Growth and structural properties of gallium oxide nanowires prepared by chemical vapour deposition

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Gallium oxide nanowires have been prepared on Si(100) substrates using metallo-organic chemical vapour deposition. Growth behaviour has been investigated with various deposition times and the structural morphologies of the nanowires have been studied. The thickness and surface coverage ratio of the deposits increased with increasing deposition time. The gallium oxide nanowires were amorphous phase, having a circular cross-section with diameter of about 50–250 nm.

Keywords: Gallium oxide, Chemical vapour deposition, Nanowires, Structural properties

Introduction

In recent times, one of the most exciting areas of research in materials science has been the study of one-dimensional nanomaterials as a result of their novel physical properties.[1–3] Up to now, many kinds of binary oxide materials such as CoO, MgO, SiO_x, In_2O_3, GeO_2, ZnO, and AlOx have been synthesised as nanowires.[4–10] As one of the most important binary oxide nanowires with a wide bandgap of 4·9 eV, gallium oxide nanowires have great potential for applications in optoelectronic nanodevices and gas sensors.[11]

Accordingly, many researchers have produced gallium oxide nanowires by different preparation procedures such as physical evaporation of Ga powders,[12] dc arc discharge of GaN powders with a transition metal catalyst,[13] thermal annealing of milled GaN powders,[14] heating a composite material of GaAs and Au,[15] and heating a mixture of Ga_2O_3 powder and graphite[16] or a mixture of Ga_2O_3 powder and active carbon/carbon nanotubes.[17]

In the present study, without employing a catalyst, gallium oxide nanowires have been prepared on Si substrates by the metallo-organic chemical vapour deposition (MOCVD) method and the growth behaviour and structural properties of the gallium oxide nanowires have been investigated. The deposits have been characterised by scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and transmission electron microscopy (TEM).

Experimental procedures

Figure 1 shows a schematic diagram of the MOCVD system used to grow the gallium oxide nanowires. For a substrate material, (100)-oriented silicon (Si) was chosen. Before insertion into the chamber, the substrate was chemically cleaned with acetone (CH_3COCH_3) and water. For the growth process, trimethylgallium (TMGa) and oxygen (O_2) have been used as the gallium and oxygen sources, respectively. Argon carrier gas flowed through the TMGa bubbler maintained at $-5°C$, with a flowrate of 30 standard cubic centimetres per minute (sccm). The flowrate of O_2 was set at 6 sccm. The substrate temperature was 650°C with deposition times in the range of 3–5 min.

Structural properties were assessed by XRD (Philips CM20T) with Cu K_{a1} radiation (λ=0·154056 nm), SEM (Hitachi S-4200) operating at 15 kV, and TEM (Philips CM-200) operating at 200 kV with energy-dispersive X-ray spectroscopy (EDS) attached. The TEM sample was prepared by dispersing the powder in alcohol. Imaging was enabled by dispersing a few drops of suspension onto a carbon coated copper grid.

Results and discussion

Figure 2*a–c* shows the plan view SEM images of the deposits with deposition times of 3, 4 and 5 min, respectively. As the whitened and blackened regions represent the deposits and the bare Si substrate, respectively, it is surmised that the surface area covered by the deposits increases with increasing deposition time. After deposition for 5 min, the whole substrate surface was found to be covered with very dense deposits.

Figure 3*a–c* shows cross-sectional SEM images of the deposits on the Si substrate with deposition times of 3, 4 and 5 min, respectively, revealing that this deposit has a wool-like shape, consisting of aggregates of nanowires. The average thicknesses of the wool-like deposits with deposition times of 3, 4, and 5 min were 13·0, 15·3 and 18·2 μm, respectively, indicating that the thickness of the deposits increases with increasing deposition time. The SEM images reveal that the wirelike nanostructures

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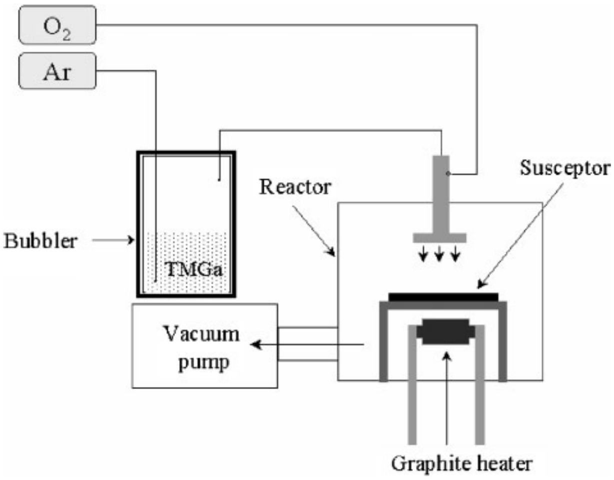
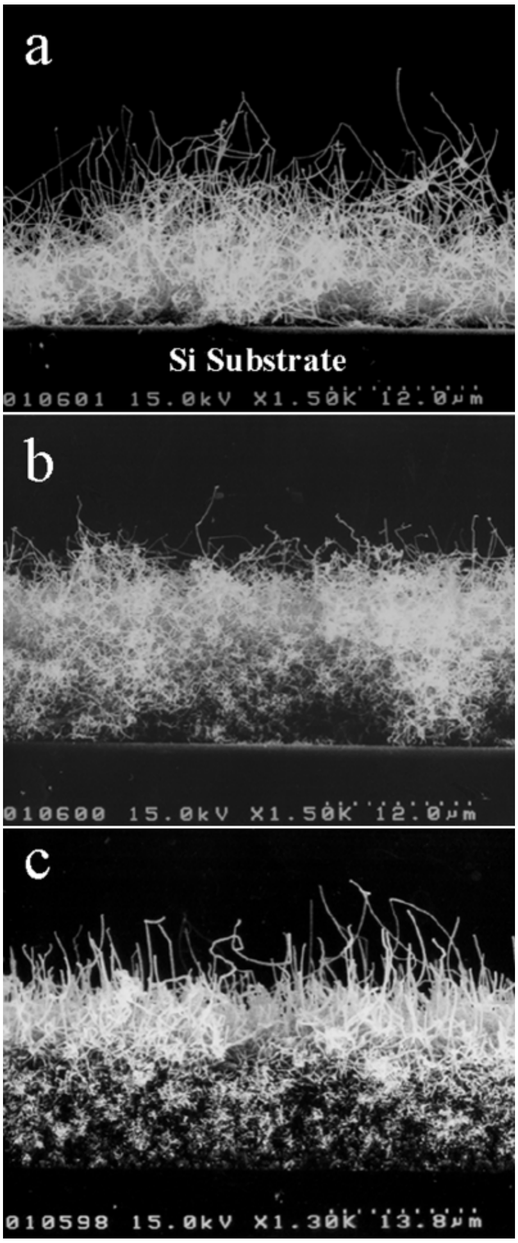
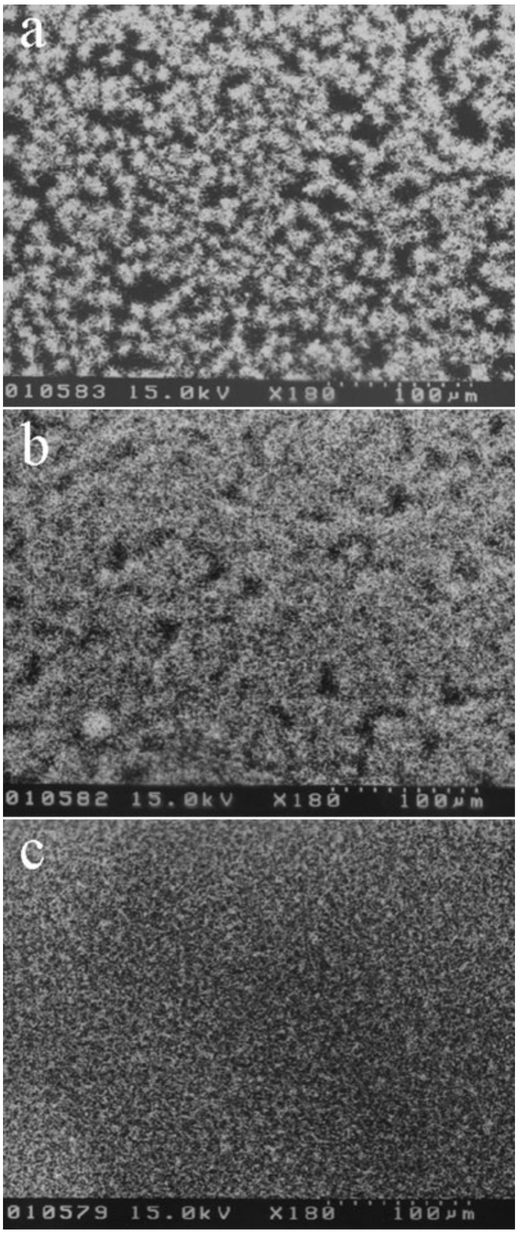


1 Schematic diagram of MOCVD system



2 Plan view of SEM images of deposits on surface of Si substrate with deposition times of *a* 3 min, *b* 4 min and *c* 5 min

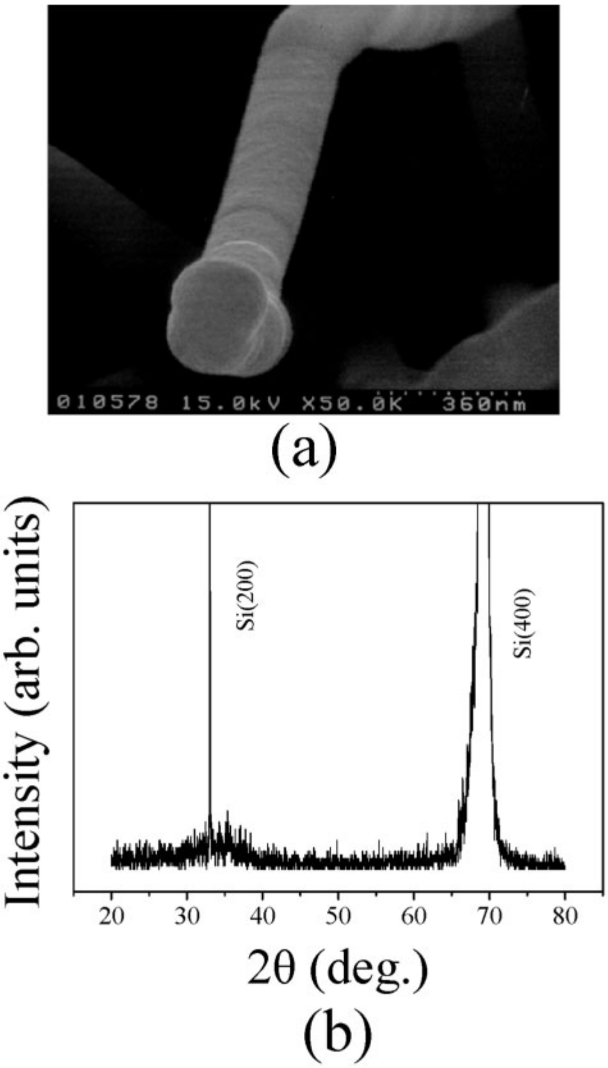


3 Cross-sectional SEM images of deposits on Si substrates with deposition times of *a* 3 min, *b* 4 min and *c* 5 min

have uniform diameters along the randomised growth direction and the nanowires are dense and continuous. Statistical analysis of many SEM images has shown that the nanowires have diameters ranging from 50 to 250 nm, regardless of deposition time.

Figure 4*a* shows a high magnification SEM image of a nanowire grown at a substrate temperature of 650°C for 5 min, revealing that the cross-section of the nanowire has a circular shape with no nanoparticles at its tip. Figure 4*b* shows the XRD patterns of the nanowires on Si substrates, revealing that the nanowires are fully amorphous. No reflections are clearly discerned other than (200) and (400) peaks from the Si substrate.

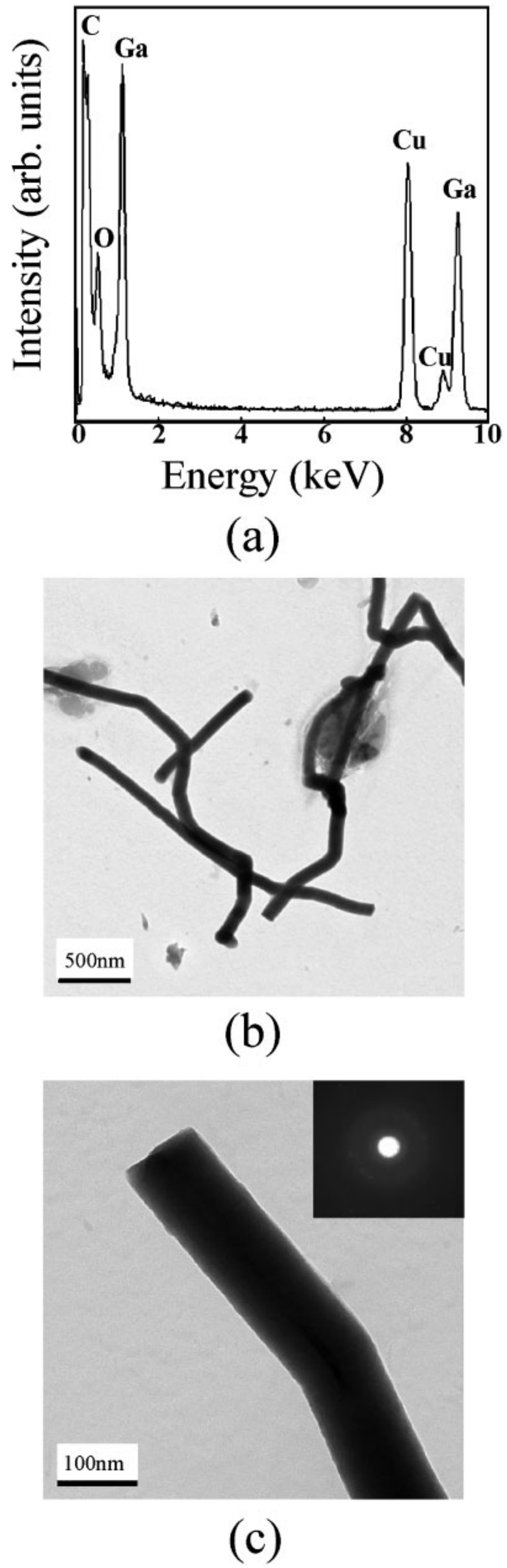
TEM analysis has been carried out for further characterisation of the nanowires. Figure 5*a* displays the typical EDS spectrum collected from the nanowires, clearly showing the peaks of Ga, O, C and Cu. The C and Cu-related peaks are the result of contamination from the carbon-coated copper grids while preparing



4 ***a*** **High magnification SEM image of nanowire;** ***b*** **XRD pattern recorded from nanowires**

TEM specimens, indicating that the components of the nanowire are only Ga and O. Figure 5*b* shows a low magnification TEM image of the gallium oxide nanowires, indicating that they display wirelike shapes with diameters of about 50–120 nm, and no spherical droplets can be seen at the tips of these nanowires, in agreement with SEM images. Figure 5*c* shows a high resolution TEM (HRTEM) image with corresponding selective area electron diffraction (SAED) pattern. Since there are no lattice fringes inside the nanowires and they have the highly diffusive SAED ring pattern, the HRTEM image and SAED pattern coincidentally identify that they are of amorphous nature.

Since no catalysts were intentionally used for the growth of these nanowires and no nanoparticles or impurities were clearly observed on the tips of the synthesised nanowires, it is surmised that the growth of gallium oxide nanowire is a self-catalytic process and is not dominated by the conventional V-L-S mechanism,[18] in which a metal-containing particle as a catalytic site is located at the growth front of the wire. Further systematic study is under way to derive the detailed mechanism for the growth of gallium oxide nanowires by the MOCVD method.



5 ***a*** **EDS spectrum showing chemical compositions of nanowires;** ***b*** **low magnification TEM image of gallium oxide nanowires;** ***c*** **high resolution TEM image with corresponding SAED pattern**

Conclusions

We have demonstrated the deposition of thin films of high density gallium oxide nanowires on Si substrate using the MOCVD technique. The thickness and surface coverage ratio of the thin films of nanowires increase with increasing deposition time. SEM observation revealed that these nanowires are dense and continuous. SEM and TEM studies confirmed that the average diameter of gallium oxide nanowires obtained by this method ranges from 50 to 250 nm with no nanoparticles at their tips. The as-prepared gallium oxide nanowires are of amorphous nature.

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