Three-dimensional AlN microroses and their enhanced photoluminescence properties†

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Received (in Cambridge, UK) 3rd June 2008, Accepted 22nd July 2008
First published as an Advance Article on the web 12th September 2008
DOI: 10.1039/b809380f

Novel three-dimensional AlN microroses, for the first time, have been synthesized *via* direct reaction between Al and N_2 in arc plasma without any catalyst and template.

Since the discovery of carbon nanotubes (CNTs), one-dimensional (1D) nanostructures with various morphologies, such as wire, rod, belt and tube, have attracted considerable attention due to their potential usage as building blocks for fabricating nanoscale electronic, optoelectronic, electrochemical and sensor devices.[1–4] Recently, it has been found that the properties of nanomaterials may have strong dependence on their size, morphology, and shape.[5,6] Therefore, the synthesis of novel complex nanostructures is of great interest because of their fascinating properties and potential applications. In addition, understanding the formation mechanism of these novel complex nanostructures should lead to developments in advanced functional nanomaterials. To date, most of the three-dimensional (3D) nanostructures have been produced by stacking 1D or two-dimensional (2D) inorganic nanostructures with simple morphologies into hierarchical 3D architectures, usually through self-assembly routes.[7–9] Therefore, it is still a great challenge to prepare high-quality complex 3D nanostructures directly through one-step techniques, rather than the simple assembly of 1D or 2D nanostructures.

III-Nitrides with various structures and morphologies have attracted increasing attention in recent years due to their significant applications, such as optoelectronic and field-emission devices.[10–12] As an important candidate of these compounds, aluminium nitride (AlN) with the highest band gap of about 6.2 eV, has various unique properties such as excellent thermal conductivity, high chemical resistance, high melting point, and has gained considerable interest.[13,14] In particular, AlN nanostructures have shown novel physical and chemical properties, for example, small electron affinity, strong piezoelectricity, high surface acoustic wave (SAW) velocity and a tunable band gap, which are essential for applications in field emitters, flexible pulse-wave sensors and ultraviolet nanolasers.[15–18] Recently, some researchers have reported the photoluminescence (PL) properties of AlN nanostructures and indicated that the efficient visible luminescence of AlN in the 2–4 eV region makes it a promising material for light-emitting applications.[19] To date, various AlN nanostructures such as nanobelts, nanotubes, nanocones and hierarchical comb-like structures, have been synthesized *via* different processes.[20–23] However, there has been only few reports on the formation of high-quality complex 3D AlN nanostructures. In this communication, we report for the first time the direct synthesis of novel complex 3D AlN microroses without any catalyst and template. The subsequent characterization of photoluminescence emissions reveal that these AlN microroses have a much higher relative intensity of emission as compared with AlN nanowires, indicating potential applications in light-emission devices.

The XRD pattern of the as-synthesized AlN microroses is shown in Fig. 1(a). All observed peaks can be indexed to a pure hexagonal phase (space group: $P6_3mc$ (186)) of AlN (JCPDS file No. 08-0262) with calculated lattice constants $a = b = 3.120$ Å, and $c = 4.984$ Å. No peaks of any other phases or impurities were detected. The chemical composition of the microroses was further determined by energy-dispersive X-ray spectroscopy (EDS) (Fig. 1(b)). Only peaks of the elements Al and N are present in the EDS spectrum with an approximate ratio of 1 : 1, implying the stoichiometry of AlN.

The morphologies of the sample can be seen in the scanning electron microscope (SEM) images in Fig. 2. The sample has an interesting rose-like morphology, a large number of complex 3D AlN microroses were formed on the substrate as shown in Fig. 2(a). It is noteworthy that the microroses may be manually separated from the substrate with ease. It can be seen that these microroses have a hemispherical 3D structure with diameters ranging from 10 to 50 μm. Such a 3D microrose structure of AlN has not been reported anywhere before. As shown in the enlarged image of an individual microrose (Fig. 2(b)), the morphology of the rose-like sphere has two parts: 'corolla' and 'torus'. The 'torus' part has a pyramidal shape, which acts as substrate for the growth of the 'corolla'

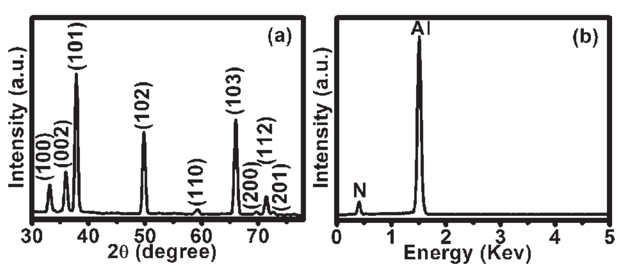

Fig. 1 (a) The corresponding X-ray powder diffraction pattern and (b) EDS spectrum of the as-synthesized AlN microroses.

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† Electronic supplementary information (ESI) available: Experimental section and PL spectrum of the annealed AlN microroses and nanowires. See DOI: 10.1039/b809380f

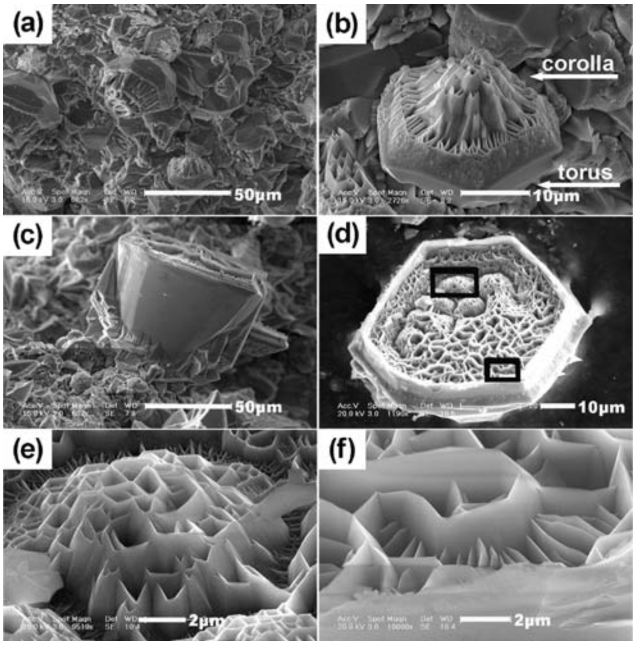

Fig. 2 (a) SEM image of a rose-like nanostructured AlN substrate. (b) Close-up image of an individual rose-like spherical structure. (c) Side-on view of the 'torus' part. (d) Close-up image of another individual rose-like spherical structure of a different shape. (e) Highly magnified image of the big boxed area in panel (d). (f) Highly magnified image of the small boxed area in panel (d).

part. The 'corolla' part is composed of vertically standing and smooth petal-like structures, which presumably arise from the several dozens of nanopetals conglomerating with each other and eventually forming the 3D microrose. The thickness of the layered structures and the apertures between them were found to be about 200–500 nm. The side-on view of the 'torus' part was shown in Fig. 2(c). It can be seen that the size of the 'torus' part was about 50 μm in height and the surface is smooth.

To explore the formation mechanism of the complex AlN microroses, we manually separated a single AlN microrose from the aggregates, shown in Fig. 2(d). This AlN microrose has a different type. It clearly shows that the 'corolla' part of this microrose is underdeveloped, but it has the petal-like structure. We speculate this microrose may be in an early stage of the growth process. The enlarged image of a big box shown in Fig. 2(e) indicates that the petal-like structure has a corolla-like shape. Fig. 2(f) shows that the highly magnified image of an area marked with a small box in Fig. 2(d), from which we can clearly see the petal-like structures arranged in a row. The thickness of the nanopetals is not uniform but decreases gradually from the bottom to the top to form a knife-edge shape. Based on our observations, we suggest a formation mechanism of the complex AlN microroses which involves the following growth processes: (1) initial nucleation of AlN, (2) formation of the 'torus' part with a pyramidal shape, (3) growth of the 'corolla' part of 2D structured nanopetals in a quasi-1D manner, and (4) formation of high-quality complex 3D AlN microroses. In step 1, as the processing temperature increases, thermal decomposition of N_2 and evaporation of the Al column results in the formation of Al and N vapors, and the Al and N vapors are transported by N_2 carrier gas to a certain temperature zone to grow AlN crystals. In this process, the heat convection and temperature gradient produced by arc discharge plasma provide a chemical vapor transport and condensation process, which is responsible for nucleation of AlN.[24] The AlN nuclei will then deposit on the anode aluminium column, resulting in continuing growth of 3D AlN microrose nanostructures. In step 2, the 'torus' part is formed with continuous supply of AlN vapors, which act as substrate for the growth of the 'corolla' part. Further, the 'corolla' part is formed by the nanopetals in a quasi-1D manner from the core of the substrate, *i.e.* step 3.

For the growth of AlN microroses, the 'torus' part and 'corolla' part exhibit asymmetrical growth behaviors along the $\pm[0001]$ directions. It has been reported that the N polar $(000\bar{1})$ surface is stable under N-rich conditions. In contrast, the Al polar (0001) surface is energetically favorable under Al-rich conditions.[25,26] Being heated by the arc, Al is evaporated drastically. As a result, an Al-rich condition is created in the growth of the 'torus' part. Under such conditions, the 'torus' part is formed with a continuous supply of AlN vapors on the Al polar (0001) surface, which is a thermodynamic equilibrium process. As the reaction goes on, more and more AlN is produced and eventually the Al substrate is covered with AlN, which hinders the evaporation of Al and creates a N-rich condition in which the growth process of the 'corolla' part takes place. Under this condition, the 'corolla' part is formed on the N polar $(000\bar{1})$ surface by the nanopetals in a quasi-1D manner.

To further analyze the structural characteristics of the as-synthesized AlN microroses, a HRTEM image was obtained, as shown in Fig. 3. The inset in Fig. 3 is a magnified image of the rectangular outlined section. The interplanar spacing is 0.271 nm (marked between the two arrows), which matches the d-spacing of (100) planes of AlN, in good accordance with our XRD results.

Raman scattering is a useful tool for the characterization of nanomaterials. Six Raman-active modes may be predicted by group theory, *i.e.*, $1A_1(TO) + 1A_1(LO) + 1E_1(TO) + 1E_1(LO) + 2E_2$, because AlN belongs to the space group $P6_3mc$. Fig. 4(a) shows the Raman spectrum of the as-grown AlN microroses. Three distinct peaks centered at 609.8 cm^{-1}, 654.2 cm^{-1}, and 666.9 cm^{-1} are correlated to the first-order vibrational modes of A_1(TO), E_2(high), and E_1(TO), respectively. The low-intensity broad peak around 904.8 cm^{-1} is assigned to the overlap of the modes A_1(LO) and E_1(LO). These results are in good agreement with the results for AlN nanobelts.[20]

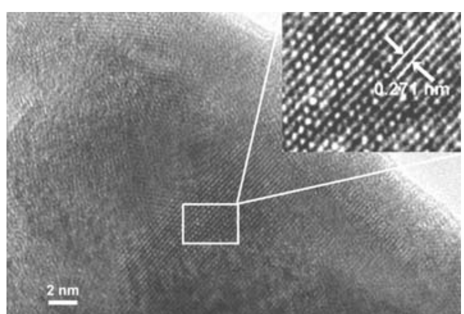

Fig. 3 HRTEM image of the as-synthesized AlN microroses.

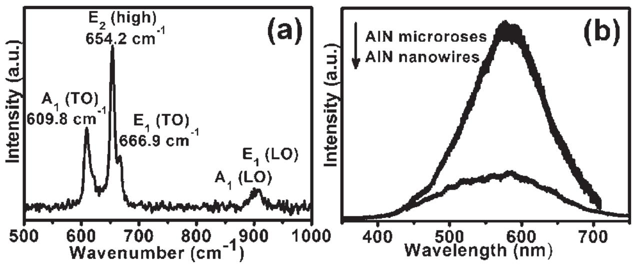

Fig. 4 (a) The corresponding Raman spectrum of the as-synthesized AlN microroses. (b) Photoluminescence spectrum of AlN microroses and nanowires at room temperature.

Fig. 4(b) presents the photoluminescence spectrum of the AlN microroses, which is excited by 325 nm UV light from a He–Cd laser at room temperature. The PL emission from these microroses was compared to high quality AlN nanowires grown in arc plasma[24] as shown in Fig. 4(b). The emission peak at around 580 nm is detected for both AlN microroses and nanowires. Obviously, this band is not the direct band gap emission, but is referred to as deep-level or trap-level emission. Clearly, the emission has generally been attributed to the nitrogen vacancy and the radiative recombination of a photon- (or electron-) generated hole with an electron occupying the nitrogen vacancy,[27] this phenomenon has also been observed previously in AlN nanocones.[22] Compared with the AlN nanowires, the emission intensity of the microroses drastically increases, as shown in Fig. 4(b). Such high emission intensity in AlN microroses may be related to a higher density of nitrogen vacancies. Similar work has also been reported by Yang[28] in which the weak green emission from thicker ZnO nanowires is suggested to be due to the lesser surface oxygen vacancy concentration. We believe that the microroses with vertically standing nanopetals may favor a higher level of surface and subsurface nitrogen vacancies. In addition, the vertically standing nanopetals of these microroses can form the Fabry-Perot microcavities, which may enhance the optical gain and radiation recombination probability.[29–31] To test these hypotheses, we intentionally annealed the AlN microroses and nanowires in high purity N_2 and their PL is shown in Fig. S1 (ESI).† The morphology of the microroses did not change, as shown in the inset of Fig. S1 (ESI).† Compared with the unannealed AlN microroses and nanowires, the emission intensity of the annealed AlN microroses and nanowires shows a marked decrease. The decrease of the emission intensity may be ascribed to the decrease of nitrogen vacancies on the surfaces of the AlN microroses and nanowires after nitridation in N_2. However, the emission intensity of the AlN microroses also appears stronger than that of AlN nanowires, which further confirms that the intensive emission of the AlN microroses mostly attribute to the novel structure with vertically standing nanopetals. The stong PL emission indicates that the AlN microroses have potential applications in light-emitting devices.

In summary, we reported the synthesis of novel complex 3D AlN microroses through direct nitrification of the aluminium metal in arc plasma without any template or catalyst. The morphology of our sample has a novel 3D microrose shape ranging from 10 to 50 μm with two parts: 'corolla' and 'torus'. Furthermore, intensive light emission from AlN microroses has been observed. With excellent photoluminescence properties, the novel AlN microroses have potential applications in electronic and optoelectronic devices.

This work was financially supported by the Natural Science Foundation of China (No. 50772043) and the National Basic Research Program of China (Nos. 2005CB724400 and 2001CB711201).

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