Comparison between optical properties of doped and undoped GeO_x Nanowires

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Abstract: Cr-doped germanium oxide nanowires, germanium oxide nanowires have been synthesized using physical vapor deposition method. For growth of nanowires and Cr-doped nanowires the experimental conditions were similar except doping source. The doped germanium oxide nanostructures such as Cr-doped germanium oxide nanowires will be effective in influencing the optical properties of germanium oxide nanostructures, since they may tune their band gap energy.

Keywords: Germanium oxide; Doping; Nanowires; Nanotubes; Optical properties.

I. Introduction

One-dimensional (1D) nanostructures are very promising candidates because of their potential for elucidating promising applications in magnetic, optical, and electronic devices [1]. Owing to contribution to understand fundamental concepts in mesophysics and potential applications in nanoelectronic devices, recently special attention has been paid to 1D nanostructures such as nanotubes and nanowires. Germanium oxide (GeO_x) is of particular interest, since it is a transparent conducting oxide (TCO) with high potential in optoelectronics communication devices such as optical waveguides for integrated optical systems [2]. The linear coefficient of thermal expansion and refractive index of GeO_2 glass is higher as compared to SiO_2 glass [3]. The GeO_X is a blue luminescent material and plays vital role in vacuum technology. Hence fabrications of GeO_X nanostructures are always useful for future optical nanodevices. The low-dimensional nanostructures of GeO_X, such as nanowires, nanoneedles, nanowhiskers or nanotubes [4,5] are potentially useful for various industrial applications. Using various physical and chemical methods such as physical vapor deposition, carbothermal reduction, laser ablation and thermal oxidation, different nanostructures: nanowires, nanoneedles, nanotubes and nanowhiskers of GeO_x have been prepared by germanium (Ge) and GeO_2 precursor powders [6-8]. The doping in GeO_X nanostructures with rare earths elements, transition metal elements (Er and Eu) and metal impurities (Sn and Mn) shows that doping impurities can tune the optical properties of GeO_X nanostructures [9-13]. The Ge nanowires, GeO_X nanowires and nanotubes have been synthesized and their optical properties were investigated [14, 15]. The GeO_X nanostructures have wide band gap energy and their optical properties promised interesting applications as in fabrication of optoelectronic devices. The doped GeO_X nanostructures (nanowires and nanotubes) will be effective in influencing the optical properties of GeO_X nanostructures since they may tune their band gap energy. As suitable impurities can affect physical properties of GeO_X nanostructures, the waveguiding behavior of undoped and doped germanium oxide nanowires and nanotubes would be interesting and will be useful to fabricate future optical nanodevices.

In view of this, in present work, GeO_X nanowire and Cr doped GeO_X nanowires are synthesized by using a simple vapor transport nanotubes in the visible region is explored.

II. Experimental

The commercial germanium (Ge), germanium oxide (GeO_2), chromium oxide (Cr_2O_3), (all from Alfa Aesar and 99.99 % pure) powders were used as precursor materials. The p-type silicon (001) wafer was ultrasonically cleaned in ethanol for 15 min. The 3 nm thick gold film was deposited on wafer at room temperature (RT) by using an electron beam evaporation

system at a pressure ~ 6 x 10^{-6} Torr. These gold coated silicon wafers were used as substrates for further experimentation. The GeO_X nanowires, Cr-doped GeO_x nanowires, were grown on silicon wafer substrates by a vapor transport method using a three zone furnace. For preparation of GeO_X nanostructures, mixture of Ge and GeO_2 with a 1:3 ratio was placed in an alumina boat and heated at 1100 ^oC (zone-I) at a rate of 20 ^oC/min with the reaction time of 60 min. and with 100 sccm Ar flowing through the tube. During this, gold coated silicon wafer substrates were placed in zone-II (at 750 ^oC) and to zone-III (at 850 ^oC) to grow GeO_X nanowires. After completion of reaction, the furnace was allowed to cool naturally to room temperature (RT). Similarly, for the preparation of Cr-doped GeO_x nanowires, the mixture of Ge, GeO_2, CrO_3 in 3:9:3 ratio was used and gold coated silicon wafer substrates were placed in zone-II (at 750 ^oC) and gold coated silicon wafer substrates were placed in zone-III (at 850 ^oC).

The morphological study of the resultant films was done by using field emission scanning electron microscope (FESEM, JEOL JSM-6500F, accelerating voltage = 10 kV) and transmission electron microscope (TEM, JEOL JEM-2010, 200 kV) equipped with an energy-dispersive spectrometer (EDS). EDS was used for analysis of chemical composition of undoped and doped GeO_x nanowires. The influence of Cr, dopant on the photoluminescence properties of undoped and doped GeO_X nanowires in the visible region have also been explored.

III. Result and Discussion

The substrate temperature plays vital role in the morphological change in GeO_X nanostructures. The white products were obtained on substrates during experimentation at temperatures of 750 and 850 ^0C. Figure 1 (a) shows FESEM image, corresponding TEM image and EDS spectrum of the GeO_X nanowires. It confirms the growth of nanowire structure with diameter and length in the range of 25 - 30 nm and 10 - 15 µm respectively for product obtained at 750 ^oC. The insets of figure 1(a) show TEM image of the nanowires with the gold tip and EDS spectrum of corresponding nanowires. The EDS spectrum confirms the composition of Ge and O. Thus at substrate temperature of 750 ^0C, GeO_X nanowires are formed. Figure 1(b) depicts FESEM image of Cr-doped GeO_X nanowires, corresponding TEM image and EDS spectrum as insets. The FESEM image of the product obtained at 750 ^oC confirms the growth of high density nanowire structure with diameter and length in the range of 25 - 30 nm and 10 - 15 µm respectively. The insets of figure 1(c) show TEM image and EDS spectrum of corresponding nanowires. The EDS spectrum confirms the doping of Cr in GeO_X nanowires.

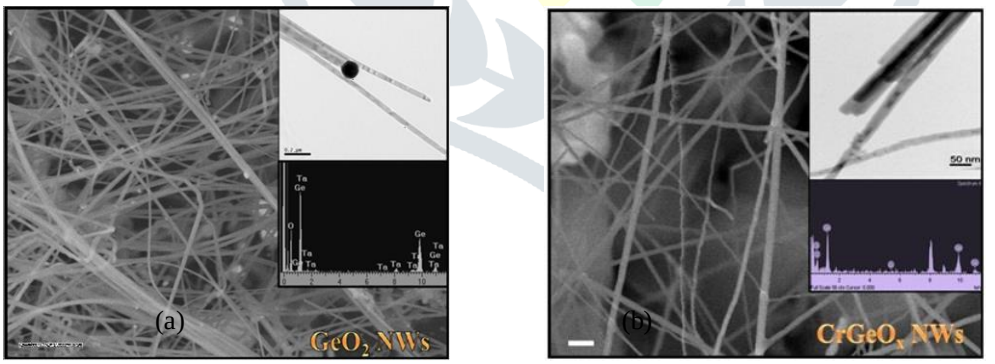

Figure 1 FESEM image (scale bar = 1 µm) of GeO_X nanowires (Insets: corresponding TEM image and EDS spectrum), (b) FESEM image (scale bar = 100 nm) of Cr-doped GeO_X nanowires (Insets: corresponding TEM image and EDS spectrum)

Figure 3 (a) shows that photoluminescence (PL) emission spectrum of the as-prepared GeO_X nanowires measured upon photoexcitation at 325 nm. In order to have closer insights for the origin of emission, spectral feature are fitted with Gaussian functions. In case of GeO_X nanowires, the best fit of the emission was obtained with two Gaussian functions, with the peaks centered at 420 nm (in blue region) and 472 nm (in bright blue region). Similarly, in case of Cr-doped GeO_X nanowires [Figure 2 (b)], the peaks are centered at 424 nm (in blue region) and 476 nm (in bright blue region).

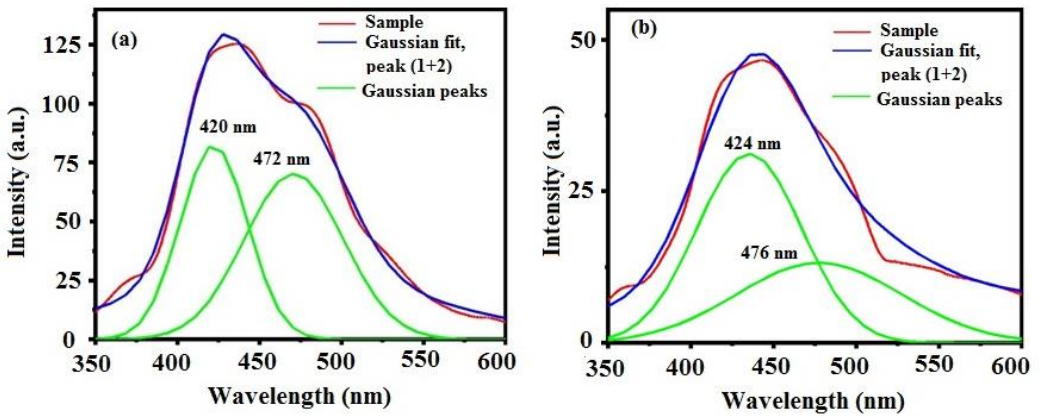

Figure 3 PL spectra of (a) GeO_X and (b) Cr-doped GeO_X nanowires at RT

Since the GeO_X nanowires and Cr-doped GeO_X nanowires are prepared at high temperature (1100 ^oC) and GeO is volatized at this point, the oxygen vacancies and oxygen-germanium vacancy pairs easily exist in the products. It is thus reasonable that the blue light emission and bright blue emission can be attributed to oxygen vacancies and oxygen-germanium vacancies centers. The shift in peak position illustrates that the Cr-doping can slightly tune the structure of energy level and band gap of GeO_X nanomaterials. Further, Cr-dpoing can increase the defects and oxygen vacancies in GeO_X nanomaterials.

IV. Conclusions

The undoped GeO_X nanowires and Cr-doped GeO_X nanowires are synthesized by using a simple vapor transport method at high temperature. The red shift in photoluminescence spectrum of Cr-doped GeO_X nanowires as compared to undoped GeO_X nanowires shows that the optical properties of the GeO_X nanowires can be tuned by Cr doping. It suggests the possible control of defects in nanowires and oxygen vacancies in GeO_X nanowires. Thus the optical properties of the GeO_X nanowires can be controlled by using different doping elements, which will improve their application region in functional devices.

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