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Growth and characterisation of epitaxially ordered zinc aluminate domains on *c*-sapphire

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Abstract

Epitaxially ordered zinc aluminate domains with sub-micron dimensions are formed on bare *c*-sapphire substrates using a vapour phase method (with vapour generated by carbothermal reduction of ZnO) at various temperatures and growth durations. A zinc aluminate ($ZnAl_2O_4$) layer is formed by reaction of the source materials (Zn and O) with the substrate. We observe crystallites with a well-defined epitaxial relationship on the sapphire substrate in addition to polycrystalline material. The epitaxially oriented deposit displays the form of characteristically twinned (singly or multiply) grains of sub-micron dimensions with three variants, consistent with the *c*-sapphire substrate symmetry. Scanning electron microscopy and transmission electron microscopy studies show that the formation of these grains is associated with the presence of extended defects in the sapphire substrate. Epitaxially ordered grains formed at higher temperatures show a change in the nature of the twin boundaries and epitaxial relations as a function of growth time, attributed to the effects of annealing during growth.

Keywords: Zinc aluminate; Spinel; Epitaxy; Sapphire; Growth; SEM; TEM

1. Introduction

Controllable growth of oxide materials is an important research area, with applications ranging from photonic devices, transparent conducting oxides (TCO) and high temperature electronics (HTE) to catalysis and biocompatibility applications [1,2]. Among these oxides, spinel materials (of the type AB_2O_4) have been widely studied, with their growth mechanisms and structural properties the subject of extensive investigations. Zinc aluminate ($ZnAl_2O_4$) is a spinel of particular interest technologically, given its wide potential functionality [3]. A recent report has used zinc aluminate as a platform material to demonstrate a generic technique for core-shell nanostructure synthesis using the nano-Kirkendall effect, indicating the great potential this material has for nanoscale applications [4]. Its wide bandgap (~3.8 eV) may lead to applications in TCO and HTE, and, when doped with rare-earth elements, it may function as an effective luminescent material for phosphor applications [5,6]. Zinc aluminate is also being considered for optical coating applications in aerospace technology, is used in many catalytic applications, including cracking, dehydration of saturated alcohols, synthesis of methanol and other alcohols in addition to acting as a support for catalysis [7,8]. The catalytic functionality of materials, particularly for sub-micron particles, is known to be affected by the microstructure, and various facets show substantial differences in catalytic activity [9]. Controllable, ordered growth of microstructured catalytic material on a chemically and physically robust substrate is therefore an important technological focus.

We report results that demonstrate the formation of zinc aluminate domains with well-defined epitaxial relationships on *c*-sapphire substrates. Our data show that we can control the degree of faceting and the epitaxial relationships by controlling

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the growth conditions, thus potentially controlling the functionality of zinc aluminate microstructures on sapphire. The aluminate microstructures formed also show a number of intrinsically interesting features, including a strikingly symmetrical appearance in scanning electron microscope (SEM) images, enhanced diffusional transport along the lower density "open" twin boundary and two well-defined types of twin boundary, related to the epitaxial relationships mentioned above.

2. Experimental details

Zinc aluminate was grown on *c*-sapphire substrates by vapour phase transport. Most of the substrates used were obtained from Testbourne Ltd, Hampshire, UK, although substrates from other suppliers were also used. The substrates are ultrasonically cleaned before growth and are not coated with gold (note: some reference samples have been covered with gold to catalyse the formation of wurtzite phase ZnO nanorods by the vapour–liquid–solid mechanism, using otherwise similar growth conditions) [10]. A ZnO/graphite powder mix (1:1 wt.) is placed at one end of a quartz boat and the substrate is placed ~0.5 to 5.0 cm from the source in a single zone horizontal tube furnace with argon carrier flow (90 sccm). The nominal temperature of the furnace is set in the range 950–1125 °C and the set temperature is achieved in ~15–20 min. The actual substrate temperature is 35 °C lower than the nominal temperature for growth at 950 °C and 50 °C lower for growth at 1125 °C, due to the temperature gradient of the furnace.

Samples were characterised by SEM and field emission (FE-) SEM (LEO Stereoscan 440 operating at 15 kV and Hitachi S-4300 Field Emission operating either at 5 kV or 20 kV), atomic force microscopy (AFM: Nanoscope IIIa, Digital Instruments; contact mode) and transmission electron microscopy (TEM: JEOL2000FX operating at 200 kV). Sections for TEM microstructural evaluation were made using standard focused ion beam thinning (FEI FIB 200 workstation operating at 30 kV using a Ga ion source with currents of 11 nA and 150 pA for box milling and final polishing, respectively; see Ref. [11]). X-ray diffraction measurements were made using a Bruker AXS D8 advance texture diffractometer (using Cu K_α radiation). Laue patterns were acquired at the Fluo-Topo X-ray topography beamline of the ANKA (*Å*ngström *Ka*rlsruhe) at the Institute for Synchrotron Radiation, in Karlsruhe, Germany, using the continuous spectrum of synchrotron radiation from a 2.5 GeV storage ring at typical currents of 100–180 mA, and at the Institute for Crystal Growth in Berlin, Germany; details are given in Ref. [12].

3. Results

The results section describes the characterisation of zinc aluminate microstructures and is divided into three subsections, based on the growth durations and substrate preparation (Section 3.1 describes growth for 30 min duration, Section 3.2 describes 60 min duration growth and Section 3.3 describes the effects of substrate preparation).

3.1. 30 min growth duration

A series of SEM images of samples grown for 30 min at furnace temperatures of 950 °C (A) and (B) and 1125 °C (C) and (D) are shown in Fig. 1 (A)–(D). Prominent structures with a linear appearance are seen with a high secondary electron contrast, aligned in *three* specific in-plane directions with an angle of 120° between them. These structures are uniformly distributed among these directions. The width of the linear high intensity region in all cases is ~70 nm and the length of this region is distributed in the range 400–600 nm for samples grown at 950 °C, and in the range 700–1500 nm for samples grown at 1125 °C, though shorter and longer examples are seen in both cases. We have performed atomic force microscopy (AFM) to study the surface topography, shown in Fig. 2 for a sample grown at ~1125 °C for 30 min. Three-fold symmetric structures, similar to those observed in SEM, are again visible and longitudinal and transverse height profiles are displayed from various regions of the AFM image. These show that the structures have an average height of ~90–100 nm, and that the width of the structures (at their base) deduced from these profiles is ~200 nm. This is substantially greater than the width of the bright linear regions seen SEM, and the difference is much greater than can be explained by tip-broadening effects in the AFM. Thus the bright linear structures seen in the SEM images are not solely due to contrast effects due to surface topography. Height profiles in regions of the sample with no symmetric structures (profile 4 in Fig. 2) show a substantial degree of roughness, indicating that layer deposition has taken place in this region also. Evidence of this deposition from SEM data is also shown in the circled region in the inset of Fig. 1(B) above.

The symmetric distribution of these microstructures with a three-fold symmetry suggests an epitaxial relationship to the hexagonal sapphire *c*-plane substrate. The crystallographic orientation of the *c*-sapphire substrates relative to their physical edges has been found by Laue pattern analysis and confirmed by X-ray phi scan measurements (data not shown). When the orientation of the sapphire substrates is known, the relative orientation of the nanowires thereon was found using SEM images at various magnifications, allowing comparison with the physical sample edges. We find that the long direction of the bright symmetric structures lie parallel to the $<10{-}10>$ sapphire in-plane directions in all cases studied. This alignment along a high symmetry in-plane sapphire direction further suggests that at least the portion of the deposit associated with these microstructures grows with an epitaxial relationship to the substrate.

We have performed transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements in both cross-section and plan-view mode in order to ascertain the material phase, elucidate the origin of the symmetric microstructures seen in SEM and AFM and to study the epitaxial relationships between the substrate and the deposited layer. Fig. 3 shows cross-sectional TEM data for a sample grown at 950 °C for 30 min (the sample shown in Fig. 1(A) above). Fig. 3 (A) shows a broad area at relatively low magnification which is a montage of two bright field micrographs. An immediate