature by lifting the crucible from the furnace and placing it on a metal plate in ambient conditions.

A sample prepared on a single crystal surface was included for comparison. A 5 mm x 5 mm R-plane terminated single crystal (MTI Corporation) was used as received. La₂O₃ powder was dispersed into

¹ Certain commercial products or company names are identified here to describe our study adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the products or names identified are necessarily the best available for the purpose.

isopropanol. A drop of the suspension was placed onto the surface of the crystal and allowed to dry under ambient conditions. The targeted mass of La_2O_3 deposited onto the crystal surface was approximately 11 mg, although the actual amount of La_2O_3 deposited was not independently measured. The sample was heated in the same manner as the powder samples. A TEM sample was prepared using a dual beam focus ion beam (FIB) microscope with gallium ion source. To protect the surface, a thin amorphous carbon coating was deposited using a carbon evaporation source and then a platinum/carbon layer was deposited using the electron beam at an accelerating voltage of 5 kV. Initial cuts and thinning of the lift-out sample were made using an accelerating voltage of 30 kV and final thinning was conducted at an accelerating voltage of 5 kV to mitigate surface damage.

Characterization

Powders were dispersed directly onto carbon films supported by copper grids with no additional treatment. Scanning transmission electron microscopy (STEM) data were acquired on a microscope equipped with aberration-corrected probe-forming optics. The accelerating voltage was 300 kV and the probe convergence semi-angle was 14 mrad. The probe current, as measured with a previously calibrated fluorescent screen, was typically (5 to 30) pA. High-angle annular dark field images were acquired using a Fischione Model 3000 annular detector. The inner collection semi-angle for HAADF imaging was 70 mrad. Stacks of images were acquired with dwell times of 2 μs or less. Images stacks were aligned by rigid alignment(28) and then summed using Fiji.(29, 30)

Multislice image simulations implementing the frozen phonon algorithm were computed using Dr. Probe.(31) Accelerating voltage (300 kV) and collection semi-angles (70 mrad to 190 mrad) replicated experimental conditions, all aberrations were set to zero and resultant images were convoluted with Gaussian function of 0.05 nm half width at half maximum to account for the effective source size. The

probe position sampling step size was 0.015 nm and supercell thicknesses were between approximately 18 nm and 22 nm.

Results

The α -Al₂O₃ particles were a mixture of morphologies including ellipsoids and elliptical discs, frequently with holes. Surface terminations included, but were not exclusively, C-plane (0001) and R-plane ($1\bar{1}02$).

STEM imaging of an annealed powder shows a mixture of both α -Al₂O₃ and La₂O₃ particles (Figure 1a).

When the surface normal is orthogonal to the electron beam, there is a sharp increase in the HAADF image intensity at surfaces of the α -Al₂O₃ particles (Figure 1b). In pure α -Al₂O₃ samples no such behavior was observed (Figure 1c). Because HAADF-STEM image intensity is proportional to atomic number, this indicates that La is adsorbing at the α -Al₂O₃ surface. This can be confirmed by elemental analysis.

Electron energy loss spectroscopy (EELS) detects La at the outermost atomic layer (Figure 1d), the region of increased intensity in the HAADF image.

Two different surfaces – C-plane (0001) and R-plane ($1\bar{1}02$) – were imaged with the surface normal perpendicular to the electron beam. C-plane terminated surfaces were viewed along $\langle 11\bar{2}0 \rangle$ and $\langle 10\bar{1}0 \rangle$ directions (Figure 2) and R-plane terminated surfaces were viewed along $\langle 10\bar{1}1 \rangle$ and $\langle 02\bar{2}1 \rangle$ directions (Figure 3). Atomic resolution images reveal the La atoms form a pseudomorphic adlayer, where the La atoms are in registry with the Al sublattice. Intercolumn HAADF signal variations within the La adlayer (Figure 2c) indicate the number of atoms in each column along the electron beam direction is different, that is, vacancies are present in the adsorbate layer. The presence of vacancies is not unique or unexpected as some equilibrium concentration of vacancies will exist. Rather it is distinctive that the magnitude of the intercolumn variation of the HAADF signal is easily perceptible by visual inspection. Due to dynamical scattering of the electron beam and incomplete information about the structure, quantification of the number of atoms per column (concentration of vacancies) is not possible. A crude

qualitative comparison was made with simulated images (Figure 2d), where vacancies were inserted randomly into the adlayer with a probability of 40 % at each cation site, which roughly mimicked the nature of the experimental HAADF signal variations (Figure 2c). Furthermore, these HAADF signal variations were not periodic (no additional reflections are present in the Fourier transform of the images). Making a distinction between periodic and aperiodic signal variations is relevant because a surface reconstruction (i.e., a unit cell different from the underlying bulk structure) when viewed in projection, by nature of having a unit cell different than or rotated relative to the underlying bulk structure, would potentially lead to periodic variations of the HAADF signal. Therefore, this lack of periodicity suggests that the vacancies do not exhibit long-range order and that a surface reconstruction has not formed. However, this structural assignment was made using projected images of the sample observed from only two crystallographic directions and surface reconstructions cannot be unequivocally ruled out. Extended defects (vacancy clustering) could also be possible.

Pseudomorphic adlayer models were constructed as input for multislice image simulations (results shown in Figures 2 and 3) to compare with the experimental results. In these models, representing C- and R-plane terminated surfaces, the terminating surface layer of Al atoms was replaced by La atoms to create the adlayer. Creating the surface requires terminating the bulk α -Al₂O₃ structure at a specific location within the atomic layer stacking sequence. Along the c-axis of α -Al₂O₃ where the (0001) surface is created, the α -Al₂O₃ atomic layers stack in a *R*-O-Al-Al-O-Al-Al-O-Al-Al-*R* sequence, where Al and O represent the Al and O atomic layers and *R* represents continuation of the stacking sequence of the bulk structure. Accordingly, in a sample without an adlayer or reconstructed surface, the (0001) surface is either terminated by an O layer (i.e., *R*-O-Al-Al-O), a single Al layer (i.e., *R*-O-Al-Al-O-Al) or a double Al layer (i.e., *R*-O-Al-Al-O-Al-Al). We are not able to determine if the surface is O terminated using HAADF-STEM, but we are able to distinguish if the surface is terminated by a single or double cation layer. The most frequently observed termination sequence was a double cation layer, that is, *R*-O-Al-Al-O-Al-AE,

where AE is the adsorbate element, as exemplified in Figure 2 and for the majority of the elements shown in Figure 6. However, a sample prepared using GeO_2 (Figure 6) exhibited the single cation layer termination sequence, that is, $R\text{-O-Al-Al-O-AE}$. While on R-plane or $(1\bar{1}02)$ terminated surfaces, the position in the atomic layer stacking sequence where the adlayer element substituted the Al layer was identical for all samples. The atomic layers of $\alpha\text{-Al}_2\text{O}_3$ arrange in a sequence of $R\text{-O-Al-O-Al-O-R}$ normal to the $(1\bar{1}02)$ plane and $R\text{-O-Al-O-Al-O-O-AE}$ was the observed stacking sequence (Figure 3 and Figure 7). Simulated images better replicated the experimental results for both C- and R-plane terminated surfaces when the position of the La atoms were shifted from the Al (cation) basis site in the corundum unit cell, indicating that the La atoms have relaxed. The directions of these shifts are indicated in the models of Figures 2 and 3. On C-plane terminated surfaces, the La atoms were shifted in the $[0001]$ direction away from the bulk structure. On R-plane terminated surfaces, the La atoms were shifted normal to the $(1\bar{1}02)$ plane away from the bulk structure and alternatively shifted in opposing $[\bar{1}2\bar{1}0]$ and $[1\bar{2}10]$ directions, to contract pairs of atomic columns (as viewed in projection) towards one another. Because the images are projections of the structure along the beam direction, there is some ambiguity about the directional assignment, as shifting the atoms in other directions could also produce a similar appearance of pairs of atomic columns contracting towards one another.

The magnitude of the La adlayer relaxation on R-plane terminated surfaces was compared with an adsorbate, Er, of smaller ionic radius ($\text{La}^{3+} = 0.1032 \text{ nm}$ vs. $\text{Er}^{3+} = 0.089$).⁽³²⁾ To promote more homogenous coverage of the $\alpha\text{-Al}_2\text{O}_3$ powder, the additive concentration was increased to 5 atomic percent and samples were heated at a temperature of 1100°C for approximately 20 hours. Stacks of 12 to 16 images were acquired with dwell times of $1 \mu\text{s}$ and all images used in this comparison between La and Er were acquired at the same magnification. The probe current was 5 pA or less. For each sample, images were acquired from multiple particles and in some cases more than one region of the same particle. Images were aligned using rigid registration. Short dwell times and rigid registration will

minimize but not eliminate distortions introduced by instabilities such as sample drift. However, image acquisition conditions were nominally the same for both samples, therefore the precision and accuracy of the analysis may be similar. To quantify the magnitude of the relaxation, the x-y coordinates of individual atomic columns were fit with a two-dimensional elliptical Gaussian function, enabling sub-pixel accuracy, using the program Atomap.⁽³³⁾ The absorbate-Al distance was compared to a reference region, comprised of the immediately adjacent Al-Al interplanar spacings. An example image with the atomic columns labeled is shown in Figure 4a. The distance measurements were made in pixels and to calibrate the scale, the interplanar spacing of the Al-Al atomic columns in the reference region were assumed to be equal to 0.3478 nm. A violin plot comparing data from the two samples is shown in Figure 4b. The La adlayer relaxed an average of 0.048 nm (0.018 nm) while the Er adlayer relaxed an average of 0.021 nm (0.015 nm), where the value in parentheses is one standard deviation about the mean. These distances are Euclidean; therefore, the direction of the relaxation could be both normal and lateral to the surface.

A series of experiments tested the extent of conditions under which La adlayers formed. From the original set of experimental parameters a single parameter was changed while holding everything else constant: The sample was annealed at 500 °C for 144 h rather than at 1100 °C for 2 h; the sample was annealed at 1500 °C for 20 min rather than at 1100 °C for 2 h; the sample was cooled at a rate of 20 °C h⁻¹ rather than quenched; the sample was annealed for a period of 72 h rather than for 2 h; La₂O₃ was added at a concentration of 10 atomic percent to the α -Al₂O₃ rather than at 2 atomic percent; La₂O₃ was deposited onto a R-plane terminated single crystal substrate rather than a powder. In this case two parameters were changed because the concentration of La₂O₃ was no longer 2 atomic percent. All these results on R-plane terminated surfaces (Figure 5) show a pseudomorphic layer of La atoms one atomic layer thick; the same result as the baseline set of experiments. Although, in some experiments with C- and R-plane terminated *single crystals* it was observed (not shown) other adlayer structures could form

in addition to the pseudomorphic monolayer structure. Studies on single crystals are on-going to better understand these observations.

Other oxide additives were screened, and on (0001) surfaces Ge, Ba, Ce, Pr, Nd, Sm, Eu, Gd and Dy formed pseudomorphic adlayers (Figure 6). While Ba, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er and Tm formed pseudomorphic adlayers on ($\bar{1}\bar{1}02$) surfaces (Figure 7). The limited sampling capability of TEM combined with inhomogeneous samples where adlayer coverage may not be complete can yield false negatives, which is why we are not listing samples where evidence of pseudomorphic adlayers was inconclusive. It is worth noting, there is evidence that other elements, beyond the scope of our study, can also form pseudomorphic monolayers on α -Al₂O₃. It was reported that a Te pseudomorphic monolayer formed on (0001) α -Al₂O₃ during deposition of a film.(34)

Discussion

The HAADF-STEM results showed that adsorbates formed as a pseudomorphic adlayer with a maximum thickness of one monolayer. One atomic layer is presumably the thermodynamic equilibrium of these α -Al₂O₃-pseudomorphic adsorbate systems, as increasing annealing time or the amount of additive when processing the samples did not change the result, neither did changing the annealing temperature or cooling rate. Using a simple model this monolayer limit can be understood as a balance between different energetic driving forces, strain energy and surface energy. Adsorption of the additives lowers the surface energy of the α -Al₂O₃ and this comes at a penalty of elastic strain energy. Because the adlayer formed, we can infer that the reduction in surface energy is greater than the gain in strain energy. Growth of additional layers would further increase the strain energy of the system, however, the decrease in surface energy would be based on the interfacial energy of the adlayer-vapor interface rather than the α -Al₂O₃-vapor interface, a process and energy balance similar to epitaxial film growth. Unlike thin film growth, in the present experiments, the source of the adsorbates is present in bulk form

and interspersed with the α -Al₂O₃. Therefore, if reduction of the surface energy and the total energy of the system is no longer sufficient to offset the strain energy or other energetic penalties, there will not be a net diffusion of cations from the additive particles to the α -Al₂O₃ particles and the number of adlayers do not increase beyond one.

The isovalent lanthanide adsorbates have ionic radii with a range between 0.1032 nm (La³⁺) to 0.088 nm (Tm³⁺), compared to 0.0535 nm of the Al³⁺ host cations.(32) Pseudomorphic adlayers were also able to form with aliovalent adsorbates of Ba and Ge, which have preferred formal oxidation states of 2+ and 4+, respectively. When considered from the perspective of the hard sphere model and the bond valence sum (BVS) model – where the standard bond length of the adsorbate-oxygen bond is greater than the Al-O bond lengths(35) – this suggests there are mechanisms active that enable the pseudomorphic adlayer structure to accommodate a range of adsorbate cations with different degrees of size mismatch or valence. Three experimental observations were made: (1) there was a relaxation of the adlayer atomic positions; (2) there were vacancies in the adlayer; (3) the position where the α -Al₂O₃ unit cell is truncated to create the surface was not fixed. A comparison of La and Er adlayers on R-plane terminated surfaces revealed that the magnitude of the relaxation increased as the ionic radii of the adsorbate increased, suggesting the magnitude of bond relaxation may be proportional to the ionic radius of the adsorbate. While vacancies are present in the adlayer, it was not possible to quantify the concentration and identify any trends as a function of adsorbate. However, the vacancy concentration may be proportional to ionic radius to accommodate adsorbates with ionic radii larger than host cation. The position in the atomic layer stacking sequence where the adlayer formed changed in the case of an aliovalent adsorbate (Ge) on the C-plane surface. Changing the position of the surface termination changes the local bonding environment, which, depending on the characteristics of the specific adsorbate, may better facilitate minimizing the potential energy of the system. Exploring additional aliovalent additives could help to determine if this is a prevalent phenomenon. In the absence of a

complete structure determination of the adlayer and underlying $\alpha\text{-Al}_2\text{O}_3$ we can only speculate which of these (or other) specific mechanism(s) is relevant. Complete structure determination would also illuminate how the surface atoms have been compensated such that the total valence is zero.

The observed adlayer structure is nominally the same for a range of elements, which presents opportunities for systematic studies as a function the adsorbate element. The low dimensionality of the adlayers and band offset and charge transfer between $\alpha\text{-Al}_2\text{O}_3$ and the adlayer could result in unique electronic, magnetic or chemical reactivity characteristics. Besides the possibility of possessing unique functional properties this observation may be useful for studying complexions, a term that has been recently conceived to described an “interfacial material or strata that is in thermodynamic equilibrium with the abutting phase(s) and has a stable, finite thickness”.⁽³⁶⁾ Understanding their phase-like behavior has been recognized as a “grand challenge” in ceramic science.⁽³⁷⁾ This challenge explicitly targets internal interfaces, however, studies on surfaces could provide complementary information to studies on grain boundaries, as there are structural similarities between the adlayers here and a report on the adsorption of Nd to a grain boundary in $\alpha\text{-Al}_2\text{O}_3$.⁽³⁸⁾ A total of two atomic layers of Nd were present in the grain boundary, where one atomic layer of Nd was believed to have adsorbed to each respective face of the two grains making up the grain boundary. One of the $\alpha\text{-Al}_2\text{O}_3$ grains was viewed along a $\langle 02\text{-}21 \rangle$ was terminated by a $\{1\bar{1}02\}$ plane. Nd adsorbed on the $\{1\bar{1}02\}$ plane was described as “close to the aluminum cation sites” and “position of the cations is slightly shifted from the perfect aluminum cation sites”.⁽³⁸⁾ A structure we interpret as a pseudomorphic monolayer and nominally the same structure we report on the R-plane terminated surfaces here. The other grain was not orientated appropriately for atomic resolution imaging, making it impossible to discern the relationship of that adlayer with respect to the underlying grain. Assuming the similarity of the results between the interfacial layer at a surface and an internal interface can be confirmed, joint studies of surfaces and internal interfaces may be useful. Surfaces can be characterized using a different set of techniques than

internal interfaces, such as, scanning probe, LEED, or transmission electron microscopy techniques in a plane view geometry. Additionally, surfaces may afford the opportunity to identify trends and test ideas more readily before moving onto the more complex phase space of grain boundaries.

Conclusions

Adlayers were observed to form on C- and R-plane terminated surfaces of α -Al₂O₃ particles. The adsorbed layers are pseudomorphic and one atomic layer thick. This same structure was observed for a series of different elements. Designing experiments to elucidate the complex relationships between the properties of interfaces is often challenging due to the large phase space of variables and the inability to precisely introduce variations systematically. As such, this creates an opportunity for systematic studies on properties of the adlayers themselves or how the adlayers impact functional properties or processing, such as catalysis and epitaxial growth, respectively.

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Author Contributions

Aaron C. Johnston-Peck (leader): design, sample preparation, data acquisition and analysis, writing.

Russell A. Maier (contributor): design, sample preparation, writing.

Conflicts of Interests

The authors declare no competing financial interests.

Figures

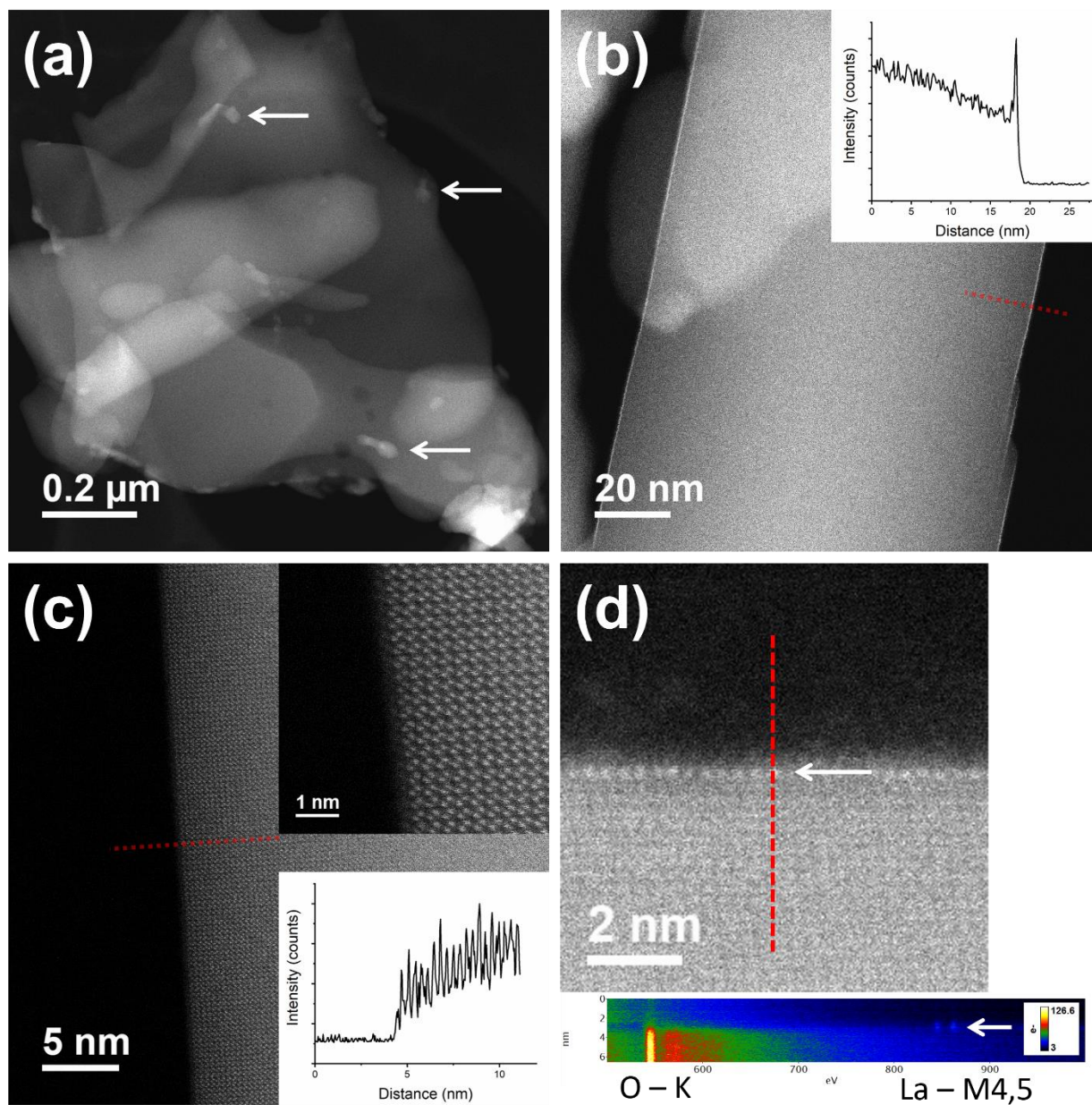


Figure 1. HAADF images of α - Al_2O_3 particles and La_2O_3 particles, examples indicated by arrows, after annealing (a). Along the surface of an α - Al_2O_3 particle (b) there is an increase in intensity indicating the adsorption of a higher atomic number element. The inset in (b) is the intensity profile along the dashed line. A undoped sample (c) has no such intensity increase at the surface. The inset in (c) is the extracted

intensity profile along the dashed line. EELS detects the presence La at the surface (d). The dashed red line indicates the location of the line scan while the arrows point to the corresponding position in the image intensity profile and the EELS data (position vs. energy loss).

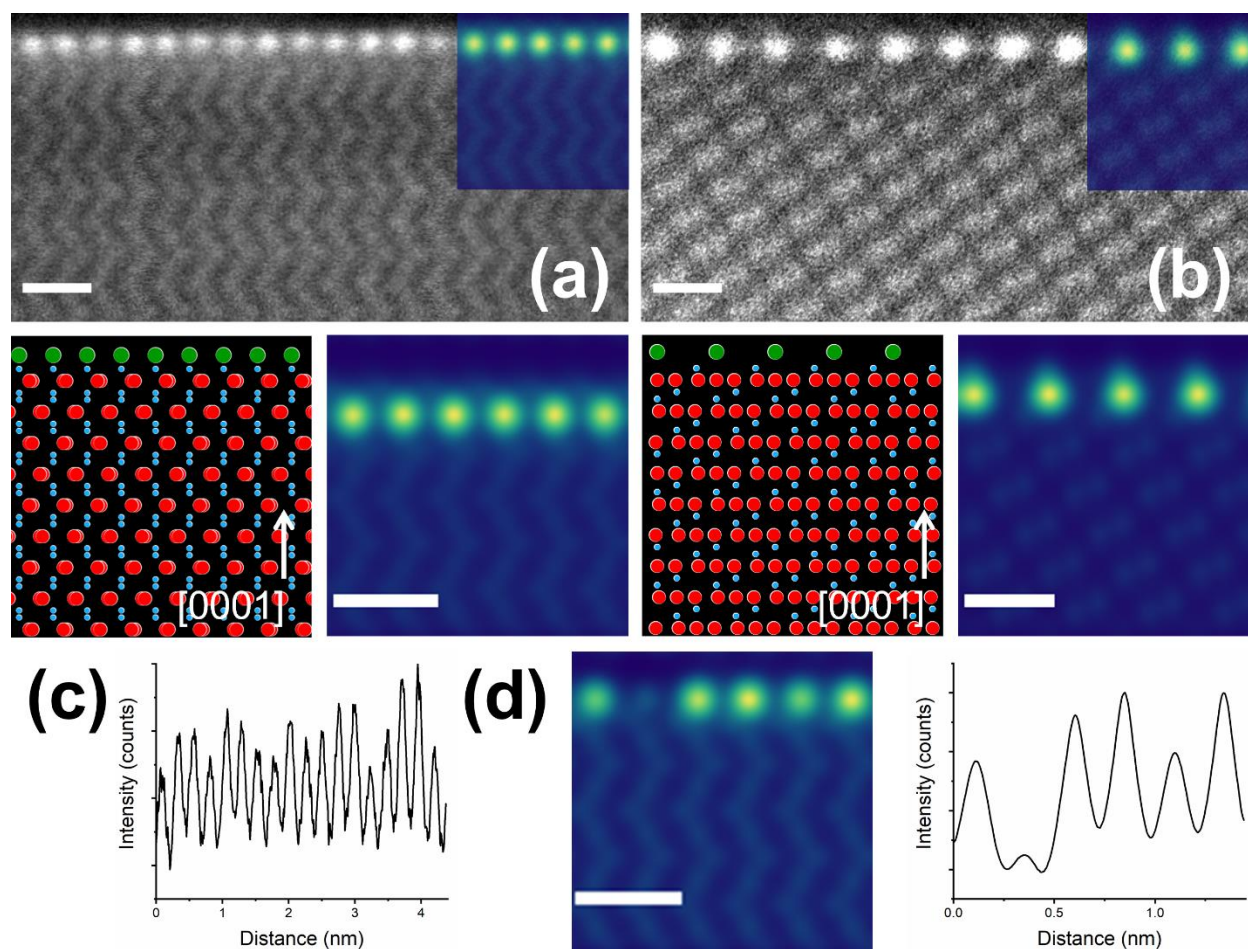


Figure 2. Images of La adlayers on α - Al_2O_3 (0001) terminated surfaces viewed along $\langle 10\bar{1}0 \rangle$ (a) and $\langle 11\bar{2}0 \rangle$ (b). Along with each HAADF image is an atomic model (Blue – Al, Red – O, Green – La) of the surface and the corresponding simulated image. The image intensity profile (c) from the La adlayer in (a) displays non-periodic variations in intensity suggesting the presence of vacancies. A multislice simulation including vacancies (d) along with the intensity profile from the La adlayer depicts similar behavior as the experimental data. A copy of the simulated image is also overlaid on the HAADF image. Scale bars are equal to 0.5 nm.

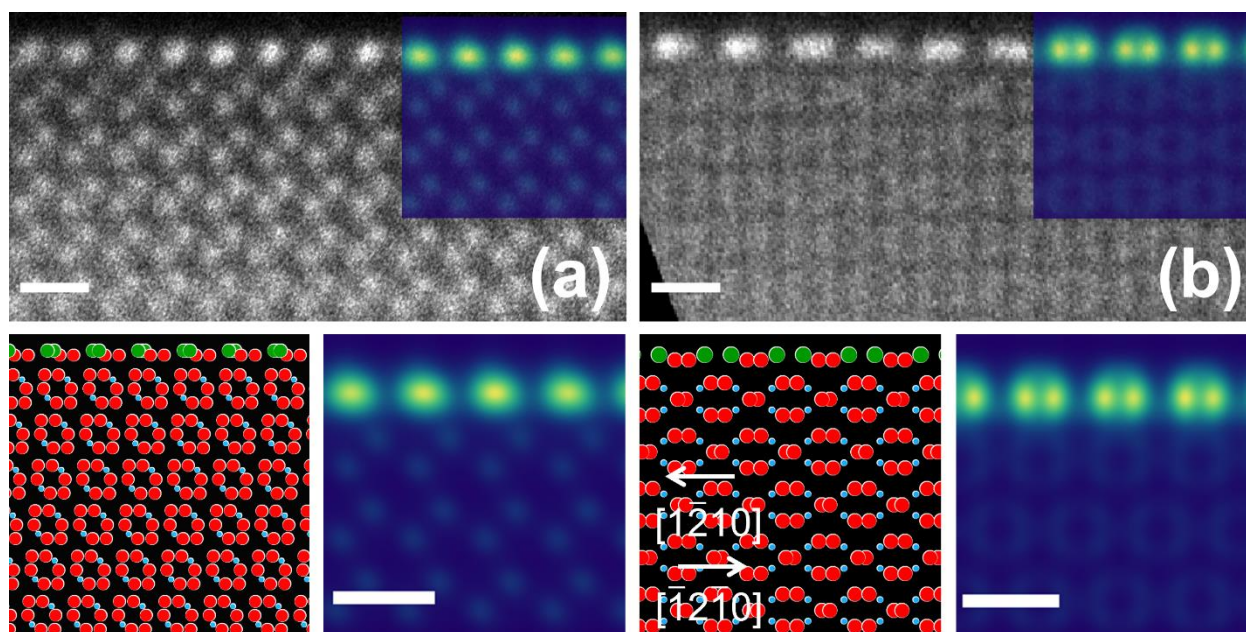


Figure 3. Images of La adlayers on $\alpha\text{-Al}_2\text{O}_3$ ($1\bar{1}02$) terminated surfaces viewed along $\langle 02\bar{2}1 \rangle$ (a) and $\langle 10\bar{1}1 \rangle$ (b) Along with each HAADF image is an atomic model (Blue – Al, Red – O, Green – La) of the surface and the corresponding simulated image. A copy of the simulated image is also overlaid on the HAADF image. Scale bars are equal to 0.5 nm.

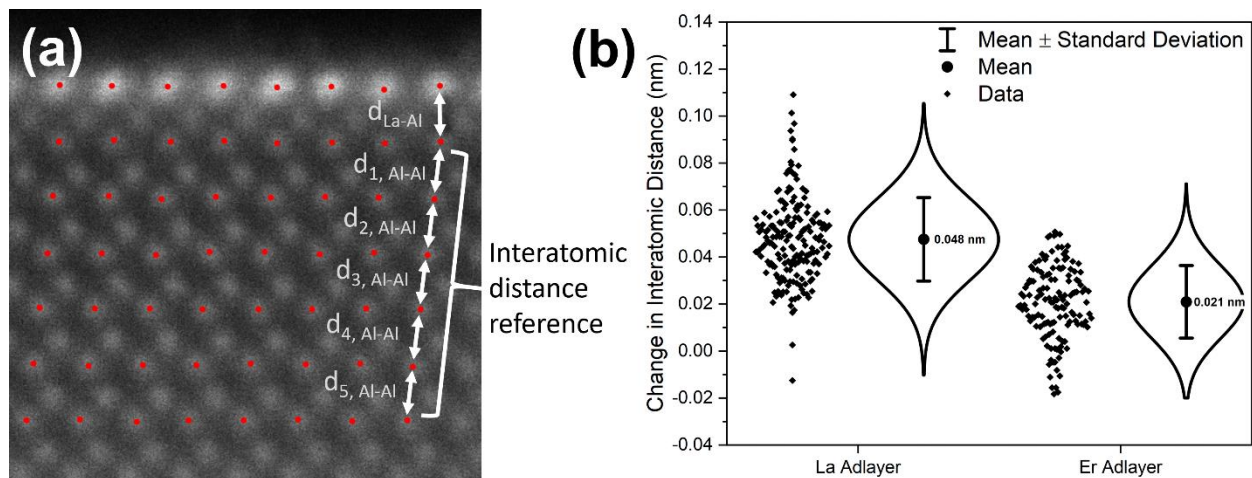


Figure 4. Example image of a La adlayer on a ($1\bar{1}02$) terminated surface used to determine the magnitude of adlayer relaxation (a). Each red dot marks the center of the two-dimensional Gaussian fit to an atomic column. The distance between the La atomic column and Al column is labeled as $d_{\text{La-Al}}$, while the distance between Al columns on adjacent ($1\bar{1}02$) planes are labeled as $d_{n,\text{Al-Al}}$ these distances were assumed to be equal to 0.3478 nm and functioned as an internal distance calibration to quantify $d_{\text{La-Al}}$. Violin plots comparing the interatomic distance of La and Er adlayers indicate that the La-Al distance is greater than the Er-Al distance (b). Data points corresponding to values from individual atomic columns are on the left while a normal distribution fit to the data is shown on the right. The mean value and a set of whiskers indicating one standard deviation about the mean is included.

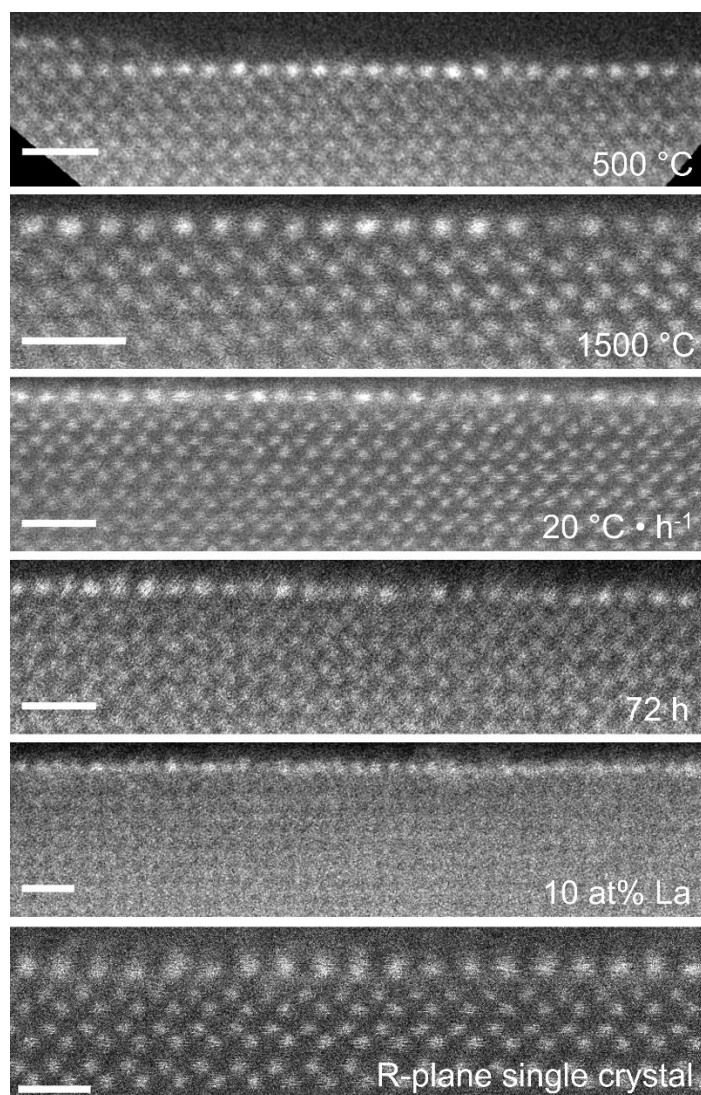


Figure 5. Formation of La adlayers on R-plane terminated surfaces as function of experimental conditions. The baseline synthesis was annealing a sample loaded with 2 atomic percent of metal oxide at 1100 °C for 2 hours and quenching the sample to room temperature. The following changes to processing conditions did not change the resultant structure: annealed at 500 °C for 144 h; annealed at 1500 °C for 20 min; cooled from 1100 °C at a rate of 20 °C h⁻¹; annealed at 1100 °C for 72 h; loaded with 10 atomic percent La; a single crystal substrate rather than powder α -Al₂O₃. Scale bars are equal to 1 nm.

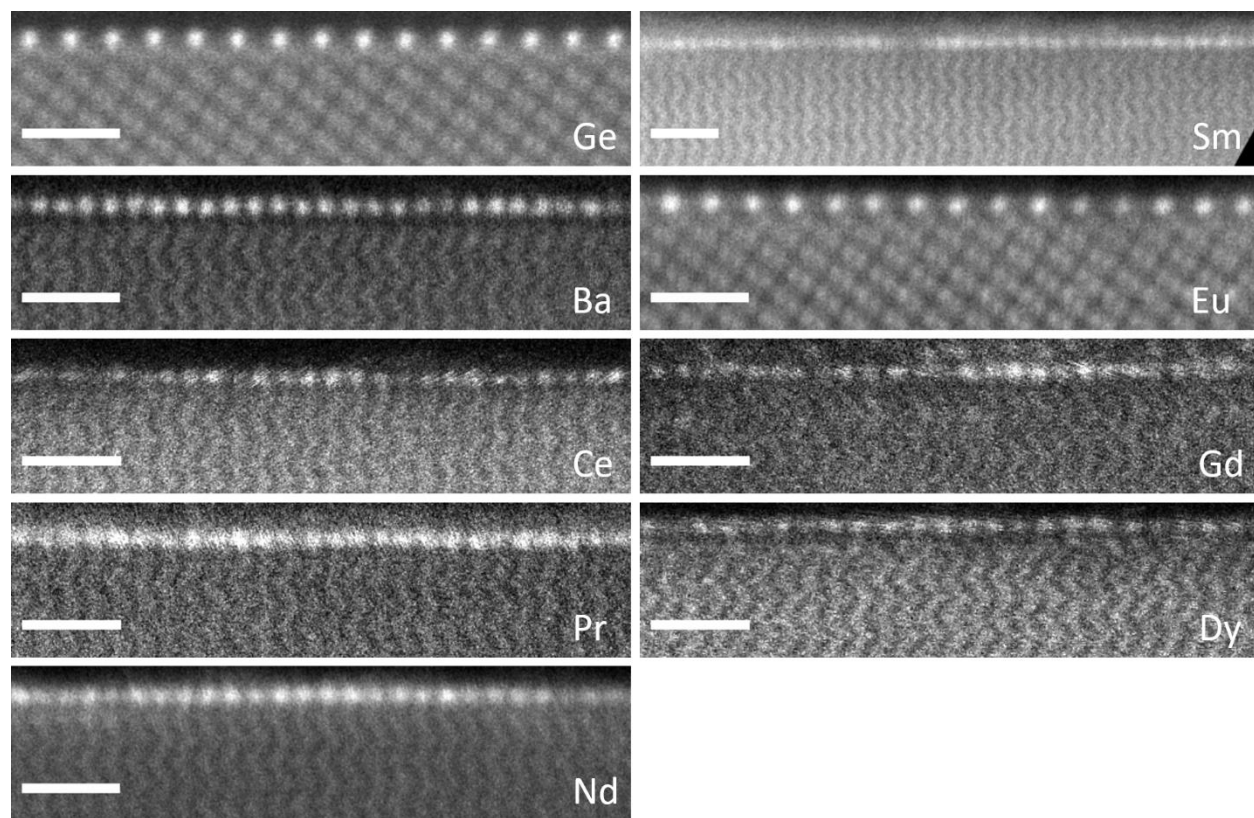


Figure 6. Formation of adlayers on C-plane terminated surfaces. Scale bars are equal to 1 nm.

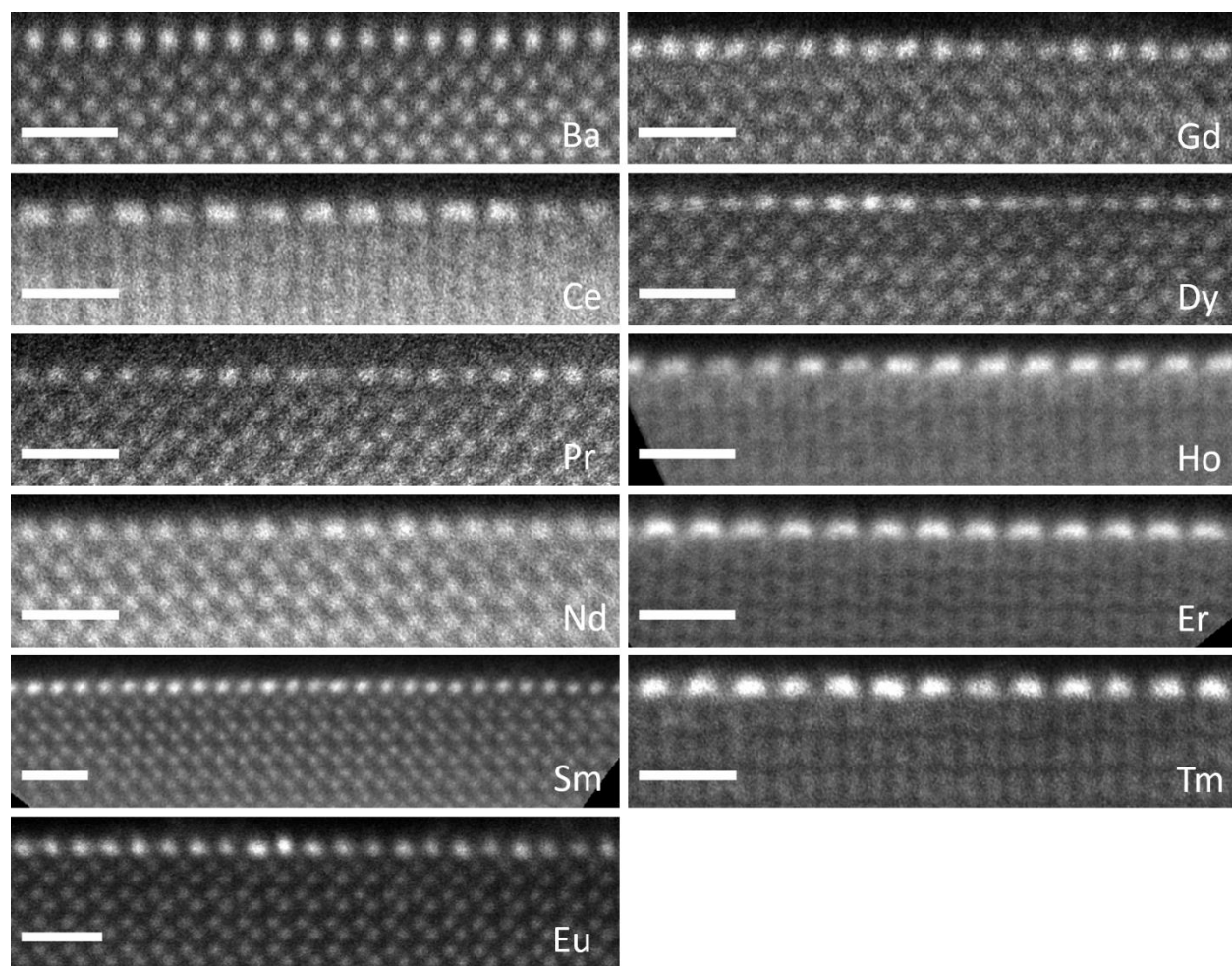


Figure 7. Formation of adlayers on R-plane terminated surfaces. Scale bars are equal to 1 nm.

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