JOURNAL OF
Materials
CHEMISTRY
Communication

Simulated amorphisation and recrystallisation: nanocrystallites within meso-scale supported oxides

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Received 14th June 2000, Accepted 7th August 2000
First published as an Advanced Article on the web 31st August 2000

We present the first simulation of an ultra-thin supported oxide, which encompasses, within a single simulation cell, all major structural features observed in a real system, including misoriented nanocrystallites, grain boundaries, dislocations and defects.

The chemical, physical and mechanical properties of a material can change tremendously when supported on a substrate material. Indeed, the exploitation of such a phenomenon remains central to applications spanning catalysis, sensors, electronics, optics and even engineering systems. Clearly, it is desirable to optimise the material properties and to help achieve this goal one must first understand the mechanisms that operate when a material is supported.

Here we employ dynamical simulations to explore the structural changes that evolve within an ultra-thin film of MgO when supported on a BaO(001) substrate. This system was chosen as a model system representative of a metal oxide supported on an oxide substrate, which has a much larger lattice parameter and, hence, the support induces strain upon the thin film. The results here will pave the way to performing similar simulations with a more industrial focus, such as supported ceria systems (automobile exhaust catalysis).

There have been many studies applying atomistic simulation techniques to investigate the structure and energetics of surfaces and interfaces (see for example ref. 1). Almost all start by defining the basic structure of the system, which is then simulated using dynamical or static methods.[2] However, since it can be difficult or indeed intractable to identify the precise atomistic structure experimentally, assumptions must be made (perhaps erroneously) with regards to the starting structure. Here, we consider an alternative approach whereby the structure of the thin film is allowed to evolve in response solely to the lattice misfit and underlying support material. To achieve this, the thin film is forced to undergo a transition to an amorphous state (loss of long range order) before recrystallising. Consequently, the final structure loses all memory of the preparatory configuration. Various mechanisms for amorphising the thin film have been explored. Here, amorphisation is induced by applying dynamical simulation, initially at a high temperature, to an MgO thin film, which is initially constrained under considerable tension.

Our calculations are based on the Born model of the ionic solid in which the ions interact *via* long-range Coulombic interactions and short-range parameterised interactions; the reliability of such simulations rests ultimately with the potential parameters.[3] In this study we have employed the potential parameters of Lewis and Catlow[4] with the additional approximation of the rigid ion model, imposed to reduce the computational expense.

Dynamical simulations, periodic in three dimensions, were performed using the DLPOLY code,[5] which includes, for surface and interface calculations, a void to represent the free surface above the thin film. A standard two-region approach is employed in which region I contains the thin film and the first few layers of the support (one MgO repeat unit for this present simulation) and ions within this region are allowed to move freely within the dynamical simulation regime. Region II contains a fixed region of the support and provides the correct crystalline environment.

To generate the MgO/BaO(001) thin film interface, eight layers of MgO were placed directly on top of a BaO(001) support. The size of the simulation cell was 154.4×154.4 Å, which corresponds to 28 BaO repeat units or 56 atoms for each side of the cell giving an interfacial area of *ca.* 24 000 Å^2 (approaching the meso-scale). The BaO was maintained at its natural lattice parameter and, in order to generate an initial coherent structure, the MgO accommodates the full +27% lattice misfit.

Dynamical simulation, with a timestep of 5×10^{-3} ps, was applied to the system for a total of 735 ps and was performed at an initially high temperature to help induce amorphisation which was then sequentially reduced, during which time the thin film recrystallised into a low energy configuration. Velocity scaling, performed at every step, was used throughout to prevent the rapid and large build up of excess kinetic energy as the thin film evolves, *via* an amorphous transition, from the highly strained initial configuration to a crystalline phase with reduced strain and a range of defects. Specifically, the dynamical simulation was run for 5 ps at 1000 K; 655 ps at 1200 K; 10 ps at 500 K; 55 ps at 100 K. A final dynamical simulation was performed at 0 K until the energy of the system converged, acting effectively as an energy minimisation. The amorphisation was controlled to ensure that the MgO thin film did not melt. In particular, amorphisation was monitored by calculating the radial distribution function; amorphous systems show no long-range order. If melted, the thin films demonstrate markedly different structural and diffusion characteristics compared with the analogous amorphous solid. For both the amorphised solid and melted systems, the calculated mean square deviations (msd) increase rapidly at the start of the simulation. However, once amorphised, the msd levels off as the diffusion reduces in the amorphous solid, whereas for the melted system, the msd continues to increase linearly. Structurally, the melted system is associated with a break up of the thin film surface which, upon prolonged dynamical simulation, extends as far as the support. The thin films were not, therefore, allowed to melt in this present study.

The structure of the MgO/BaO(001) system is presented in Fig. 1. For reasons of clarity, slightly less that 25% of the full simulation cell is shown. However, the segment is sufficient to adequately provide a flavour of the system. The final MgO thin film accommodates the rocksalt structure, as expected, and comprises *ca.* 5–6 layers; the surface of the MgO thin film is not atomically flat. Mg–O bond distances within the thin film range from *ca.* 1.8 to 2.3 Å with an average of 2.1 Å, suggesting little strain within the thin film lattice (the natural Mg–O bond distance is 2.1 Å). In addition, the average Mg–O bond

DOI: 10.1039/b004756m

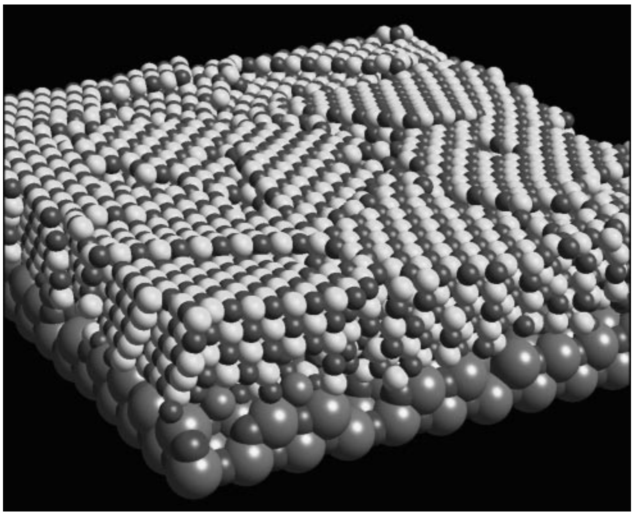

Fig. 1 Segment (25%) of the MgO/BaO(001) simulation cell. The small dark spheres are oxygen, the small light spheres magnesium and the large spheres barium.

distance for the interfacial MgO plane is *ca.* 2.0 Å, indicating that the interfacial region is strained compared with MgO regions further from the interface. Such observation is consistent with recent experimental studies on supported oxide thin films, which suggest that the strain within the thin film is not observed beyond the first few layers perpendicular to the interface.[6]

At the interfacial region, the MgO and BaO are highly defective and comprise a much lower density of ions compared with the 'bulk' material. In particular, many voids exist, up to *ca.* 200 Å^2 in size, within the MgO and BaO interfacial planes. In addition, barium ions from the support migrate from the surface to occupy either interstitial positions or magnesium lattice sites within the thin film. The displaced magnesium ions accommodate barium lattice positions within the support.

A plan view of the MgO thin film, presented in Fig. 2, shows that the MgO has formed numerous nanocrystallites, ranging from *ca.* 200 to 2 000 Å^2 in size and rotated, with respect to the underlying BaO surface normal, by various angles. The figure demonstrates the wealth of structural features that can be elucidated in such a simulation. These include nano-domains, dislocations, defects, and pseudo-hexagonal MgO, although perhaps most striking are the grain boundaries that exist where neighbouring nanocrystallites intersect.

This is the first time that simulation has been able to predict a realistic model of a thin film–oxide interface in which a whole range of crystallite orientations and sizes are observed. The structure is very similar to models of grain growth; however, in the case of grain growth, the large crystallites grow at the expense of the smaller ones. In our case, the different crystallite orientations are pinned by the underlying support. The misfit between the support and the thin film prevents them from growing any larger, as this would result in bringing like-charged ions into close proximity at the interface. The small regions thus allow favourable interactions across the interface with opposite charged ions close together.

To aid structural interpretation, graphical techniques were employed to identify, deconvolute and depict the individual features; the elucidation of such 3D atomistic detail is, at present, intractable experimentally.

The atomistic structures of the grain boundaries within the

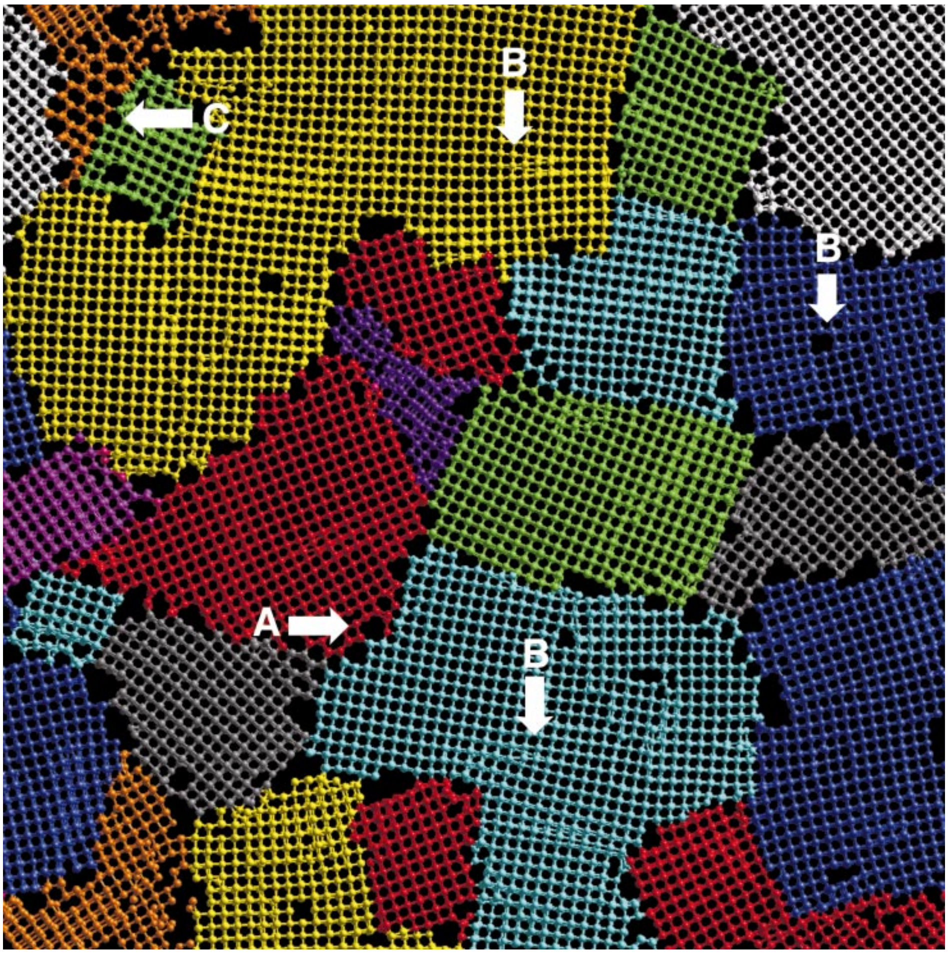

Fig. 2 Plan view of the full simulation cell (Fig. 1) depicting, for reasons of clarity, 2–3 MgO layers. To aid structural interpretation, the various nano-crystallites are coloured.

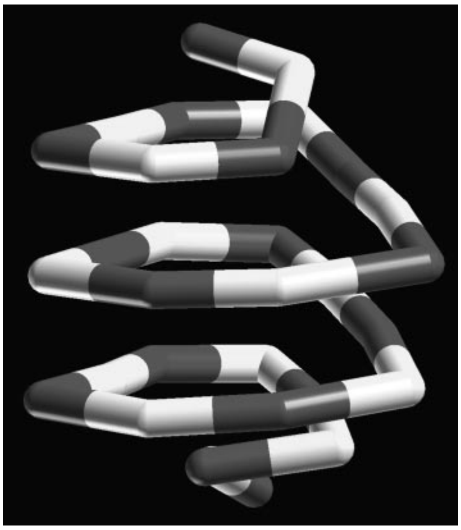

Fig. 3 Core structure of a screw–edge dislocation, as depicted by region ‘A’ in Fig. 2.

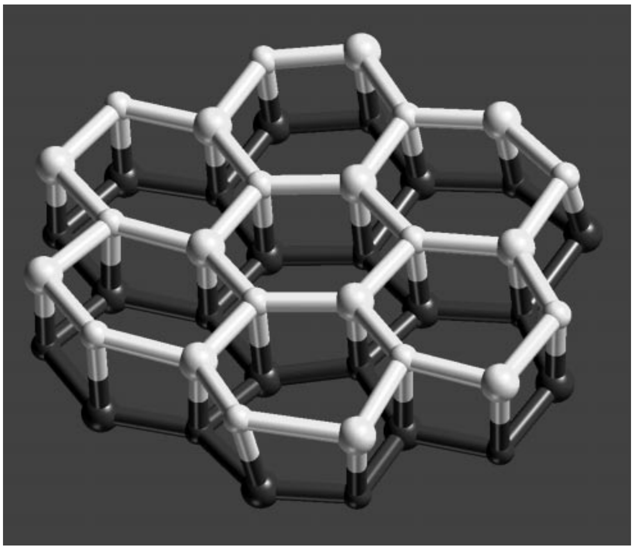

Fig. 4 MgO region accommodating a pseudo-hexagonal type structure, as depicted by region ‘C’ in Fig. 2.

MgO thin film are similar to those modelled previously in NiO (with good experimental correlation[7]). Since grain boundaries can be considered as an array of edge dislocations,[8] we have depicted the dislocation core structure of one particular grain boundary (region ‘A’ in Fig. 2) in Fig. 3. Surprisingly, the core structure is helical, which indicates that the dislocation has screw character in addition to edge character. Mixed screw–edge dislocations are also present within the nanocrystallites (regions ‘B’, Fig. 2) in addition to the domain boundaries.

Another interesting feature concerns the transformation of several MgO regions from a cubic to a pseudo-hexagonal type structure. One extended region (region ‘C’, Fig. 2) is enlarged and presented in Fig. 4. We suggest that the driving force for such a structural transformation is to help accommodate the lattice misfit; geometrically, a cubic to hexagonal transformation is associated with up to *ca.* $+30\%$ increase in the interfacial area. In addition, the hexagonal type structure provides considerable structural flexibility with regards to accommodating the lattice misfit. For example, a small change in the O–Mg–O bond angles will produce a large change in the interfacial area at low cost energetically.[9] Conversely, for cubic type structures, any compression or expansion along the direction of the bond is energetically prohibitive; rather, misfit dislocations evolve. An analogy can perhaps be drawn between these ‘pseudo-hexagonal’ type structures and a concertina.

Ultimately, one strives to optimise the properties of a supported material, and to help achieve this goal one must first understand structurally the mechanisms that operate when a material is supported. Accordingly, simulated amorphisation and recrystallisation has been used to explore the wealth of structural features that evolve within a supported oxide thin film. These include mis-orientated nanocrystallites, grain boundaries, dislocations cores and defects. Conversely, it is presently difficult, or even impossible, to visualise such structures with three-dimensional atomistic clarity, as demonstrated here, using experimental techniques. This study exemplifies the versatility of simulation in providing a unique and complementary technique to be used in conjunction with experiment.

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