Characterization of ultrathin oxidic metal layers on another surrogate metal support: A theoretical surface science approach

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The topic of the growth and characterization of ultrathin oxidic layers on metal substrates has drawn a lot of interest over the last few decades thanks to vast improvements in the resolution of surface spectroscopic and microscopic measurements. In line with the progress of nanoscale characterization, theory has also successfully provided insights to complement the experimental observations via atomistic modeling. However, close comparison between experiment and theory for the characterization of the ultrathin oxidic layer is still a huge challenge.

To address these issues, thin oxidic layers on different metal supports are investigated using first-principle density-functional theory calculations through the close comparison with experiments. Here, we introduce two examples [1, 2] of ultrathin oxidic metal layers on Au(111): (1) The interplay between oxygen gas and evaporated Cu metal atoms on another metal substrate (i.e., Au(111)) is described. Indeed, our revised *ab initio* atomistic thermodynamic model shows the impact of the evaporated metal sources on the surface phase diagrams of oxidic metal layers and provides a way of predicting new surface structures of controlled stoichiometry. (2) Various polymorphic structural models of Mo oxidic layers on Au(111) substrate are compared with recent experimental results that cover theoretical spectroscopic and microscopic approaches (with more advanced STM simulations, going beyond the simple Tersoff-Hamann approximation). We find that through the control of metal-oxygen coordination in these ultrathin oxidic O/Mo films on Au(111), the oxidation state of Mo atoms in the O/Mo layers can be reduced without the intentional creation of oxygen vacancies thanks to a unique charge transfer mechanism.

We hope to demonstrate that coupling our revised *ab initio* atomistic thermodynamic model with advanced theoretical spectroscopy/microscopy can afford a better picture of these complex oxidic surface structures – often seen in experiments under controlled growth conditions but still not well understood.

[1] **T. Lee**, Y. Lee, S. Piccinin, and A. Soon, *Ab initio* thermodynamics of surface oxide structures under controlled growth conditions, *J. Phys. Chem. C* **121**, 2228 (2017)

[2] **T. Lee**, Y.-J. Lee, K. Palotás, G. Lee, C. Stampfl, and A. Soon, Polymorphic expressions of ultrathin oxidic layers of Mo on Au(111), accepted in *Nanoscale* (2019)