Oxide-assisted growth and optical characterization of gallium-arsenide nanowires

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This letter reports the synthesis and optical characterization of GaAs nanowires obtained by oxide-assisted laser ablation of a mixture of GaAs and Ga_2O_3. The GaAs nanowires have lengths up to tens of micrometers and diameters in the range of 10–120 nm, with an average of 60 nm. The nanowires have a thin oxide layer covering a crystalline GaAs core with a $[\bar{1}11]$ growth direction. Raman scattering and photoluminescence (PL) characterizations of GaAs nanowires reveal that the spectral peaks significantly shifted and broadened from those of bulk GaAs material. The changes in these spectra are mainly attributed to impurities, defects, and residual stress in the GaAs nanowires. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1371966]

Gallium arsenide (GaAs), as a direct-band-gap semiconductor with high electron mobility, has been widely used for the fabrication of laser diodes, full-color flat-panel displays, and high-speed transistors.[1,2] Recently, the remarkable properties of one-dimensional nanostructures have stimulated intensive interest in the synthesis, characterization, and applications of GaAs nanowires.[3–6] Several methods have been applied to synthesize GaAs nanowires, including laser-assisted metal-catalytic growth,[7] nanosize-pore template or mask growth,[8,9] as well as sidewall growth based on electron-beam lithography.[10] Recently, an oxide-assisted growth method has been developed to fabricate nanowires of silicon and germanium.[11–13] This method not only produces nanowires in larger quantity than the prior methods,[14] but it also requires no metal catalysts and/or templates as usually needed in other methods. Thus, it would simplify the purification process and subsequent application of nanowires produced by this method. As such, it is of interest to extend this method to the synthesis of binary or ternary compound semiconductor nanowires. In this letter, we report that GaAs nanowires can indeed be synthesized using the oxide-assisted method.

The equipment used in the present work is similar to that we used to synthesize silicon nanowires.[11] Briefly, a quartz tube was mounted inside a high-temperature tube furnace. A target for laser ablation was made by pressing GaAs powders with 25 mol % gallium oxide (Ga_2O_3) at room temperature. The target and a polished silicon(100) substrate were placed inside the quartz tube at the center and near one end of the furnace, respectively. After the system was evacuated to 0.01 Torr, a carrier gas of high-purity argon mixed with 5% hydrogen was kept flowing through the quartz tube at 50 sccm and a pressure of 300 Torr. The system was heated to 930 °C at the central region and the temperature at the Si substrate was approximately 800 °C. A beam of a KrF excimer laser with a wavelength of 248 nm was focused by a lens onto the target. The laser energy was 400 mJ per pulse with a pulse duration of 34 ns at 10 Hz. The ablation lasted 5 h. Black color products formed on the silicon substrate.

The morphologies and structures of the nanowires were investigated by scanning electron microscopy (SEM) (Philips XL 30 FEG) and high-resolution transmission electron microscopy (HRTEM) (Philips CM200 FEG). Energy-dispersion x-ray (EDX) spectroscopy and electron diffraction (ED) analysis were also performed. Raman scattering and photoluminescence (PL) spectra were measured at room temperature with a Renishaw 2000 micro-Raman Fourier transform spectrometer using the argon laser at 514 nm as the excitation source.

Figure 1 shows a typical SEM image of GaAs nanowires deposited on silicon substrates. Large quantities of curved and randomly oriented nanowires with diameters of around 50 nm can be clearly observed in this image. The lengths of the nanowires are up to tens of micrometers. The EDX spectrum shown in the inset of Fig. 1 demonstrated that the nanowires consist only of gallium, arsenic, and oxygen. The signal of silicon came from the silicon substrate. Further insight into the structure of the GaAs nanowires can be obtained from the HRTEM lattice image of an individual nanowire, shown in Fig. 2. The corresponding electron diffraction pattern recorded perpendicular to the axis of this nanowire is shown in the inset of Fig. 2. The crystal structure and growth direction as determined from the ED pattern and lattice image of this nanowire are a zinc-blende structure and close to $[\bar{1}1\bar{1}]$, respectively. The growth direction of the present nanowires is the same as that of GaAs nanowires grown by a metal-catalyzed vapor–liquid–solid (VLS) process.[15] Figures 2 and 3 also show that the crystalline-GaAs core was wrapped by a thin amorphous layer. The chemical composition of the amorphous layer was determined to be gallium oxide (GaO_x) by using the electron energy-loss spectrometer (Gatan GIF200) attached to the HRTEM. Analysis of a number of nanowires showed that the diameter of the crystalline-GaAs cores and the thickness of the outer sheath vary from 10 to 120 and 2 to 10 nm, respec-

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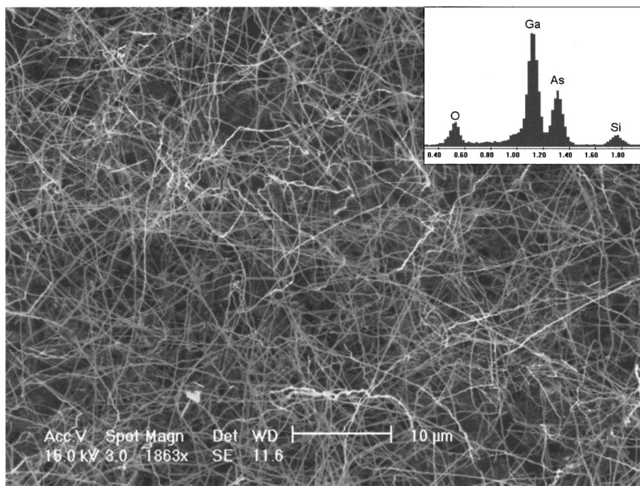

FIG. 1. Typical SEM image of GaAs nanowires. Inset shows EDX spectrum taken from GaAs nanowires, and the Si peak is from the silicon substrate.

tively. The average diameter of the core was about 60 nm, and the average thickness of the outer sheath was 5 nm.

It is known that the tips of the nanowires determine the one-dimensional growth of GaAs nanowires.[14] HRTEM image of a typical tip of GaAs nanowires shown in Fig. 3 reveals that the growth direction of the tip is along $[\bar{1}1\bar{1}]$, which is consistent with previous observations of GaAs nanowires. The crystalline tip was coated by a thin amorphous layer of GaO_x. This feature is significantly different from those GaAs nanowires synthesized by the metal-catalyzed VLS growth, in which the tips were terminated at metal-alloy nanoparticles.[15]

From the synthetic process and experimental observations, we suggest that the following stages are involved in the nucleation and growth of GaAs nanowires:

(1) Laser-induced decomposition of GaAs into Ga and As.
(2) Reaction of $4Ga+Ga_2O_3=3Ga_2O$ at the high-temperature zone.
(3) Transport of volatile Ga_2O and As to the low-temperature-deposition zone.
(4) Reaction of $3Ga_2O+4As=4GaAs+Ga_2O_3$ at the low-temperature-deposition zone leading to the nucleation and growth of the GaAs nanowires.

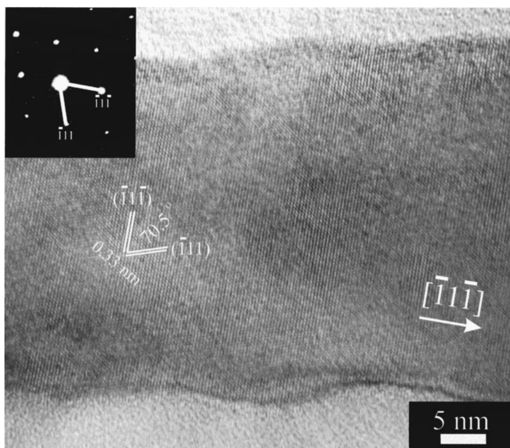

FIG. 2. HRTEM image of a GaAs nanowire. The growth axis is close to the $[\bar{1}11]$ direction. The inset is the corresponding ED pattern recorded along the [110] zone axis perpendicular to the nanowire growth axis.

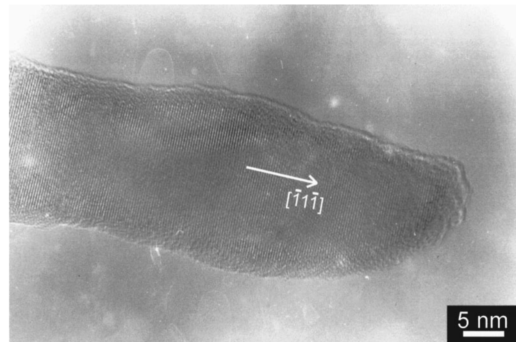

FIG. 3. HRTEM image of the tip of a GaAs nanowire. The growth direction is close to the $[\bar{1}11]$ direction (white arrow).

It can be seen from above that gallium oxide (Ga_2O_3) takes part in the oxidation–reduction reaction (2) to form the volatile Ga_2O. This reaction is indispensable for the synthetic process. To support this claim, an experiment was performed with the same conditions except that a target made of pure GaAs powder, but no Ga_2O_3, was used. No nanowires were obtained. This result showed clearly that Ga_2O_3 mixed in the target and the oxidation–reduction reaction are essential for the nucleation and growth of nanowires. In step (4), when GaAs and Ga_2O_3 are formed, the two products would separate in order to reduce the surface energy between them. As amorphous materials usually have much lower surface energies than crystalline materials, the amorphous-oxide layer would form on the outside of the crystalline-GaAs core to further reduce the surface energy of the system.

The optical properties of nanowires are important in understanding the physics of low-dimensional systems and their potential applications to optoelectronics.[16] The Raman scattering spectra of the GaAs nanowires [Fig. 4(a)] show first-order modes of transverse optical (TO) phonons and longitudinal optical (LO) phonons at 269 and 290 cm^{-1}, respectively.[17] Both LO and TO bands are broadened, and

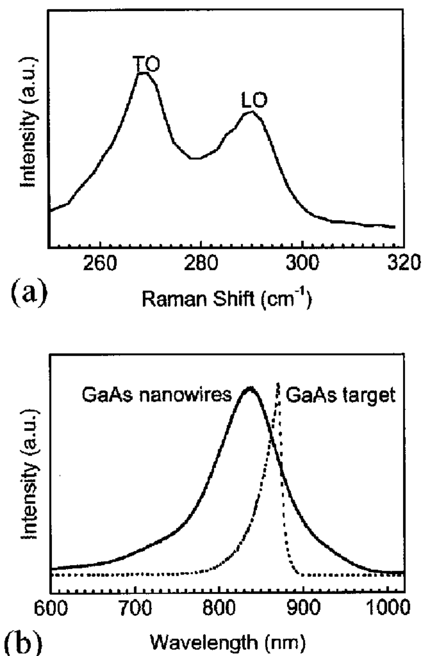

FIG. 4. Room-temperature Raman spectrum (a) of GaAs nanowires and PL spectra (b) of GaAs nanowires and GaAs bulk crystal.

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only the LO peak observably shifted by about 40 cm^{-1} toward lower wave numbers relative to that of bulk crystalline GaAs. In general consideration for Raman scattering of one-dimensional structure, the downshifts of the Raman peaks are mainly attributed to the size-confinement effect.[18,19] However, the 60 nm diameter of the present GaAs nanowires is not small enough to produce the 40 cm^{-1} downshift in phonons via the size-confinement effect. Furthermore, the downshift was observed only for the LO but not the TO phonon modes. Thus, the downshift cannot be mainly caused by the size-confinement effect, although a few nanowires with diameters smaller than the phonon-confinement size would contribute to some downshift in Raman scattering. Impurities and defects, such as point defects, twins, and stacking faults, would also cause small downshifts in phonon scattering. On the other hand, the downshifts caused by both the size-confinement effect and defects are the major reason for broadening the phonon modes.[20] Another possible cause for the downshift of the LO phonon mode may be the residual stress within GaAs nanowires,[19] which originated from the lattice distortion in GaAs nanowires. This distortion might be established during and after the growth of the nanowires as a result of a difference of the thermal expansion coefficients of the crystal GaAs core and the amorphous GaO_x outer sheath. Since the stress in nanowires is anisotropic, the effect of the stress on Raman scattering may vary among the phonon modes. This may be the reason that the downshift was only observed in the LO phonon mode.

The PL spectra of GaAs nanowires and bulk GaAs are shown in Fig. 4(b). It can be observed that the spectrum of GaAs nanowires is dominated by a broadened spectral feature at about 838 nm. A more than 30 nm upshift was induced relative to that of bulk GaAs. In the oxide-assisted synthesis, oxygen may remain in the GaAs crystal core as an impurity when the GaAs phase was formed and separated from the gallium-oxide phase. The oxygen impurity may broaden and blueshift the PL peak. It is known that oxygen as an n-type impurity could produce a Burstein–Moss effect, which would cause a blueshift in the PL of GaAs.[21] Thus, for GaAs nanowires synthesized by the oxide-assisted approach, the oxygen impurity is expected to be the main cause of the PL blueshift. In addition, the exciton radius of GaAs is larger than that of elemental semiconductors, such as Si and Ge. According to theoretical calculations, blueshifts in PL caused by the size effect would only be observed when the diameter of the GaAs nanowires is less than 10 nm.[1,22] Clearly, the average diameter (60 nm) of the GaAs nanowires is not small enough to produce such a large blueshift via the size-confinement effect, although it may be operative in those nanowires with diameters less than the Bohr radius of GaAs. Nevertheless, these blueshifts could contribute to the broadening in the PL of the GaAs nanowires.[20] On the other hand, the free-electron-to-neutral-acceptor impurity recombination and the possible unresolved neutral-donor-to-acceptor features at longer wavelengths also produced broadening in the PL.[22]

In summary, GaAs nanowires were synthesized by the oxide-assisted method via the laser ablation of a mixture of GaAs and Ga_2O_3. Neither metal catalysts nor templates were used in this process. The length of the GaAs nanowires was up to tens of micrometers. The GaAs nanowire was composed of a crystalline core of 60 nm in diameter clothed by a thin amorphous-oxide layer with an average thickness of 5 nm. The growth was explained by a growth mechanism based on an oxidation–reduction reaction. Significant shifts and broadening were observed in the Raman and PL peaks, which were mainly attributed to stress, impurities, and defects in the GaAs nanowires.

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