Synthesis, characterization and electrical properties of hybrid Zn$_2$GeO$_4$–ZnO beaded nanowire arrays

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Abstract
We report the syntheses of vertically aligned, beaded zinc germinate (Zn$_2$GeO$_4$)/zinc oxide (ZnO) hybrid nanowire arrays via a catalyst-free approach. Vertically aligned ZnO nanowire is used as a lattice matching reactive template for the growth of Zn$_2$GeO$_4$/ZnO nanowire. The morphology and structure of the as-prepared samples were characterized using X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). TEM studies revealed the beaded microstructures of the Zn$_2$GeO$_4$/ZnO nanowire. The thickness and microstructures of crystalline beads could be easily controlled by tuning the growth duration and temperature. The photoluminescence spectrum of the Zn$_2$GeO$_4$/ZnO nanowires is composed of two peaks, i.e., the ultraviolet (UV) peak and the defect peak. For longer treatment duration of the samples, both the UV and defect peak intensities decrease dramatically. One application of the as-prepared Zn$_2$GeO$_4$/ZnO nanowire is to use the nanowire as template for the growth of three-dimensionally (3D) aligned, high-density ZnO nanobranches en route to hierarchical structure. The study of field emission properties of the as-prepared samples revealed the low turn-on voltage and high current density electron emission from the 3D ZnO nanobranches as compared to the ZnO nanowires and Zn$_2$GeO$_4$/ZnO nanowires. Furthermore, the electrical transport behavior of single hybrid nanowire device indicates the formation of back-to-back Schottky barriers (SBs) formation at the contacts and its application in white-light response has been demonstrated.

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1. Introduction
One dimensional (1D) metal oxide nanostructures have attracted attention due to their interesting properties with potential in various nanoscale electronic and optoelectronic devices [1,2]. Promising applications include memory cells [3], solar cells [4], sensors [5], detectors [6,7], field-effect transistors [8], etc. Nanostructure of ternary metal oxides often shows interesting properties and functionalities, which are less pronounced or even absent in the common binary metal oxide system [9–18]. Among the many ternary systems Zn$_x$GeO$_4$ has interesting properties which make it suitable for applications such as visible-blind deep-ultraviolet photodetection [19,20], high-capacity anode material of lithium battery [21], bright white-bluish luminescence [22], photocatalytic water-splitting [23,24], photocatalytic reduction of CO$_2$ into renewable hydrocarbon fuel [25]. Recently, Yan et al. has reported the deep-UV detection performance of Zn$_2$GeO$_4$ nanonetworks with good wavelength selectivity [19].

However, synthesis of 1D ternary nanostructure with pure phase and desirable stoichiometry is considerably more challenging in comparison with the synthesis of 1D structures of their binary counterparts. Recently, the axial growth mechanism of Zn$_2$GeO$_4$–ZnO nanowire heterojunction and crystallographic alignment of ZnO nanorod arrays on Zn$_2$GeO$_4$ nanocrystal have been studied [26,27]. The most conventional way to synthesize the ternary oxide nanowire in chemical vapor deposition (CVD) technique is the high temperature co-evaporation of either the mixture of the constituent powders or dual-source deposition onto appropriate substrates [28,29]. A few research groups [12,14,30,31] have demonstrated the synthesis of crystalline ternary oxide nanowire or nanotubes by using their binary oxide nanowires as template. Typically the template synthesis of ternary nanowires essentially consists of three major steps; (1) preparation of binary oxide 1D nanostructures, (2) coating/deposition of the constituent metal or metal oxide to form a core-shell structure and (3) post treatment to facilitate the formation of ternary hybrid compound. Multitwinned Zn$_2$TiO$_4$ nanowires
have been synthesized by thermal annealing of Ti coated ZnO nanowires [12]. Yang et al. has shown the formation of similar multitwinned Zn2TiO4 by thermal annealing of ZnO–TiO2 core-shell nanowires, where atomic layer deposition (ALD) technique was utilized to coat the shell [32]. Similarly, the transformation of the MgO–Al2O3 core-shell nanowires into MgO–MgAl2O4 core-shell nanowire has been reported [30].

In this work, we report the controlled synthesis of beaded Zn2GeO4/ZnO hybrid nanowire arrays via a vapor-solid reaction using CVD technique. Here vertically aligned ZnO nanowires were used as a lattice matching reactive template for the growth of hybrid nanowires. Instead of preparing hybrid ternary nanowires via three-step process; our method of synthesis is a two-step process, where the coating and in-situ annealing is carried out simultaneously in controlled gaseous environment. Upon completion of the synthesis, each vertically standing ZnO nanowire has transformed into beaded chain with non-periodic beads like structure. The hybrid nanowires are slightly bent and curved. However, we did not observe any cracks, voids or, tubes morphology from further detail analysis. The morphology of final product is not sensitive to the temperature variation but depends significantly on the duration of the heating at fixed temperature. We also demonstrated the performance of a single hybrid nanowire in a photoconductive device for applications in nanoscale photodetectors.

2. Experimental methods

The synthesis process was carried out in a horizontal tube furnace (Carbolite CTF 12/75/700) using thermal evaporation and condensation method. Firstly vertically aligned and well faceted ZnO nanowire arrays were synthesized via vapor-solid (VS) method as reported earlier [33]. Mixture of ZnO (99.99%, Aldrich) and graphite (size < 20 μm, synthetic, Aldrich) powders in 1:1 weight ratio was loaded at the closed end of a quartz tube (one-end closed tube; diameter 0.15 cm and length ~25 cm). Pieces of Si (100) wafers pre-deposited with ZnO seed layer (~200 nm in thickness) by pulsed laser deposition were placed nearer to the open end as growth substrates. This quartz tube was inserted into the large alumina working tube of the tube furnace. Ar gas mixed with 0.25% O2 by volume with a total flow rate of 80 sccm (standard cubic centimeter per minute) was used as transport media. The temperature of the furnace was ramped to 900 °C at the rate of 25 °C/min and maintained for 30 mins with inside pressure of 2.0 mbar. The resultant ZnO nanowire array was used as templating substrate for the second step. Fig. 1 shows a schematic of the experimental setup with the templating substrate at the middle of the one end closed quartz tube. To synthesize the beaded Zn2GeO4/ZnO hybrid nanowires, a small piece of Ge wafer was used as source material and the above synthesized vertically aligned ZnO nanowire on Si was used as reactant substrate. The Ge source wafer was inserted in the quartz tube at downstream position with a separation of 1 cm from the template substrate. Purified Ar gas was flowed through the vacuum sealed tube furnace (at a flow rate of 100 sccm and a pressure of 1 mbar) loaded with the quartz tube, for 1 h before ramping the temperature to 850 °C at a rate of 15 °C/min. The synthesis of Zn2GeO4/ZnO nanowires was conducted at 850 °C for different growth durations.

3. Results and discussion

The hexagonal facet of the ZnO nanowires on the ZnO seed layer/Si substrate is clearly visible in the SEM images (see for example Fig. 2(a)). The as-obtained pristine ZnO nanowires have diameters ranging from 60 nm to 100 nm and lengths around 1–2 μm. Fig. 2(b–c) show SEM images of the ZnO nanowires taken after treating with the Ge vapor. It is evident that the smooth facets of pristine ZnO nanowires were transformed to beaded structures. The SEM images with 20 degree tilted view of the beaded Zn2GeO4/ZnO hybrid nanowires are shown in Fig. 2(c–d), which show that the hybrid nanowires are still vertically oriented.

We prepared samples with growth durations of 5 mins, 30 mins, 60 mins and 120 mins for systematic comparison of the final products, TEM, selected-area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS) measurements were performed. Fig. 4(a–b) show the TEM image of the beaded nanowires, indicating the diameter of the beaded nanowires ranging from 60 nm to 100 nm. Fig. 4(b) indicates the presence of planer defects in the region between two adjacent beads. The corresponding SAED pattern of the nanowire is shown as the inset in Fig. 4(b), in which a series of small and weak diffraction spots are found among the main spots. The lattice spacing between the adjacent lattice planes (Fig. 4(c)) is measured to be approximately 0.71 nm, which is consistent with the (110) planer separation of Zn2GeO4 crystal, confirming the direction of growth of the nanobeads to be along [110] direction. It is also clear from the TEM image (Fig. 4(c)) that the crystalline planes are continuous through interface between two beads, which indicates that the beads are single crystals with same orientation. The fast Fourier transform (FFT) pattern inserted in the bottom-right corner of Fig. 4(c) matched with the FFT of Zn2GeO4 (110) plane. EDS spectrum (Fig. 4(d)) shows that the beaded nanowires consist of only three elements, namely, Zinc, Germanium and Oxygen with atomic percentage of 29.8, 14.9 and 55.3, respectively. This is approximately in the ratio of 2:1:4, consistent with the stoichiometry of Zn2GeO4 compound.

We proposed the following growth mechanism for the formation of beaded ternary oxide nanowire (Fig. 5). Firstly, the ZnO...
nanowire (Fig. 5(i)) was exposed to Ge vapor at high temperature and the surface of the nanowire was coated with Ge as shell material (Fig. 5(ii)). For nanoscale solid-state reaction, surface diffusion is the dominating transport process over the volume diffusion since the surface diffusion coefficient is normally several orders of magnitude larger than their bulk components. Likewise the interplay of Ge into ZnO matrix most likely facilitates the growth of Zn$_2$GeO$_4$ ternary crystallites. An extreme case of the Kirkendall effect represents one-way diffusion of Ge into ZnO and formation of epitaxial Zn$_2$GeO$_4$ shell with excess Ge clusters (Fig. 5(iii)) on hexagonal ZnO surfaces by solid state reaction. Upon suitable matching of the thickness of the core with shell, crystalline beaded Zn$_2$GeO$_4$ (Fig. 5(iv)) nanowire can be obtained. The originally smooth hexagonal ZnO nanowires were roughened...
and become curved due to the strain produced at the core-shell interface during the second step of growth as a result of lattice mismatch of ZnO (Hexagonal, $a=3.25$ Å, $c=5.21$ Å) and Zn$_2$GeO$_4$ (Rhombohedral, $a=14.23$ Å, $c=9.53$ Å). As the synthesis temperature is much lower than the melting point of Ge $\sim 940$ °C, the lack of Ge vapor will control the morphology of the sample by controlling the solid-state reaction.

Fig. 6 shows the XRD patterns for the ZnO nanowires (curve a) and as grown Zn$_2$GeO$_4$/ZnO hybrid nanowires (curve b). All peaks in ‘curve a’ can be indexed with wurtzite ZnO crystal with lattice constants of $a=3.25$ Å, $c=5.21$ Å [JCPDS Card No. 00-0075]. The peaks in ‘curve b’, can be indexed with rhombohedral zinc germanium oxide (Zn$_2$GeO$_4$) crystal with lattice constants of $a=14.23$ Å, $c=9.53$ Å [JCPDS: PDF File No. 00-011-0687], in addition to the substrate peak corresponding to Si(110) substrate and peaks of the ZnO template [JCPDS: PDF File No. 01-070-2551]. Fig. 7 shows the room temperature photoluminescence spectrum (PL) of the samples with different growth durations (He-Cd laser, 325 nm excitation). The spectrum reveals the heterostructures have one prominent ultraviolet peak at 380 nm and a broad visible band centered at wavelength 540 nm. The inset shows the relative intensity of the peak centered at 380 nm for samples...
grown at different durations. The deep level (green) emission from ZnO is due to the presence of various defects, such as interstitial oxygen and oxygen vacancies [37]. Compared to the pristine ZnO nanowires, the PL spectrum recorded from Zn$_2$GeO$_4$/ZnO beaded nanowire arrays shows different features. Due to the increase of growth duration, the volume of unconsumed ZnO will reduce, which will effectively reduce the excitonic peak intensity. After 5 mins of growth, the intensity of defects peak increased compared with pristine ZnO sample, which can be attributed to the increase in surface defects. After longer growth treatment, the defect peak intensity is found to decrease suggesting the Zn$_2$GeO$_4$ creasing process greatly reduces the surface area. The UV emission with a peak at ~380 nm is due to the near band edge emission of ZnO [34]. The samples with longer treatment durations does not display any detectable shift to the near band edge emission peak at 380 nm, which confirms that Ge doping in the core ZnO grains is absent in our samples [35,36].

We also explored the further growth of ZnO nanostructures on the backbone of Zn$_2$GeO$_4$/ZnO beaded nanowires. Zn$_2$GeO$_4$/ZnO beaded nanowires synthesized by 120 mins of treatment were used as template for the deposition of ZnO using the same tube furnace. The deposition of high-density 3D ZnO nanostructures was carried out for 30 mins in the same conventional way of synthesizing ZnO nanowires, as described earlier. Fig. 8(a) shows the SEM image of primary Zn$_2$GeO$_4$/ZnO hybrid nanowires used for the ZnO deposition. After the vapor phase deposition of ZnO, the primary Zn$_2$GeO$_4$/ZnO beaded nanowires were uniformly covered with thin ZnO nanobranes (Fig. 8(b)). The higher magnification SEM images of the high-density heterostructures were shown in Fig. 8(c–d). The ZnO nanowire branch with sharp nano-needle structure (length ~100–250 nm, diameter ~10–20 nm) can be clearly viewed from Fig. 8(d). These results strongly support the crystallographic relation of the ZnO nanobranes grown on the backbone of Zn$_2$GeO$_4$/ZnO beads. The crystalline Zn$_2$GeO$_4$/ZnO beaded nanowires serve as an ideal substrate for ZnO nanobranes growth. The [110] crystallography planes of growth Zn$_2$GeO$_4$ beads on (100) faced plane of ZnO allow epitaxial growth of ZnO nanowires [27].

The field emission (FE) performance of the ZnO nanowires, Zn$_2$GeO$_4$/ZnO hybrid nanowires and 3D ZnO nanobranes were carried out inside a high-vacuum chamber ($2 \times 10^{-6}$ Torr) at room temperature with a two-parallel-plate configuration, as detailed elsewhere [39]. Fig. 9(a) shows a plot of emission current density versus the applied field ($J$-$E$) of these three samples, obtained when the anode-sample distance was 100 µm. It is revealed that the emission current density ($J$) exponentially increases with an increase in the applied field ($E$). The turn-on electric field (the average applied field corresponding to an
emission current density of 10 μA/cm² is 10.98 V/µm, 10.30 V/µm and 6.43 V/µm for ZnO nanowires, Zn₂GeO₄/ZnO hybrid nanowires and ZnO nanobranches, respectively. In addition to the turn-on voltage, the ZnO nanobranches on Zn₂GeO₄/ZnO hybrid nanowires yielded a maximum current density of 300 μA/cm² under a field of 8.9 V/µm. These results suggest that the ZnO nanobranches array have better field emission property compared with pure ZnO nanowires and Zn₂GeO₄/ZnO hybrid nanowires.

The FE characteristics were further analyzed with the Fowler-Nordheim (FN) theory [40] described by

\[ J = (A\beta^2 E^2 \phi) \exp(-B_0 \beta^{3/2} / \beta E) \]  

\[ \ln(J/E^2) = \ln(A\beta^2 \phi) - B_0 \beta^{3/2} / \beta E \]  

where \( J \) is current density from the emitting source, \( A = 1.54 \times 10^{-6} \text{ A V}^{-2/3} \text{ cm}^{-1/2} \), \( B = 6.83 \times 10^{4} \text{ eV}^{-3/2} \text{ V} \text{/µm} \), \( E \) is the applied field, \( \phi \) is the work function of the emitting materials, and \( \beta \) is the field enhancement factor. Fig. 9(b) shows the FN plots (\( \ln(J/E^2) \) versus \( 1/E \)) and the linear fit near the turn-on field indicating the quantum tunneling process of the electron emission from the emission tips. Field-enhancement factor, \( \beta \), is an important parameter in describing FE, which depends on several parameters such as, the emitter geometry, crystal structure, vacuum gaps, and the spatial densities of emitters. \( \beta \) can be determined by fitting the slope value of the FN plot and inserting the available \( \phi \) value.

By substituting the \( \phi \) (setting ZnO work function [38] as 5.3 eV) in the slope of FN plot (Eq. (2)) for branched ZnO nanowire heterostructures, \( \beta \) can be estimated to be 1331. The ZnO nanobranches with sharp nano-needle heads would be main contributing factor for the observed higher current density at low turn-on field, as compared with pure ZnO nanowires and Zn₂GeO₄/ZnO hybrid nanowires.

The single nanowire devices were fabricated on heavily n-doped Si substrate (resistivity ~ 1–10 Ω cm) coated with thin (~100 nm) insulating layer of SiO₂. The gold (Au) electrodes of thickness ~100 nm were designed on the substrate with two probe configuration using standard optical lithography technique. The spacing of the electrodes was ~30 µm. The nanowires were placed between the (Au) electrodes by using micromanipulator probe station (Cascade Microtech™). The sharp tungsten tip (size ~75 nm) was able to pick the single nanowire separately from their growth substrates and placed one by one on the SiO₂/Si substrate. The free ends of the single nanowire were electrically connected separately with the prefabricated gold electrodes by depositing uniform Pt metal (~300 nm). The focused electron beam (FEI Quanta 200-3D FIB/SEM; electron beam induces deposition (EBID), electron beam as decomposing source for organometallic platinum at 5 kV, 0.18 nA current) was used to deposit Pt metal on the contacts, separately. The electrical measurements and photoconductivity measurements were performed at room temperature using Keithly 6430 under vacuum (2 × 10⁻⁴ mbar).

The typical I–V curve of the hybrid nanowire for a continuous voltage sweep of 5 V to –5 V under vacuum and dark conditions at room temperature is shown in Fig. 10(a). The nonlinear and asymmetry positive current and negative current of I–V characteristic of the semiconducting hybrid nanowire indicates the bead nanowire makes two asymmetrical Schottky barrier contacts with the Pt metal. From the inset of Fig. 10(a), we can see that ln I is linear with V in the intermediate bias voltage for both positive and negative currents, which indicates the typical I–V characteristic of back-to-back SB structure [41]. Photosresponse of the single nanowire device was also studied under the illumination of a halogen white light source (for a fixed light intensity of 3 ± 0.3 mW/cm²). Fig. 10(d) shows the photocurrent-time (I–t) characterization of the nanowire device. The photocurrent of the nanowire device reduced quickly from 10.5 pA (under white light illumination) to a dark current of 7.3 pA. The average photoresponse time \( \tau_1 \) (rise time) and \( \tau_2 \) (decay time) are estimated to be approximately 2.3 and 2.3 s. (Fig. 10(e)), respective, indicate the fast white light sensitive property of the single hybrid nanowire device.

4. Conclusion

In summary, we have demonstrated the growth of vertically oriented beaded Zn₂GeO₄/ZnO hybrid nanowires in a two-step method. The microstructures, morphology and composition of as-prepared samples were characterized using XRD, SEM, EDS, and TEM analysis. PL spectrum of the samples with different treatment durations shows no detectable shift to the near band edge emission of ZnO. In contrast, for longer treatment duration of the samples, both the UV and defect peak intensities decrease dramatically. In addition, we have demonstrated the feasibility of using the Zn₂GeO₄/ZnO beaded nanowires as a template to form high density heterostructures of Zn₂GeO₄/ZnO 3D nanosstructures. We have also demonstrated the efficiency of field emission properties for branched ZnO heterostructured nanowires, which is better than the pure ZnO nanowires and the hybrid nanowires. Eventually in the same method of preparing Zn₂GeO₄/ZnO beaded nanowires, we can transfer the ZnO...
nanobreaches into Zn$_2$GeO$_4$/ZnO beaded nanobreaches, which will effectively produce 3D heterostructures of Zn$_2$GeO$_4$–ZnO nanowires. 3D aligned high-density, hierarchical nanostructures with Zn$_2$GeO$_4$/ZnO backbones and ZnO nanobreaches attribute higher surface area for realizing multifunctionality of nanostructures. We also demonstrated the performance of the single hybrid nanowire in a photoconductive device for applications in nanoscale photodetectors.

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