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Letter

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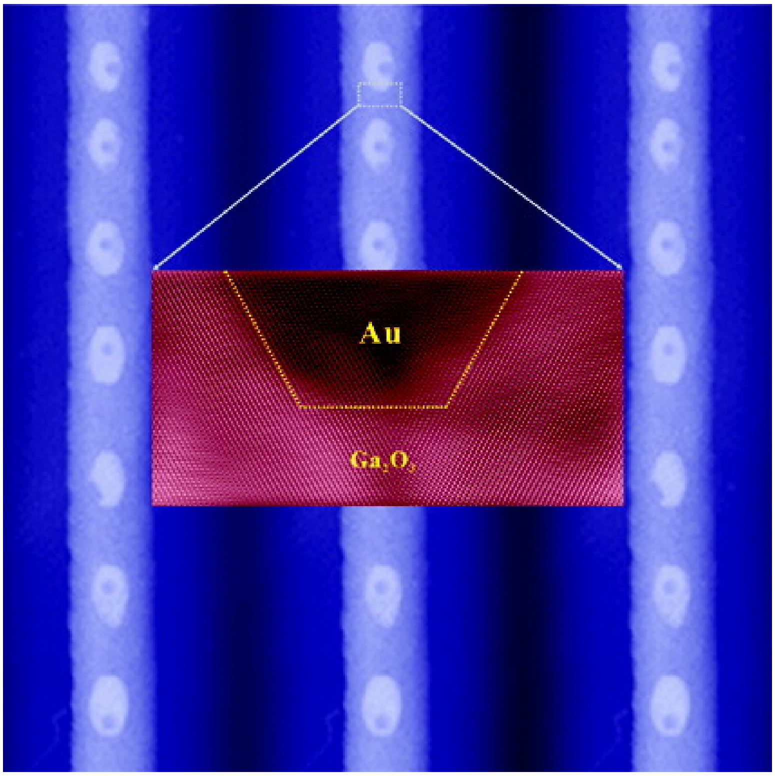
Nano Lett., **2008**, 8 (10), 3081-3085• DOI: 10.1021/nl0731567 • Publication Date (Web): 17 April 2008



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VOLUME 8, NUMBER 10, OCTOBER 2008

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Nanophotonic Switch: Gold-in-Ga_2O_3 Peapod Nanowires

Chin-Hua Hsieh,[†] Li-Jen Chou,[*,†] Gong-Ru Lin,[‡] Yoshio Bando,[§] and Dimitri Golberg[§]

Department of Materials Science and Engineering, National Tsing Hua University, No. 101, Section 2 Kuang-Fu Road, Hsinchu, Taiwan 300, Republic of China, Graduate Institute of Electro-Optical Engineering and Department of Electrical Engineering, National Taiwan University, No. 1, Section 4, Roosevelt Road, Taipei 106, Taiwan, Republic of China, and Advanced Materials Laboratory and Nanomaterials Laboratory, Nanoscale Materials Center, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Received December 4, 2007; Revised Manuscript Received January 31, 2008

ABSTRACT

A novel metal–insulator heterostructure made of twinned Ga_2O_3 nanowires embedding discrete gold particles along the twin boundary was formed through a reaction between gold, gallium, and silica at 800 °C during simple thermal annealing. The Au-in-Ga_2O_3 peapods spontaneously crystallized under phase separation induced by the formation of twin boundaries. The nanostructures were analyzed by field emission scanning (FESEM) and transmission electron microscopes (FETEM), and their photoresponse was investigated using a double-frequency Nd:YAG laser with a wavelength of 532 nm on a designed single-nanowire device. The surface plasmon resonance (SPR) effects of embedded Au nanoparticles are proposed to be responsible for the remarkable photoresponse of these novel structures.

Optical computing is becoming an eminent technology as nanoscale setups, including logic gates, switches, interconnections, and memories, are swiftly reaching maturity. Recently, the response of an optical switch has been pushed to the terahertz regime. A laser transistor[1] is a good successful example, but there are many problems that still need to be solved. For construction of such complicated nanoscale hybrid systems, we propose a new approach: a vertical ultrafast optical switch architecture composed of Au nanoparticles embedded in oxide nanowires. Being stimulated by the numerous discoveries with respect to the richness of carbon nanotube novel properties, the research on diverse one-dimensional nanostructures have been placed in the forefront of nanotechnology. The studies of these may shed an additional light on many fundamental issues related to dimensionality and space-confined transport phenomena. Nanostructures, such as nanodots, [2] nanobelts,[3] and nanowires,[4] have successfully been analyzed in many reports. Among those, the nanowires are thought to be the most

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[*] Corresponding author. E-mail: ljchou@mx.nthu.edu.tw.

[†] Department of Materials Science and Engineering, National Tsing Hua University.

[‡] Graduate Institute of Electro-Optical Engineering and Department of Electrical Engineering, National Taiwan University.

[§] Advanced Materials Laboratory and Nanomaterials Laboratory, Nanoscale Materials Center, National Institute for Materials Science.

10.1021/nl0731567 CCC: $40.75

functional with a wide range of applications. Possible applications include $TaSi_2$[5] and NiSi[6] nanowires as interconnectors in future integrated circuits, ZnO nanowires[7] as nanogenerators, and GaN nanowires[8] as versatile optoelectronic materials. To date, the synthetic approaches for 1-D nanostructures have relied on various physical or chemical methods, including vapor–liquid–solid (VLS) growth,[9] self-catalytic vapor–liquid–solid (SC-VLS) growth,[10] vapor−solid (VS) growth,[11] oxide-assisted (OA) growth,[12] and hydride vapor phase epitaxy (HVPE).[13] To precisely control the size of nanowires by a metal catalyst, the vapor–liquid–solid (VLS) mechanism has most effectively been utilized. Furthermore, the hybrid nanostructures such as core–shell nanowires[14] and nanopeapods[15] have attracted extensive attention due to their unique optical and electrical properties. Recently, Hu et al.[16] have reported that Au nanoparticles encapsulated in silica nanowires exhibit a wavelength-dependent photoresponse due to the surface plasmon resonance (SPR) effect.[17]

In this study, we report on crystalline gold nanoparticles periodically encapsulated in monoclinic single-crystalline Ga_2O_3 nanowires during VLS growth. Moreover, a single-nanowire optical device was designed and its photonic characteristics were studied. These revealed a remarkably high on/off photocurrent ratio during a response to a Nd:YAG laser light with a 532 nm wavelength. The whole structure exhibits a bandgap of 4.9 eV. The present synthetic approach is direct and simple, provides a solution for the fabrication of diverse functional 1-D hybrid nanowire devices, and opens new prospects in nanoscale optoelectronics.

To form the Au-in-Ga_2O_3 peapods, commercially available Ga powders (purity 99.9999%) and Au nanoparticles were used as a Ga vapor source and a catalyst, respectively. The quartz tube was heated in a horizontal furnace to 800 °C with a ramping rate of 20 °C/min. Subsequently, Ga powder and an amorphous SiO_2 substrate covered with well-dispersed 150 nm Au nanoparticles were placed into the quartz tube. The reaction temperature of 800 °C was held at a pressure of 1×10^{-2} Torr for 30 min. For HRTEM analysis, the as-synthesized nanowires were ultrasonically dispersed in a methanol solution. A few drops of the mixture were dripped on a C-coated Cu TEM grid. The morphologies and crystal structures were analyzed by field-emission scanning (FESEM, JSM-6500F) and transmission electron microscopes (FETEM, JEM-3000F). The FETEM operated at 300 kV and having point-to-point resolution of 0.17 nm was equipped with a high-angle angular dark field (HAADF) detector and an energy dispersion spectrometer (EDX). The studies of a photoresponse were carried out using a double-frequency Nd:YAG laser (Laser Century Technology, model GL532T), externally modulated at 1 kHz by a chopper controller (Stanford Research Systems, SR540) as an excitation source, with a wavelength of 532 nm and maximum power of 1 W. To minimize an illuminating spot size, an excited laser beam was coupled into a single-mode lens fiber and focused on the peapod nanowires. Under a constant bias of 2 V, the photocurrent produced by a single nanowire was enhanced in a programmable lock-in amplifier (Stanford Research Systems, SR830) with a constant load resistance of 56 MΩ. All measurements were performed at room temperature and atmospheric pressure.

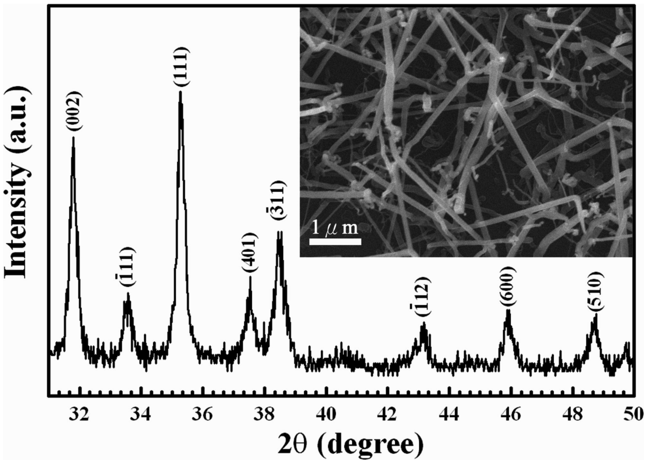

Figure 1. XRD spectrum of Au-in-Ga_2O_3 peapod nanowires grown on a silica substrate. A top-view SEM image is shown in the inset.

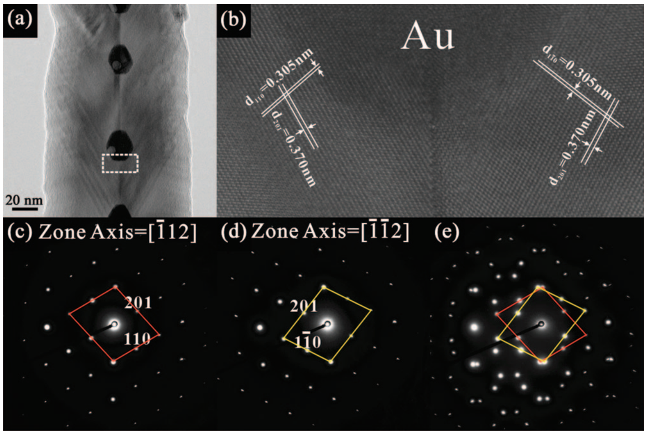

Figure 2. (a) Typical low-magnification TEM image of an individual Au-in-Ga_2O_3 peapod nanowire. (b) High-resolution TEM image of the area framed in (a). (c,d) Corresponding diffraction patterns taken from the left- and right-hand-side parts of the wire divided by the twin boundary. (e) Corresponding diffraction pattern of the entire peapod structure.

High-density Ga_2O_3 nanowires with a fairly uniform diameter were obtained, as shown in the inset to Figure 1. The peaks in a XRD spectrum, Figure 1, are indexed as (002), ($\bar{1}$11), (111), (401), ($\bar{3}$11), ($\bar{1}$12), (600), and (510) reflections of a monoclinic β-Ga_2O_3. The lattice parameters of $a = 1.223$ nm, $b = 0.3039$ nm, $c = 0.5808$ nm, and $\beta = 103.82°$ are consistent with the standard values (JCPDS card: no. 41-1103).

A representative TEM image of a single nanowire is shown in Figure 2a. A twin boundary with a rather rough surface is visible in the nanowire center. In Figure 2b, a HRTEM image of the framed area in Figure 2a shows an Au nanoparticle embedded in the Ga_2O_3 nanowire within the twin boundary interface. Electron diffraction patterns (DPs) taken from the left- and right-hand-side portions of the nanowire are displayed in Figure 2c,d. These were indexed

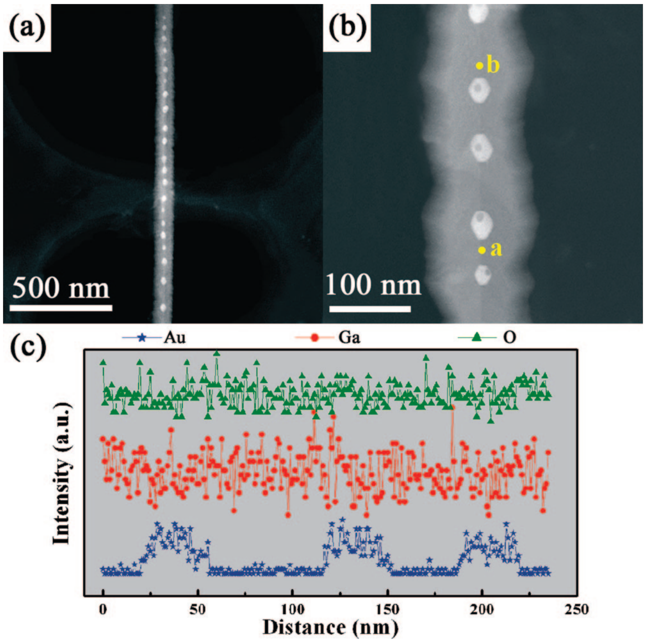

Figure 3. (a) Low-magnification HAADF TEM image of an individual Au-in-Ga_2O_3 peapod nanowire with the Au nanoparticles embedded along the twin boundary. (b) Zoom-in view of HAADF in (a). (c) Corresponding elemental line-scan profiles of Au, Ga, and O, respectively.

as β-Ga_2O_3 $[\bar{1}12]$ and $[\bar{1}\bar{1}2]$ zone axes, respectively. This is in good agreement with the XRD results. A DP of the entire nanowire, Figure 2e, reveals the mirror symmetry of β-Ga_2O_3 with the twin boundary.

Analytical HRTEM techniques were utilized to get further insights into the structure of gold-embedded nanowires. A HAADF image in Figure 3a displays a clear difference in the optical contrast between Au, Ga, and O elements. It is worth noting that, in the Wu et al. report, in order to minimize the surface energy of an Au_2Si nanoparticle within the surrounding amorphous SiO_2 matrix, the ball-like particles were embedded in SiO_2 during the VLS process.[18] However, in our study, the Au nanoparticles appeared to be hexagonally faceted. This specific morphology is suggested to be due to the minimization of total surface energy during the present peapod growth. The compositional line profiles of Au, Ga, and O elements (in spots a−b), recorded in the STEM mode, are shown in Figure 3c.

In previous reports, the usage of Ga and SiO_2 mixtures as a source material has been documented to be effective to generate Ga_2O vapor and to grow Ga_2O_3 nanowires.[19] However, it is rather difficult to control the unstable Ga_2O vapor production during a reaction between Ga and SiO_2 powders. In the present work, we found that due to a relatively stable surface area, a molten Ga ball had acted as a stable and continuous Ga vapor source. The formation mechanism of the present structures is suggested as follows: according to the Au−Ga phase diagram,[20] a liquid Au−Ga alloy droplet is formed by incorporating a small amount of Ga in an Au nanoparticle as the temperature rises above 400 °C. Once Ga vapor reaches a silica surface, the Ga_2O vapor is produced through a reaction between Ga and SiO_2.[21]The possible chemical reactions involved are:

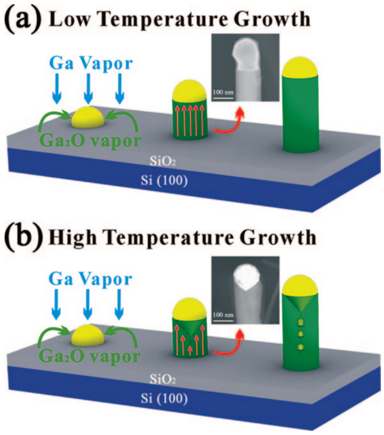

Figure 4. Schematics of the standard nanowire growth (a) and the Au-in-Ga_2O_3 peapod nanowire growth (b).

$$4Ga(g)+SiO_2(s) \rightarrow 2Ga_2O(g)+Si(s) \tag{1}$$

$$3Ga_2O(g) \rightarrow Ga_2O_3(s)+4Ga(s,l) \tag{2}$$

The processing temperature is the dominant factor affecting the supersaturation of a Au−Ga droplet. In the lower temperature range, 400−600 °C, the uniform supersaturation (Figure 4a) occurs at the interface between the droplets and silica substrate resulting in the formation of single-crystalline Ga_2O_3 nanowires. However, the nonuniform supersaturation takes place during the significant fluctuations in temperature near 800 °C. As a result (Figure 4b), the supersaturation prevails around the droplet edge rather than in its central area. Consequently, a single Ga_2O_3 nanowire with the internal twin boundary is formed. The dendrite-like twinned growth is suggested to reflect the difference in the nucleation rate, which is documented by the inhomogeneous Ga_2O concentration profile. As a result, the Au-in-Ga_2O_3 nanopeapods crystallize under the fluctuations of Ga_2O concentration and twin boundary formation. Interestingly enough, a HAADF image (Figure 3b) illustrates that there is a hole in each embedded Au nanoparticle. We suggest that these voids have been formed during the whole structure cooling stage.

Parts a and b of Figure 5 present the optoelectronic device composed of an individual Au-in-Ga_2O_3 peapod nanowire. Compared to the Hu et al. results on the Au-in-SiO_2 peapod nanowires, the present device reveals the strong absorption of 532 nm visible light. We assume that this is due to the pronounced surface plasmon resonance (SPR) effects of Au−Ga nanoparticles. In general, the monoclinic Ga_2O_3 with a wide bandgap of 4.9 eV is considered to be good insulator. The present $I-V$ measurements also verified a high resistance of 8000 GΩ of a single-crystalline Ga_2O_3 nanowire. The enhanced photoconductivity of a peapod nanostructure is demonstrated in Figure 5c. The improved electrical conductivity and optical response of a dielectric matrix with encapsulated noble-metal nanoparticles can be explained by the large electromagnetic field enhancement in the vicinity of the metal surface, which enhances the third-order nonlinear susceptibility of the noble-metal nanoparticles. The incident photons excite surface plasmon polaritons (SPP) at the Au−Ga_2O_3 interface; consequently, the electromagnetic field of surface plasmon polaritons decay exponentially into the

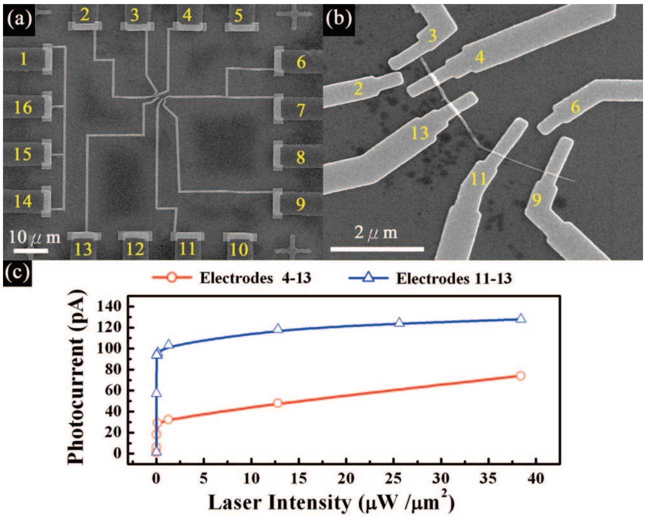

Figure 5. (a,b) Low-magnification and an enlarged SEM images of the photoswitch made of an individual Au-in-Ga_2O_3 peapod nanowire, respectively. (c) Photoresponse of the device at different pumping powers between nos. 4–13 and nos. 11–13 electrodes.

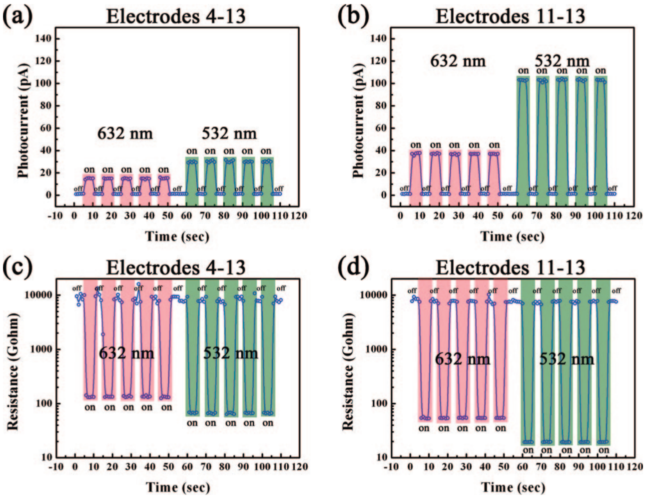

Figure 6. (a,b) Photoresponse behaviors during illumination-on and -off cycles between no. 4–13 and no. 11–13 electrodes, respectively. (c,d) Replotted corresponding figures of resistance vs time.

interior of Au$-$$Ga_2O_3$$-$Au junction. The electrons generated by the SPR effect drift to the Ga_2O_3 barrier and tunnel to the counter electrode. Moreover, the photoresponse is determined by the generation rate of the hot electrons in Au nanoparticles and by the tunneling rate through the Ga_2O_3 barrier. As a result, the response of a photocurrent is proportional to the pumping power from 1.28 to 38.4 μW/μm^2 with a slope of 0.63 μm^2 pA/μW. Moreover, parts a and b of Figure 6 show the reversible transient curves of a photocurrent under different wavelength pumping light soucres, yielding a maximum photocurrent of 103.25 pA with an on/off ratio of 500. The instant photoresponse of the present peapods under illumination over 5 s is illustrated by a sharply rising photocurrent followed by a small fluctuation. In addition, the corresponding resistance vs time replotted figures are shown in parts c and d of Figure 6, respectively. Because the frequency of the nanoswitch is controlled by the pumping light source, a vertical optical nanosystem can be realized by integrating the nanoswitch into the active light source such as a laser transistor.

In summary, a novel 1-D photoswitch made of Au-in-Ga_2O_3 peapod nanowires was designed. The wires were produced in line with the vapor–liquid–solid (VLS) growth using a reaction between metal Ga and silica at 800 °C and gold as a catalyst. HRTEM and XRD studies indicate that the nanowires are twinned single crystals and have discrete Au nanoparticles periodically embedded along the twin boundary. A gold particle surface plasmon resonance (SPR) enhanced photoresponse nanodevice made of an individual nanostructure was tested using a double-frequency Nd:YAG laser with a wavelength of 532 nm as the illumination light source. This reveals a high on/off ratio during a photoresponse. The developed simple and straightforward synthetic approach may be highly valuable for the generation of diverse optoelectronic devices.

Acknowledgment. This research was supported by the National Science Council through Grant Nos. NSC 95-2221-E-007-245-MY2 and NSC 96-ET-7-007-002-ET.

Supporting Information Available: Au-Ga phase diagram; PL spectrum of pure Ga_2O_3 nanowire on a SiO_2 substrate; low- and high-magnification SEM images of a nanowire device; photoresponse behaviors with and without pure Ga_2O_3 nanowires on a SiO_2 substrate; high-magnification SEM image and photoresponse behaviors of the gold-peapodded Ga_2O_3 nanowires; blank device, pure Ga_2O_3 nanowire, and gold-peapodded Ga_2O_3 nanowire device and their corresponding $I-V$ curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL0731567