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Direct Observation of Tunnelled Intergrowth in SnO$_2$/Ga$_2$O$_3$ Complex Nanowires

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Abstract

β-Ga$_2$O$_3$ intergrowths have been revealed in the SnO$_2$ rutile structure when SnO$_2$-Ga$_2$O$_3$ complex nanostructures are grown by thermal evaporation with a catalyst-free basis method. The structure is formed by a Ga$_2$O$_3$ nanowire trunk, around which a rutile SnO$_2$ particle is formed with [001] aligned to the [010] Ga$_2$O$_3$ trunk axis. Inside the SnO$_2$ particle, β-Ga$_2$O$_3$ units occur separated periodically by hexagonal tunnels in the (210) rutile plane. Orange (620 nm) optical emission from tin oxide, with a narrow linewidth indicating localized electronic states, may be associated with this β-Ga$_2$O$_3$ intergrowth.

Keywords: wide band gap oxides, transmission electron microscopy, tunnelled intergrowth

1. Introduction

Significant advances in semiconducting metal oxides for optoelectronic applications have been recently reported$^1$. The wide band gap of the monoclinic β-Ga$_2$O$_3$ (4.9 eV) and rutile SnO$_2$ (3.7 eV), make these metal oxides suitable for applications in the ultraviolet range. These thermodynamically stable phases are easy to produce and chemically stable. Additionally, Ga and Sn are more abundant than e.g. indium in the Earth's upper continental crust$^2-3$ providing a potential alternative to rare-metal free transistors$^3$. These oxides offer a wide range of optoelectronic applications including photodetectors$^4$, solar cells$^5$, photocatalysis$^6$ and biomedical usages$^7,8$.

Currently, nanoscale structures are at the forefront of research. New architectures of mixed dimensionality and materials combination open up new and versatile applications. Our previous work has clearly demonstrated the growth of complex oxide structures, based on Ga$_2$O$_3$ and SnO$_2$ using thermal evaporation and careful choice of growth parameters (gas flow, temperature and Cr doping)$^9-11$. Different architectures have been reported involving these two metal oxides, which constitute the first steps in the design of novel hierarchical oxide nanostructures with wide band gap and tailored functionalities.

Previous work showed that β-Ga$_2$O$_3$ reacts with oxides possessing the rutile structure to form coherent intergrowths$^{12-15}$. These structures can be described as sheets of β-Ga$_2$O$_3$ between slabs of rutile (SnO$_2$, GeO$_2$, or TiO$_2$)$^{16}$. Here, we report the observation of similar tunnelled intergrowth structures in a SnO$_2$/Ga$_2$O$_3$ nanostructure. In our case, the intergrowth of Ga$_2$O$_3$ sheets in SnO$_2$ produces 1-D hexagonal tunnels lying parallel to the $b$-axis of the intergrowth. These tunnels may be suitable hosts for small-to-medium cations$^{17}$, with potential application as battery electrodes, or strongly anisotropic ionic conductors. In addition to studying the intergrowth structure, we also use cathodoluminescence (CL) to shed some light on previously unreported luminescence bands of tin oxide.
2. Materials and Methods

Ga$_2$O$_3$/SnO$_2$ nanostructures were synthesized via catalyst-free thermal evaporation. The precursor material was a mixture of 90 wt.% Ga$_2$O$_3$ and 10 wt.% SnO$_2$ powders compacted into a disk of 5 mm diameter. Some pure metallic Ga was placed on the upper surface of the pellet to enhance the growth of Ga$_2$O$_3$ nanowires. The pellet was introduced into a furnace and heated under flowing argon for 8 hours at 1100 °C. The formation mechanism is a vapor-solid process, which produces many nanostructures on the pellet surface. Most structures have a characteristic morphology of a Ga$_2$O$_3$ nanowire, or trunk, decorated with small SnO$_2$ particles around, in a skewer-like (SK) arrangement. In previous work we studied SK structures formed by adding tin oxide powders on a pure gallium oxide pellet instead of incorporating them into the substrate. We show here that such slight changes in the sample preparation procedure can alter the microstructure of the final product.

The SK nanostructures were transferred into a TEM copper grid with a lacy carbon support for scanning electron microscopy (SEM) characterization and cathodoluminescence (CL) spectroscopy, using a Gatan MonoCL4 spectrometer attached to a Zeiss Supra 55VP SEM operating at 10 kV (using a spectral resolution of 5nm). Focused ion beam (FIB) sections of selected SK nanostructures were fabricated in a JEOL 4500 FIB-SEM and characterized by scanning transmission electron microscopy (STEM) in a doubly corrected JEOL ARM200F working at 200 kV. Energy dispersive X-ray spectroscopy (EDX) analyses in STEM mode were performed with probe currents of approximately 200 pA and a windowless Oxford Instruments X-Max Silicon Drift Detector with an area of 100 mm$^2$.

3. Results and discussion

Fig. 1 (a) shows a secondary electron image of a typical SK structure. An elemental EDX map (Sn orange, Ga yellow) confirms that the thin Ga$_2$O$_3$ nanowires (<100nm diameter) thread through the larger SnO$_2$ particles. As we demonstrate below (Fig. 3b) the Ga$_2$O$_3$ NW axis is [010], parallel to the [001] direction of the SnO$_2$ particles. The SnO$_2$ particles have well-defined facets, with characteristic (100) and (101) planes. This does not fully agree with the theoretical calculations for SnO$_2$ surface energies that predict that the (110) rutile surface has the lowest energy, and is therefore the most stable thermodynamically. The calculated surface stability in the SnO$_2$ rutile is (110)<(010)<(101)<(001). Nevertheless, the formation of SnO$_2$ crystals with (101) facet planes has been previously reported$^{20}$. Using vapor-solid growth and different temperatures, Zhou et al$^{20}$ were able to tune the [101] facet ratios of SnO$_2$ polyhedra, demonstrating similar structures to the SnO$_2$ particles grown on the Ga$_2$O$_3$ nanowires reported in this article.

Fig. 2 Comparative room temperature CL spectra of the SnO$_2$/Ga$_2$O$_3$ structure. 1 and 2 indicate the points where the cathodoluminescence spectra were taken. SnO$_2$ polyhedron facets are also indicated. (b) and (c) EDS mapping for the Sn and Ga respectively.

Fig. 2 shows room temperature CL spectra recorded from the SnO$_2$ particles at points 1 and 2 in Fig. 1a and compared with the spectrum recorded from a SnO$_2$ wire taken as a reference. SnO$_2$ usually contains a high number of oxygen vacancies that are responsible for its complex luminescence features. Furthermore, in the case of small particles the large surface/volume ratio may affect luminescence properties.
Here, we observe that the isolated SnO$_2$ wire displays luminescence involving broad green-blue (~480 nm) and orange (580-620 nm) emission bands (blue line in Fig. 2). These components have been reported in SnO$_2$ nanowires and in sintered SnO$_2$. The orange emission is usually attributed to oxygen vacancies and/or related states, while coupling of surface states with oxygen vacancies have been proposed for the green-blue emission$^{21,22}$. In the case of SnO$_2$ particles, we find that the CL spectra (red and green lines) from points 1 and 2 in Fig. 1. show two distinct features in comparison with the isolated SnO$_2$ wire. First, the dominant luminescence is the blue-green band, which is consistent with the role that surface states play in this emission. And, on the other hand, the broad orange band is replaced by a narrow emission line at 620 nm.

Previous photoluminescence (PL) studies in SnO$_2$ nanoribbons obtained by laser ablation reporteda strong broad luminescence peak around 620 nm$^{23-25}$ associated with oxygen vacancy – tin interstitials leading to formation of trapped states in the bandgap$^{25}$. Here, we observe that orange emission narrows, what suggests local changes in the electronic levels probably as a consequence of changes of the local crystal microstructure of the SnO$_2$ particles attached to the Ga$_2$O$_3$ nanowire. In order to elucidate this point, we have carried out high-resolution transmission electron microscopy in a cross-section of the SK SnO$_2$/Ga$_2$O$_3$ nanostructures.

A focused ion beam (FIB) section perpendicular to the axis of the Ga$_2$O$_3$ nanowire and containing one of the SnO$_2$ particles was fabricated. A low magnification annular dark field (ADF) image of this section is shown in Fig. 3a, showing the Ga$_2$O$_3$ nanowire centered in the SnO$_2$ particle. To determine the crystallographic relationship of the Ga$_2$O$_3$/SnO$_2$ heterojunction, high magnification ADF images were recorded such as the one shown in Fig. 3b. Here, the projection indicates that the [010] Ga$_2$O$_3$ axis is parallel to [001] SnO$_2$. This orientation relationship is slightly different to previous investigations of similar growths, in which Ga$_2$O$_3$ nanowires had a [110] axis$^{10,11}$. Both orientations are quite common in Ga$_2$O$_3$ due to the anisotropy of the lattice in the b direction. In the current case the Ga$_2$O$_3$ nanowires with a [010] axis act as a lattice-matched substrate for the SnO$_2$.$^{10}$

Dark lines, marking boundaries along {210} planes$^{12}$ of the SnO$_2$ (e.g. marked by a green square in Fig. 3b) were observed. Antiphase$^{26}$ and twin$^{27}$ boundaries in SnO$_2$ have been reported previously. Nevertheless, the atomic structure of the dark lines does not correspond with either of these defects, since it cannot be described as a simple displacement of the SnO$_2$ crystal lattice. Hexagonal tunnels, with a diameter < 3 Å and period of approx. 1 nm, can be seen in the boundaries. To get a better understanding of these boundaries, EDX elemental mapping was recorded as shown in Fig. 4a. Here, two dark boundaries are separated by six unit cells of SnO$_2$.

**Fig. 3.** (a) Low magnification ADF-STEM cross-section image of the area of the SK structure prepared by FIB. (b) Atomic resolution ADF image of the heterojunction between the Ga$_2$O$_3$ nanowire and the SnO$_2$ particle, overlapped with the cation balls model for Ga$_2$O$_3$ (yellow) and SnO$_2$ (orange).
This type of intergrowth was not observed in previous structures grown under similar conditions. On the other hand, this tunnelled intergrowth of $\beta$-Ga$_2$O$_3$ into the SnO$_2$ could explain the luminescence features observed in Fig. 2. It is known that deep centers associated with native defects, such as vacancies, have localized wave functions induced by the broken bonds and strain associated with the displacement of atoms. Here, the tunnelled intergrowth may modify the electronic states structure and promote the narrowing of the orange emission at 620 nm, which was not observed in single SnO$_2$ wires or in previous SnO$_2$ particles on Ga$_2$O$_3$ trunks. This may have been because the particular orientation relationship between the Ga$_2$O$_3$ trunk and SnO$_2$ particle was different. Single Ga$_2$O$_3$ nanowires can present several wire axis orientations, such as [010], [001], [110] or [40-1], usually depending on the synthesis route. In our previous works, either [001] Ga$_2$O$_3$/[10-1] SnO$_2$ or [1-10] Ga$_2$O$_3$/[010] SnO$_2$ relationships were found, whereas in the current case the $\beta$-Ga$_2$O$_3$ [010] nanowire axis is aligned with SnO$_2$ [001] as demonstrated in Fig. 3b. The distribution of hexagonal tunnels in these structures make them good candidates to host ions and could serve as one-dimensional conduction pathways.

Fig. 4. (a) ADF image of an area of the SnO$_2$ particle containing Gallium intergrowth (b) Ga (yellow) and Sn (orange) overlaid EDS map of the same area. (c) superimposed ADF and EDS maps

Fig. 5. (a) Structure of $\beta$-Ga$_2$O$_3$ columns (yellow) coherently incorporated in the rutile SnO$_2$ (orange). (b) Atomic resolution ADF images overlapped with ball model crystal intergrowth structure. Oxygen atoms are not shown in (b). (c) Multislice ADF simulation of the structure described in (a).
4. Conclusions

In summary, Ga$_2$O$_3$/SnO$_2$ material systems grown by thermal evaporation using a catalyst-free method showed $\beta$-
Ga$_2$O$_3$ intergrowths in the SnO$_2$ rutile nanostructure formed
around Ga$_2$O$_3$ nanowires. Electron microscopy shows planar
$\beta$-Ga$_2$O$_3$ units separated by hexagonal tunnels with a diameter
< 3 Å and period of approximately 1 nm in the (210) rutile
plane. Room temperature cathodoluminescence emission was
obtained in the SnO$_2$ particles. Blue and green luminescence
dominate the spectrum because of the surface to volume ratio.
In addition, the CL spectrum at selected points in the SnO$_2$
particles reveals a narrower orange band emission than
previously observed in bulk-like material. The presence of
gallium oxide mono-layers inside the tin oxide lattice could
modify the electronic states and therefore the luminescence
features.

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