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Misfit accommodation in oxide thin film heterostructures ☆

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Abstract

Complex oxides are of intense interest due to their diverse properties, such as colossal magnetoresistance and superconductivity. Their complexity arises not only from the number of constituent elements, but also from their tolerance of non-stoichiometry and the structural complexity of these perovskite-based materials, e.g. the distortions and rotations of the oxygen octahedra surrounding the B-site cation. For these reasons, misfit accommodation in these materials is far more complex than in simpler materials, and can involve several different mechanisms simultaneously. In some cases, interfaces can be free from any misfit dislocations, lattice mismatch being accommodated via incorporation of oxygen vacancies, which take an ordered periodic arrangement. Interfaces may also present a perturbation to the octahedral rotations that can dramatically affect properties, not just close to the interface but through the entire film. In oxygen ion conducting materials, the oxygen sublattice may even melt in some situations.

Keywords: Thin films; Defects; Dislocations; Misfit relaxation

1. Introduction

The explosion of interest in the field of oxides, especially the so-called complex oxides, is due to the wealth of new phenomena they exhibit, such as colossal ionic conductivity and magnetoresistance, and the emergence of new superconducting, magnetic and electronic properties [1–3]. Even more exotic phenomena have been found at interfaces in oxide heterostuctures. For example, the seemingly simple interface between the two insulators $LaAlO_3$ and $SrTiO_3$ can be metallic [4], ferromagnetic or superconducting [2,5]. Even more degrees of freedom exist in complex oxide heterostructures, where octahedral distortions and associated changes in orbital occupation can take place, e.g. the orbital reconstruction observed in superconducting/ferromagnetic cuprate/manganite heterostructures [1,6].

Misfit accommodation can be similarly complex. Generally, stress in thin films is relaxed by dislocations, which nucleate at free surface steps and glide to the interface. Thus, kinetics of dislocation nucleation and propagation play a critical role in thin film relaxation processes. Surface steps play a critical role in dislocation nucleation, and lattice frictional stress determines propagation [7,8]. Only when a component of the film stress, known as the critical resolved shear stress, acting on dislocations in the glide plane, exceeds the yield stress/lattice frictional stress will the dislocation propagate. The critical resolved stress is given by $\sigma_f \cos\varphi\cos\lambda$ (Schmid factor), where σ_f is the planar stress, φ is the angle between the stress direction and the glide direction, and λ is the angle between the stress

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direction and the glide plane normal. For certain film/substrate orientations, the Schmid factors may be too small or zero for available slip systems. This would prevent the generation of misfit dislocations. Under these conditions, films having large misfits can grow without dislocations up to a certain thickness without a fracture/crack. In complex oxides there are many additional possible mechanisms. Dislocation cores can be non-stoichiometric, and the entire misfit may be accommodated by alternative means, for example through the introduction of oxygen vacancies, which can lead to lattice parameter changes [9]. In addition, mismatch can occur not only in the lattice parameter but, in the case of perovskites, also in the octahedral tilt network, again radically influencing the film properties. A detailed atomic resolution characterization of the interface atomic and electronic structure, ideally coupled to electronic structure calculations, is critical to understand and control the structure–property relations in these materials.

Scanning transmission electron microscopy (STEM) is ideally suited to a study of this nature as it is able to provide multiple signals simultaneously at atomic resolution [10], specifically, the Z-contrast image (through a high- or medium-angle annular detector [11–13]), a bright-field (phase-contrast) image [14] and electron energy loss spectroscopic (EELS) images reflecting the elemental composition and electronic structure [15,16]. With the successful correction of objective lens aberrations, the spatial resolution, precision and sensitivity of these measurements have been dramatically improved, as described in a number of recent reviews [17,18]. However, particularly in the case of dislocation cores, it must be remembered that not all contrast is Z-contrast [19–21]. The high strain fields of the dislocation cores can disturb the crystal orientation, either directly or through surface relaxations, leading to image contrast. Depending on the detector angle, such contrast can be bright or dark; indeed, it is possible to determine the nature of the Burgers vectors from the symmetry of the contrast [22–24]. Similar contrast effects will be present in EELS signals, so that quantitative interpretation of composition maps at dislocation cores is also difficult. In addition, although it is generally assumed that the fine structure shown by EELS can be interpreted in terms of oxidation states – particularly useful for the transition metal L edges – the influence of diffraction/channeling conditions on such signals has yet to be rigorously established in the case of atomic resolution.

Here, we use these techniques to illustrate the rich variety of misfit accommodation processes utilized by oxide thin films and heterostructures. We show an example of domain matching epitaxy [25], with the formation of misfit dislocations and additional strain relief through dislocation core segregation. We then show examples of the formation of metastable intermediate phases at interfaces, and of misfit accommodation via vacancy arrays, which avoids the formation of misfit dislocations entirely. We then show how, in perovskite films, the additional order parameter represented by the octahedral tilt network provides a new mechanism for misfit accommodation that has a major influence on interfacial properties. Finally, we show an extreme example where the O ion sublattice actually disorders, or melts, with a colossal increase in ionic conductivity.

2. Dislocation core structures at a non-polar ZnO/Al_2O_3 interface

Non-polar ZnO and GaN films are of interest for light emission applications since they avoid the strong piezoelectric polarization fields which tend to separate electrons and holes, thus reducing the internal quantum efficiency [26–29]. This system is actually a classic example of so-called domain matching epitaxy [25] in which a high mismatch can be fully relaxed during film growth by matching different integer numbers of planes in the two materials. Choosing the *r*-plane of sapphire ($(1\ \bar{1}\ 0\ 2)$ Al_2O_3) as a substrate, ZnO grows epitaxially with its *a*-plane ($(1\ 1\ \bar{2}\ 0)$ ZnO) parallel to the sapphire *r*-plane, with in-plane orientations of $[0\ 1\ \bar{1}\ 0]$ ZnO // $[2\ \bar{1}\ \bar{1}\ 0]$ Al_2O_3 and $[0\,0\,0\,1]$ ZnO // $[\bar{1}\ 1\ 0\ 1]$ Al_2O_3 [30–32]. The lattice mismatch in these two directions is quite different – 18.3% for the former direction but only 1.5% for the latter direction – and, perhaps surprisingly, it is the high mismatch that is relaxed completely during the growth process. The explanation is that in the high mismatch direction it is simple to nucleate dislocations during film growth because the critical thickness is below one monolayer. Such relaxation has been commonly

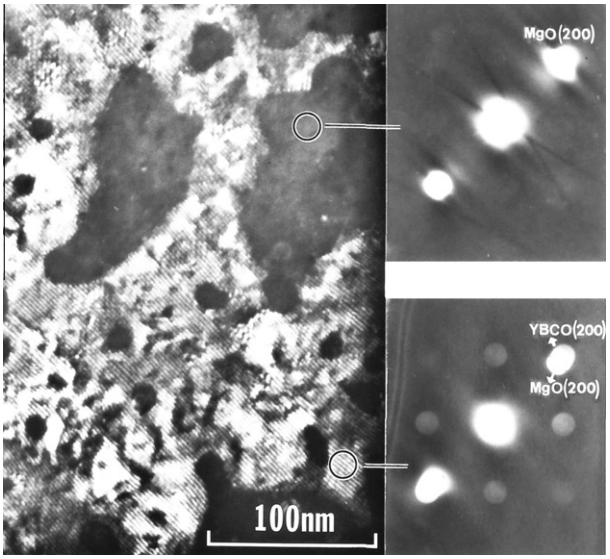

Fig. 1. Dark-field plan-view TEM image from a three unit cell $YBa_2Cu_3O_{7-x}$ (YBCO) film deposited on MgO taken with a YBCO {100} reflection, which is forbidden in MgO, with microdiffraction patterns from the bare substrate (top) and a portion of the YBCO film (bottom). The dark regions in the image represent bare substrate, and the intensities from the YBCO film are quantized, indicating single, double and triple unit cell regions. Moiré fringes indicate that relaxation has occurred even in the single unit cell regions of the film. The misfit is 9.3 and 7.6% along the *a* and *b* directions of the YBCO, respectively. Reproduced from Ref. [34].