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Defect assisted thermal synthesis of crystalline aluminum borate nanowires

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Aluminum borate is attractive in that the material has excellent mechanical properties, chemical inertness, high temperature stability, and a low coefficient of thermal expansion. Moreover, aluminum borate has advantages over a more traditional material, SiC, in that it does not readily oxidize at high temperature and can be produced at lower cost. In this study, we demonstrate a facile route to grow single crystal aluminum borate nanowires directly on bare sapphire surfaces without the need for a catalyst. Our findings point to a growth mechanism in which lattice defects allow B or B2O3 diffusion. The nanowire formation occurs as a means to relieve residual stress that arises due to thermal expansion mismatch between the aluminum borate and alumina phases. Indeed, at a more local scale, the same stress process facilitates diffusion. By adding iron oxide, which has a high diffusion rate in sapphire, one can accelerate this process. The growth mechanism is fundamentally different to the more usual fabrication routes which employ vapor-solid-liquid or vapor-solid growth processes.

INRODUCTION

Quasi one-dimensional nanostructures have drawn significant attention over the last decades because of their potential for technological application as well as for being ideal systems to test and study physical phenomena such as electronic and heat transport or optical properties in constrained dimensionalities. The mechanical properties of nanowires (NWs) or whiskers are also of interest, in particular, as a strengthening material in composites. Aluminum borate is attractive in that the material has excellent mechanical properties, chemical inertness, high temperature stability, and a low coefficient of thermal expansion. Moreover, aluminum borate has advantages over a more traditional material, SiC, in which it does not readily oxidize at high temperature and can be produced at lower cost.

A number of synthesis routes are available for the fabrication of aluminum borate nanowires. For example, a sol-gel process followed by annealing led to single crystal Al2B2O5 and Al18B4O33 nanowires. The choice of temperature provided a degree of control over the nanowire stoichiometry such that at 750 °C Al2B2O5 nanowires were formed, while the higher temperature of 1050 °C led to Al18B4O33 whisker formation with slightly larger diameters. The authors argued that growth occurred through a self-catalytic mechanism. However, usually metal based catalyst systems are employed to drive the reactions. Catalytic routes in which the thermal evaporation of Al2O3, B2O3, and B powders or B2O3, B in the presence of Fe2O3 catalyst nanoparticles supported on alumina substrates have been shown yield Al18B4O33 and Al4B2O9 nanowires, respectively. A chemical vapor deposition (CVD) route using NiB and Pt as the catalysts over sapphire substrates led to the formation of Al18B4O33 and Al4B2O9 nanowires and nanotubes. A comparative vapor study by Cheng et al. employed the use of powdered precursors (boron and boron oxide or simply boron oxide) mixed with aluminum powder to yield Al18B4O33 nanowires. In addition, they successfully grew whiskers with the further addition of Fe2O3 as a catalyst. In the case that nanowires were synthesized without a catalyst (Fe2O3). In all these studies, the authors argued that the formation of the aluminum borate nanowires occurred through the vapor liquid solid (VLS) or vapor solid (VS) mechanisms. In the VLS growth route, a nanowire is extruded from the catalyst particle whose size dictates that diameter of the nanowire. The catalyst also captures and supplies feed material from the vapor phase. In the VS process, the catalyst is in a molten state during nanowire growth while in the VS mechanism the catalyst remains in the solid state. Molecular dynamic and experimental studies suggest the ratio of the VLS growth rate to the VS growth rate strongly depends on the feed material supply rate.

In this study, we investigate the effect of boron feedstock material in the vapor phase over sapphire single crystals at elevated temperature. The procedure leads to the formation of Aluminum borate nanowires through surface reconstruction of the substrate. The addition of Fe2O3 accelerates the process. The formation of the nanowires does not occur through VLS or VS pathways but through dislocation mechanisms.

EXPERIMENTAL

A mixture of commercial B and B2O3 powders in a 3:4 weight ratio were ground together with a pestle and mortar.
The ground mix served as the precursor material. The substrates consisted on r-plane sapphire wafers. Both their polished and unpolished surfaces were explored with and without the presence of commercial Fe$_3$O$_4$ nanoparticles (15-20 nm) on their surface. To form a thin film of the iron oxide nanoparticles on the sapphire substrates, they were first dispersed in ethanol, sonicated for 30 min, and then a drop of the suspension was placed over the substrate surface and then left to dry in ambient conditions. The samples were then mounted into an alumina tube with the precursor a few millimeter upstream from the samples. The alumina tube loaded with precursor mix and samples was then loaded in a quartz tube furnace. A two-step thermal reaction was implemented. First, a pre-heating step during which the temperature was held at 400°C for 30 min was applied. This was followed immediately by a second temperature increment to the desired reaction temperature (700°C, 900°C, and 1100°C) which was then maintained for 3 h. During the reaction, an N$_2$ flow of 350 sccm was applied from the moment that the oven reached 400°C and was held there until the overall reaction time (3 h) was completed. Finally, the reactor and sample cooled naturally to room temperature.

Scanning electron microscopy (SEM) investigations were conducted on a JEOL JSM 6510. High resolution transmission electron microscopy studies (HRTEM) were conducted on a JEOL 2010 retrofitted with two CEOS third-order spherical aberration correctors for the objective lens (CETCOR) and the condenser system (CESCOR). The microscope was operated using an acceleration voltage of 80 kV. Electron energy loss (EELS) investigations were completed on a FEI Tecnai HRTEM operating at 300 kV. The HRTEM samples were prepared by scraping surface material off the substrate surface with a spatula. The removed material was then sonicated in ethanol for 30 min and then a few drops were placed onto standard lacey carbon TEM grid which was then allowed to dry naturally. For the x-ray diffraction (XRD) studies, a Rigaku Miniflex diffractometer was used. The stochiometric evaluation of aluminum borate structures, it has recently been shown that Al$_{18}$B$_4$O$_{33}$ is inaccurate. The updated more accurate stochiometry is Al$_5$BO$_9$ (Ref. 18) which we use when describing our structures.

RESULTS AND DISCUSSION

SEM analysis of the samples allows a relatively facile and useful evaluation of the morphological changes on the substrate surface from the different synthesis parameters (reaction temperature, substrates initial surface roughness, and use or not of a catalyst).

Figure 1 shows a series of SEM micrographs which reveal the surface morphology of the polished and unpolished surfaces of the sapphire substrates in their pristine condition and after the reaction for different temperatures (reaction time 3 h) with no catalyst being implemented. At 700°C, there are no observable differences on either the polished or unpolished surfaces as compared to the pristine crystal. At 900°C, clear changes can be observed. Both surfaces show a corrugated surface with random directions. Generally, the corrugations are narrower, more defined, and at times even show nanowire structures protruding from the surface for unpolished sapphire surfaces. At 1100°C, the corrugations on the surface are better defined as compared to samples prepared at 900°C and have higher yields of nanowire formation. Overview micrographs from a sample prepared at 1100°C on a polished surface shown in Figure 2 highlight large regions packed with nanowires. Again the average nanowire/corrugation width is smaller for the unpolished surfaces as compared to the smooth surface. Moreover, they are narrower than those obtained at the lower temperature of 900°C. The change in corrugation/nanowire width with temperature and surface are summarized in Table I.

For comparison, we performed an identical set of experiments but this time with Fe$_3$O$_4$ nanoparticles deposited on the sapphire surface. Representative SEM micrographs are
provided in the supplementary material, Figure S1. As with the first set of experiments, no observable differences are found with a reaction temperature of 700°C. At 900°C and 1100°C, clear corrugation and nanowire formation can be seen. Again, nanowire development is better at 1100°C. Moreover, in general, the nanowire formation is richer (higher yield) as compared to equivalent samples produced without any Fe3O4 nanoparticle deposition on the surface. In terms of the mean diameters and range of the nanowires/corrugations, in general, the trend is similar to that obtained when using no Fe3O4, namely, the diameters are reduced at higher temperatures. However, the range is broader when Fe3O4 is used and, in addition, the mean value is slightly higher. These differences are highlighted in Table I.

SEM investigations at higher magnifications show the nanowires possess a variety of polygonal cross-sections, most of which are triangular, square, or rectangular (Figures 3(a) and 3(b)). Occasionally, one can observe structures which apparently have hollow cores (Figures 3(c) and 3(d)). Panels e and f show nanowires in a development stage.

HRTEM investigations from numerous nanowires revealed that the nanowires are single crystalline along their entire length. No distinct orientation along their long axis was observed. Lattice information derived from the d-spacings, selected area electron diffraction (data not shown), and Fourier transforms of the crystalline nanowires (e.g., Figure 4) suggests the nanowires are predominantly Al6BO9 with a small fraction of Al5B2O9 nanowires. XRD studies confirmed the presence of crystalline Al6BO9 nanowires (see Figure S2 in the supplementary material). The presence of Al6B2O9 is less easy to determine since its XRD signatures overlap with those from Al5BO9. However, the relative intensities of certain peaks suggest Al5B2O9 is present. For example, Al4B2O9 has a peak at 26.5° and Al5BO9 has a pair at 26.5° and 27°. The relative intensity of this pair in the as produced samples differs from the reference Al5BO9 pair, in that, the peak at 26.5° is significantly stronger which would be expected if a contribution from Al4B2O9 nanowires existed.

Local EDX studies on the nanowires confirmed the presence of Al and O; however, EDX as an elemental analysis technique is not sensitive to B (see Figure S3 in the supplementary material). Hence, we conducted local EELS investigations as this spectroscopic route is sensitive to boron. The studies confirmed the presence of boron along with Al and O in the nanowires. Figure 5 shows energy filtered elemental mappings for two nanowires. Examples of local EELS studies on the nanowires are provided in Figure S4 in the supplementary material. It is worth noting that no Fe was detected in the nanowires for samples formed in the presence of Fe3O4. Moreover, no Fe-based particles in any form were ever observed at the ends of the nanowires.

The lack of any evidence of catalyst particle at the end of the nanowires and, indeed, the ability of developed synthesis route to yield single crystal aluminum borate nanowires even without the presence of Fe3O4 suggest the traditional VLS and VS growth mechanisms are not pertinent in this synthesis route. Moreover, the surface restructuring in which first corrugations develop and then further evolve into nanowires indicates a fundamentally different formation mechanism. The fact that the corrugation and nanowire development occurs more readily on the unpolished surfaces provides us an important clue, namely, structural defects (e.g., step sites and possibly cracks) play a role. In addition, the surface not only restructures but as it does so it forms a new material, viz., it changes from single crystalline alumina to single crystalline aluminum borate nanowires. This tells us that B incorporates into the sapphire substrate. At elevated temperatures, the precursor mix (B and B2O3) result in the formation of B2O2 in the vapor phase—see Reaction (1).

| TABLE I. Diameter ranges and averages of the NWs at an intermediate formation stage (900°C) and at their fully developed state (1100°C). |
|---|---|---|---|---|---|---|---|
| Back side | 900°C | 1100°C | Polished side | 900°C | 1100°C | 900°C | 1100°C |
| Range (nm) | Mean (nm) | Range (nm) | Mean (nm) | Range (nm) | Mean (nm) | Range (nm) | Mean (nm) |
| Without Fe3O4 | 400–1500 | 1000 | 150–1600 | 550 | 450–4000 | 1600 | 450–3000 | 950 |
| With Fe3O4 | 400–3000 | 1100 | 200–2200 | 650 | 450–400 | 1300 | 150–1300 | 550 |

FIG. 3. Panels A through D provide SEM micrographs illustrating the different types of cross-sections for the nanowires. Panels E and F show nanowires in a development stage.
Thus, the B₂O₂ must either decompose at the alumina surface and lead to B to diffusion into the alumina and/or B₂O₂ diffuses directly into the alumina. The diffusion process will be easier at lattice defects, such as dislocations/nanocracks. The process will be self-propelling once B or B₂O₂ diffuses into the alumina as the thermal expansion mismatch between the matrix material (alumina) and the diffused material forming provide residual stress which leads to bond breakage which in turn facilitates further diffusion.¹⁵,¹⁶ Thus, there will be an incremental breaking of bonds and diffusion. This process will also lead to fracture formation which initially forms surface corrugation and eventually nanowires. In other words, as the aluminum oxide changes to aluminum borate, the nanowire formation takes place to relieve the inherent stress build-up in the process. The observation that the corrugation widths and nanowire diameters are smaller when further developed (at higher temperatures) fit nicely with the above description and also explains why the nanowire formation is slower on the polished surface (fewer defects). The enhanced yield of aluminum borate nanowires upon the inclusion of Fe₃O₄ on the surface of the alumina further corroborates the proposed nanowire growth mechanism. Iron oxide is known to be highly soluble in alumina and in the process of diffusing in will form surface defects as well as nanocracks due to thermal expansion mismatch.¹⁵,¹⁷ These defects will enhance the diffusion of B or B₂O₂ and thus accelerate aluminum borate nanowire formation. Presumably, the simultaneous incorporation of iron and boron is unfavourable and hence Fe is never detected in the nanowires. It may be that the iron diffusion is simply so rapid that the opportunity for simultaneous incorporation is limited. Further studies are required to better elucidate this aspect.

In summary, contrary to previous predictions,¹² our findings conclusively show that one can grow single crystal aluminum borate nanowires directly on bare sapphire surfaces without the need for a catalyst. The data point to a growth mechanism in which lattice defects allow B or B₂O₂ diffusion. The nanowire formation occurs as a means to relieve residual stress that arises due to thermal expansion mismatch between the aluminum borate and alumina phases. Indeed, at a more local scale, this same stress process facilitates diffusion. The growth mechanism is fundamentally different to the more usual fabrication routes which employ VLS or VS growth processes.

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See supplementary material at http://dx.doi.org/10.1063/1.4737115 for further micrographs of catalyst assisted aluminum borate nanowires, x-ray diffraction data (XRD), and electron energy loss spectroscopy (EELS) data.