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Cite as: APL Mater. 5, 086103 (2017); https://doi.org/10.1063/1.4992004
Submitted: 25 June 2017 . Accepted: 28 July 2017 . Published Online: 08 August 2017

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Exposing high-energy surfaces by rapid-anneal solid phase epitaxy

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(Received 25 June 2017; accepted 28 July 2017; published online 8 August 2017)

The functional design of transition metal oxide heterostructures depends critically on the growth of atomically flat epitaxial thin films. Often, improved functionality is expected for heterostructures and surfaces with orientations that do not have the lowest surface free energy. For example, crystal faces with a high surface free energy, such as rutile (001) planes, frequently exhibit higher catalytic activities but are correspondingly harder to synthesize due to faceting transitions. Here we propose a broadly applicable rapid-anneal solid phase epitaxial synthesis approach for the creation of nanometer thin, high surface free energy oxide heterostructures that are atomically flat. We demonstrate its efficacy by synthesizing atomically flat epitaxial RuO$_2$(001) and TiO$_2$(001) model systems. The former have a superior oxygen evolution activity, quantified by their lower onset potential and higher current density, relative to that of more common RuO$_2$(110) films. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

Transition metal oxides (TMOs) exhibit a broad range of properties with numerous potential applications. These properties come about due to strong interactions between lattice, charge, and spin degrees of freedom. Efforts to tailor their functionality have therefore focused on creating nanoscale epitaxial TMO heterostructures that manipulate the atomic structure, electronic band-width and band-filling, and exchange interactions. The well-controlled epitaxial oxide film growth that is necessary for such advanced tailoring critically hinges on morphological control of the growth front, which needs to be kept atomically flat. This prerequisite has limited the availability of two-dimensional (2D) oxide heterostructures largely to material systems grown in morphologically stable orientations with a low surface free energy, e.g., the perovskite (001) and rutile (110) surfaces. For nanoscale two-dimensional (2D) heterostructures, where the surface to volume ratio diverges, the surface free energy thus increasingly restricts the crystallographic phase space for 2D heterostructure synthesis to those with low surface energies. A synthesis approach that is able to overcome this limitation would open new possibilities in producing novel 2D heterostructures and functionally important surface orientations, e.g., for oxide electronics and catalytic applications.

In this work, we demonstrate that it is possible to circumvent these limitations and epitaxially synthesize atomically flat, high surface free energy single crystal transition metal oxide films by means of a modified approach to solid phase epitaxy (SPE); rapid-anneal solid phase epitaxy (RASPE). In conventional SPE, film deposition occurs at temperatures low enough to produce flat, amorphous films which are subsequently epitaxially crystallized by a conventional post-annealing treatment, facilitating the creation of high doping levels and sharp doping profiles, as well as the synthesis of phases with crystal structures or stoichiometries that are otherwise not accessible. However,
for materials with a high surface free energy, the post-annealing treatment enables a transition to a faceted morphology. Here, our purpose is to synthesize atomically flat oxide heterostructures in crystallographic orientations exposing surfaces with high surface energies that are not achievable with conventional SPE. Specifically, by keeping the annealing temperature and time sufficiently low and short, respectively, the amorphous film crystallizes epitaxially while the atomic diffusion length is adequately limited, preventing the formation of a lower energy, faceted surface. Since the minimum temperature necessary for crystallization does necessarily allow for some atomic mobility, the critical ingredient is to keep the annealing time exceedingly short. This is made possible using a laser-based fast heating system incorporated in the ultra-high vacuum (UHV) growth chamber that allows us to constrain the kinetics of the crystallization process much more than in conventional SPE.

We utilize rutile TiO$_2$(001) substrates, featuring the highest surface free energy among the rutile low index facets,$^{20}$ to grow and characterize atomically flat epitaxial RuO$_2$ and homoepitaxial TiO$_2$ thin films. Furthermore, since RuO$_2$ is known to be a good catalyst for the oxygen evolution reaction (OER) and CO oxidation,$^{21-24}$ and the surface free energy is a potential descriptor of catalytic activity,$^{25-27}$ we compare the OER activity of these high surface free energy, (001)-oriented RuO$_2$ films with that of low surface energy, atomically flat RuO$_2$(110) thin films that were grown using conventional oxide molecular beam epitaxy (MBE). The results show a superior OER activity on the RASPE-grown RuO$_2$(001) surface, with a significantly reduced onset potential and an enhanced current density. While the results presented here are based on a model system of single crystalline RuO$_2$(001) films, they firmly establish rapid-anneal solid phase epitaxy as an approach that expands the access to novel 2D oxide heterostructures with improved functionality and suggest a path toward improved OER active RuO$_2$ catalysts.

While conventional MBE growth of RuO$_2$(110) results in high quality films,$^{28}$ attempts to duplicate this in the (001) orientation consistently result in a faceted morphology, even when the growth temperature is reduced to the point that grainy films are grown, see supplementary material Notes 1, 2, and 3. We have therefore constrained the growth kinetics even more using RASPE. Specifically, we deposit amorphous ruthenium oxide (am-RuO$_2$) with a thickness of ~1.5 nm at room temperature (RT) and subsequently flash-anneal the as-deposited film to 220 °C for a very short time of ~10 s in an O$_2$ pressure of 6.0 × 10$^{-6}$ mbar, after which the heating is switched off. These steps can be repeated to grow thicker films. RHEED reveals that after one cycle of RASPE, the pattern of fractional order spots from the TiO$_2$(001)-c(7√2 × 5√2)R45° reconstruction$^{20}$ has developed into a pattern of parallel streaks with a set of weak fractional order streaks from a (√2 × √2)R45° surface reconstruction, see Figs. 1(a) and 1(b), respectively. AFM and STM data recorded on a ~3.0 nm thick film grown in two RASPE cycles [Figs. 1(c)–1(e)] reveal an atomically flat large-scale step-terrace morphology [compare, e.g., to the morphology of atomically flat SrTiO$_3$(001), (110), and (111) surfaces]$^{30-32}$ as well as the formation of domains with a (√2 × √2)R45° surface reconstruction. We emphasize that this is the first report of an atomically flat and reconstructed high-energy RuO$_2$(001) surface.$^{33}$

We further investigated the bulk structure of a thick RuO$_2$(001) film, grown using 14 RASPE cycles, by X-ray scattering. Figure 2(a) presents X-ray reflectometry data from which a film thickness of 21.0 nm is deduced. Figure 2(b) shows that the film is single crystalline, and that no impurity phases are present. In Fig. 2(a) the X-ray reflectivity (XRR) oscillations for the (001) oriented film do not extend as far as that for the (110) film [Fig. S2(a) of the supplementary material], suggesting a morphology that is more islanded for the thick (001) film, consistent with the absence of Kiessig fringes for the (001) film in Fig. 2(c), and the appearance of transmission spots in RHEED patterns after 3 RASPE cycles, see Fig. S5(d). Finally, the offset between the RuO$_2$(002) and the TiO$_2$(002) peaks indicates that the film has partially relaxed, although the lattice parameter of 3.061 Å along the [001] surface normal, as compared to the equilibrium bulk spacing along of 3.107 Å,$^{34}$ shows that tensile epitaxial strain is still present in the film.

To elucidate how the crystallization progresses through the amorphous film during the flash-anneal of the am-RuO$_2$ film on TiO$_2$(001), we performed a scanning transmission electron microscopy (STEM) experiment on a selected area of a 21.0 nm thick film in which the crystallization was frozen before it was completely finished, effectively creating a snapshot of the crystallization process. The STEM projection along the [010] direction reveals a partially crystallized film with a...
FIG. 1. (a) and (b) RHEED patterns before and after the first cycle of RASPE growth of a ∼1.5 nm RuO$_2$(001) film. Red arrows in (b) indicate the streaks from ($\sqrt{2} \times \sqrt{2}$)R45° surface reconstruction. (c) AFM image, (d) STM image, and (e) line profile along the red line in (d) measured on the surface of a ∼3.0 nm thick RuO$_2$(001) film. The separation between adjacent stripes on the RuO$_2$(001) surface is ∼0.65 nm in (e), consistent with reconstructed RHEED pattern in (b). STM scanning parameters in (d) are +1.5 V, 5 pA.

FIG. 2. (a) XRR, (b) XRD, and (c) θ-2θ scans around (002) reflection of a thick (21.0 nm) RuO$_2$(001) film. (d) Cross-sectional Z-contrast STEM image of a partially crystallized RuO$_2$(001) film.

trapezoid-shaped, faceted growth front that is covered by the remainder of the am-RuO$_2$, see Fig. 2(d). The well-crystallized lower half of the film below the residual am-RuO$_2$ is epitaxial to the TiO$_2$(001) substrate. The sides of these trapezoids are formed by slanted (101) and (−101) planes, whereas a (001) plane terminates the apex. We infer that the crystallization nucleates from the interface with the TiO$_2$(001) substrate, as expected, and progresses fastest along the [001] direction due to the high surface energy of the (001) plane.$^{35}$ The appearance of {101} facets on the sides of
these growing islands may be explained by their relatively low surface free energy.\textsuperscript{36} We do note, though, that such calculated surface energies are generally based on an interface with the vacuum, and here an interface with am-RuO\textsubscript{2} exists, which is likely to alter the interfacial free energy balance. Upon further crystallization, the small $\sim$4.0 nm (001) oriented facets at the top of the trapezoids will eventually reach the surface of the deposited film. The limited but finite atomic diffusion length during the short flash-annealing treatment allows for a limited lateral growth of these coherently crystalline surface domains, until the annealing is terminated when the last amorphous areas have crystallized. For thicker films needing a longer annealing time, this limited surface diffusion produces an islanded surface. RHEED data (not shown) indeed reveal that after complete crystallization, these 21 nm thick films are islanded but not faceted, similar to the surface of a $\sim$4.5 nm thick film [see Fig. S5(d) of the supplementary material]. However, for nanoscale thin films with thicknesses at least up to $\sim$3.0 nm, the result is a RuO\textsubscript{2}(001) surface consisting of relatively small terraces of exposed (001) crystal planes, as revealed by the atomically resolved STM data in Fig. 2(b). These data clearly demonstrate that RASPE allows the growth of RuO\textsubscript{2} films with exposed high surface free energy (001) planes and even produces atomically flat heterostructures for the thinnest films.

To investigate whether the RASPE approach is more generally applicable, we have performed preliminary experiments of TiO\textsubscript{2}(001) homoepitaxial growth using this approach. Supplementary material Note 4 demonstrates that indeed atomically flat TiO\textsubscript{2}(001) can also be grown homoepitaxially using this method. The successful growth of atomically flat homoepitaxial TiO\textsubscript{2}(001) film verifies the universality of RASPE in preparing (oxide) heterostructures in crystallographic orientations exposing surfaces with a high surface free energy.

Next, we compare the oxygen evolution properties of the RuO\textsubscript{2}/TiO\textsubscript{2}(001) and RuO\textsubscript{2}/TiO\textsubscript{2}(110) heterostructures. RuO\textsubscript{2} is one of the best catalysts for large scale water splitting, but the oxygen evolution (partial) reaction limits the water splitting rate.\textsuperscript{37} Recently, it was suggested that the surface free energy of crystal surfaces can be used as a descriptor for catalytic activity,\textsuperscript{27} exhibiting a volcano-relations akin to the Sabatier principle.\textsuperscript{38} Some early work\textsuperscript{39–42} on various nominally low index RuO\textsubscript{2} facets did not include a characterization of the surface morphologies, thus leading to questionable interpretations in terms of surface energies. Recently, Stoerzinger et al. reported that for RuO\textsubscript{2} films, the (100) surface indeed has a higher OER activity than the lower energy (110) surface.\textsuperscript{22} We exploit the novel capability to synthesize atomically flat, epitaxial thin RuO\textsubscript{2}(001) and (110) films with a comparable roughness, to evaluate the relative OER activity of these two surfaces that have the highest and lowest surface energy of the RuO\textsubscript{2} low index facets. We use $\sim$3.0 nm thick RuO\textsubscript{2}(001) and (110) films prepared by RASPE and MBE as described above, respectively, as electrodes because scanning probe data indicate that these have a similar surface roughness, facilitating a direct comparison of electrochemical oxygen evolution currents.\textsuperscript{22}

Figures 3(a) and 3(b) present the cyclic voltammetry (CV) measurements of the RuO\textsubscript{2}(001) and (110) electrodes. Since our RuO\textsubscript{2} films are atomically flat, the active area can be assumed to be equal to the exposed geometric area of the sample. Therefore we divided the measured current by the exposed area to obtain the current density. Figure 3(a) [see also Fig. S7(a) of the supplementary material] shows that the current density in the RuO\textsubscript{2}(001) sample decreases gradually in the first few cycles, and becomes stable at the ninth cycle. For the RuO\textsubscript{2}(110) sample, the current density increases from the first to the second cycle and remains essentially unaltered thereafter [Figs. 3(b) and S7(b)], which is consistent with the report in Ref. 22. After these OER experiments, the surface roughness of the two studied samples was investigated by using the [Fe(CN)\textsubscript{6}]\textsuperscript{3+/4–} reaction in a 5 mM mediator. As displayed in Fig. S9, both RuO\textsubscript{2} surfaces show a very similar charge density for the outer sphere redox couple [Fe(CN)\textsubscript{6}]\textsuperscript{3+/4–} [3.48 and 3.43 mC/cm$^2$ for RuO\textsubscript{2}(001) and RuO\textsubscript{2}(110), respectively], implying that the surface area of both orientations, and hence their roughness, remains comparable under the OER conditions employed here.

The origin of the different behavior in the initial aging of the two samples, observed before the reaction is stabilized in the first 10 CV cycles, remains elusive. A potential roughening of the surface through e.g., electrode corrosion\textsuperscript{43} as a cause of the observed initial aging of the RuO\textsubscript{2}(001) OER activity is unlikely because the RuO\textsubscript{2}(001) and (110) samples have a similar roughness after OER experiments (Fig. S9 of the supplementary material), whereas only the RuO\textsubscript{2}(001) surface
FIG. 3. (a) and (b) CV curves recorded in the first and in the final, stabilized cycles for RuO$_2$(001) and (110) surfaces in O$_2$-saturated 1 M KOH at 1600 rpm at 10 mV/s at 300 K. (c) Log(J) vs. E plot used to determine $V_{\text{onset}}$ for the first and final, stabilized CV cycles. Note that the residual current (straight dashed lines) has not been subtracted from the current density data presented in [(a)–(c)]. (d) Tafel plots derived from the catalytic CV current density after subtracting the linear residual current. In (d), the red and blue dots are the raw data, and black lines are fits.

decreases in activity. We also note that the OER onset potential of the TiO$_2$ is significantly larger than that of RuO$_2$,
 and the OER onset potential observed in our samples (see below), indicating that the observed aging is not related to exposure of the underlying TiO$_2$ substrate after dissolution of the RuO$_2$ films. Instead, this initial aging could be related to our observation of the formation of oxygen gas bubbles accumulating on the RuO$_2$(001) surface, decreasing the effective surface area available for the OER until a steady state is reached [at the 9th cycle, see Fig. S7(a)], similar to the OER behavior observed on Ni–Fe oxide catalysis. Indeed, a larger concentration of bubbles was observed on RuO$_2$(001) than on the RuO$_2$(110) surface. While an in-depth analysis of the known aging behavior of RuO$_2$ during the OER, and its dependence on crystallographic orientation is beyond the scope of this work, at the very least the model system provided by this newly accessible RuO$_2$(001) surface exhibits a significantly higher OER activity in its most pristine form (i.e., in its first OER cycle), than the RuO$_2$(110) surface.

To quantify the potential (vs. the reversible hydrogen electrode, RHE) beyond which the OER commences ($V_{\text{onset}}$) on these two surfaces, we define $V_{\text{onset}}$ as the potential at which the measured current starts to deviate from the level measured in the region where no oxygen is generated. Using the average of the anodic and cathodic current traces we find $V_{\text{onset}}$-(001) = 1.36 V and $V_{\text{onset}}$-(110) = 1.46 V as shown in Fig. 3(c) for the RuO$_2$(001) and RuO$_2$(110) surfaces, respectively, i.e., the overpotentials for these facets are only 130 and 230 mV. We note that $V_{\text{onset}}$ is independent of the “aging” observed in the CV cycles in our experiment, and that the $V_{\text{onset}}$-(110) is consistent with the data presented in Ref. 22. Even if the choice of the method to define $V_{\text{onset}}$ootnote{Note 5} might slightly affect the absolute values extracted from the $J$($E$) curves, the difference in $V_{\text{onset}}$ between the two sample orientations remains significant, independent of the chosen method (see supplementary material Note 5). The pronounced decrease in $V_{\text{onset}}$-(001) of 100 mV with respect to $V_{\text{onset}}$-(110) shows that the RuO$_2$(001) surface is remarkably more active than the RuO$_2$(110) surface.

A measure for the activity for the OER was estimated from the $J$($E$) curves by quantifying the specific current density at a constant overpotential of 0.3 V (i.e., 1.53 V vs. RHE), $J_{0.3V}$. These
Both the RuO$_2$ surface free energies prevent conventional growth of flat heterostructures. This was demonstrated in the synthesis of epitaxial transition metal oxide heterostructures with atomically flat surfaces even when high deposition rates were employed. A more thorough analysis of the overpotential dependence of OER kinetics at these surfaces is left for future investigation. Clearly, atomically flat films do not expose sufficient surface area to reach commercially valuable absolute oxygen evolution rates. However, the results presented by this model system suggest that the functional properties of transition metal oxides such as RuO$_2$ catalysts, already a benchmark material, can still be improved upon by novel synthesis approaches. Moreover, access to an expanded set of crystal facets for fundamental catalysis studies could aid in a better understanding of the processes that determine the overall efficiency. Specifically, a comparison of the relative magnitude of the surface free energies of the RuO$_2$(110), (100), and (001) facets with their OER activity, suggests that RuO$_2$(001) either is situated at the apex of the volcano (Sabatier) relation for catalytic activity as a function of surface free energy proposed in Ref. 27, or has not even reached the best possible performance of RuO$_2$. In the latter case further optimization may only be possible by synthesizing high Miller index facets of the rutile RuO$_2$ structure.

In conclusion, the results reported here illustrate that rapid-anneal solid-phase epitaxy, consisting of cycles of room temperature deposition and subsequent rapid flash-annealing, allows the synthesis of epitaxial transition metal oxide heterostructures with atomically flat surfaces even when high surface free energies prevent conventional growth of flat heterostructures. This was demonstrated in both the RuO$_2$/TiO$_2$(001) heteroepitaxial and the TiO$_2$(001) homoepitaxial systems. For the case of RuO$_2$/TiO$_2$(001), the crystallization of the amorphous film proceeds through faceted trapezoids that

| CV cycle  | $J_{0.3\text{V}}$ (µA/cm$^2$) | $J_{0.3\text{V-res.curr.subtr.}}$ (µA/cm$^2$) |
|-----------|-----------------------------|-----------------------------------|
| 1st-(001) | 835                         | 811                               |
| 1st-(110) | 354                         | 218                               |
| Final-(001) | 481                      | 472                               |
| Final-(110) | 356                     | 200                               |

*Current density at overpotential of 0.3 V after subtracting the residual current.*
nucleate epitaxially at the interface with the substrate and the resulting large-scale surface morphology is comparable to that of conventional MBE-grown atomically flat RuO$_2$(110) films, at least for films with a thickness up to 3.0 nm. This novel capability expands access to epitaxial transition metal oxides with strain states and crystal symmetries at the surface that were hitherto not available due to roughening instabilities, which is expected to allow for further tuning of their physical and chemical properties. In particular, we demonstrate here that the OER characteristics of these novel RuO$_2$/TiO$_2$(001) heterostructures are superior to those of RuO$_2$/TiO$_2$(110), measured by their 100 mV lower OER onset potential, as well as the 2–4 times higher OER current density. These results are consistent with the recently proposed relation between surface free energy and catalytic activity and offer suggestions for potential further improvement of the OER activity of the benchmark RuO$_2$ catalyst.

See supplementary material for growth and characterization details, conventional MBE growth of epitaxial RuO$_2$(110) on TiO$_2$(110), conventional MBE growth of RuO$_2$(001) films on TiO$_2$(001), RASPE growth of atomically flat rutile TiO$_2$(001) film, and determination of the onset potential of OER on RuO$_2$(001) and (110) films.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division (Y.W., A.H., M.F.C., T.Z.W., H.H.W., and P.C.S.). Part of this research (OER measurements by Y.S., R.P., and Z.W.) was performed at the Center for Nanophase Materials Sciences, a DOE Office of Science User Facility.

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

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It should be pointed out that upon increasing the number of deposition and annealing cycles to synthesize thicker films, transmission spots appear in RHEED [Fig. S3(d)], indicating that the surface evolves into a more islanded morphology. However, the absence of slanted streaks in the RHEED pattern due to diffraction from facet surfaces [compare red arrows in Fig. S4(a) with Fig. S3(d) of the supplementary material] indicates that the exposed surface crystallographic planes of the islands are parallel to that of the substrate. This means that the presence of islands on the surface is not due to a faceting transition, and the surface still exposes the (001) crystal plane.

34 Seeing JCPDS Card No. 40–1290 and JCPDS Card No. 21-1276 for RuO$_2$ and TiO$_2$, respectively.

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