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Letter

Large scale, low temperature hotplate synthesis of germanium dioxide nanowires

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ABSTRACT

A low temperature ~350 °C, low cost germanium dioxide (GeO_2) nanowire (NW) synthesis process has been developed under ambient conditions. Nanowires can be grown on a number of different surfaces including silicon, quartz, Al_2O_3 and aluminum nitride (AlN) by first coating the substrates with a thin layer of gold. The as grown NWs are tens of microns long and ~50–200 nm in diameter and exhibit characteristics of the vapor–liquid–solid (VLS) growth mechanism.

1. Introduction

One dimensional structures have gained much attention in the last decade due to material properties that differ from their bulk counter parts, e.g. oxide NWs have been found to have different bandgap than bulk oxides [1]. They are better candidates for sensors because of higher surface to volume ratio which allow larger surface activities and accumulation of charge species which can modify transport properties [2]. Germanium dioxide nanomaterials exhibit blue photoluminescence [3] and GeO_2 NWs have been reported with photoluminescence an order of magnitude higher than GeO_2 powder [4]. GeO_2 NWs have a bandgap of 2.44 eV and have higher refractive index ($n = 1.63$) than silicates [5] which makes them attractive for optoelectronic applications. This material can be used as optical waveguides [6] and GeO_2 NWs have been used as substrate for surface enhanced Raman spectroscopy (SERS) [7]. Several routes of GeO_2 NWs synthesis have been reported in the literature that include physical evaporation [8], laser ablation [9], thermal oxidation [10], carbon nanotube confined reaction [11], and thermal annealing of Ge under oxidizing environment [12]. These synthesis procedures require heating above sublimation temperature of GeO (710 °C) to generate sufficient vapor pressure of source material. Nanowire growth can occur rapidly under these typical growth conditions and for added control, vacuum growth chambers are commonly used which might include process gas control instrumentation, vacuum pumps and furnaces (internal or external to the chamber). Here we report on a low cost, low temperature, hotplate NWs synthesis method with minimum process variables for good repeatability.

2. Experimental

A hotplate capable of reaching ~350 °C temperature was used to grow GeO_2 NWs on the following substrates: quartz, alumina, AlN and Si wafers each coated with 9–28 nm of gold (Au). The experimental setup is shown in Fig. 1. To fabricate the NWs a gold coated substrate was placed on hotplate facing upward and a small piece of an undoped Ge wafer was placed on top of the substrate. Aluminum foil was used to cover the sample on the hotplate taking care not to touch the samples with the aluminum. The hotplate was then heated to ~350 °C for about 2 h then switched off and allowed to cool down to room temperature before the substrate was removed. Through an optical microscope, a white wool-like growth could be observed on the substrate.

3. Results and discussion

The product was characterized by JEOL 6400 SEM, energy dispersive spectroscopy (EDS) (Oxford Instruments), JEOL 3010 transmission electron microscope (TEM), powder X-ray diffraction (XRD) (Rigaku) and Raman spectroscopy (EZ Raman). Nanowires were tens of micron long and ~50–200 nm in diameter. For TEM analysis a Cu TEM grid (Pelco 100 mesh with lacy carbon) was placed on an AlN piece having NWs on its surface and the TEM grid was moved several millimeters to scrape some of the NWs onto the grid. TEM image in Fig. 2(a) shows NW with Au tip confirming VLS growth mechanism. The obtained diffraction pattern during TEM imaging is shown in Fig. 2(b) indicating that NWs are crystalline in nature. After 2 min of imaging, the diffraction pattern was lost which is in agreement with what has been reported elsewhere [8].

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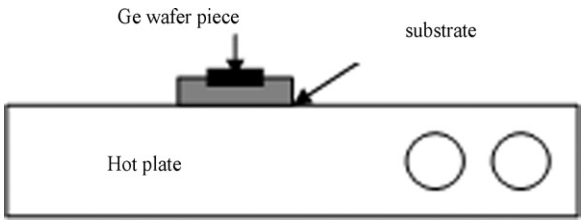

Fig. 1. Hotplate setup for GeO_2 nanowire synthesis.

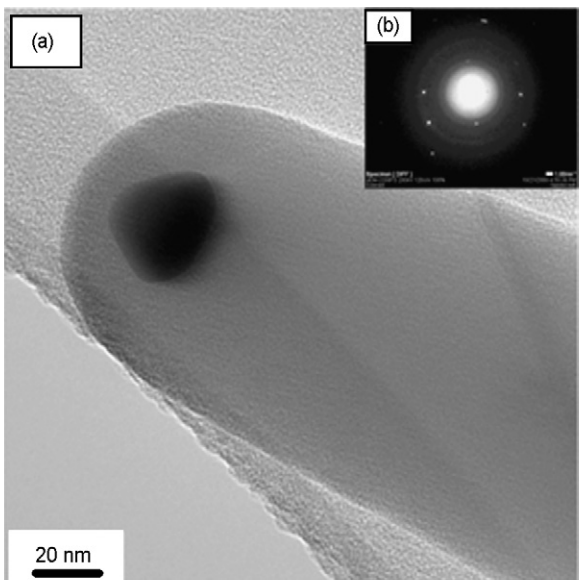

Fig. 2. (a) TEM image showing Au tip on GeO_2 NW and (b) diffraction pattern indicating nanowires are crystalline.

SEM images of GeO_2 NWs grown on aluminum nitride (AlN) and alumina (Al_2O_3) are shown in Fig. 3(a) and (b). SEM images of NWs on quartz and silicon (Si) wafer are shown in Fig. 4(a) and (b) respectively. It can be clearly seen that growth on Si wafer and quartz are sporadic whereas on alumina and aluminum nitride there is uniform layer of NWs. A closer look reveals that later substrates have thin wires with more uniform morphology. We believe it is because AlN and Al_2O_3 have rough surfaces providing more edges for a dense growth. Fig. 5(a) shows the Raman spectra indicating that NWs are trigonal in structure [7,13]. Fig. 5(b) shows the XRD spectrum peaks relating to GeO_2. The EDS spectrum in Fig. 6 indicates that Ge and O are close to 1:2 in ratio (31:67) confirming the product is GeO_2.

4. Growth mechanism

In Addition to GeO_2 we also synthesized ZnO NWs using a hotplate which grew only on the zinc source and any efforts to grow NWs on catalyst coated substrate were not successful. The growth on Zn source can be explained by self-catalytic nucleation and tip growth process [14] which clearly is not a VLS growth mechanism. Whereas in the case of GeO_2, NWs could be synthesized only on a catalyst coated substrate and not on source itself. It appears that a catalyst is necessary for low temperature growth of GeO_2 because melting point of Ge is 915 °C but melting point of Au–Ge eutectic is 356 °C (at 27 at.% Ge) [15] which is well below the sublimation point of germanium. There are previous reports of hotplate metal oxide NW growth; however, to our knowledge it is the first report of GeO_2 NWs synthesis using hotplate. Cheong et al. [16] synthesized WO*x* NWs on hotplate by heating tungsten (W) foil

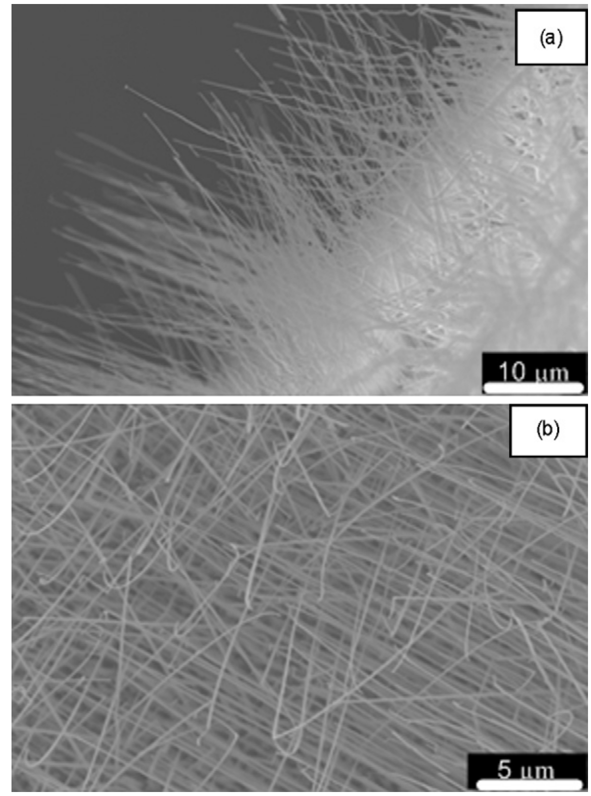

Fig. 3. SEM images of GeO_2 nanowires on gold coated. (a) Aluminum nitride (AlN) surface and (b) alumina (Al_2O_3) substrate.

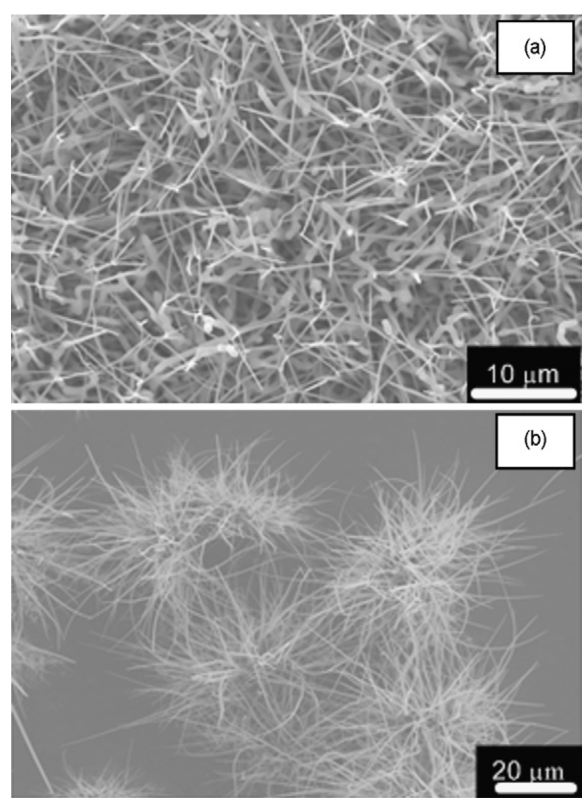

Fig. 4. SEM images of GeO_2 nanowires on gold coated. (a) Quartz surface and (b) silicon (Si) substrate.

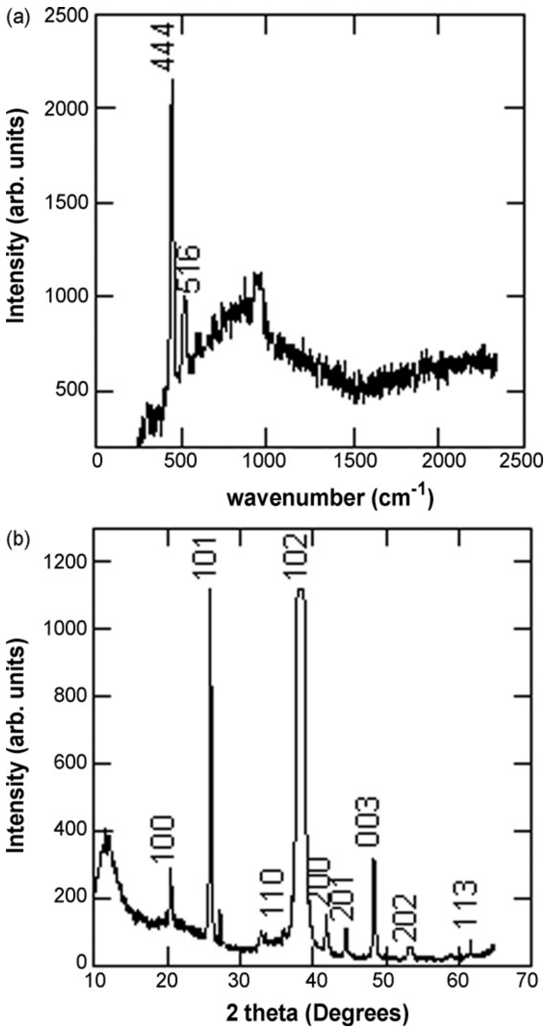

Fig. 5. (a) Raman spectra of GeO_2 NWs indicating that NWs are trigonal in structure and (b) XRD spectrum indicating NWs are GeO_2.

and collecting NWs on glass slide without any catalyst. They have proposed solid–vapor–solid (SVS) growth mechanism for their synthesis process. Zhu et al. [14] and Yu et al. [17] have reported metal oxide NWs including ZnO, CuO, α-Fe_2O_3 and CoO_x nanostructures through direct heating of source on hotplate without using any catalyst. They have ascribed solid–liquid–solid (SLS), self-catalytic nucleation and tip growth mechanism for their NWs. We believe our synthesis mechanism is different from these reports because of the Au catalyst presence. We believe it is VLS mechanism where first GeO evaporates from Ge source. GeO then travels in vapor form to the substrate and forms eutectic with Au droplet. The captured GeO combines with oxygen from air to form the GeO_2 NWs. Because of close proximity of source and catalyst, Ge vapors quickly supersaturate Au droplet which is necessary for nanowire nucleation and growth [18]. No growth was observed when the substrate was placed farther from Ge source which indicates that GeO rapidly condenses out of the gas phase. This could be caused by low vapor pressure of the GeO, and the time to formation of GeO_2 in the gas phase. Nanowire growth is only observed when source is in intimate contact with catalyst coated substrate.

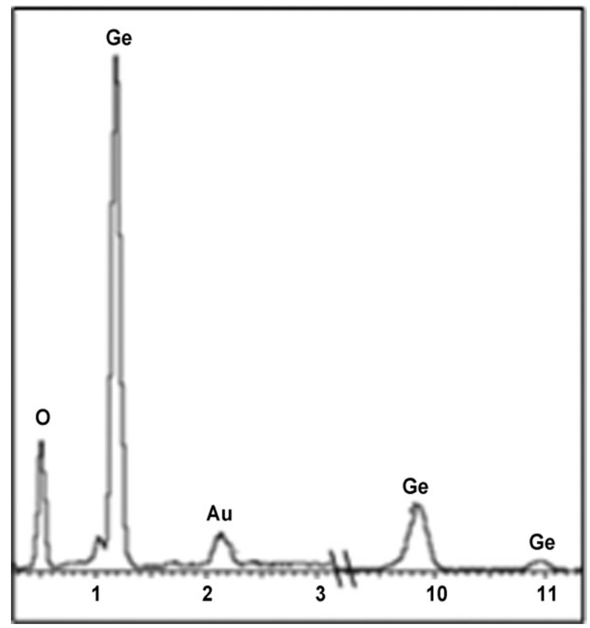

Fig. 6. EDS spectrum indicating germanium and oxygen ratio.

5. Conclusion

We have synthesized GeO_2 NWs using a simple hotplate technique. This synthesis is different from previous hotplate reports as it needs catalyst for nanowire growth and Au catalyst metal at the tips of the nanowires supports the vapor–liquid–solid growth mechanism. This low cost technique can be used for large scale synthesis of GeO_2 nanowires for various applications.

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