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A General Synthetic Route to III–V Compound Semiconductor Nanowires**

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III–V compound semiconductor wires with nanometer diameters have attracted much interest in recent years for their potential applications in high-electron-mobility nano-electronic devices and full-color flat panel displays.^[1] Several approaches have been successfully developed for the fabrication of these nanowires. These include vapor–liquid–solid (VLS) growth,^[2] metal-catalyzed growth assisted by laser ablation,^[3] and template-induced growth.^[4] Recently, we have developed the oxide-assisted growth approach for bulk-quantity synthesis of high-quality crystalline silicon and germanium nanowires.^[5,6] Metal catalysts and/or templates as used in other methods are not needed in the oxide-assisted growth method. The diameters of the nanowires produced by the oxide-assisted growth are quite uniform.

In this paper, we introduce a general method to synthesize III–V binary compound nanowires based on the oxide-assisted growth approach, and propose that the method may be generally applicable for the synthesis of other one-dimensional nanomaterials. Gallium arsenide nanowires with zinc-blende structure were fabricated by laser ablation of GaAs powders mixed with gallium oxide (Ga_2O_3) (no metal catalyst used). Transmission electron microscopy (TEM) examinations show a thin gallium oxide layer wrapped around the GaAs nanowire and its tip. No metal catalyst particle was found on the tip of the nanowires. Based on the experimental observations, a growth mechanism is proposed. The model is further substantiated by the successful synthesis of gallium phosphide and gallium nitride nanowires by a similar approach. Our

results suggest that this general method may be extended to fabricate other binary or ternary compound semiconductor nanowires.

Experimental details of the synthesis can be found in the experimental section. Figure 1a is a typical scanning electron microscopy (SEM) image of the products. It shows that the prod-

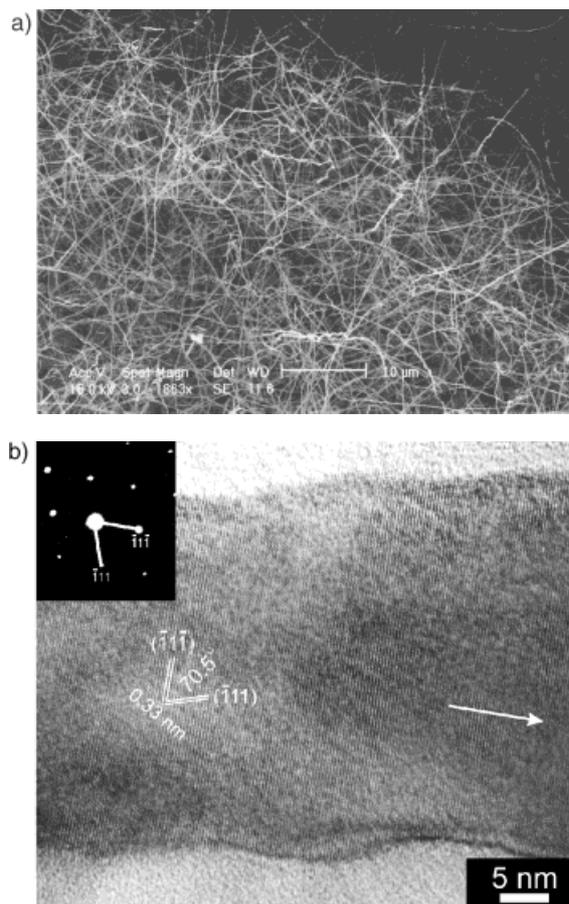


Fig. 1. a) A typical SEM image of the GaAs nanowires synthesized by the oxide-assisted method. b) A HRTEM image of a GaAs nanowire. The growth axis is close to the $[\bar{1}1\bar{1}]$ direction (white arrow). The inset is the corresponding ED pattern recorded along the $[110]$ zone axis perpendicular to the nanowire growth axis.

uct consists of wire-like structures with lengths up to 10 μm and diameters on the order of 50 nm. An energy-dispersion X-ray spectroscopy (EDX) facility attached to the scanning electron microscope was employed to analyze the chemical composition over a large area. The results revealed that the products consisted only of gallium, arsenic, and oxygen.

Further insight into the structure of the nanowires was obtained from high-resolution transmission electron microscopy (HRTEM) characterization. Figure 1b is a representative lattice-resolved image of the GaAs nanowire. The corresponding electron diffraction (ED) pattern recorded perpendicular to the axis of this nanowire is shown as the inset. The ED pattern can be indexed as the $[110]$ zone axis of single-crystal GaAs with a zinc-blende structure. The spacing of the crystallographic planes measured from the HRTEM image is 0.33 nm,

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as indicated in Figure 1b. It corresponds to the {111} lattice planes of the crystalline GaAs. The angle between the ($\bar{1}11$) and ($\bar{1}\bar{1}\bar{1}$) crystallographic planes was measured to be 70.5° (see Fig. 1b). The growth direction of the nanowire was close to the $[\bar{1}\bar{1}\bar{1}]$ direction, which is consistent with the ED observation. A thin amorphous layer that wrapped around the outside of the GaAs nanowire could be observed. The chemical composition of the sheath was determined to be gallium oxide (GaO_x) by an electron energy-loss spectrometer (EELS) facility (Gatan GIF200) attached to the high-resolution transmission electron microscope. Analysis of a number of nanowires showed that the diameters of crystal GaAs cores and the thickness of the outer sheath vary from 10 to 120 nm and 2 to 10 nm, respectively. The average diameter of the core was about 60 nm, and the average thickness of the outer sheath was 5 nm. The interface between the crystal core and amorphous sheath has an undulant contour. This undulation may be a naturally occurring configuration of the surrounding facets of the GaAs nanowire when it develops along the growth direction. This kind of morphology has also been observed in germanium nanowires.^[6]

To further reveal the growth mechanism of GaAs nanowires synthesized by this novel oxide-assisted method, the tip of the GaAs nanowire was examined by HRTEM; a typical image is shown in Figure 2. No nanoparticle on the tip was observed. The lattice planes with a spacing of 0.33 nm

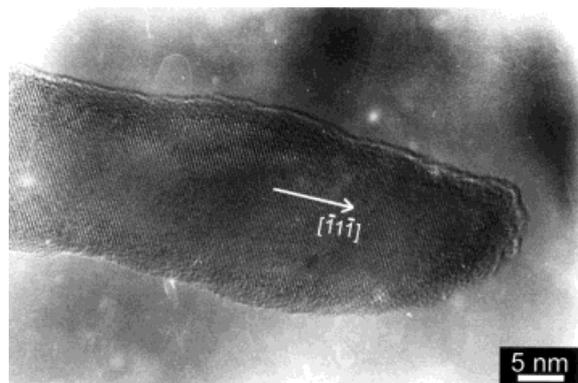


Fig. 2. A HRTEM image of the tip of a GaAs nanowire. The growth direction is close to the $[\bar{1}\bar{1}\bar{1}]$ direction (white arrow).

corresponding to the (111) plane of GaAs are nearly perpendicular to the nanowire axis. This reveals that the tip of the GaAs nanowires also grows along the $[\bar{1}\bar{1}\bar{1}]$ direction, which is consistent with the growth direction of the bulk wire observed above. It is important to note that the tip is clothed by a thin amorphous sheath with a chemical composition of gallium oxide (GaO_x). These features differ significantly from those of the GaAs nanowires synthesized by metal-catalyzed VLS growth, in which an alloy nanoparticle is invariably formed on the tip of the nanowires.^[2,3] The characteristics of the tip observed here are very similar to those observed in silicon or germanium nanowires prepared by the oxide-assisted method.^[6,7]

Considering all the above structural characteristics, we propose a four-stage growth process leading to the formation of GaAs nanowires as follows:^[8–10] 1) GaAs in the target is first decomposed into Ga and As upon laser ablation. 2) The resulting Ga atoms react with the Ga_2O_3 in the target to produce Ga_2O via the reaction $4\text{Ga} + \text{Ga}_2\text{O}_3 = 3\text{Ga}_2\text{O}$. 3) As Ga_2O is much more volatile than Ga_2O_3 at the processing temperature, Ga_2O vapor can be readily transported to the deposition zone by the carrier gas. At the same time, the As also volatilizes and is easily transported to the deposition zone. 4) Ga_2O and As react at the deposition zone via the reaction $3\text{Ga}_2\text{O} + 4\text{As} = 4\text{GaAs} + \text{Ga}_2\text{O}_3$ to finally form GaAs wires.

A test was done with the same experiment parameters except that a target made of pure GaAs powders with no oxides (Ga_2O_3) was used instead. No nanowires were obtained, which showed that the Ga_2O_3 mixed in the target is essential for the formation of GaAs nanowires. The result can be understood as follows. Since the amount of Ga vapor formed from GaAs decomposition by laser ablation is much lower than the amount of Ga in the Ga_2O at the present experimental temperature,^[8] if no Ga_2O_3 is present in the target, a smaller amount of Ga will be transferred to the growing zone. Therefore, the critical role of Ga_2O_3 in the target is to react with Ga to form the volatile Ga_2O . It is important to note that even if GaAs were ablated directly by the laser and transferred to the growing zone by the carrier gas,^[3] the GaAs one-dimensional growth could not be developed, as there is neither a suitable chemical reaction nor a metal catalyst, which is required for the growth of GaAs nanowires. Thus, the above analysis also implies that the chemical reaction $3\text{Ga}_2\text{O} + 4\text{As} = 4\text{GaAs} + \text{Ga}_2\text{O}_3$ is essential in the nucleation and growth of GaAs nanowires.^[7]

Further support for the above mechanism would be obtained if it could be extended to the synthesis of one-dimensional nanostructures of other binary compounds, such as the III–V compound semiconductors. For this purpose, the synthesis of gallium phosphide (GaP) and gallium nitride (GaN) nanowires was attempted by the same oxide-assisted approach. GaP and GaN targets mixed with 25 mol-% gallium oxide (Ga_2O_3) were laser ablated at 890°C and 1000°C , respectively. Other experimental parameters were kept the same as those used in the synthesis of the GaAs nanowires. GaP and GaN nanowires were similarly obtained from these experiments. Figure 3 and 4 show typical HRTEM images of the GaP and GaN nanowires, respectively. A TEM image of GaP nanowires and a SEM image of GaN nanowires are shown as insets in Figures 3 and 4, respectively. The GaP nanowires have an average diameter of 22 nm and the growth direction is close to the $[0\bar{1}\bar{1}]$ direction. On the other hand, the GaN nanowires with a zinc-blende structure have an average diameter of 80 nm and growth along the $[\bar{1}\bar{1}\bar{1}]$ direction.^[11] Both kinds of nanowires had a thin layer of amorphous gallium oxide (GaO_x) wrapped around them, and assumed a structure similar to that of GaAs nanowires. The formation of GaP and GaN nanowires can be understood

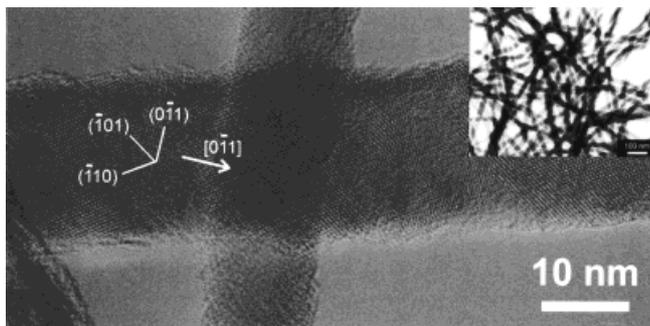


Fig. 3. A typical HRTEM image of GaP nanowires grown at about 750 °C on a silicon (100) substrate. The growth direction is close to the $[0\bar{1}1]$ direction. The inset is a TEM image of GaP nanowires.

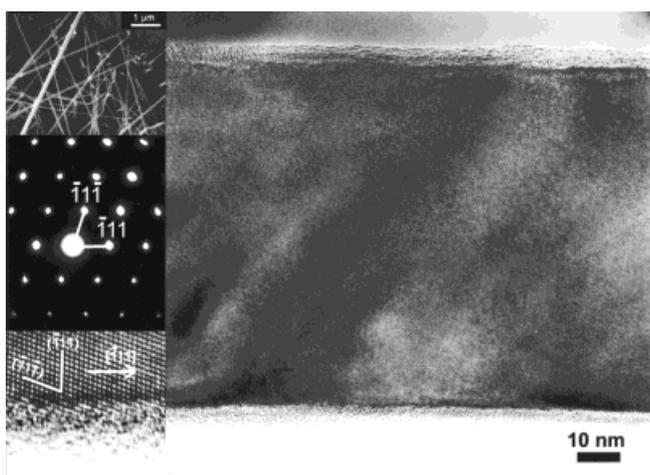


Fig. 4. A HRTEM image of a GaN nanowire grown at about 900 °C on a silicon (100) substrate. The insets are a SEM image (top), the corresponding ED pattern (middle) recorded along the $[\bar{1}\bar{1}\bar{1}]$ zone axis perpendicular to the nanowire growth axis, and the local enlarged HRTEM image (bottom). The growth direction is along the $[\bar{1}\bar{1}\bar{1}]$ direction (white arrow in bottom inset).

using a analysis similar to that of the formation of GaAs nanowires, replacing As by P and N, respectively. The critical reactions responsible for the formation of GaP and GaN nanowires are, respectively, $3\text{Ga}_2\text{O} + 4\text{P} = 4\text{GaP} + \text{Ga}_2\text{O}_3$ and $3\text{Ga}_2\text{O} + 4\text{N} = 4\text{GaN} + \text{Ga}_2\text{O}_3$.

In conclusion, the oxide-assisted method has been successfully used to synthesize binary compound semiconductor nanowires. Using the compound materials mixed with an oxide as the target, the corresponding binary compound nanowire was produced. In this process, the critical role of the oxide in the target is to react with an element (formed from the laser ablation of the target) to form a volatile oxide. The situation is similar to the oxide-assisted synthesis of Si (or Ge) nanowires,^[5,6] in which the responsible volatile oxide SiO (or GeO) was formed by reacting Si (or Ge) with SiO₂ (or GeO₂) during laser ablation of the Si (or Ge) target mixed with SiO₂ (or GeO₂). Furthermore, the syntheses of various semiconductor nanowires mentioned above all involve a similar oxidation–reduction reaction, in which an appropriate oxide also serves as a reactant. It appears that such a chemical reaction is indispensable in the nucleation and growth of the nanowires in the oxide-assisted growth process.^[7] The chemical reaction–

induced nucleation and growth of nanowires is an essential feature that differentiates oxide-assisted growth from conventional metal-catalyst VLS growth. A chemical reaction is needed in the oxide-assisted growth, while a metal template or tip is required in the metal-catalyst VLS growth. That a metal catalyst is unnecessary in the oxide-assisted growth is an advantage, since it would simplify the process for the purification and subsequent applications of the nanowires produced by this method.

Experimental

The equipment used for the synthesis of GaAs nanowires has been described in detail elsewhere [12]. A target was made by pressing GaAs powders mixed with 25 mol-% gallium oxide (Ga₂O₃) at room temperature for 24 h with a hydraulic press. The target and a polished silicon (100) substrate were placed inside a quartz tube at the center and near one end, respectively. The tube was placed into a tube furnace with the tube center in the central region of the high-temperature zone. After the system had been evacuated to 0.01 torr by a rotary pump, a carrier gas of high-purity argon mixed with 5 % hydrogen was kept flowing through the quartz tube from one end to the other, where the silicon substrate was located. The gas flow rate was 50 sccm (standard cubic centimeters per minute) and the pressure was kept at 300 torr. The system was heated to 930 °C at the central region. A temperature gradient was established from the center to the ends of the quartz tube with the temperature of the Si substrate at approximately 800 °C. After the temperature and pressure had stabilized, the laser ablation process was started. A KrF excimer laser beam of 400 mJ per pulse and a pulse width of 34 ns at 10 Hz was used to ablate the target. The size of the laser spot on the target was about 0.5 mm × 4 mm. The total duration of the ablation was 5 h. Black products were formed on the silicon substrate. Firstly, the product directly on the silicon substrate was observed by SEM (Philips XL 30 FEG). The nanowires were then scraped from the substrate and mounted onto copper grids for HRTEM (Philips CM200 FEG) observation.

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Photochemical Pattern Transfer and Patterning of Continuous Zeolite Films on Glass by Direct Dipping in Synthesis Gel**

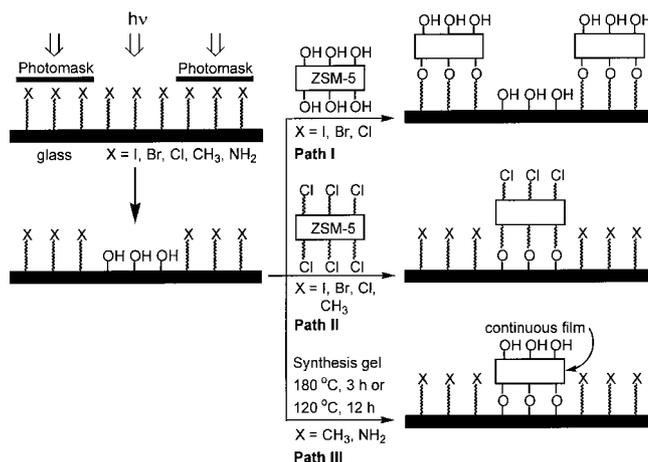
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Ceaseless exploration of new applications of zeolites and related porous materials is indispensable for the continual development of the science and technology of zeolites. A new breakthrough in their applications can possibly be achieved by seeking utilization of the porous materials for combinatorial catalysts and as low-dielectric packing materials for integrated circuits. One of the key steps in realizing such applications is to develop reliable methods to pattern them as thin films on various supports. However, despite the availability of a large number of methods to prepare thin films on various supports,^[1–12] the methods to pattern them are rare since they have begun receiving attention only recently. Ozin and co-workers first reported a way to selectively deposit mesoporous silica on patterned, alkanethiol-covered regions of gold by carefully positioning the substrate between the air and synthesis gel interface.^[13] Stucky and co-workers demonstrated the preparation of patterned, hierarchically ordered mesoporous silica films on silicon supports through direct heating of the patterned, micromolded precursor gel.^[14] By replacing the precursor gel with nanocrystalline microporous silica (silicalite) in the above micromolding/heating method, Yan, Zhao, and co-workers were able to prepare patterned microporous and micro-macroporous silica films.^[15] As a result of our interest in the assembly of covalently bound monolayers of zeolite crystals on mica and glass substrates,^[12] we also developed a versatile method to pattern monolayers of oriented and covalently bound zeolite crystals.^[16]

In all of the above-mentioned methods, however, microcontact printing, also known as poly(dimethylsiloxane) (PDMS) stamping, has been adopted as the only way to transfer patterns. Alternative photochemical approaches have not been explored, although, in principle, they have many intrinsic advantages over PDMS stamping, e.g., higher resolution,

reproducibility, reliability, and processability.^[17] Furthermore, zeolite film patterning by direct dipping of the supports patterned with surface-protecting organic functional groups into the synthesis gel has not been explored, although it is likely to be the most practical and simplest method to pattern continuous zeolite films on supports. We now report that photochemical degradation of various organic functional groups tethered to glass plates is a highly versatile and effective way of preparing glass plates patterned with organic functional groups and that direct dipping of the patterned glass plates into the synthesis gel readily leads to glass plates patterned with continuous zeolite films.

First, we prepared glass plates with tethered 3-iodopropyl (IP) groups via siloxane linkages (see Experimental section), with the intention of transferring the pattern through photochemical decomposition of IP groups. The glass plates with tethered IP groups were then exposed to UV light generated by a high-pressure Hg lamp with a photomask on top of each glass plate as depicted in Scheme 1 (left). As a test, we employed grids as convenient photomasks. We also adopted our



Scheme 1. The procedures for patterning covalently bound monolayers of ZSM-5 crystals (I and II) and continuous ZSM-5 films (III).

previously reported zeolite film patterning method^[16] as a test procedure to check the validity of our photochemical pattern transfer. Thus, after exposure to UV light for 1 h, the IP-tethered glass plates were allowed to come into contact with plain ZSM-5 crystals in boiling toluene for 3 h. The scanning electron microscopy (SEM) image of the glass plates, after sonication for 2 min, revealed that the ZSM-5 crystals are attached only on the masked regions, as shown in Figure 1A (left). The image of the zeolite film at a higher magnification ($\times 10$) clearly reveals that the film consists of a monolayer of ZSM-5 crystals.

Upon switching from plain ZSM-5 crystals to those with tethered 3-chloropropyl (or any 3-halopropyl) groups, only the unmasked spots became covered with the monolayers of ZSM-5 crystals (Fig. 1B). Thus, these results verify that the above photochemical approach is an excellent procedure for transferring patterns for patterning glass plates with covalently assembled monolayers of zeolite crystals on glass as

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