

Thermochemical analysis on the growth of NiAl₂O₄ rods

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Experimental Details:

In order to fabricate NiAl₂O₄ submicron-sized rods on sapphire (0001) substrates, we have heated a mixture of graphite and NiO powders. The NiO (Nickel(II) oxide) powders were purchased from Aldrich Chemical Co. Ltd. By means of SEM observation, the NiO powders are polyhedron-shaped with their sides and edges being slightly rounded. The size of the powders are estimated to be in the range of 100 nm-10 μm. The growth was conducted in a quartz tube that has been described in detail in an earlier report [H. W. Kim, N. H. Kim, J. H. Myung, S. H. Shim, *Phys. Stat. Sol. (a)*, 2005, **202**, 1758]. A Au film (with a thickness of 3 nm) was deposited on sapphire (0001) substrates by means of sputtering. Both the substrate and the powder mixtures were placed in an alumina boat that has been loaded in a horizontal tube furnace with a distance between substrate and powders of approximately 10 mm. The growth tube was kept at the reaction temperature for 1 h under a constant flow of air (flow rate: 20 sccm) and Ar (flow rate: 100 sccm). In our preliminary study, submicron-sized rods could not be attained by means of this process with temperatures in the range of 1000–1400 °C (Fig. S1). Accordingly, the growth of NiAl₂O₄ rods was carried out at higher temperatures of 1500 and 1600 °C.

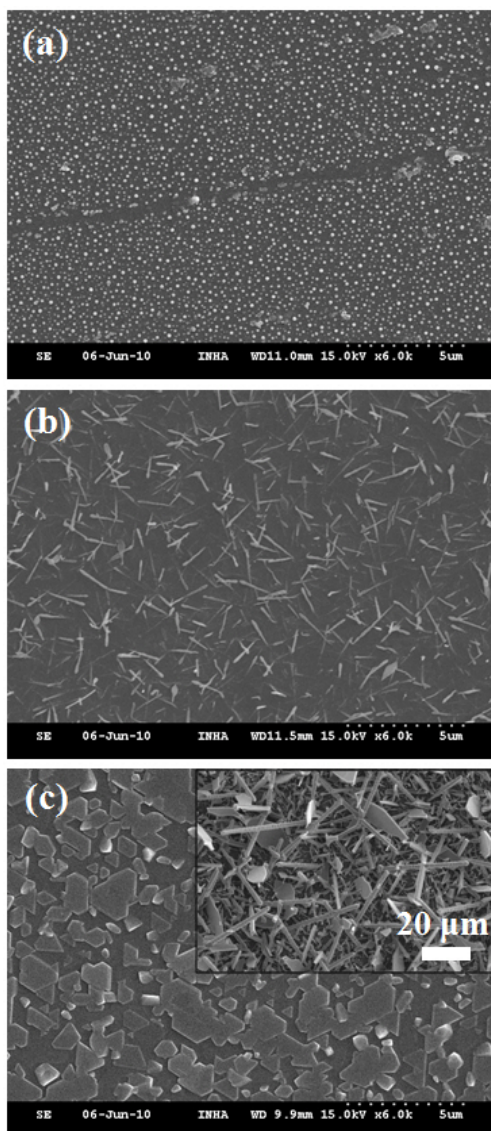


Fig. S1. SEM image of the products synthesized at (a) 1000, (b) 1200, and (c) 1400°C. The inset shows a detailed image describing some part of the product synthesized at 1400 °C. There exist rod-like structures with a diameter in the range of 2–10 μm.

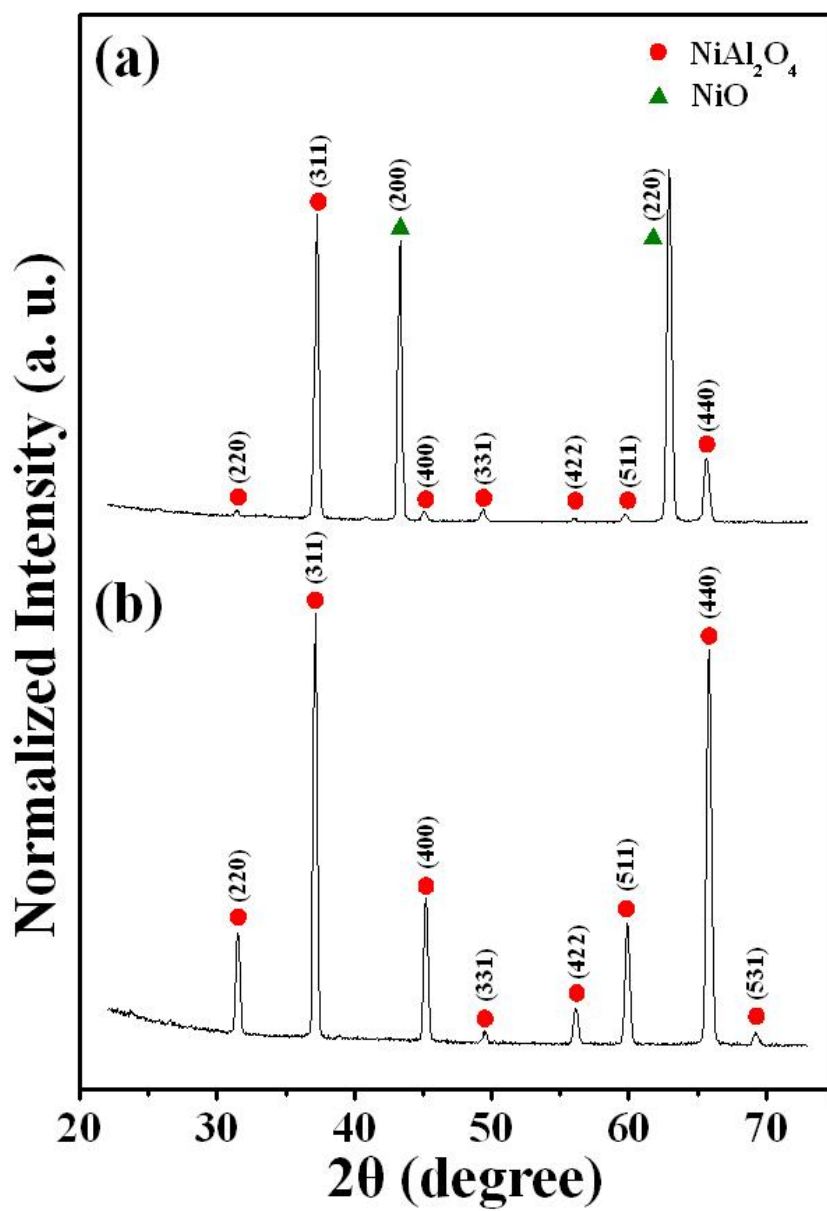


Fig. S2. XRD spectra of the products grown at (a) 1500 and (b) 1600 °C.

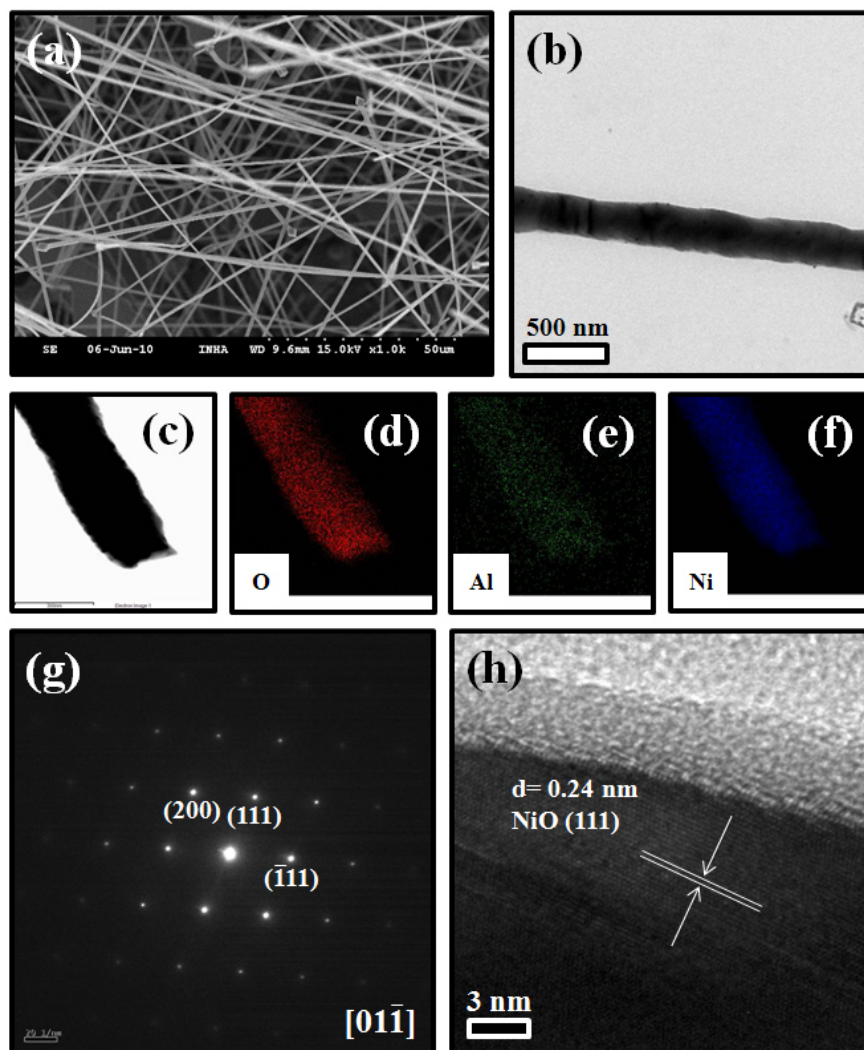


Fig. S3. (a) SEM image and (b) Low-magnification TEM image of 1500°C-grown rods. (c) Typical TEM image of the tip part of the rod and corresponding EDX elemental maps of (d) O, (e) Al, and (f) Ni elements. (g) SAED pattern and (h) lattice-resolved TEM image enlarging the squared box in (b).

Fig. S3(a) shows a top-view SEM image of the product grown at 1500 °C, indicating that the material consists of 1D structures. Fig. S3(b) is a low-magnification TEM image of a rod with a diameter of 270–290 nm. Fig. S3(c) reveals that no particle is attached to the tips of the 1D structures. Fig. S3(d–f) shows TEM–EDX elemental maps of the elements O, Al, and Ni, respectively. Fig. S3(g) is a selected area electron diffraction (SAED) pattern of the rod grown at 1500 °C and taken along the $[01\bar{1}]$ axis, which shows that diffraction spots correspond to the (200), (111), and $(\bar{1}11)$ lattice planes of the cubic NiO phase. In addition, the presence of clear lattice fringes indicates a highly single-crystalline quality of the rods with no noticeable structural defects, such as dislocations and stacking faults (Fig. S3(h)). The spacing of 0.24 nm between adjacent lattice planes corresponds to the distance between two $\{111\}$ crystal planes of the NiO phase.

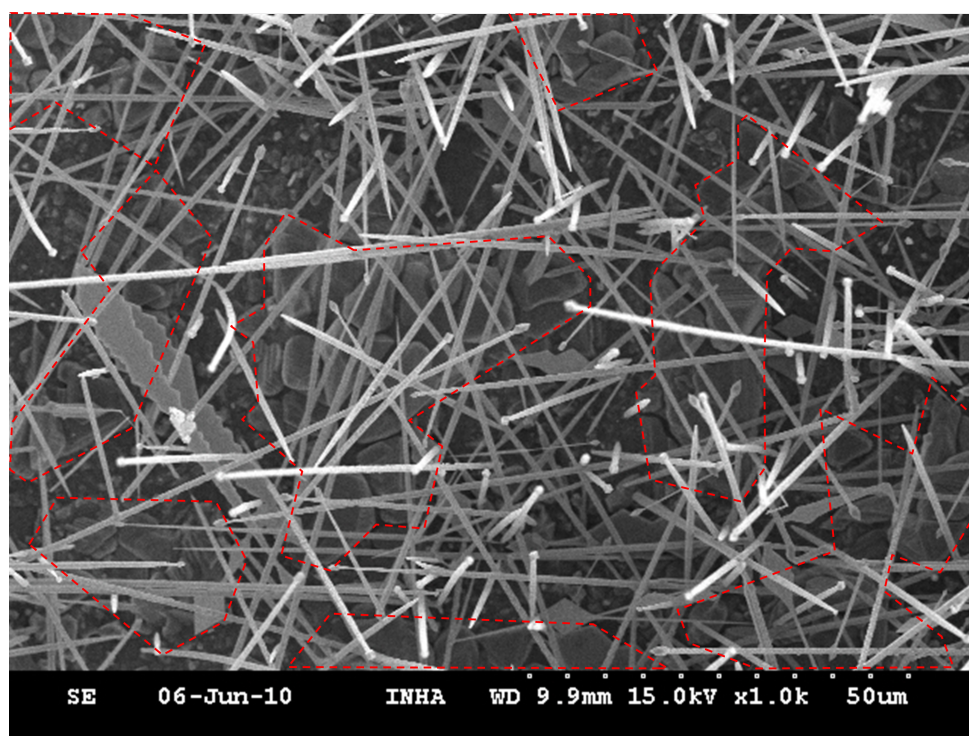


Fig. S4. Plan-view SEM image of the product prepared at 1500 °C. The red dotted areas exhibit the file-like or cluster-like structures on top of the substrate.

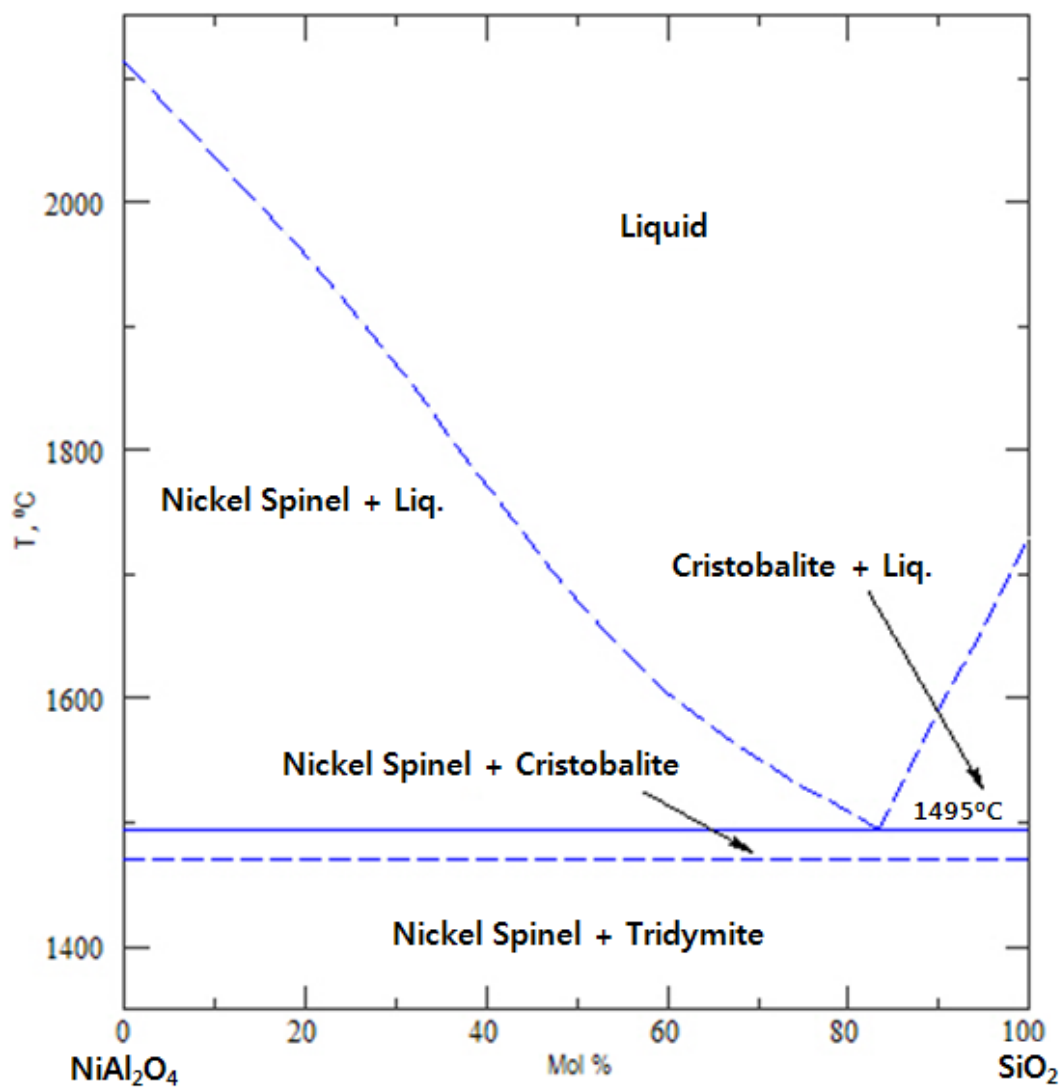


Fig. S5. NiAl₂O₄-SiO₂ phase diagram [B. Phillips, J. J. Hutta, I. Warshaw, J. Am. Ceram. Soc. 46 (1963) 579-583].

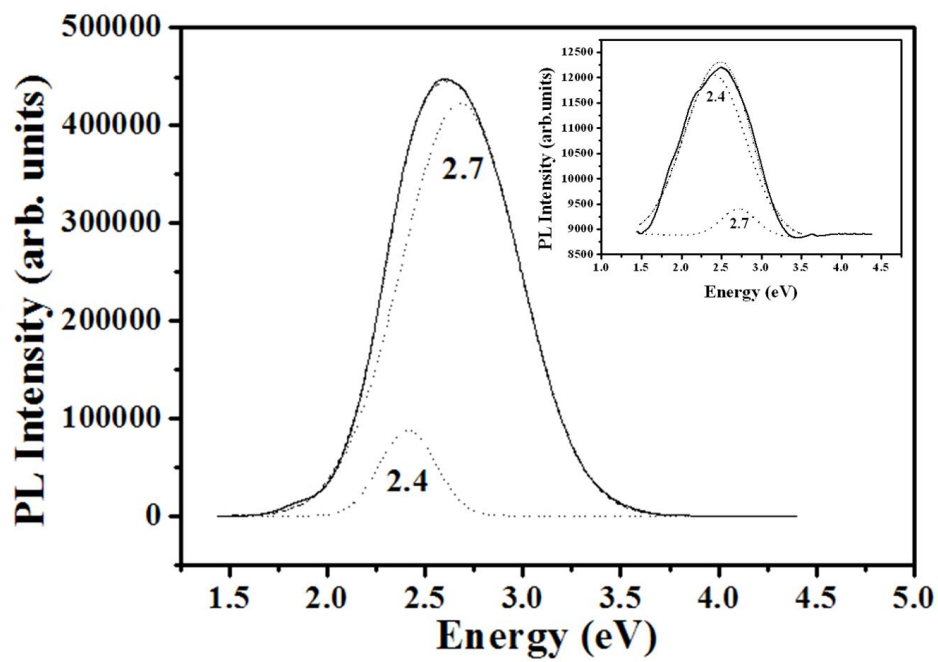


Fig. S6. Room-temperature PL spectrum of rods grown at 1600 °C and (inset) at 1500 °C.

It can be seen that the overall intensity, as well as the peak position, of the band around 2.4 eV were almost invariant when increasing the growth temperature from 1500 °C to 1600 °C. Since the rods grown at 1500 °C are mainly comprised of NiO and only partly of NiAl₂O₄, with the NiAl₂O₄ phase not contributing to the PL emission, we surmise that the band located at 2.4 eV can be mainly attributed to the NiO phase. Similarly, the peak at 2.4 eV has previously been observed in the cathodoluminescence spectrum of NiO [Diaz-Guerra, A. Remon, J. A. Garcia, J. Piqueras, *Phys. Stat. Sol. (a)*, 1997, **163**, 497]. This emission has been assigned to the magnetic exciton state 3d⁸2p. By comparing the PL spectra of the rods grown at 1600 °C and at 1500 °C, we infer that the relative strong band peaked around 2.7 eV exclusively originates from the rods synthesized at 1600 °C. On the basis of the XRD patterns, it has been revealed that the main component of the rods prepared at 1600 °C corresponds to the cubic NiAl₂O₄ phase with some minor contribution of the cubic NiO phase. However, The TEM analysis (Fig. 1) indicates that the rod tip is mainly composed of SiO_x. Because PL of the cubic NiAl₂O₄ phase has not been reported so far, we suggest that the peak at 2.7 eV arises from the SiO_x phase of the rod tips. A similar blue emission with a peak position in the range of 2.6–3.0 eV has been previously observed in PL spectra of SiO_x nanowires [Y. W. Wang, C. H. Liang, G. W. Meng, X. S. Peng, L. D. Zhang, *J. Mater. Chem.*, 2002, **12**, 651; D. P. Yu, Q. L. Hang, Y. Ding, H. Z. Zhang, Z. G. Bai, J. J. Wang, Y. H. Zou, W. Qian, G. C. Xiong, S. Q. Feng, *Appl. Phys. Lett.*, 1998, **73**, 3076; Z. Q. Liu, S. S. Xie, L. F. Sun, D. S. Tang, W. Y. Zhou, C. Y. Wang, W. Liu, Y. B. Li,

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X. P. Zou, G. Wang, *J. Mater. Res.*, 2001, **16**, 683; G. Z. Ran, L. P. You, L. Dai, Y. L.

Liu, Y. Lv, X. S. Chen, G. G. Qin, *Chem. Phys. Lett.*, 2004, **384**, 94].