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Controlled side coupling of light to cladding mode of ZnO nanorod coated optical fibers and its implications for chemical vapor sensing

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ABSTRACT

Controlled light coupling from surrounding to the cladding mode of zinc oxide (ZnO) nanorod coated multimode optical fiber induced by the light scattering properties of the nanorod coating and their applications of sensing are reported here. A dense and highly ordered array of ZnO nanorods is grown on the cladding of silica fibers by using low temperature hydrothermal process and the effect of the hydrothermal growth conditions of the nanorods on the light scattering and coupling to the optical fibers is experimentally investigated. The nanorod length and its number per unit area are found to be most crucial parameters for the optimum side coupling of light into the fibers. Maximum excitation of the cladding mode by side coupling of light is obtained with ZnO nanorods of length ~2.2 μm, demonstrating average coupling efficiency of ~2.65%. Upon exposure to different concentrations of various chemical vapors, the nanorod coated fibers demonstrated significant enhancement in the side coupled light intensity, indicating the potential use of these ZnO nanorod coated fibers as simple, low cost and efficient optical sensors. The sensor responses to methanol, ethanol, toluene and benzene vapor were investigated and compared, while the effect of humidity in the sensing environment on the sensor performance was explored as well.

1. Introduction

Zinc oxide (ZnO) is a group II–VI wide bandgap (E_g ~3.37 eV) semiconductor material with high electron mobility (~200 $cm^2 V^{-1} s^{-1}$) and exciton binding energy (~60 meV), which makes it an interesting material for a variety of optoelectronic applications [1–3]. Among the various nanostructured ZnO reported in the literature, one-dimensional (1-D) nanorod structure is particularly attractive because of its high surface to volume ratio. Due to the polar nature of the (002) crystal plane of ZnO, anisotropic growth of ZnO to obtain nanorod structure can be easily achieved using solution phase or gas phase synthesis techniques [4–6]. Low temperature hydrothermal growth is one of the most widely used techniques because of the simplicity, low cost and potential to produce highly ordered arrays of ZnO nanorods in large scales [7]. However, majority of the reported research till date limits to the growth of the nanorods on flat surfaces, like glass [8], silicon wafer [9] and sapphire substrates [10]; while very few studies have been done on the growth of the nanorods on curved surfaces.

ZnO nanorods grown on silica fibers have shown light coupling into nanorod waveguides due to its higher refractive index ($n_{ZnO} \sim 2$) than silica ($n_{silica} \sim 1.5$), enabling its potential application as an optical sensor [11–13]. In this context, Liu et al. [14] has reported a humidity sensor based on ZnO nanorods coated silica fibers and demonstrated enhanced interaction between the light coupled to the nanorods and the surrounding. Similarly, application of ZnO nanorod arrays as out-cladding coating on a long period grating to sense ethanol was reported by Konstantaki et al. [15].

Herein, we report controlled side coupling of light into a multimode optical fiber with dense array of ZnO nanorods as an out-cladding coating. The side coupling of light was achieved from

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the surrounding to the cladding mode utilizing the scattering property of the one-dimensional ZnO nanorods, which reduces the complexity in sensor designing. The ZnO nanorods scatter the incident light at an angle larger than the critical angle of the surrounding and the cladding, allowing the excitation of the cladding mode [16]. In the present work, by controlling the length, diameter and surface coverage of the ZnO nanorods, modulated thru their hydrothermal growth conditions, the light scattering and coupling into the cladding mode is experimentally investigated. Finally we have demonstrated a model chemical vapor sensor based on the ZnO nanorod coated fibers which lead to an increase in the output power of the fiber (cladding mode) in the presence of different chemical vapors.

2. Experimental details

All the chemicals used in this study are of analytical grade and used without any further purification. Standard multimode (MMF) optical fibers, acquired from Thorlabs, USA (item no. FG105LCA) are used during the study, having visible to IR transmission in the range of 400–2400 nm with maximum attenuation of 12 dB/km at 850 nm. The fibers feature a pure silica core with diameter 105 μm ± 2% and a fluorine doped silica cladding of 125 ± 1 μm diameters. The plastic buffer on the fibers were stripped in acetone in an ultrasonic bath, followed by cleaning the fibers with successive sonication for 15 min in soap water, acetone, ethanol and deionized (DI) water. For some experiments microscopic glass slides were used, which were cleaned by using the same process as described for the fibers.

2.1. ZnO seeding

A zinc acetate solution prepared in ethanol was used to prepare the seed layer of ZnO nanoparticles which serves as the nucleation sites for the hydrothermal growth of the ZnO nanorods. Zinc acetate concentration was varied from 1 mM to 6 mM in order to study the effect of the seed layer on the light scattering and coupling by the nanorods. In order to deposit the seed layer, the cleaned fibers were placed on a hot plate maintained at 60 °C and 100 μl of the zinc acetate solution was drop casted on the fibers followed by slow drying of the solvent. The dropping process was repeated 10 times and at the end of the process the fibers were annealed at 350 °C for 1 h in ambient conditions. The deposition of the seed layer on the glass substrates were also carried out by following the same process where the optical fibers were replaced by the glass substrates.

2.2. Hydrothermal growth of ZnO nanorods

ZnO nanorods were grown on the seeded fibers as well as on the seeded glass substrates by using hydrothermal process, where an aqueous solution containing 10 mM zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and 10 mM hexamethylenetetramine or HMT ($(CH_2)_6N_4$) was used as precursor solution. The seeded samples were dipped in 100 ml of the precursor solution in a beaker and heated to 90 °C. The hydrothermal reaction time was varied from 5 h to 20 h, and in order to maintain a constant growth rate of the nanorods the old precursor solution was replenished with new solution every 5 h till the end of the hydrothermal process [17]. Finally the as-obtained ZnO nanorods coated fibers and glass substrates were retracted from the precursor solution and rinsed thoroughly with DI water several times, followed by drying in oven at 90 °C. The as obtained ZnO nanorods coated substrates were then characterized by scanning electron microscopy (SEM; model: JEOL JSM-6301F) and X-ray diffraction spectroscopy (XRD; model: JEOL JDX-3530 with Cu Kα radiation).

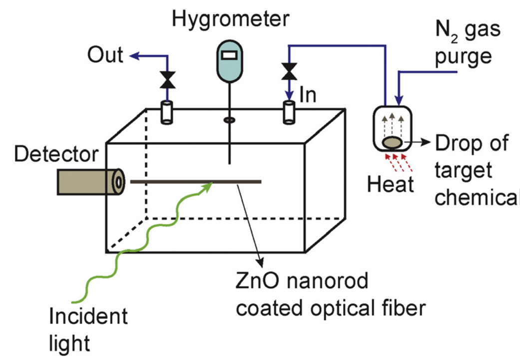

Fig. 1. Schematic diagram depicting the sensing setup.

2.3. Light scattering measurements

The presence of the ZnO nanorods on flat substrate or optical fiber causes the incident light to scatter angles larger than the incident angle. The angular spectrum distribution of the scattered light depends strongly on the shape and density of the nanorods. Optical scattering is characterized through scattering cross section, C_{sc}, and phase function $p(\theta,\phi)$. Cross section is the ratio of the total scattered field to the incident light represented as an area normalized to unit area. Phase function is a probability distribution function of the light scattering at radial and azimuthal angles θ and ϕ. To evaluate C_{sc} and p of the grown ZnO nanorods on glass substrate, an optical nephalometer was built. The details of the nephalometer setup are given in the Supplementary information (Fig. S1).

In the experiment, a collimated fiber coupled white light LED source is used to shine light on the sample. An optical detector is placed at the end of a rotating arm to measure the optical power as a function of the azimuthal angle, ϕ (radial symmetry is assumed as the direction of the rods is along the direction of incident light). The average scattering cross section for one rod, C_{sc}, is estimated from the measured ratio of the total scattered power to the incident light, divided by the density of nanorods (number of rods per unit area, ρ_a). This density is determined from the SEM images (details given in the Supplementary information). Knowing C_{sc} and ρ_a, the scattering coefficient (defined as the scattering loss per unit length of propagation) can be represented as $\alpha_s = C_{sc} \times \rho_a/L$, where L is the average length of the rods measured from the SEM images. This quantity is important especially when dealing with optical fibers, as will be explained in the next section.

2.4. Sensing tests

ZnO nanorod coated fibers were used for chemical vapor sensing, where the nanorods were grown using the optimum synthesis conditions which led to the maximum light coupling efficiency. Fig. 1 shows the schematic diagram of the sensor test bench. During the measurement of sensor characteristics, nitrogen (N_2) was used as the carrier gas, which serves as both reference and diluting gas. Initially, N_2 gas was passed through the test chamber until a steady-state condition was obtained. A known amount of methanol vapor was then evaporated in a small vial and introduced to the test chamber as the target gas. Same procedure was adopted for other chemicals as well. The concentration (C) of the target vapor in ppm was calculated by using the following equation [18]:

$$C = \frac{V_t \times D_t \times T}{M_t \times V} \times 8.2 \times 10^4 \quad (1)$$

where, V_t, D_t and M_t represent the volume (μl), density (g ml^{-1}) and molecular weight (g mol^{-1}) of the target gas, V represents the volume of the test chamber and T is the sensor operating temperature