CONTROLLING THE INTERFACIAL LAYER FORMATION DURING DEPOSITION OF CUO ON AL(111) USING A MULTI-LEVELS MODELING APPROACH

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CONTEXT

Miniaturization of devices coupled to the technological capacity to produce nanoscale multi-layered materials imposes an absolute control at the atomic scale, of the technological processes, of the composition of the layers, and of the nature of the interfaces that impact decisively and ensure the final properties of the material.

This is notably the key issue in so-called energetic materials. Energetic materials are substances, which store chemical energy and return it on demand after ignition through an appropriate stimulus (mechanical, thermal, electrical, optical, actuation). The studied energetic material is Al/CuO thermites elaborated as stacked nanometer thick layers using vapor-like deposition process. In multi-layered energetic materials, the interfacial layers, shown as barrier layers are known to determine the reactivity, the stability and the available total energy to be released, of the material. Barrier layers appear here as the technological and scientific issues since they are irreparably formed during vapor deposition process and their formation is still not controlled. Being able to design nanoenergetic materials morphology (structure, composition) layers should lead to tailored energetic performances for targeted applications.

Our challenge is to propose a predictive modelling to fill in the gaps in experiments and to guide technological process at the atomic scale through **multilevel strategy** [1], where ***ab initio* calculations** are used to probe and unravel (identification and characterization) the atomic scale events occurring during the growth of materials and where **kinetic Monte Carlo-based in house code** is developed to simulate the growth and link the design of the materials to the elaboration process parameters.

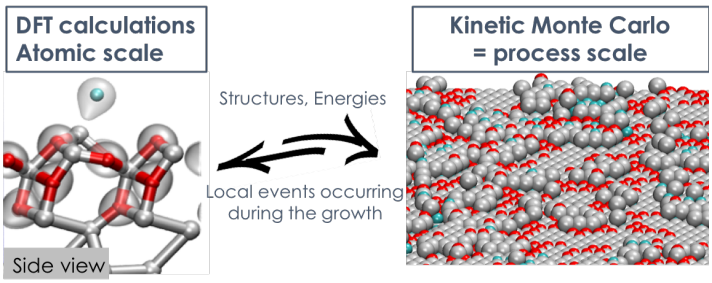

Figure 1: Multi-levels modeling approach.

RESULTS

DFT calculations: an insight into atomistic mechanism occurring during the growth

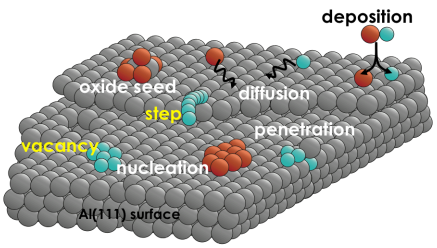

Figure 2: Schematic view of atomic scale diffusions involved during deposition of CuO (blue and red respectively) on Al substrate (grey).

DFT [1] highlights that:

- The adsorption of molecular CuO on Al surface is dissociative
- Atomic Cu and O diffuse on Al surface, O associated with a thermally activated diffusion, Cu without any measurable diffusion barrier
- The two species Cu and O tend to cluster
- At higher coverage, oxide nuclei are formed thanks to extraction of Al atoms – no O insertion is observed
- Cu inserts deep into the Al bulk thanks to a vacancy-enhanced diffusion
- Oxide nuclei appear as traps for Cu atoms, avoiding them to insert into Al substrate

These DFT calculations reveal the complex chemistry encountered during the formation of the interfacial layer during CuO deposition on Al. Here, we need to go beyond DFT.

kMC simulations: linking design to elaboration process parameters

DFT results were used as input data to parameterize the in house kinetic Monte Carlo code developed in the team. This kMC code is able to simulate the growth of the interfacial layer formed during the deposition of CuO on Al at the macroscopic scale. This code is able to deal with millions of atoms and takes into account external technological parameters as can be applied during the deposition process. It is thus possible to directly compare the simulation results with the experimental ones.

The Figure 3 shows the impact of the choice of the technological process parameters on the nanostructuring of the material, notably on the thickness of the interfacial layer formed during the deposition process. Here the temperature of the substrate is varied from 300 K to 200 K. We notice the crucial effect due to the temperature variations on the thickness. A thickness of roughly 60 Å is obtained at room temperature, whereas our simulation results reveal that it is possible to elaborate net and perfect interfaces without the formation of interfacial alloyed layer when the substrate is cooled at 200 K.

In this predictive modeling work, we have identified a critical temperature around 200-210 K to control the interfacial layer growth.

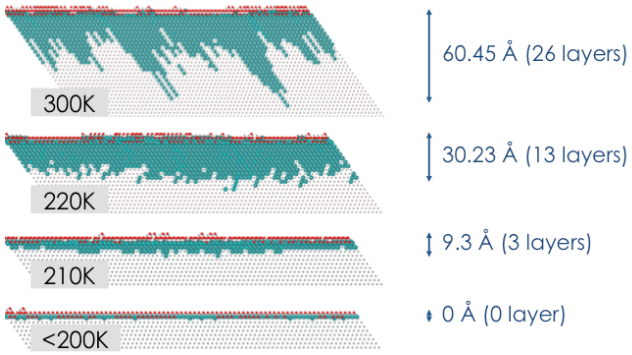

Figure 3: Impact of the applied temperature during process deposition on the thickness of interfacial layer formed during deposition of CuO on Al(111).
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CONCLUSIONS

We demonstrate that a tailored material nanostructuring can be achieved only if the impact of the applied technological process parameters on the nanostructuring can be exactly predicted. The pre-knowledge of the effects of technological process parameters can be well predicted using a multi-levels modeling approach, combining DFT calculations with kMC approach.

We highlight that the nanostructuring can be driven by the control of the kinetics of the atomic diffusions involved during the growth. Authorizing or not the atomic diffusions by choosing a targeted temperature allows the control of the thickness of the achieved interfacial layer, and thus opens a new route toward designed materials for dedicated applications.

The knowledge obtained with the large amount of conducted DFT calculations to identify all the atomistic events involved during the growth is the key issue!

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