Preparation and photoinduced wettability conversion of superhydrophobic β-Ga_2O_3 nanowire film

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High-yield uniform β-Ga_2O_3 nanowire films with mesh structure on GaP substrate have been synthesized via heat treating porous GaP preevaporated Au under low vacuum. The single-crystalline β-Ga_2O_3 nanowires have uniform diameters of about 100 nm and a preferential [001] growth direction along the axis. The as-prepared β-Ga_2O_3 nanowire film reveals a superhydrophobic property. The remarkable photoinduced surface wettability conversion at β-Ga_2O_3 nanowire film was found, which can be explained by the cooperation of the surface photosensitivity and the special nanostructure. © *2007 American Institute of Physics*.
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The wettability of solid surfaces is a very important property and is governed by the chemical composition as well as the geometric structures of the surface.[1,2] In recent years, the superhydrophobic surfaces have received much attention because of their unique properties[3–6] and promising applications in self-clean surface,[7] gene delivery,[8] microfluidic channels,[9] and nonwetting liquid transfer.[4]

As one of the important semiconductor materials with a wide band gap (E_g=4.2–4.9 eV), quasi-one-dimensional nanostructured β-Ga_2O_3 has attracted increasing interest due to its diverse range of high technological applications.[10–14] However, nearly all of the applications are based on its optical or electronic properties. In this letter, we present an approach to synthesize high-yield uniform β-Ga_2O_3 nanowire films on semiconductor substrate. It was found that these as-prepared β-Ga_2O_3 nanowire films have superhydrophobicity. The remarkable phenomenon of photoinduced surface wettability conversion from superhydrophobicity to superhydrophilicity was observed in this β-Ga_2O_3 nanowire film. A similar remarkable surface wettability transition was only observed on ZnO (Refs. 5 and 15) and TiO_2 (Ref. 16) films. This surface with controllable wettability is of great importance for both fundamental research and practical applications.

High-yield uniform β-Ga_2O_3 nanowire films with mesh structure on GaP substrate were synthesized via heat treating porous GaP preevaporated Au under low vacuum. Porous layers were prepared by two-step etching methods using sulfur-doped (111) *n*-type GaP with a doping concentration of 4×10^{-17} cm^{-3}. The GaP wafers were first anodized in a 0.5*M* H_2SO_4 solution for 45 min at a current density of 20 mA/cm^2. Then, the samples were etched in a mixture solution ($3HCl+1HNO_3$) for 60 min. Figure 1(a) shows scanning electron microscope (SEM) (Philips XL30FEG) image of the etched GaP, which indicates that pores with an average size of about 150 nm were formed on the surface of GaP.

After that, the porous GaP coated with about 10 nm thick Au layer was placed into a horizontal quartz crucible which was then placed in a quartz tube of a tubular furnace. First, the quartz tube was evacuated for 10 min by a vacuum pump. The furnace was heated at a rate of 15 °C/min to 900 °C. Then, it was maintained at this temperature for 1 h before being cooled to room temperature. High purity Ar and O_2 were kept flowing at a rate of 240 and 80 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. Uniform white films were found on the surface of the GaP substrate.

Figures 1(b) and 1(c) show the SEM image of the white product. It can be seen that high-yield uniform nanowire (diameters of about 100 nm and lengths of several micrometers) films have been grown on GaP subsrate. The results of the transmission electron microscope (TEM) (JEOL JEM-2100F) image [Fig. 2(a)] and corresponding electron diffraction pattern [Fig. 2(b)] of a single nanowire confirm that the nanowires are single-crystalline β-Ga_2O_3 nanowires and indicate that the nanowires preferably grew along the [001] direction.

The evolution of β-Ga_2O_3 nanowires involves two fundamental steps: nucleation and growth.[17] The reaction is complicated. Ga vapor was generated from the decomposition of porous GaP. Meanwhile, multiple Au–Ga eutectic liquid droplets formed on the surface by alloying reaction between the Au clusters and the Ga (Ref. 18) and nuclei grown into one-dimensional structures from the bottom by using of

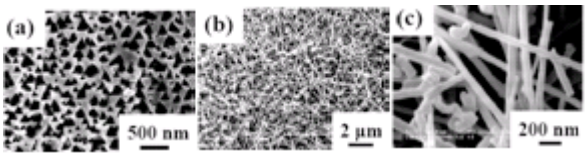

FIG. 1. (a) SEM image from the top surface of porous GaP wafer. [(b) and (c)] SEM images of β-Ga_2O_3 nanowires grown on GaP substrate.

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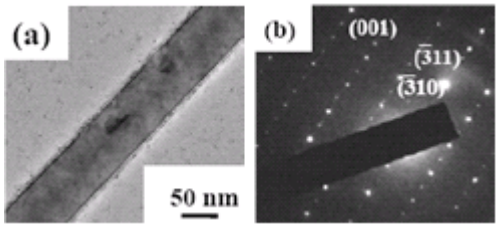

FIG. 2. (a) TEM image of a single β-Ga_2O_3 nanowire. (b) Corresponding electron diffraction pattern.

dissolved matters. As a result, high-yield mesh-structured β-Ga_2O_3 nanowire film was formed.

The hydrophobicity of the β-Ga_2O_3 nanowire film was measured by means of the water contact angle (CA) using an OCA 20 contact angle system (Data Physics instrument, GmbH, Germany) at ambient temperature. The CA value is about 155°, which clearly shows that the as-prepared β-Ga_2O_3 nanowire film has superhydrophobic property. The shape of water droplet on the film was shown in Fig. 3(a). Conventionally, the hydrophobicity of a surface is enhanced by modifying the surface with low-surface-energy materials (e.g., fluorinated or silicon compounds).[19–21] For a given material, CA is usually related to the surface roughness.[22] It is believed that the superhydrophobic feature of β-Ga_2O_3 nanowire film could be ascribed to the surface with network structures to trap air in the interspaces.[23] In general, the CA can be described by Cassie and Baxter's equation,[24]

$$\cos\theta' = f_1 \cos\theta - f_2, \tag{1}$$

where θ is the CA on a flat solid surface, while θ' is the equilibrium CA on a rough surface made of the same material as the smooth surface. f_1 and f_2 are the fractions of the surface under the water droplet occupied by solid material and air, respectively ($f_1+f_2=1$). From Eq. (1), it is clear that a rough surface of nanostructure implies a high fraction of f_2 and minimizes the fraction of contact area between water and the film, resulting in a highly hydrophobic surface. In addition, the surface of a metal oxide is a high-energy surface. The Ga_2O_3 nanowire film is not avoidable, exposed in atmospheric environment and organic contaminations such as oil droplets from vacuum pumps and bioeffluents that could be absorbed on it, enhancing hydrophobicity,[25] similar to hydrophobic modification.

The photoinduced wettability conversion property of the β-Ga_2O_3 nanowire film is further explored. UV illumination was carried out using a 250 W Hg lamp with wavelength centered at 365 nm with two subpeaks at 254 and 405 nm respectively. After the film was exposed to UV light of 20 mW/cm^2 under ambient conditions for 2 h, water droplet immediately spreads on the film, exhibiting CA of about 0°, as shown in Fig. 3(b). These results clearly demonstrate that the remarkable photoinduced surface wettability conversion

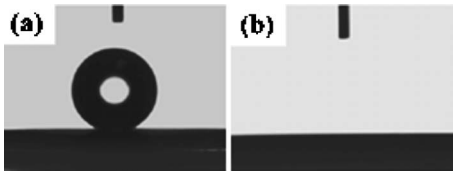

FIG. 3. Photographs of water droplet shape on the β-Ga_2O_3 nanowire films (a) before and (b) after illumination.

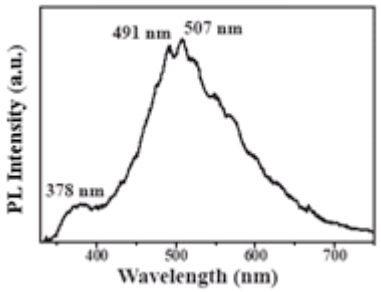

FIG. 4. Room temperature PL spectrum of β-Ga_2O_3 nanowires.

phenomenon takes place on β-Ga_2O_3 nanowire film. This special wettability conversion property has also been found in ZnO nanorod array films and TiO_2 thin films after the UV radiation.[5,15] To date, the mechanism of the photoinduced superhydrophilicity observed for TiO_2 and ZnO is still being debated.[26,27] Sun *et al.* suggested that band gap illumination generated electron-hole pairs in ZnO and TiO_2 and some of the holes could react with lattice oxygen to form surface oxygen vacancies which contribute to hydrophilic feature of the surface.[15] Recent work[28,29] points out that the decomposition of organic contaminations should play a role in the UV-induced hydrophilicity phenomenon. It has also been demonstrated that the photocatalytic reactivity of powdered Ga_2O_3 can occur under sub-band-gap excitation.[30] To make clear whether sub-band-gap excitation contributes to the superhydrophobic-superhydrophilic conversion in β-Ga_2O_3 nanowire film, UV light below 300 nm is removed by near-stoichiometric $LiTaO_3$ crystals. After UV illumination for 2 h at a light intensity of 20 mW/cm^2, the contact angle is about 23°, which demonstrates that the sub-band-gap excitation is also an important factor resulting in the superhydrophobic-superhydrophilic conversion.

For further analysis of the origin of photoinduced wettability conversion of β-Ga_2O_3 nanowire film under sub-band-gap excitation, photoluminescence (PL) spectrum of as-prepared β-Ga_2O_3 nanowires was measured through Jobin Yvon LabRam HR 800UV system with a 325 nm He–Cd laser, as shown in Fig. 4. One small UV peak at about 378 nm and two strong blue peaks at 491 and 507 nm are observed, which indicate the presence of midgap energy levels originating from oxygen vacancies in the Ga_2O_3 nanowires.[31–33] Therefore, the UV irradiation with energy less than band gap can stimulate electron-hole pairs in Ga_2O_3 nanowires. As reported,[5,15] in the process of illumination, these electrons and holes can recombine to emit photons. Conversely, some of the holes can also react with lattice oxygen, leading to the formation of surface oxygen vacancies, while some of the electrons react with lattice metal ions (Ga^{3+}) to form Ga^{2+} defective sites (surface trapped electrons). In ambient conditions, as time goes by, more and more oxygen vacancies were formed by the reaction between the holes and lattice oxygen. The defective sites are kinetically more favorable for hydroxyl adsorption.[15,34] Meanwhile, upon UV illumination, photoexcitation of Ga_2O_3 nanowires can cause formation of surface electron and surface hole active centers which participate in surface chemical processes, e.g., in the photoadsorption of O_2. Moreover, carrier trapping by preexisting defect centers in Ga_2O_3 nanowires generates color centers.[35] Photoexcitation of the colored sample within this newly formed band leads to

photostimulated adsorption of O_2.[30] Molecules such as H_2O and O_2 absorbed on the surface interact with the carriers to form hydroxyl radicals and O_2^-. As the reactive energy of hydroxyl radicals exceeds the bond energy of organic contaminations on metal oxides, contaminations can be decomposed. As a result, the surface hydrophilicity of β-Ga_2O_3 nanowire film is greatly improved. In addition, for a mesh-structural β-Ga_2O_3 nanowire film, water will enter and fill the interspaces of the films, leaving only the upper part of the nanowires not in contact with the liquid. This effect also contributes to the superhydrophilicity of the surface. Namely, combining with photoproduction of surface defects, the removal of adsorbed organic contaminations by photooxidation and special nanostructure, the UV irradiation causes the surface wettability of β-Ga_2O_3 nanowire films to change from superhydrophobicity to superhydrophilicity.

In summary, superhydrophobic β-Ga_2O_3 nanowire film has been prepared using Au as catalyst and porous GaP as source material. The technique used is an effective approach for the large-scale formation of β-Ga_2O_3 nanowires on semiconductor substrate, which can also be used to synthesize other metal oxide semiconductor nanowires for practical application. It was demonstrated that excitation illumination with energy less than band gap can also result in the photoinduced wettability conversion on β-Ga_2O_3 nanowire film, which is ascribed to the presence of mid-band-gap levels in β-Ga_2O_3 nanowires. These special properties will extend the applications of β-Ga_2O_3 films. This work would be conducive to further understanding the mechanism of wettability conversion of metal oxide semiconductors by UV illumination.

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