Doped spiral alumina nanowires

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Spiral alumina nanowires, doped with Cr and Si, are directly and reliably produced in bulk quantities via annealing of high entropy alloys.

Various oxide nanowires have recently become important in the fabrication of nano-scale devices, for example Ga2O3, MgO, In2O3, SiO2, and ZnO nanowires and/or nanobelt structures have been successfully generated and tested.1 Researchers continue to explore other oxides materials, e.g. the alumina nanowires, which exhibit good photo-luminescence performance.1 The alumina nanowires are normally made via transition metal catalysis.1–3 Interestingly, the direct heating of SiO2 and Al mixture can also produce the alumina nanowires doped with Si.4 When the concentration of Si-dopants increases the alumina nanowires become amorphous.5 In this Communication, we report a simple route to bulk yields of doped spiral alumina nanowires, which has been accidentally discovered during the annealing of high entropy alloys. Studies of traditional alloys have recently focused on the multi-element system, so-called the high entropy alloys (HEAs).6 HEAs, usually made from an equimolar mixture of more than five different elements, have been tested and have realized a higher degree of hardness, resistivity, thermal stability and anti-corrosion than the common binary and ternary systems.6 However, atoms with differing radii are difficult to pack simultaneously within a unit cell, thus, the HEAs often exhibit a quasi-crystalline structure and their configurational entropy (∆Sconf = R \ln n, R: gas constant, n: the number of elements) is 2.2R–2.7R, ca. three times greater than the normal alloy systems (~1.1R).

Our experiments were initially focused on the enhancement of HEA crystallinity via the annealing process, so the atoms are allowed to rearrange via Frenkel and Schottky defects. Unexpectedly, the spiral nanowires, grown on the HEA surfaces, are present. Our routine experiments focus on the Ti–Si–Ni–Zr–Cr–Al–Fe system and experimental procedures are as follows. An equimolar mixture of granular Ti, Si, Ni, Zr, Cr, Al, and Fe (purity, 99.9%), corresponding to ∼5%–35 at% for each element in bulk, was firstly melted by an induction furnace in a vacuum. The resultant bulk alloy was then ground into a powder form (dark grey, ca. 300–400 mesh) via a ball-milling system. The annealing of alloy powder (2 g, loaded in an alumina container) was carried out in a ceramic tube (55 mm in diameter and 1200 mm in length) placed in a horizontal electrical furnace. The alumina tube has been vacuated to 10–2 Torr, followed by the introduction of a 100 sccm Ar–H2 flow (9:1, 100 sccm). The furnace temperature was first raised to 950 °C for 1 h, and further increased to 1350 °C for 1 h. The furnace was then allowed to cool to room temperature. We find that the annealing results in a sintered layer formation on the HEA surfaces and the removal of the sintered layer exposes brown–yellow powders, which are collected for electron microscopy and other related analyses.

SEM images show nanowire coverage of the HEA matrix (Fig. 1a and b) and the close-up image reveals that the nanowires

Fig. 1 (a) A SEM image of As-made sample. (b) a close-up SEM image from the nanowire coverage. Insert: a close-up SEM image at the HEA surface. (c) SEM image of an individual nanowires, which clearly shows a spiral surface morphology. (d) HRTEM image of a spiral nanowire. Square: a highlighted HRTEM image from the Fig. 1d. (e) Selected electron diffraction of a nanowire. (f) an EDX profile of nanowire.

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actually sprout from the bulk phase (insert, Fig. 1b). Note: the heating of alumina in the presence of Fe/Co contaminants can also produce nanowire materials,\(^2\), the insert in Fig. 1b immediately rules out the possible generation of nanowires from the furnace tube. The nanowires are fairly uniform in length (3–5 \(\mu\)m) and diameter (30–45 nm). Interestingly, the surface morphology of nanowires is spiral-like (Fig. 1b–c), which has been further verified by HRTEM investigations. The clear and continuous lattice fringes shown in the TEM image (Fig. 1d) suggest that the nanowires are likely to be a single crystal, also supported by the electron diffraction (ED, Fig. 1e). The ED pattern reveals the following features. Firstly, the indexed spots are well-fitted by a polycrystalline structure. The spiral morphology is unlikely to be due to the screw dislocations, because no twin-boundaries or large defective lattices are present (square, Fig. 1d), which is consistent with the ED pattern. EDX analyses of the individual nanowires show strong signals of O and Al, together with small Si and Cr peaks. The Cu and C arise from the TEM grid and carbon coated film, respectively. EDX analysis has been repeatedly carried out on the individual nanowires and the result is similar. The detection of Al, Si and Cr in the nanowires is consistent with the starting material and the origin of O is possibly the residual trapped air.

The outcome of the EDX and ED analyses seems to suggest that the nanowires are essentially \(\alpha\)-Al\(_2\)O\(_3\), doped with Si and Cr. Firstly, the \(\alpha\)-Al\(_2\)O\(_3\) is mostly a hcp structure, which is consistent with the ED profile. Secondly, the Al and O lattices can be partially substituted by the Si and Cr without significantly disturbing the hcp structure.\(^7\) For example, when the Si substitutes Al the SiO\(_2\) segments are produced (i.e. O–Al–O \(\rightarrow\) O–Si–O). Likewise, the replacement of Al by Cr leads to the O–Cr–O formation. Since the heating of SiO\(_2\)/Al mixture can also produce the Si-doped alumina nanowires, the novelty presented in the current study is that the nanowires are spiral and are automatically doped with Cr, which have not been previously achieved. The low-melting-point metal (Al) is firstly zone-refined (i.e. precipitation) during annealing process,\(^8\) the nanowires can therefore grow on the basis of the following equations.\(^2\),\(^9\)

\[
2\text{Al}(g) + x\text{SiO}_2(g) \rightarrow 2\text{AlO}_x(g) + x\text{Si}(g) \quad (1)
\]
\[
\text{Al}(g) + x\text{SiO}_2(g) \rightarrow \text{AlO}_x(g) + x\text{SiO}(g), \text{ or} \quad (2)
\]
\[
4\text{Al}(l) + 3\text{SiO}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s) + 3\text{Si}(s). \quad (3)
\]

The subsequent zone-refining element, Cr, relative to the Ti, Zr, Ni and Fe, thus precipitates the nanowire growth. The above description explains the automatic incorporation of Cr into the Si-containing alumina nanowires. SEM examinations reveal that the pitch of current spiral nanowires is ca. 10–15 nm. This value does not change by varying the annealing temperature (1250–1400 °C). According to the Madelung equation \(U_l = \lambda \exp(-R/\rho) - q^2/2R\), \(\lambda\) and \(\rho\): empirical parameters, \(R\): the nearest-neighbor distance, \(q\): charge, the binding energy of an ionic crystal is exponentially dependent on \(R\) and decreases with \(q^2\), which means that the incorporation of a covalent entity (Si) into the alumina induces local structural stress. Consequently, the unidirectional growth of nanowires, triggered by the VLS mechanism, is modified. If the localized stress is concentrated along the \(c\)-axis then the solidification of a saturated droplet at the L–S interface preferentially adopts an asymmetric deposition, which produces wavy-like surfaces on the nanowires. This description is similar to the growth of contact angle anisotropy (CCA) at the L–S interface, reported by McIlroy et al.\(^10\) Repeat experiments produced similar spiral nanowires, indicating a reliable production method. The materials have been made in bulk quantities to test their photo-luminescence (PL) and electronic field emission properties.

The blue emission from alumina has been widely studied.\(^11\)–\(^13\) The emission is mainly caused by the electronic transitions at the energy levels of \(F^\prime\) (i.e. the singly ionized O-vacancies).\(^11\)–\(^13\) The blue- and red-shifts, due to variation in the \(F^\prime\) concentration and existence of impurities, have also been observed.\(^11\)–\(^13\) On the other hand, the silica nanowires emit a green light.\(^14\) Since our nanowires consist of both oxides, a combined PL profile of silica and alumina is therefore anticipated. A nanowire compacted film excited by an UV at 325 nm wavelength shows a broad band centered at 500 nm, together with a distinguishable peak at 662 nm (Fig. 2a). They correspond to blue–green and yellow light, respectively.
blue–green band centered at 500 nm is consistent with the combined PL profile of silica and alumina, as mentioned above, whereas, the small band at 662 nm has not been previously reported. Previous workers have reported that when the alumina plates are doped with Cr, two transitions take place, i.e. $^4A_2 \rightarrow ^4T_2$ (U-band) at 410 nm and $^4A_2 \rightarrow ^4T_2$(Y-band) at 565 nm, respectively, which is inconsistent with the 662 nm band seen here. The small emission at 662 nm is unlikely to be due to the Cr-dopants, because the substitution of Al$^{3+}$ by Cr$^{3+}$ (i.e. O–Al–O → O–Cr–O) leads to a Cr$^{3+}$-transition between the excited state $^4T_2$ (or $^4T_1$) and lowest $^2E$ state, which is a phonon emission process. The small 662 nm band probably arises from an additional transition, due to the charge transfer between the Cr and Si. The energy involved in this additional electronic transition is expected to be smaller than 2 eV, because the Cr–Si bond is a weak-dipole character.

The electronic field emission measurements on a spiral nanowire film exhibit a slightly lower threshold field (3–4 V μm$^{-1}$, Fig. 2b) than values obtained from other oxides (ZnO, W$_{18}$O$_{48}$) by ca. 2–10 V μm$^{-1}$. The F–N plot is essentially linear (insert, Fig. 2b), indicating a vacuum tunneling mechanism.

In summary:

(1) Novel spiral alumina nanowires are produced via the annealing of HEAs.
(2) Cr is automatically incorporated into the alumina during the nanowire growth.
(3) Nanowires emit blue–green light, together with a small emission at 662 nm.
(4) Nanowires show a well-defined field emission profile and a lower threshold field than zirconia and tungsten oxide.

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Notes and references