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Fabrication of lateral electrodes on semiconductor nanowires through structurally matched insulation for functional optoelectronics

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Abstract
A strategy of using structurally matched alumina insulation to produce lateral electrodes on semiconductor nanowires is presented. Nanowires in the architecture are structurally matched with alumina insulation using selective anodic oxidation. Lateral electrodes are fabricated by directly evaporating metallic atoms onto the opposite sides of the nanowires. The integrated architecture with lateral electrodes propels carriers to transport them across nanowires and is crucially beneficial to the injection/extraction in optoelectronics. The matched architecture and the insulating properties of the alumina layer are investigated experimentally. ZnO nanowires are functionalized into an ultraviolet photodiode as an example. The present strategy successfully implements an advantageous architecture and is significant in developing diverse semiconductor nanowires in optoelectronic applications.

1. Introduction
Semiconductor nanowires have emerged as potential active materials [1–3]. Techniques that produce suitable electrodes are essential in the application of nanowires to electrical and functional devices [4]. Optoelectronic applications rely on the accurate architecture of electrodes for carrier injection/extraction to motivate photoelectric interaction within nanowires. Vertical nanowire arrays [5, 6] and dispersed nanowires [7, 8] are usually fabricated with electrodes at both terminal ends, at which carrier transports are conducted along the axial direction of the nanowires. In spite of several functional prototypes, the geometric design of the nanowires has limited optoelectronic applications. Electronic injection/extraction and output power may be limited by the fractional electrodes at the ends of the nanowires [9]. Moreover, photoelectric interaction is affected by natural surface states of nanowires, such as ambient absorption/desorption [10], as carriers transport along the nanowires. A satisfactory architecture is conceived to deposit electrodes at opposite lateral sides of nanowires, so that numerous carriers can transport across the diametrical direction in a short path and proceed along the whole sides [11]. The implementation of such architecture is significant to facilitate the application of the present nanowires in photodiodes, photovoltaic cells, and light emitting diodes (LEDs) [12]. Previous studies have reported on nanowire light emitting devices using an analogous architecture [9, 13–17]. Various nanowires were laterally injected from the complementary substrate using insulators fabricated by thin film spin-coating or deposition between electrodes. Duan et al achieved lasing in a single nanowire [13]. However, the electrical contacts of the electrodes are not reliable because of the simple mechanical contact of the nanowires on the substrate [18–20]. Insulator residues probably remained in...
The inserted layer after etching. In addition, precise placement of a thin insulation layer between two lateral electrodes at the nanometric scale is difficult.

In this work, a new strategy is presented to fabricate electrodes on the lateral sides of semiconductor nanowires. Nanowires are embedded in aluminum (Al) thin film to form a nanowire–film composite. From the composite, structurally matched alumina insulation is formed by selective anodic oxidation. Electrodes are consequently deposited via direct evaporation of metallic atoms onto opposite sides of the nanowires. Furthermore, zinc oxide (ZnO) nanowire ultraviolet (UV) photodiodes are functionalized to demonstrate the feasibility of optoelectronic devices based on this architecture. Carriers are transported across the nanowires in the architecture, and their efficient injection/extraction is studied. Corresponding morphology of the architecture and the properties of the alumina layer, as well as those of the UV photodiode, are investigated. The strategy increases the potential uses of semiconductor nanowires in optoelectronic applications.

2. Experiments
The strategy was formulated to expose the lateral sides of nanowires for two-step evaporation of reliable electrodes. A selective and controllable anodic oxidation was applied to form a matched nanowire insulator layer in the architecture. ZnO nanowires, as representative building blocks, were selected in the strategy.

The fabrication process is schematically illustrated in figure 1. ZnO nanowires were directly grown on a GaN/sapphire substrate via a vapour transport process [21]. The nanowires were dispersed from the as-grown substrate to a Si slice using a mechanically printed slide [22, 23]. The Si slice was utilized as a transfer substrate. One of the lateral sides of the horizontal nanowire on the slice was exposed (figure 1(a)). A 300 nm thick Al film was then deposited by thermal evaporation when the sample stage was tilted. The nanowire was entirely overlaid and embedded into the Al film forming a nanowire–film composite (figure 1(b)). Al reliably formed an electrode on one side of the nanowire without any preceding process. This composite was then attached onto another Si substrate using an adhesive (figure 1(c)). The total adhesion of the composite was weak on the transfer substrate because the interfacial strength of the evaporated Al was poor on the Si [24, 25] with only the van der Waals interaction with the ZnO nanowire. The composite was peeled and reversed from the transfer substrate under an external lift force. Hence, the reversed composite exposed another lateral side of the nanowire (figure 1(d)).

Anodic oxidation [26–29] was subsequently applied to form an alumina layer on the surface of the reversed composite. During this step, a 0.1 mol l$^{-1}$ tartarate–glycol–water solution was used as electrolyte with the pH value buffered by ammonia. A 40 nm thick alumina was achieved under constant anodic voltage of 30 V within 10 s (figure 1(e)). Another electrode on the nanowire can be formed via any suitable deposition on the surface of the composite (figure 1(f)). Finally, lateral electrodes were fabricated on the opposite sides of the ZnO nanowire using the native alumina layer to separate the two electrodes.

Patterned top metallic electrodes were fabricated through a shadow mask to measure the electrical properties of the alumina insulator and the UV photodiode. The related structure and morphology of the architecture were observed under a scanning electron microscope (SEM, JOEL 7000F) and an atomic force microscope (AFM, Veeco IMS). The alumina was analysed using x-ray photoelectron spectroscopy (XPS, PHI 5000). Electrical properties were identified using a semiconductor parameter analyser (Agilent, 4156C) at room temperature.
3. Results and discussion

3.1. Architecture and morphology

The accomplished architecture with lateral electrodes on the nanowires is investigated. Figure 2(a) illustrates the SEM image of the as-fabricated cross-section with an additional evaporated Al film. This Al film is used to define the thickness of the alumina layer and protect the nanowire from flaking. A 170 nm wide hexagonal ZnO nanowire is fabricated with the top and bottom electrodes at opposite lateral sides and a uniform 40 nm thick alumina layer between the electrodes. Energy dispersive x-ray spectroscopy (EDS) maps show the elemental distribution of Zn, O, and Al in figure 2(b), which clarify the ZnO nanowire, alumina layer, and Al electrodes in the architecture. Thermal evaporation is a well-known classic vacuum deposition technique for fabricating high-quality thin films [30]. According to the experimental procedure above, in which both electrodes are fabricated by direct evaporation onto the bare nanowire, the lateral electrodes are evidently reliable. These reliable electrodes, which are supplied over the whole area of the nanowire, are suitable for electronic injection/extraction.

The components, including the nanowire, insulator layer, and lateral electrodes, should match each other to be constructed in an integrated architecture. Structurally matched alumina insulation is introduced to achieve an insulator layer between the opposite lateral electrodes. This insulation is based on anodic oxidation. At the portion with plain Al in the composite, cations and anions move to the electrolyte/Al and the Al/alumina interfaces driven by the potential gradient. Al is consumed, and the alumina grows at both interfaces following the basic mechanism under a high-field regime [26]. At the portion with the embedded nanowire, the highly crystalline ZnO nanowire acts as a barrier. Ions do not migrate through the ZnO nanowire at the applied anodic voltage [31]. Thus, the directional growth of alumina relies on the absence of ion motion at this part. Consequently, the Al below the nanowire, which acts as the native bottom electrode, is not anodized, whereas the top side of the nanowire is kept exposed for subsequent fabrication of another electrode.

Furthermore, anodic oxidation is a self-inhibited process in which uniform thickness can be achieved by the given anodic voltage [26, 32]. The alumina layer facilitates precise spacing, unlike the non-selective insulation by rigorous coating and etching residual [13–15]. Alumina insulation is natively selective on the plane and is controllable in the depth of the composite, which matches the nanowire in the architecture. The native bottom electrode and the subsequently fabricated electrode also match. Significantly, the alumina layer between the lateral electrodes separates them and conducts the electrical path through the nanowire.

The morphology before the fabrication of the top electrode is evaluated using an AFM. The typical topography of the reversed composite with embedded nanowires is shown in figure 2(c). The root mean square roughness of the plain alumina is calculated as 0.5 nm. The planar surface is attributed to the smoothness of the reversed composite and the moderate anodic oxidation. The nanowire is embedded substantially in the Al film, and its lateral side is exposed. A line profile across the nanowire indicates the relative height of the nanowire on the plane. The side of the nanowire and the surface of the alumina layer differ by only a few nanometres. The composite is continuous at the surface with no observable damage in the nanowire. This condition indicates that the strategy is compatible with various nanowires. The good coplanar surface makes the strategy favourable for the deposition of any material for the electrodes on the nanowires, such as ultrathin gold (Au) electrodes. Evidently, various semiconductor nanowires can be supplied with diversely lateral electrodes or junctions and further functionalized as diverse devices.

3.2. Alumina layer

The alumina layer is the most important component because it serves as the structural and electrical insulator within the architecture. A plain alumina layer is prepared from the reversed Al film using the same procedure as in the experiment. The XPS results shown in figure 3(a) illustrate the binding energy of Al 2p. The related fitted curve reveals that the as-prepared alumina layer consists of γ-Al2O3 [33]. Serial thickness data measured from cross-sectional SEM images are plotted in figure 3(b). The thickness increases with the applied anodic voltage. A linear relationship is evident in the curves,
which agrees with the high-field model [26]. The formation factor calculated from the slope is 1.4 nm V⁻¹. Alumina layers with varied thicknesses are investigated with patterned top Al electrodes on the layers as a metal–insulator–metal structure to analyze the electrical properties of the alumina. Capacitances are measured at 1 MHz, as shown in figure 3(b). The experimental plots are in accordance with the reciprocal function, in contrast to voltages and thicknesses. Based on the plate capacitor model, the relative permittivity of 9.3 is calculated, which is within the range of the value for Al₂O₃ (from 8 to 10) [34–36]. The results prove that the controllable alumina layer has high-quality composition and structure.

Electrical leakage is evaluated to examine the insulating properties of the alumina layer. Figure 3(c) shows the leakage current densities measured from samples with varied thicknesses that ranged from 20 to 105 nm. Normally, all leakage curves show an increment with increasing bias voltage. A drop in the current density is observed for thicker layers. Direct and Fowler–Nordheim tunnelling [37] are not relevant to thick insulator layers in the low-field region. Filamentary conducting paths [38, 39] formed during anodic oxidation are responsible for the leakage. The current drop is caused by the low probability of through paths occurring in thicker layers. Despite the measured current, the leakages of all samples are less than 10⁻¹⁸ A cm⁻² until the field bias voltage of 8 V. This result is similar to that prepared by thermal oxidation or atomic layer deposition [34, 35].

Furthermore, the breakdown field intensity versus thickness is measured in figure 3(d). Several thin samples show a breakdown field intensity of approximately 15 MV cm⁻¹, whereas 70 and 105 nm thick samples do not exhibit breakdown until the maximum voltage of the measured system. The inset of figure 3(d) shows that the currents follow Frenkel–Poole emission before breakdown [40], expressed as

$$J = CE \exp \left( \frac{-q\left(\Phi - \sqrt{qE/\pi \varepsilon}\right)}{k_B T} \right)$$

where $J$ is the current density, $E$ is the electric field, $q$ is the elementary charge, $\Phi$ is the voltage barrier, $\varepsilon$ is the dynamic permittivity, $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $C$ is a constant. This equation implies that the conduction is related to the thermal carrier emission at localized traps under high field. Point defects formed at the alumina/Al interface are associated with the final catastrophic breakdown [41, 42]. The breakdown field of the fabricated 40 nm alumina layer in the final architecture is 16 MV cm⁻¹. Therefore, the obtained alumina insulation can isolate the top and bottom electrodes. The excellent insulating properties satisfy the requirement of the bias applied on semiconductor nanowires for photodiodes or LEDs.

3.3. ZnO nanowire UV photodiode

ZnO nanowires are functionalized as a UV photodiode in a demonstration based on the proposed architecture. The schematic diagram and microscopic image in figure 4(a) depict one photodiode cell patterned by cross-linked SiO₂ and Au stripes. SiO₂ acts as a buffer beneath the ultrathin Au for subsequent probing measurements. The 20 nm thick patterned ultrathin Au spreads from the SiO₂ buffer to overlay the window and forms the top electrodes of the nanowires.
inside. As a result, one typical cell comprises several tens of nanowires.

This photodiode is a front illumination device. The ultrathin Au serves as a semi-transparent electrode, which renders good transmittance among metal materials [43]. Incident UV light transmits through this electrode and excites electron–hole pairs in the ZnO nanowires. Given the difference in the work functions between Au (5.1 eV) and ZnO (4.15 eV), Au/ZnO forms a Schottky junction, whereas Al (4.1 eV) and ZnO almost have no barrier between them. Compared with the nanowire devices [7] with electrodes at both ends, ZnO nanowires are fabricated with electrodes on opposite lateral sides. This architecture allows Schottky junction and electrical transport across nanowires rather than along the axial direction. Hence, the as-fabricated nanowire photodiode is a Schottky type in a diametrical structure.

The properties of electrical transport and UV response are characterized as bias voltage applied to the Au electrode against the Al electrode. Room temperature \( I-V \) curves are measured in the dark and under 175 \( \mu \)W cm\(^{-2}\) 365 nm UV, as shown in figure 4(b). The plain alumina layer has no response under illumination (not shown). The rectified current in the dark indicates the typical Schottky transport [44] with strong rectification. Currents at forward bias are plotted and discussed on a log–log scale in figure 4(c). In the dark, the plots suggest different regions of electrical transport. An exponential relationship at low bias is related to the thermionic emission mechanism at the Schottky junction. At high bias, the transport shows a nonlinear \( I-V \) characteristic of \( I-V^m \) \( (m = 3.5) \), which is ascribed to the space charge limited current (SCLC) [45]. This characteristic is explained by the numerous carriers injected from the electrodes, which exceeded the concentration of free carriers in the ZnO nanowires. Under UV illumination, the photo-excited carriers greatly increase the carrier concentration. However, the superlinear current \( (m = 2) \) presents the remaining SCLC conduction, which implies the abundant number of injected carriers. The electronic injection into the nanowires that contributed to the lateral electrodes and the reliability of electrodes is efficient in the architecture.

The current increases significantly under UV illumination at reverse bias. An on/off ratio of 6000 at \(-1\) V is obtained. The energy band diagram illustrated in the inset of figure 4(b) shows that the photo-excited pairs can be efficiently separated by both the built-in field and the applied bias. The photocurrent increases with bias because more carriers are spatially separated at higher bias. The carriers are collected by electrodes to contribute to the photoresponse current when the dark current is prohibited by the Schottky barrier.

Repeating photosresponse is observed with periodic switching of UV light. Remarkably, photocurrent is measured at zero bias in figure 4(d). A reducing current is seen during each illumination. This phenomenon is involved with the
built-in field reduction and the surface state equilibrium of the ZnO nanowires. Given the absorbed oxygen on the ZnO nanowires, the Schottky junction of the photodiode is affected by the interfacial states [46–48]. The depleted surface of nanowires induces a higher Schottky barrier and stronger built-in field. Once the illumination is on, primary photocarriers are separated by the original built-in field. Electrons reach the Al contact and become the primary photocurrent. Holes migrate to the interface of the ZnO nanowires, and some discharge the negative charges of the absorbed oxygen. The discharged oxygen changes the interfacial states and reduces the built-in field. This condition increases the probability of carrier recombination and leads to photocurrent reduction. In addition, oxygen in the vicinity can be reabsorbed on the nanowires. The equilibrium process is slow because of oxygen diffusion. The photocurrent reduces gradually until the built-in field stabilizes.

The present architecture is more favourable in achieving zero bias photocurrent, compared with the nanowire Schottky photodiode illuminated by laser [49]. The space charge region (SCR) occupies a much greater volume of the ZnO nanowire along the lateral electrode. A large number of electron–hole pairs are excited and separated in the SCR. Moreover, these carriers are readily transported to the electrodes through the short path at the diametrical direction to avoid surface-related absorption. Reliable electrodes along the whole lateral sides of the nanowires prompt the extraction of carriers, which has recently been theoretically modelled [111]. The radial distribution of the electrical field determines the transport behaviour of the electrons and holes. Both carriers directly drift to the electrodes, rather than recombining during their diffusion along the axial nanowires. With the advantages of efficient injection and extraction, the proposed architecture is beneficial in enhancing photoelectric interaction in nanowires. Various semiconductor nanowires can be further developed using the present strategy for their applications in optoelectronic devices.

4. Conclusions

In summary, the proposed architecture with electrodes on the lateral sides of semiconductor nanowires has been successfully accomplished through structurally matched alumina insulation. This strategy begins with a nanowire-embedded Al film composite. An alumina layer that serves as an insulator between the electrodes is formed by selective anodic oxidation. Subsequently, electrodes are produced by directly evaporating metallic atoms onto the opposite sides of the nanowires. The architecture thus achieved is investigated with every matched component. The alumina layer exhibits excellent controllability and insulating properties. As an example of optoelectronic applications, ZnO nanowires are functionalized as UV photodiodes. The architecture with lateral electrodes is beneficial in transporting carriers across the diametrical direction and in electronic injection/extraction. The present results suggest that the proposed strategy has significant potential for the application of semiconductor nanowires in optoelectronics.

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