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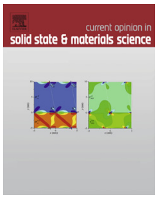

Two-dimensional metamaterials for epitaxial heterostructures

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ABSTRACT

We review the use of two-dimensional pseudomorphic materials to accommodate an extraordinary range of misfit and allow novel new phases to be grown epitaxially. These materials assume the structure of the substrate and can thus be regarded as metamaterials. We illustrate these principles through a number of systems, including a detailed structural and spectroscopic study of epitaxial VO_2/NiO heterostructures. In this case the metamaterial is VO_{1+x} which is structurally and electronically distinct from the bulk of the VO_2 film. In the transition region the crystal structure adopts that of the NiO layer, while the oxidation state of vanadium increases from ~3+ to ~4+ with thickness, accompanied by increasing lattice disorder. The formation and evolution of this interfacial phase, VO_{1+x}, accommodates the change in crystal symmetry across the interface from the rock-salt structure of NiO to the rutile structure of VO_2. The use of two-dimensional metamaterials opens a wealth of new opportunities for the growth of new materials with novel properties.

1. Introduction

The physical properties of ultrathin films can be remarkably different from their corresponding bulk materials not only owing to the spatial confinement but also to constraints imposed from the use of substrates of dissimilar materials. For example, studies have shown that epitaxial strain can increase the ferroelectric transition temperature (T_c) by hundreds of degrees in both $SrTiO_3$ [1] and $BaTiO_3$ [2] and nearly double the superconducting transition temperature in $La_{2-x}Sr_xCuO_4$ [3,4]. With current state-of-the-art technology, accurate control of the growth of ultrathin films is possible. Therefore the study of interfacial phenomena resulting from substrate constraints becomes more and more relevant not only to the understanding of solid state physics, but also to potential device applications. Heteroepitaxy, a fundamental process in the integration in microelectronic devices, involves two materials with mismatch at the interface in lattice spacing, composition and sometimes in lattice symmetry as well. Lattice spacing mismatch introduces biaxial strain, which can be relieved by generating misfit dislocations when the critical stress is reached [5]. Symmetry mismatch, however, may require a large degree of bond bending in order to maintain a coherent interface. Often, especially in the latter case, forming an intermediate phase with a structure compatible to the substrate appears to be a more favorable path for strain relief than generating misfit dislocations. Indeed, phases that are not stable or even do not exist in bulk have been found formed as a result of epitaxial stabilization, such as γ-Fe_2O_3 on MgO (001) [6], Co_2O_3 corundum phase on α-Al_2O_3 (0001) [7], hexagonal $DyMnO_3$ on $ZrO_2(Y_2O_3)$ (111) [8], and V_2O_3 and Ti_2O_3 on α-Al_2O_3 (0001) [9,10].

This review focuses on growth mechanism of metastable, psuedomorphic, two-dimensional transition metal oxides. Transition metal compounds have many intriguing electrical, superconducting, ferroelectric, magnetic and catalytic properties. The unique two-dimensional psuedomorphic metamaterials are expected to exhibit a further range of novel properties with exciting potential for next-generation solid-state devices. In the future, special emphasis will be to integrate these novel materials on Si (100) to enhance and impart smart functionality to computer chips. The structure of these psuedomorphic materials can be tuned by templating the structure of the underlying growth substrate. The psuedomorphic layer assumes the structure of the substrate up to a certain thickness, above which thermodynamic chemical free energy takes over and the structure reverts to the equilibrium phase. This critical thickness is determined by the competition between the chemical free energy and the strain free energy. The even more exciting aspect of these materials is that their

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composition can be further controlled by growth parameters and chamber pressure ambient, while keeping the unique structure dominated by the substrate.

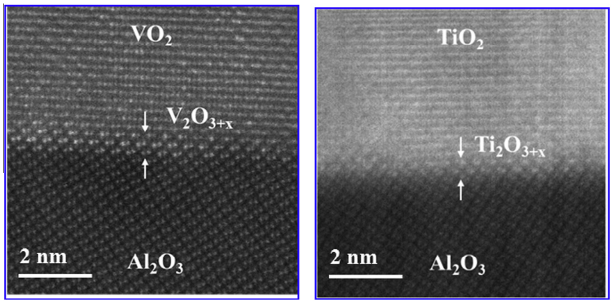
We will first summarize the psuedomorphic growth of V_2O_3 and Ti_2O_3 on (0001) sapphire, and then present a detailed illustration of the case of VO_{1+x} on NiO. As one of the most versatile members of the transition metal family, vanadium has four principal oxides VO, V_2O_3, VO_2 and V_2O_5, with the crystal structure symmetry varying from cubic (VO) through corundum (V_2O_3, at $T > T_c = 168$ K) and rutile (VO_2, at $T > T_c = 340$ K) to orthorhombic (V_2O_5) [11–13]. Furthermore, V_2O_3 and VO_2 experience a crystal structure change at T_c, from high temperature corundum (V_2O_3) and rutile (VO_2) to low temperature monoclinic [11–13]. This structural diversity brings a great variety of physical and chemical properties. For instance, there is a semiconductor–metal transition (SMT) accompanying the crystal structure change near room temperature in VO_2 [11], which makes the oxide a material of great interest for applications such as electrical and optical switching devices, light and temperature sensors. This large structural diversity also makes vanadium oxide a favorable subject for the study of interface mediated phases.

2. Examples of transition metal oxide psuedomorphic metamaterials

In our earlier studies with aberration-corrected scanning transmission electron microscopy (STEM) [14–16], we have observed ultrathin transition layers at both VO_2/Al_2O_3 [9] and TiO_2/Al_2O_3 interfaces [10], as shown in Fig. 1(a) and (b). The transition layers at both interfaces were found to have rhombohedral corundum symmetry, suggesting a V_2O_3 and a Ti_2O_3-like phase, despite using standard VO_2 and TiO_2 growth conditions. Electron energy loss spectroscopy (EELS) from the V_2O_3-like region revealed that the phase is nonstoichiometric and highly defective [9]. We speculated that this transitional layer was formed to serve as a structural buffer for the epitaxial growth of VO_2/TiO_2, fulfilling the symmetry transition from that of rhombohedral corundum in Al_2O_3 (*R-3c*) to that of rutile in VO_2/TiO_2 ($P4_2/mnm$) [9,10,17]. In this transition phase the V (Ti) atoms in the corundum structure sit on the Al sites, making the transition region show brighter than the substrate. The transition phase also looks brighter than the VO_2 because the VO_2 is not in a low index orientation and the columnar density in the beam direction is lower. The presence of the interface mediated phase shows how materials with chemical and structural mismatch can form metastable interfacial phases (metamaterials) to accommodate the differences.

3. The case of VO on NiO

To illustrate the mechanisms involved in the growth of psuedomorphic metamaterials we present the results of our recent detailed study on another vanadium oxide heterostructure interface. This illustrates the strain relief mechanism in detail, and highlights the potential of psuedomorphic metamaterials for epitaxial stabilization of novel phases. For this purpose we choose the system comprising epitaxial VO_2 ($P4_2/mnm$) on NiO (*Fm-3m*). NiO has a rock-salt structure (*Fm-3m*), the same as that of VO and therefore it was expected to serve as a symmetry modulating layer, inviting the growth of a VO-like structure at the interface. Furthermore, owing to the increased critical thickness resulting from the reduced misfit (~2% between stoichiometric VO and NiO compared with ~4% between V_2O_3 and Al_2O_3), the transition region in VO_2/NiO heterostructures was expected to be wider, which would allow a more detailed spectroscopic study to be conducted.



(a) (b)

Fig. 1. High resolution high angle annular dark field (HAADF) interface images of (a) VO_2/Al_2O_3 heterostructure (adapted from Ref. [9]) and (b) TiO_2/Al_2O_3 heterostructure (adapted from Ref. [10]) along the Al_2O_3 $[2\bar{1}\bar{1}0]$ crystal direction showing a V_2O_3-like interface region and a Ti_2O_3-like interface region, respectively. The vanadium and titanium columns in VO_2 and TiO_2 are not clearly resolved because this viewing direction is one of the high index directions.

NiO and VO_2 were successively deposited on single crystal *c*-cut Al_2O_3 substrates by pulsed laser deposition (PLD) with a KrF excimer laser ($\lambda = 248$ nm) under optimized conditions as reported elsewhere [18]. The interface structure was determined with high angle annular dark field (HAADF/STEM-Z) imaging using two aberration-corrected scanning transmission electron microscopes: a Nion UltraSTEM™ 100 equipped with a 5th order aberration corrector operating at 100 kV and a dedicated VG Microscopes HB 603U STEM equipped with a 3rd order Nion aberration corrector operating at 300 kV. The former was also used for interface electron energy-loss spectroscopic (EELS) study. STEM samples were prepared in cross-sectional geometry by standard mechanical polishing and ion milling.

3.1. Atomic and electronic structure from STEM-EELS

Preliminary results of this study have been reported in Ref. [19]. As shown in Fig. 2(a), there is indeed a wide transition region (indicated by an arrow) at the interface with a significantly reduced intensity compared to that of the VO_2 film. This reduced intensity is consistent with the expected formation of a VO phase, since V is lighter than Ni. Note however that the darkest patches in the images are probably indicative of some damage from the electron beam. The transition region is continuous with a thickness varying from ~2 nm to 5 nm. Two representative atomic resolution HAADF images of the VO_2/NiO interface along an Al_2O_3 $[01\bar{1}0]$ zone axis are shown in Fig. 2(b) and (c). The bright columns in the upper part of the image are V columns with the configuration expected when viewing down the VO_2 [100] direction (Fig. 2(b)) and VO_2 [101] direction (Fig. 2(c)). The even brighter columns in the lower part of the image are Ni columns with the configuration expected when viewing NiO along its [110] zone axis. The O columns bonded with V atoms are barely visible next to the bright V and Ni columns in both images. The cation configurations are in agreement with the orientation relationship determined by XRD [18]. The coexistence of more than one in-plane orientation originates from the oxygen sublattice matching between the film and the substrate [9]. It is evident that the bulk phases on either side of the interfacial region have very different cation configurations and an interfacial phase is present with a lattice resembling that of NiO.

EELS investigation shows that except for a narrow (V,Ni)O mixed region at the NiO side of the interface, this interfacial phase is indeed vanadium oxide [19]. The V-$L_{3,2}$ edges and O-K edges of the spectra obtained inside the interface region compared with those from V_2O_3 and VO_2 reference spectra are shown in Fig. 3. The reference V_2O_3 and VO_2 samples were deposited under