

GaS and GaSe nanowalls and their transformation to Ga₂O₃ and GaN nanowalls

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Two-dimensional nanowalls of GaS and GaSe are obtained by thermal exfoliation around 900 °C, and transformed to Ga₂O₃ and GaN nanowalls upon reaction with air and ammonia respectively at 800 °C, while maintaining dimensional integrity.

Recent investigations of nanostructures by-and-large pertain to zero-dimensional (0D) nanocrystals, and one-dimensional (1D) nanowires and nanotubes.¹ There are only a few studies on the two-dimensional (2D) nanostructures of materials, which are not only important because of possible technological applications, but also because they may define a stage in the formation of other nanostructures, such as nanotubes. In case of carbon having a layered structure in bulk forms fullerenes and onions which are the 0D nanostructures, while the nanotubes are 1D nanostructures. Carbon nanowalls, which are 2D nanostructures, were reported recently.² The growth of carbon nanowalls occurs during the formation of nanotubes by microwave plasma-enhanced chemical vapor deposition.³ These nanowalls have been used as templates to deposit magnetic nanoparticles.⁴ There have also been reports of ZnO nanowalls, and it has been found that ZnO nanorods grow from the nodes of nanowalls.⁵ ZnO nanoflowers of wall-like structure have been prepared hydrothermally in the absence of any organic reagent.⁶ Besides nanowalls, which generally stand vertically on solid substrates and are interconnected, 2D nanosheets of materials such as Zn, CuS, ZnS, Al₂O₃ and Ga₂O₃ are also known.^{7–11} GaS and GaSe, with layered structures similar to graphite, have been considered as ideal for forming nanotubes.^{12–14} We would therefore expect these two materials to also form nanowalls. In this communication, we report the successful synthesis of the nanowalls of GaS and GaSe and their reactions with oxygen and ammonia.

On heating GaS powder in a sealed quartz tube at 900 °C at a rate of 1 °C min⁻¹, we obtained solid deposits at the cooler end of the tube where the temperature was ~400 °C.† An investigation of the deposits showed that they contained beautiful wall structures, as revealed by the scanning electron microscope (SEM) images presented in Fig. 1a and Fig. 1b. The walls form smooth curved surfaces and are well connected, creating an extended network, as shown in the high magnification SEM image in Fig. 1b. The identity of the walls was established from energy dispersive X-ray analysis (EDAX) and X-ray diffraction (XRD) patterns. The

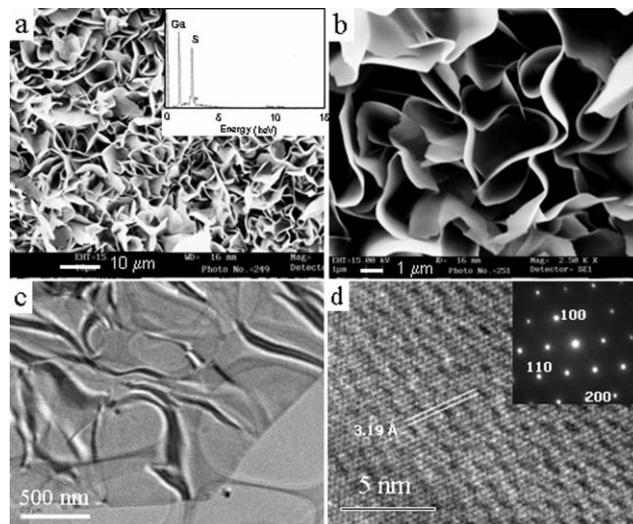


Fig. 1 (a) Low-magnification SEM image of GaS nanowalls covering a large area. Inset shows the EDAX spectrum of the nanowalls. (b) High magnification SEM image of the nanowalls exhibiting a smooth surface—an extended network and intricate curvatures. (c) TEM and (d) HREM images of a nanowall. Inset shows the SAED pattern.

EDAX spectrum (shown as an inset in Fig. 1a), recorded at various locations of the sample, confirmed the Ga : S ratio to be 1 : 1. The XRD pattern of the sample (Fig. 2a) could be indexed on a hexagonal phase ($a = 3.59 \text{ \AA}$, $c = 15.5 \text{ \AA}$) in the space group $P6_3/mmc$ (JCPDF no. 30-0576). We show the transmission electron microscope (TEM) image of a nanowall in Fig. 1c. TEM observations reveal that the walls are transparent, especially at the edges, indicating a thickness of around a few nanometers, just as in the case of carbon nanowalls.⁴ The nanowalls are single crystalline, as established by the high resolution electron microscope (HREM) images as well as the selected area diffraction (SAED) patterns. Fig. 1d shows a HREM image with an inter-layer spacing of 3.19 \AA , corresponding to $d(100)$ (3.106 \AA). The powder left over at the hot end of the sealed tube did not change in appearance, and was found to be pure GaS by XRD and EDAX analysis. It should be noted that there was no evidence of the formation of Ga₂S₃ in the various zones of the reaction tube.

Heating GaSe powder at 900 °C in a sealed tube at a rate of 1 °C min⁻¹ for 6 h gave solid deposits at the cooler (400 °C) end of the tube.† The deposits contained GaSe nanowalls, as shown in Fig. 3a. The GaSe nanowalls cover larger areas than GaS nanowalls, and have a thickness of a few nanometers at the edges. The XRD pattern could be indexed on the hexagonal GaSe phase ($a = 3.76 \text{ \AA}$, $c = 15.91 \text{ \AA}$) (JCPDF no. 37-0931). Some of the

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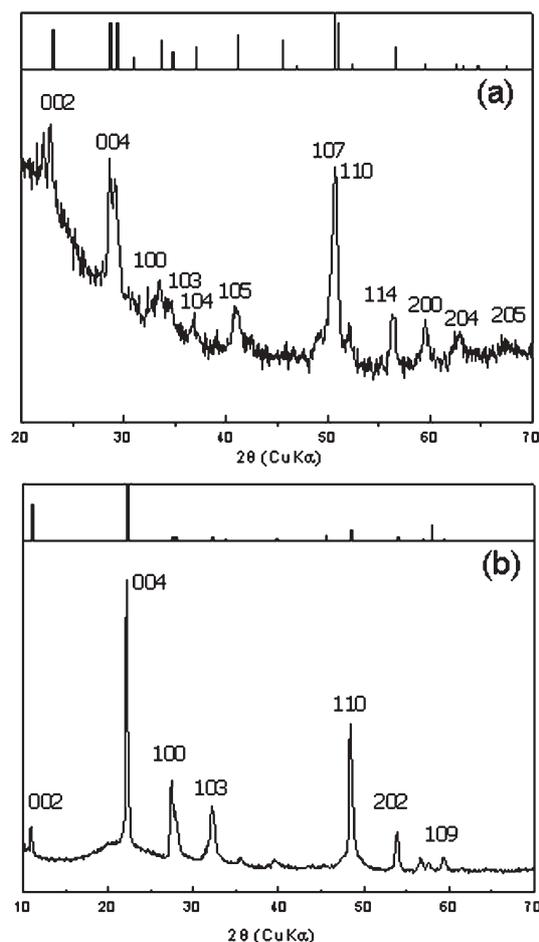


Fig. 2 XRD patterns of the (a) GaS and (b) GaSe nanowalls. The top panels indicate predicted peak positions.

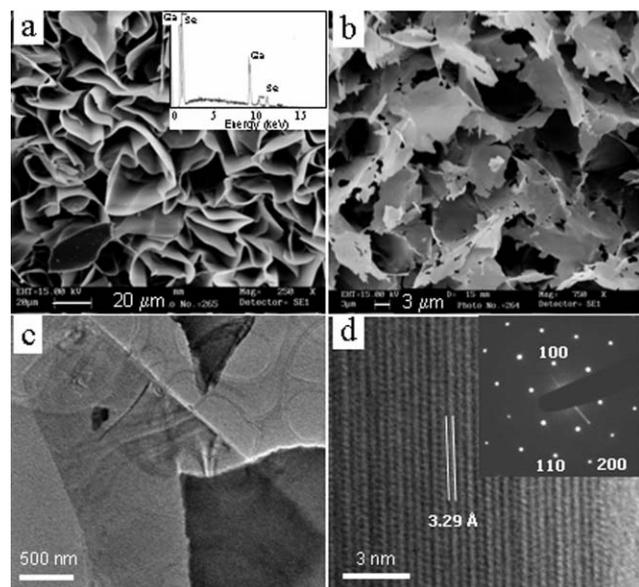


Fig. 3 (a) SEM image of GaSe nanowalls deposited at 400 °C covering a large area. Inset shows the EDAX spectrum of the nanowalls. (b) SEM image of the nanowalls deposited at ~500 °C. (c) TEM and (d) HREM images of a nanowall. Inset shows the SAED pattern.

non-[001] peaks exhibit high relative intensities due to orientational effects, the peak at $2\theta = 48.5^\circ$ being typical. The deposits obtained at the cooler end of the reaction tube, where the temperature was ~500 °C, had nanowalls containing holes (Fig. 3b). However, the composition was stoichiometric throughout, as found by EDAX analysis (inset in Fig. 3a). We show the TEM image of a GaSe nanowall in Fig. 3c. The single crystalline nature of the walls is confirmed by an HREM image (Fig. 3d) and their SAED pattern (inset in Fig. 3d). The lattice spacing observed in the HREM image of 3.29 Å corresponds to the separation between the [100] planes (=3.229 Å) of hexagonal GaSe in the space group $P6_3/mmc$. The SAED pattern also confirms that the GaSe sheets are exfoliated along the c-axis.

Careful observation showed that the cooler end of the reaction tube also contained deposits with the appearance of frozen droplets. Fig. 4a and Fig. 4b show SEM images of these GaS and GaSe droplets respectively, obtained after 1.5 h reaction time. The inset in Fig. 4b shows a flower-like nanostructure formed around a droplet. Extended growth of nanostructures at higher temperatures is known to take place by the vapor-liquid-solid (VLS) mechanism, when a metal catalyst is used, or otherwise by the vapor-solid (VS) mechanism.¹ In the present case, the mechanism of formation of the nanostructures appears to be somewhat different. Thermally-exfoliated sheets of GaS and GaSe fly to the cooler end of the reaction tube due to the temperature-induced pressure gradient. These sheets, initially in a semi-molten state, may form continuous films (underneath the nanostructures), as is evident from the SEM and EDAX observations. Even though the melting points of the bulk materials are high, the exfoliated sheets would be expected to melt at a considerably lower temperature. Smaller nuclei emanate out of the films due to the temperature gradient present between the tube walls and centre. The various nanostructures are thus formed from the nuclei, and accordingly we observe scrolls and tubular structures emerging from the droplets (Fig. 4c, Fig. 4d and Fig. 4e).

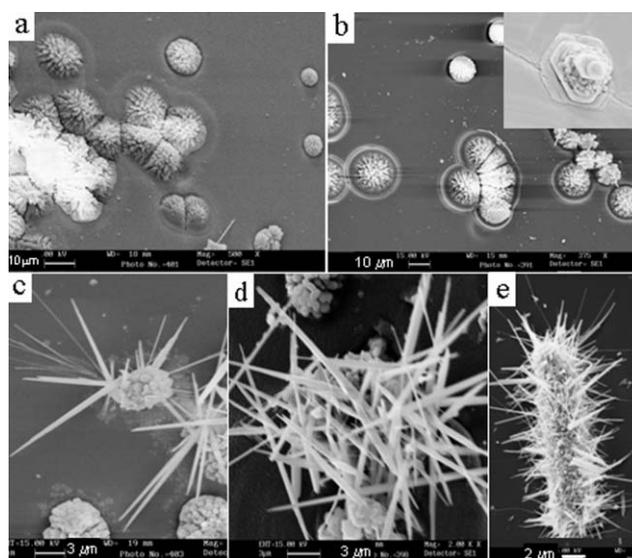


Fig. 4 Droplets of (a) GaS and (b) GaSe obtained at the cooler end of the reaction tube. Inset shows a GaSe nanostructure forming around a droplet. SEM images of (c) GaS and (d)/(e) GaSe scrolls and tubules.

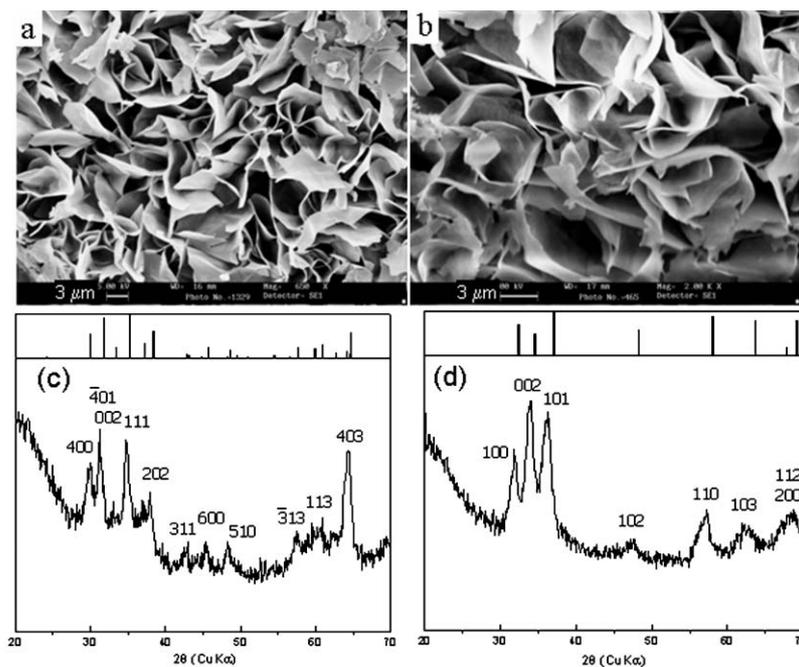


Fig. 5 SEM images of (a) Ga_2O_3 and (b) GaN nanowalls obtained by heating GaS nanowalls in air and ammonia respectively. XRD patterns of the (c) Ga_2O_3 and (d) GaN nanowalls. The top panels indicate predicted peak positions.

We have carried out reactions of GaS and GaSe nanowalls with air and NH_3 . We obtained Ga_2O_3 nanowalls by heating GaS and GaSe nanowalls in air (Fig. 5a).† The XRD pattern of the product (Fig. 5c) is readily indexed on monoclinic Ga_2O_3 in the space group $C2/m$ (JCPDF no. 43-1012). The EDAX spectrum confirmed the composition of the sample. On heating the GaS and GaSe nanowalls in NH_3 , GaN nanowalls were obtained (Fig. 5b).† The XRD pattern of the product (Fig. 5d) is characteristic of hexagonal GaN ($a = 3.20 \text{ \AA}$, $c = 5.19 \text{ \AA}$) (JCPDF no. 02-1078). To our knowledge, this is the first report of extended 2D nanostructures of Ga_2O_3 and GaN. It may be noted that Sn nanoflowers are transformed to SnO_2 nanoflowers by thermal oxidation.¹⁵

In conclusion, GaS and GaSe nanowalls have been obtained by thermal treatment of bulk powders, thereby demonstrating how these materials are quite similar to graphite in that they form 0D, 1D and 2D nanostructures. It is noteworthy that we have obtained Ga_2O_3 and GaN nanowalls from GaS and GaSe nanowalls without the loss of dimensional integrity.

Notes and references

† Nanowalls of GaS were obtained by heating GaS powder in a sealed quartz tube as follows: In a typical reaction, 0.02 g of finely ground GaS was sealed in a 30 cm long quartz tube under vacuum (5×10^{-6} Torr). The tube was placed in a horizontal furnace with a temperature gradient. The furnace was slowly heated to $900 \text{ }^\circ\text{C}$ at a rate of $1 \text{ }^\circ\text{C min}^{-1}$ and then maintained at that temperature for 6 h. The temperature of the cooler end of the tube varied over a range of temperatures ($300\text{--}500 \text{ }^\circ\text{C}$), the tip being at $300 \text{ }^\circ\text{C}$. Most of the solid deposits studied by us were collected from the region where the temperature was $400 \text{ }^\circ\text{C}$. These deposits contained GaS nanowalls. The GaSe nanowalls were obtained in a similar fashion. Nanowalls thus obtained were characterized by scanning electron microscopy, transmission electron microscopy, EDAX analysis and X-ray diffraction. Ga_2O_3 nanowalls were obtained upon heating the

nanowalls at $550 \text{ }^\circ\text{C}$ in air. GaN nanowalls were obtained by heating the GaS and GaSe nanowalls at $800 \text{ }^\circ\text{C}$ for 6 h in a furnace under a 100 sccm NH_3 gas flow (99.999% pure). Quartz pieces containing the nanowalls were sputter-coated with gold for SEM imaging using a JEOL scanning electron microscope. TEM images were obtained using a JEOL (JEM3010) transmission electron microscope, operating with an accelerating voltage of 300 kV. For this purpose, the nanowalls were scraped-off the quartz tube, dispersed in CCl_4 and deposited on a holey carbon grid. XRD patterns were recorded on a Siemens 5005 diffractometer employing the reflection Bragg–Brentano geometry with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$).

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