Single-crystalline mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) nanowires have been synthesized on silicon substrates by forcing aluminum and chromium chloride powders to react under an ammonia gas flow. The diameter and length of the nanowires have uniform diameters of $<100$ nm and several micrometers, respectively. High-resolution transmission electron microscope and selected-area electron diffraction analyses indicated that the nanowires were almost structural defect free and had a single-crystalline phase with a $\langle 0001 \rangle$ growth direction. The photoluminescence spectra showed that the mullite nanowires reached an emission peak at the center wavelength of 442 nm originating from the Al–O bonds in preference to the Al–O and Si–O bonds in the mullite bonding structure. Comparison of the photoluminescence between as-synthesized, oxygen–annealed, and plasma-etched nanowires indicates that the nanowires have few defects (i.e., oxygen vacancies).

I. Introduction

Dimensionality, shape, and size have been known to play a significant role in determining the properties of materials.\textsuperscript{1–3} In this regard, one-dimensional nanostructures such as nanotubes and nanowires have been the focus of considerable research into their use to improve the physical and mechanical properties.\textsuperscript{4–6} Recently, carbon nanotubes (CNTs) have been reported as potential elements for reinforcement in ceramic matrix composites (CMCs).\textsuperscript{7–10} However, the whiskers are limited by whisker damage during the course of processing and densification of composites. Such problems may be solved by using mullite nanowires that could have excellent mechanical properties due to a perfect single-crystalline nature free from defects. Their nano-size could be also useful for processing applications due to a perfect single-crystalline nature free from oxygen vacancies.

II. Experimental Procedure

The growth of the single-crystalline mullite nanowires was performed in a horizontal hot-walled CVT system (Fig. 1). Si/SiO$_2$ substrates oxidized by the wet oxidation method were used. The solid Al (purity 99.5%) and CrCl$_2$ (purity 99.9%) powders placed in quartz susceptors, respectively, were inserted into the center of a quartz tube at 2 in. intervals. The oxidized substrates, deposited with a 0.2-nm layer of Ni by sputtering, were placed in the quartz tube at a distance of 2 in. from the Al powders. The temperature of the furnace was increased at a heating rate of 50 C/min from room temperature to the reaction temperature of 1000 C under a flow of ammonia gas at a rate of 20 cm$^3$/min, maintained for 10 min under a constant flow of ammonia, and then cooled down to room temperature. The quartz tube was then degassed and purged with argon gas.

The morphologies and crystal structures of the nanowires grown on the substrates were characterized using scanning electron microscopy (SEM) and X-ray powder diffraction. Further structure and stoichiometry analyses of the nanowires were performed using high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDS). The photoluminescence (PL) spectra were measured at room temperature with an excitation wavelength of 325 nm (He–Cd CW laser).

III. Results and Discussion

Figure 2 shows the SEM images of the typical mullite nanowires synthesized on the substrates using a CVT process. The nanowires with a high aspect ratio were distributed over the entire area of the substrates (Fig. 2(a)) and had uniform diameters of $<100$ nm and lengths of several micrometers (Fig. 2(b)). The overall crystalline nature of these nanowires was confirmed as a high-quality mullite structure using an X-ray diffraction pattern. The low-magnification TEM image in Fig. 3(a) shows that most nanowires have uniform diameters of $<100$ nm and lengths of several micrometers. Although Ni was used as the catalyst and it
Fig. 2. Scanning electron microscopy images of mullite nanowires grown on substrates by annealing at 1000°C for 10 min. (a) Low and (b) high magnification.

Fig. 3. (a) A low-magnification transmission electron microscopy (TEM) image of mullite nanowires. (b) Energy-dispersive X-ray spectroscopy (EDS) spectrum of a selected individual nanowire in the image (a). (c) High-resolution TEM image of mullite nanowire. The inset shows the selected area electron diffraction pattern of the wire, recorded along the [110] zone axis.
clearly contributed to the growth of the nanowires, no Ni globules or elements in the nanowires were identified in the SEM observations and the EDS analysis. The failure to observe any Ni globules or elements suggests that the catalysts were etched out by the chloride vapors during the growth of nanowires. As shown in Fig. 3(b), the EDS analysis of a selected individual nanowire shows that it is composed of Al (80.7 wt%), Si (19.3 wt%), and O elements, which correspond to the stoichiometric composition of 3Al$_2$O$_3$·2SiO$_2$. The HRTEM observation (Fig. 3(c)) also shows that the mullite nanowires are smooth and almost structural defect free. The SAED analysis, recorded along the [110] zone axis, further demonstrated that the nanowires are a single-crystalline form of the orthorhombic Pham structure with a ⟨0001⟩ growth direction (inset of Fig. 3(c)). The HRTEM lattice image shows that the fringe spacing of the mullite nanowire corresponding to the interplanar distance of {0001} planes is 2.95 Å. This lattice expansion on the [0001] plane compared with the bulk mullite may be ascribed to the quantum confinement effects and/or stresses generated on the curved surfaces of the nanowires, which is expected to be significant as the size approaches the nanometer scale.

In the present process, the major vapor species in the CVT reactor are SiCl$_4$, AlCl$_3$, NH$_3$, H$_2$O, and HCl. Therefore, the overall reactions for the mullite nanowire growth could be as follows:

$$2\text{SiCl}_4(v) + 6\text{AlCl}_3(v) + 13\text{H}_2\text{O}(v) = 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s) + 26\text{HCl}(v)$$

(1)

The SiCl$_4$, AlCl$_3$, and H$_2$O vapors can be formed through the sub-reactions as follows:

$$2\text{Al}(s) + 9\text{CrCl}_2(s) + 4\text{NH}_3(v) = 2\text{AlCl}_3(v) + 12\text{HCl}(v) + 9\text{Cr}(s) \downarrow + 2\text{N}_2(v)$$

(2)

$$3\text{SiO}_2(s) + 6\text{CrCl}_2(s) + 4\text{NH}_3(v) = 3\text{SiCl}_4(v) + 6\text{H}_2\text{O}(v) + 6\text{Cr}(s) \downarrow + 2\text{N}_2(v)$$

(3)

As the reactants in Eq. (3), SiCl$_4$ and H$_2$O vapors as the silicon and oxygen sources originate from the amorphous silica thin film on the oxidized substrate formed during wet oxidation. The CrCl$_2$ powder remains in the Cr powders on the quartz susceptor of the CVT reactor after the reaction and thus acts as a chloride source for the overall CVT process.

Figure 4 shows a typical PL spectrum from the mullite nanowires in the as-synthesized state, annealed at 600°C in O$_2$ for 2 h, and plasma etched by a CF$_4$+O$_2$ mixed gas at room temperature. The excitation wavelength was 325 nm at room temperature. All spectra show a strong PL peak at the center wavelength of 442 nm (2.8 eV in photon energy) that can be attributed to the quantum confinement effects and/or the Al–O–Si bonds of the mullite bonding structure. The intensity of the PL peak of annealed nanowires is similar to that of the as-synthesized, as-synthesized, annealed in oxygen, and plasma etched nanowires. This result implies that the radiative centers leading to the measured PL are generated from the Al–O–Si bonds in the mullite bonding structure. Peng et al. observed that Al$_2$O$_3$ nanowires and nanobelts have various emission intensities in different thermal annealing atmospheres such as O$_2$ and H$_2$ owing to the optical transitions in oxygen-related defects, F$^+$ (oxygen vacancy with one electron) center. In the mullite nanowires, however, the PL peak intensity and the position for the annealed nanowires were barely changed. This may be due to the fact that the mullite nanowires synthesized in this study had a perfect single-crystalline nature with few defects (i.e., oxygen vacancies). On the other hand, the increase of the PL intensity as well as red shifting of the peak position in the plasma-etched nanowires can be principally attributed to the increase of the oxygen vacancy density, resulting from the destruction of the Si–O bonds in the nanowires. It has been reported that with the increase of the oxygen vacancies, the band gap of the silica becomes narrow dramatically. Similarly, an increase of the oxygen vacancies in the nanowires may induce a narrow band gap. As the mullite nanowires synthesized in this study are single crystalline with few defects, they could be used as novel reinforcements for high-temperature CMCs.

IV. Conclusions

The mullite nanowires with high aspect ratios were synthesized on the substrates using CVT process. The nanowires had uniform diameters of ∼100 nm and a length of a few micrometers. The TEM characterization and PL measurements from the nanowires with as-synthesized, annealed in oxygen, and plasma etched by a CF$_4$+O$_2$ mixing gas indicate the single-crystalline and defect-free nature of nanowires. The mullite nanowires could offer good opportunities for highly toughened ceramic, metal, and polymer composites.

References


