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REVIEW

Micro- and nanophotonic structures in the visible and near infrared spectral region for optical devices

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Abstract
In this paper we present some research results on the micro and nano-photonic structures in the visible and near infrared spectral region for optical devices that have been done within the framework of Nanoscience and Nanotechnology Program of Institute of Materials Science. In the first part, we report the design and fabrication of 1D photonic structure based on porous silicon layers fabricated by electrochemical etching method and some of their potential applications such as optical filters, microcavity and optical sensors for distinguishing the content of bio-gasoline. In addition, we demonstrate some results on preparation of the 2D and 3D nanophotonic structures based on silica opal layers prepared by sol–gel and self-assembled methods. In the second part, we demonstrate the results of lasing emissions of erbium ions in the visible and near infrared zone from microcavity. The observation of emission of single-mode green light at the wavelength of 537 nm from erbium ions in the microcavity is interesting for the study of atom–photon interaction phenomenon. In the last part, we will show some new results of design and fabrication of nanocomposite based on nanoscale TiO$_2$ and/or ZnO and nanoparticles of semiconductors and metals, which are oriented to the fabrication of energy conversion and photo-reactor devices.

Keywords: micro- and nanophotonic structure, photonic devices, sensor

Classification numbers: 5.04, 6.04

1. Introduction
Micro- and nanophotonics have received an increasing interest in recent years due to the foreseen possibility of merging electronics and photonics on the same chips. Significant breakthroughs have been demonstrated on optical waveguides and passive optical devices to distribute light, filter optical signal as well as in the field of active structures for light emitters, modulators and detectors. The main potential applications of the micro- and nanophotonic devices are optical communications, energy conversion, optical sensors and reactors. In terms of physical properties, photonic structures are characterized by a periodical change of refractive indices between core and cladding, leading to a strong miniaturization of the waveguide cross-sections in the deep-submicron scale, which controls spontaneous emission, zero-threshold lasing, very sharp bending of light, and trapping of photons in the high-$Q$ cavity. In addition, the use of plasmonic phenomenon based on corrugation of nanoscale metals and photonic materials, leading to enhanced optical near field, is perceived as a very interesting and
promising approach. In this paper we review the investigation results on the micro- and nanophotonic structures in the visible and near infrared range for optical devices that have been done within the framework of Nanoscience and Nanotechnology Program of Institute of Materials Science. The primary aims addressed the design and fabrication of 1D photonic structure based on porous silicon layers fabricated by electrochemical etching method and some of their potential applications such as optical filters, microcavity and optical sensors for distinguishing the content of bio-gasoline and/or light emitters. This concept will be extended to the 2D and 3D nanophotonic structures based on silica opal layers prepared by sol–gel and self-assembled methods. In the second part, we demonstrate the results of lasing emissions of erbium ions in the visible and near infrared zone from microcavity. The observation of single-mode green light at the wavelength of 537 nm from erbium ions in the microcavity is interesting for the study of atom–photon interaction phenomenon. In the last part, we will show some new results of design and fabrication of nanocomposite based on nanoscale TiO2 and/or ZnO and nanoparticles of semiconductors and metals, which are oriented to the fabrication of the energy conversion and photo-reactor devices.

2. Photonic crystal structure on nanoporous silicon multilayer and silica opals

2.1. Interference filter based on nanoporous silicon multilayer structure

Porous silicon (PS) has attracted increasing research interest in physics as well as applications since 1990 when Canham reported on the efficient visible photoluminescence (PL) of porous silicon [1]. Structurally, PS consists of many pores and silicon residuals and can usually be described as a homogeneous mixture of silicon, air and even silicon dioxide. Based on porosity, PS can be classified into three types: nano-, meso- and macropores. From the viewpoint of photonic structure, because the value of porosity is directly linked to the effective refractive index of the PS layer, this layer appears as an effective photonic medium, where the refractive index has a tunable value between the refractive index of bulk Si and that of the air (pores). The porous silicon thin films were formed from silicon wafers by electrochemical etching in hydrofluoric acid, without the necessity of any deposition process [2]. During this anodization process a part of the silicon is dissolved and the remaining crystalline silicon forms a sponge-like structure with porosity between some tens of a per cent up to more than 90%. The nano PS size depends upon the doping level of the silicon wafers: the use of low-doped p-type Si-substrates results in porous silicon (with pore and crystallite size less than 2 nm) and the use of highly doped substrates results in mesoporous silicon (of size 2–50 nm) [3]. The effective refractive index of the porous silicon thin films is mainly determined by the porosity which can be varied by several anodization parameters. In our work we concentrated on developing the nanoporous silicon multilayer structure for optical filters and microcavity. The nanoporous silicon layers with different refractive index are formed by electrochemically etching a highly doped p-type silicon wafer (resistivity of 0.01-0.1 Ω cm) in an aqueous HF:ethanol electrolyte. The pores are large enough (10–50 nm) to allow infiltration of other species but interconnected and small enough to allow porous silicon to be treated as an effective photonic medium for visible and infrared light. The electrolyte with concentration of 10–30% HF and ethanol of ratio 1:2 is chosen because of the large porosity variation obtained by varying the electrical current. The electrochemical etching process was controlled by computer using Galvanostat equipment, so precise control over electrical current density and etching time was achieved, then it resulted in a good control of the refractive index and thickness over the individual layers forming the multilayer [4]. The PS interference filters are usually formed from different depth profiles of the refractive index of PS multilayers which act as Bragg reflectors. The optical thickness of the high and low refractive index layers (nH1, nL1) are 1/4 of the filter wavelength, so that these structures are usually called quarter-wave-stacks [5]. The most suitable way to formation of various porous layers is changing the anodization current density, since high current density results in high porosity and low refractive index of the layer. By Bruggeman effective medium approximation [6], the relation between effective refractive index (εPSi) of the pore layer, silicon refractive index (εSi), void refractive index (εvoid) and porosity (P) is presented as follows:

\[(1 - P) \frac{\varepsilon_{\text{Si}} - \varepsilon_{\text{PSi}}}{\varepsilon_{\text{Si}} + 2\varepsilon_{\text{PSi}}} + P \frac{\varepsilon_{\text{void}} - \varepsilon_{\text{PSi}}}{\varepsilon_{\text{void}} + 2\varepsilon_{\text{PSi}}} = 0,\]

where P is a value in the percentage.

In practice, the porosity of a single layer is determined by weight method with an accuracy of 5%. In addition, the porosity can be estimated by surface image of materials. Figure 1 shows the field emission scanning electron microscopy (FE-SEM) image of porous silicon and/or silicon-rich silicon oxide layers, which were prepared by thermal annealing of the PS layer. The porosity of nanoporous silicon layers is commonly of 20–70%. The porous silicon multilayer was formed by periodically varying the applied current density between two levels (J1 and J2) of 64 and 19 mA cm⁻², respectively [7]. The number of periods for each filter was from 6 to 18. Figure 2 shows a FE-SEM image of the completed porous silicon 12-period filter fabricated by ratio of current densities J1/J2 = 64/19 and duration time of 6.33 and 12.3 s, respectively. As seen in figure 2(a), the typical sizes of the silicon residuals and air voids are about 50 nm. This allows us to describe the PS layers as ‘an effective medium’, whereby its optical properties mainly depend on its porosity. The SEM image of the multilayer displays different gray levels depending on the porosity of the layers (see figure 2(b)). Because of this, the layers of the stack are distinguished and therefore the thickness of each layer can be experimentally determined.

Figure 3 displays the reflection spectra of multilayer filters with different thickness levels. The curves (a), (b), (c) and (d) display the reflection spectra of 12-period filters with a total thickness of 8.1, 6.0, 5.4 and 4.5 µm, respectively. The difference in the thickness of interference filters and therefore, the thickness of the layer in the stacks causes the shift of the center wavelength at which the reflectance would be maximal.
Figure 1. FE-SEM image of core and cladding of PS layer (a, c), and of silicon-rich silicon oxide layer (b, d), which was obtained before (a, c) and after (b, d) thermal annealing in order to estimate their porosities.

Figure 2. Cross-sectional SEM images of silicon pores (a) and multilayer structure of the interference filter with period number $N = 12$ (b).

Figure 3. Shifting the reflection spectra of 12-period filter by varying the thickness of the layers in the stacks: (a) $h = 8.1 \, \mu m$; (b) $h = 6.0 \, \mu m$; (c) $h = 5.4 \, \mu m$; and (d) $h = 4.5 \, \mu m$.

Figure 4. Reflection spectra versus period numbers of stacks: curves a, b and c from multilayer filters with 6, 18 and 12 periods, respectively.

Figure 4 demonstrates the reflection spectra at wavelength of 1550 nm range from three filters with different period numbers. As seen from this figure, when period number increases, the spectra become shaper, narrower and the refractivity increases. This result relatively corresponds to our simulation using the transfer matrix method [7].
The difference in the characteristics of filter spectra from the simulation and experiment occurs in the filters having too few or too many periods \((N)\). In the case of filters having too few periods \((N \leq 6)\), reflection from the interfaces, especially from the interface between air and the top layer, becomes more important in those filters, so that the imperfections of interfaces created by electrochemical etching can cause a deformation of the reflective spectrum as seen in curve \((a)\) of figure 4. In the case of the filters having too many periods \((N \geq 18)\), the long anodization time causes a deformation of the nanostructure of surface layers, whereas the nano- and microstructure of the bottom layers can be affected by the slower transport of etching substances. The interference filters have a significant potential of applications not only for fiber-optic communication, but also for bio-chemical sensory.

### 2.2. Microcavity based on nanoporous silicon multilayer structure

The structure of microcavities, also called Fabry–Perot filters, consists of two parallel distributed Bragg reflectors (DBRs) separated by a spacer layer (or defect layer), whose reflective index can be the same or different to the ones used for the DBRs. The optical thickness of the spacer layer can be \(\lambda\) or \(\lambda/2\) [8]. The reflectivity spectrum of this structured material is characterized by a very narrow pass-band centered in a high reflectivity wavelength range. Microcavities can be used as band-pass filters with a tuned position of the peak, tunable mirrors and high-sensible detectors of organic substances among others [9, 10]. In this subsection we review the results of fabrication and investigate the wavelength-selective characteristics of DBR microcavity based on nanoporous silicon multilayer structures. In addition, the potential applications of nanoporous silicon microcavity as bio- and chemical sensors are also reported. Fabry–Perot nanoporous silicon microcavity has been formed on highly doped p-type silicon substrates by electrochemical etching method, as shown above. Nanoporous silicon microcavities are formed by first etching a top DBR with alternating \(\lambda/4\)-thickness layers of low and high porosities (high and low refractive indices, respectively), then etching a \(\lambda/2\)-thickness spacer layer with the designed refractive index, and finally etching a bottom DBR with the same conditions as the top DBR [11]. Detailed electrochemical etching conditions are presented in table 1. The PS microcavities used in our cases typically consist of 4.5/5 period upper/lower DBR. The PS microcavity samples have been rinsed in methanol and isopropanol after anodization process and dried in nitrogen ambient.

The micro- and nanostructures of the prepared nanoporous silicon microcavity have been analyzed by using the FE-SEM Hitachi 4800.

Figure 5 shows the SEM cross-section of a PS microcavity fabricated by electrochemical etching condition shown in table 1. It can be observed in figure 5(a) that the SEM image shows the dark and bright layers that have a low and high porosity, respectively. Based on this difference, the layers of the stack are distinguished and therefore the thickness of each layer can be determined as about 165 nm. As seen in figure 5(b), the typical sizes of the silicon residuals and air voids are less than 30 nm. The simulated and measured reflection spectra of nanoporous silicon microcavity are shown in figure 6. The spectrum is characterized by a transmission band at 506 nm between two high reflection bands. In experiment the reflective distinction ratio of 25% and the full-width at half-maximum (FWHM) of the band-pass at 10 nm were observed in nanoporous silicon microcavity.

The prepared microcavity has been used as bio-chemical sensor for detection of organic solvent content. The principal operation of sensor based on the nanoporous silicon microcavity is the determination of resonant wavelength shift \((\Delta \lambda)\) caused by the liquid ambients with different refractive indices, when the sensor is immersed into them. A change of refractive index of the nanoporous silicon layers due to the substitution of air with liquid in the pores results in the red shift of resonant wavelength of reflective spectrum. For testing bio-chemical sensor, the

---

**Table 1.** Electrochemical etching conditions for preparing PS microcavities.

<table>
<thead>
<tr>
<th>Description</th>
<th>Current density (mA cm(^{-2}))</th>
<th>Etching time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBR on top (4.5 periods)</td>
<td>(J_1 = 15) (J_2 = 50)</td>
<td>4.762</td>
</tr>
<tr>
<td>DBR on bottom (5 periods)</td>
<td>(J_1 = 15) (J_2 = 50)</td>
<td>4.762</td>
</tr>
</tbody>
</table>

---
device is dipped into different organic solvents with known refractive indices. Table 2 presents resonant wavelength shifts when the sensor is immerged into organic solvents such as methanol 99.5%, ethanol 99.7%, and isopropanol 99.7% and methylene chloride 99.5% with known refractive indices. The important parameter of the liquid sensor is the refractive index change of the porous layer which depends upon the refractive index of the liquid as well as the porosity of the porous layer. Using formula (1), we calculated the porosity of high- and low-refractive index layers using experimental data. Figure 7 shows the characteristics of the bio-chemical sensor which depended upon the porosity of different layers. The experimental curve agrees with calculation, when the ratio of porosity of high- and low-refractive index layer is of 34/72, respectively. The micropority sensors were applied to detection of different solutions such as methanol and ethanol in various commercial gasolines. A wavelength shift of 4.85 nm between A92 and E5, and of 10.45 nm for A92 and A92 added 15% methanol is found. From these experimental data we suppose that the elaborated bio-chemical sensor can distinguish a change of 1% in concentration of ethanol and methanol in gasoline.

2.3. Photonic crystal based on silica opals

The ordered dielectric structures with periodically modulated refractive index in two- and three-dimensions have attracted considerable interest for applications in photonics because the propagation of electromagnetic waves can be manipulated by defining allowed and forbidden energy gaps in the photon dispersion spectrum. Various important scientific and engineering applications of 2D and 3D photonic crystals such as control of spontaneous emission, zero-threshold lasing, very sharp bending of light, trapping of photons, are expected by utilizing the photonic band-gap (PBG) [12]. The fabrication of photonic crystal (PhC) with a PGB in the visible and near-IR wavelengths usually needs an enormous effort, since the spatial periodicity in the PhC is required to be on the order of the light wavelength. However, 3D PhC using an opal structure may be rather simply produced by employing a vertical deposition of mono-dispersive colloidal silica spheres through gravity sedimentation. The resulting opal structure on a substrate forms an fcc lattice of close-packed spheres with the (111) plane parallel to the substrate surface [13]. Because of this, the optical properties of self-assembled silica opal films have been extensively investigated due to their ease of manufacture and their potential applications as photonic devices. Of course, opal is known to show only a photonic pseudogap or photonic stop band, i.e., the PBG only in a certain direction at its first order band structure, and the applicability of the opal photonic crystal has been believed to be rather limited compared to other PhC structures.

In our work, opal PhC films were prepared from silica colloidal particles exploiting the self-assembly method. Silica particles were obtained using the standard Stöber synthesis process. The SiO$_2$ particles were obtained through this process resulted in spheres of about 300 nm diameter, suitable for the photonic pseudogap in the visible spectral range. Synthetic opal films were then prepared from these silica spheres by evaporating the ethanol from the silica–ethanol suspension. In order to obtain a high-quality regular assembly of the silica spheres, the ethanol was then evaporated very slowly at sufficiently low temperature. The opal crystals thus obtained were then dried naturally at room temperature for several weeks to form the opal films. The structural properties of the opal films were characterized by FE-SEM observation. The structural parameters were also obtained from the analysis of the dependence of the optical reflection peak wavelength on the incident angles of white light. Figure 8 presents the FE-SEM image of the opal photonic crystal prepared from silica spheres of 298 nm diameter.

The typical reflection spectra of silica opal films, measured with non-polarized white light, are shown in
Figure 8. FE-SEM images of opal photonic crystal prepared from silica spheres of 287–298 nm diameter. Note the multilayer film forming an fcc lattice (on top) and the hexagonal order present at the surface (on bottom).

Figure 9. Dependence of the reflection spectra of the silica opal films on the irradiation incident angles (a) and the fitting curves given by the modified Bragg equation ($D = 300$ nm, $n = 1.33 \pm 5\%$).

Figure 9(a) for various incident angles. It is remarkable that the reflection peak becomes larger as the wavelength becomes shorter and the background reflectance in the long wavelength region increases as the incident angle increases above $50^\circ$. From figure 9(b) we see that the data agree well with the modified Bragg equation, which was used in our work [13].

3. Microcavity lasers based on high concentration Er-doped glasses

3.1. High power and single-mode emission at wavelength of 1550 nm from microsphere glass lasers

Dielectric microcavity, in which light can be guided though whispering gallery mode (WGM), has been widely investigated for optoelectronic applications such as ultra-low threshold laser sources and narrow band spectral filters. The WGMs can exhibit high quality factor ($Q > 10^8$), and are of interest for fundamental research in cavity quantum electrodynamics (CQED), nonlinear optics, photonics and sensing. In our previous work [14], we successfully developed microspherical cavity lasers, which can emit the WGMs at wavelengths in the 1550 nm range with high optical power. In this section we show a novel and easy-to-use method to obtain peaks of high power, narrow linewidth and high side mode suppression ratio (SMSR) of the WGMs in the wavelength range of 1530–1610 nm emitted from the microsphere silica lasers with different erbium concentrations. As an application, we show a technique of controlling the quantity of the collected WGMs from the microcavity lasers by half-taper fiber. The microcavity lasers have been fabricated by multi-component silica-alumina glasses ($90\%$ SiO$_2$–6Al$_2$O$_3$ : 4Y$_2$O$_3$ : $x$Er$_2$O$_3$, where $x = 0.065–0.3$ is a molar per cent of Er$_2$O$_3$). Using molten method, the solid glass spheres rely upon surface tension to create perfect smooth dielectric boundary, along which the WGMs are confined. The equatorial diameters of glass spheres are of 40–150 $\mu$m for our study. Efficient optical coupling to the spherical microcavity both for pumping and for laser output extraction was performed with optical fiber tapers with waist diameter of 1–2 $\mu$m. We used a 976 nm laser diode with the output optical power up to 170 mW in single-mode emission (SDLO-2564-170) for excitation of the erbium ions. The pump laser beam and the emitted WGMs are coupled by different half-taper fibers. This technique has an advantage of flexibility in controlling the coupling gap between the collected fiber and sphere surface, while the position of excitation fiber was fixed. The spectral characteristics of the WGMs were analyzed by the optical spectrum analyzer (OSA): Advantest Q8384 with the resolution of 0.01 nm.

Figure 10 shows the emitted WGM spectra of the 3000 ppm Er-doped silica microsphere lasers with a full
diameter of 90 \( \mu \)m measured by the half-taper fiber configuration when the pump power was below (figure 10(a)) and at laser threshold (figure 10(b)), respectively. We can observe the laser oscillation modes of the microsphere cavity in the large wavelength range from 1510 to 1610 nm. In our experiment, the lasing emission was often a single-mode at threshold and the laser intensity strongly depended upon the Er-concentration in the silica glasses and the diameters of the microspheres. The maximum laser intensity at threshold was obtained from 2500 ppm Er-doped silica. Table 3 shows the single-mode laser intensity at the threshold of the 90 \( \mu \)m diameter microsphere lasers with the Er-concentration changing from 1000 to 4000 ppm. The WGM lasing spectra at threshold can be controlled by Er-doped concentration, and the laser intensity will be enhanced with the Er-ions doped into silica up to 2500 ppm. By increasing the pump power we obtained the multi-wavelength emission of WGMs in the large wavelength range of 1530–1600 nm. The intensities of single optical lines of WGMs were different, but the free spectral range (FSR) of the optical lines is equal and the SMSR is high enough for applications.

As applications in the spectroscopy and sensory, we used the optical coupling technique for controlling the quantity of the optical lines extracted from the microwavvity lasers. Experiment shows that the number of the WGM collected by the half-taper fiber strongly depended upon the coupling gap between the sphere surface and the extraction fiber and the taper diameter.

In our experimental scheme, the waist diameter of the extracted fiber was 1 \( \mu \)m and the coupling gap can be adjusted within the range of 0–2 \( \mu \)m with accuracy up to 10 nm by the 3D positioning system. When the coupling gap is of 0.2–0.6 \( \mu \)m, we often detected a single-mode of WGMs. Figure 11 shows the single-mode spectra extracted from a 90 \( \mu \)m diameter microsphere laser when the coupling gap was changed from 0.2 to 0.6 \( \mu \)m with the accuracy of coupling gap adjustment of 0.05 \( \mu \)m. This technique has good reproducibility in practice and we can extract any existing WGM in the microcavity for use with a suitable adjustment of the coupling gap.

Figure 12 shows the intensity of a single-mode WGM laser amplified by the erbium-doped fiber amplifier (EDFA) with the amplification coefficient of 40 dB. The intensity of a single optical wavelength in this case can reach up to +18.6 dBm and the SMSR is of 38 dB, which means the optical line corresponding to different WGMs of the microcavity can be easily filtered out, separately modulated, and used as independent optical channels in the dense wavelength division multiplex (DWDM) networks and sensors.

### Table 3. Laser intensity at threshold from 90 \( \mu \)m diameter microsphere lasers with different Er-concentrations.

<table>
<thead>
<tr>
<th>Er-concentration (ppm)</th>
<th>Optical pump threshold (mW)</th>
<th>Laser intensity (dBm)</th>
<th>Lasing wavelength range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>1.6</td>
<td>−53</td>
<td>1550–1570</td>
</tr>
<tr>
<td>2500</td>
<td>2.0</td>
<td>−51</td>
<td>1580–1600</td>
</tr>
<tr>
<td>3000</td>
<td>2.5</td>
<td>−55</td>
<td>1590–1610</td>
</tr>
<tr>
<td>4000</td>
<td>3.5</td>
<td>−68</td>
<td>1530–1550</td>
</tr>
</tbody>
</table>

WGMs. Figure 11 shows the single-mode spectra extracted from a 90 \( \mu \)m diameter microsphere laser when the coupling gap and sphere surface was of 0.2 \( \mu \)m (a), 0.3 \( \mu \)m (b), 0.4 \( \mu \)m (c), and 0.6 \( \mu \)m (d), respectively.

3.2. Up-conversion emission at wavelength of 537 nm from Er-doped glass microcavity lasers

It is very interesting for fundamental physics that we observed the up-conversion emission at 537 nm from Er-ions doped into the silica glass, because in a common case the up-conversion emission of the Er-doped silica fiber pumped...
by laser beam at 976 nm is a broad-band fluorescence emission with two peaks at wavelengths $\lambda_1 = 522$ nm and $\lambda_2 = 547$ nm, which corresponded to radiative transitions $^2H_{11/2} \rightarrow ^2I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ in erbium ions. The up-conversion emission at 537 nm from Er-ions can be obtained in a week-coupling cavity condition such as random cavity created by air-gap between the glass fiber and coated polymer layer, thin-film Au-coated fiber and/or microsphere cavity and the lasing wavelength difference is of $\pm 0.3$ nm for different cavity. Figure 13 shows experimentally observed green emission spectra from Er-ions doped in the optical fibers, with a pumping power of 70 mW at wavelength of 976 nm for both cases: (a) narrow emission mode at 537 nm obtained from random cavity created by silica glass fiber–air gap–polymer-coated layer and (b) broad-band emission spectrum with two peaks at 522 and 547 nm was obtained when the random cavity was destroyed. Figure 14 demonstrates the intensity of 537 nm narrow line-width emission as a function of the pump intensity at 976 nm. Upon increasing the pumped intensity, the 537 nm green light intensity stays in the linear lasing regime. It should be noted that the lasing threshold was very low (at pumped power of 2–3 mW). The measured line-width of laser spectra in both cases was of 0.2–0.25 nm. This means that the $Q$-factor of cavity was of 2100–2800.

For testing the formation of a random cavity which has structure of glass–air gap–polymer cover, we destroyed the air-gap by three ways: (i) removing the coated polymer cover, (ii) destroying air-gap by depressing polymer cover and (iii) covering polymer layer by water and/or alcohol. For the first two cases (without air-gap in the structure of the fiber) the emission at 537 nm disappeared, meaning that the cavity of laser was absolutely destroyed. In the last case, the 537 nm emission intensity did not disappear, but its intensity decreased by scattering on the fiber surface. Using the model of the coupled photon–atom modes in the cavity we propose that the 537 nm lasing emission from Er-ions in the fiber can appear by the followings factors: a diode laser operating at 976 nm pumps the Er-ions from their fundamental level $^4I_{15/2}$ to $^4I_{11/2}$ and a second photon transfers the excited ion to $^4F_{7/2}$. This level decays very rapidly to the levels $^2H_{11/2}$ and $^4S_{3/2}$. The splitting of these levels is only some hundreds of cm$^{-1}$ and the inversion can be achieved between the level $^4S_{3/2}$ and the upper Stark levels of the ground state $^4I_{15/2}$ [15]. In our case, the emission at 537 nm does not respond to radiative transition between excited state $^4S_{3/2}$ and fundamental state $^4I_{15/2}$, meaning that the emitted photon is a result of the interaction between the resonant cavity photon and the excited ions on the upper levels $^2H_{11/2}$ and $^4S_{3/2}$.

The Er-ion population on the state $^4S_{3/2}$ may be more than on $^2H_{11/2}$, and the different value of resonant photon energy and radiative energy of transition $^4S_{3/2} \rightarrow ^4I_{15/2}$ is very small in experiment (it is equal to 42 meV). We can obtain that the probability of interaction of photon-excited atom on state $^4S_{3/2}$ would be more than with atom on state $^2H_{11/2}$ in the cavity. This phenomenon has to be studied in detail in the future.

4. Nanocomposites for solar cell electrodes

Zinc oxide (ZnO) and titanium oxide (TiO$_2$) thin films have many applications to gas sensors, photocatalysis, piezoelectric devices and dye-sensitized solar cells. Unfortunately, the band gap of ZnO and TiO$_2$ are so large (around 3.37 and 3.2 eV, respectively), that they can only absorb a small part
A 200–300 nm thick layer of Ti was deposited by an electron beam with 6 keV energy at 10\(^{-5}\) Torr pressure and with deposition rate of 0.15 nm/s\(^{-1}\). The Ti-coated ITO substrates were subsequently annealed at 300 °C and/or 400 °C for 8 h in air. The thin film of TiO\(_2\) is typically limited to anatase and/or anatase-rutile mixed phases due to the low melting point of most glasses [17]. A 100 nm thick layer of Zn was fabricated by thermal vacuum-deposition at a pressure of 10\(^{-2}\) Torr and with deposition rate of 1.5 nm/s\(^{-1}\). Then the Zn coated ITO substrate was annealed at 450 °C in air for 7 h to obtain ZnO nanoporous thin films [18].

The optical transparent and electrically conductive indium tin oxide (ITO) coated glass substrate with a sheet resistance of 30 Ω per square was rinsed ultrasonically successively in acetone, ethanol, and distilled water.

A 200–300 nm thick layer of Ti was deposited by an electron beam with 6 keV energy at 10\(^{-5}\) Torr pressure and with deposition rate of 0.15 nm/s\(^{-1}\). The Ti-coated ITO substrates were subsequently annealed at 300 °C and/or 400 °C for 8 h in air. The thin film of TiO\(_2\) is typically limited to anatase and/or anatase-rutile mixed phases due to the low melting point of most glasses [17].

Figure 15. Photocurrent–potential (\(J–V\)) behaviors of ZnO (a), CdS/TiO\(_2\) (b) and CdS/ZnO (c) electrodes. The inset shows zoom in (\(J–V\)) of ZnO and CdS/TiO\(_2\) electrodes. The light source was halogen lamp.

Figure 16. Photocurrent–potential (\(J–V\)) behaviors of CdS/ZnO electrodes irradiated by sunlight in open air. The inset shows the PEC device with area of 5 cm\(^2\).

- Thin films of CdS with thickness from 40–300 nm deposited onto the ZnO/ITO films were fabricated by the same thermal evaporation method. The deposition rate was of 0.2 nm/s\(^{-1}\) and the CdS thin-film thickness was measured during deposition process using a conventional quartz crystal monitor. To obtain good crystallinity, the CdS films were annealed at 400 °C in air for 1 h. The optimal layer thickness of nano-size CdS film on the ITO/ZnO and/or ITO/TiO\(_2\) substrates was of 70–80 nm in our study.

- In photoelectronic studies a two-electrode PEC cell was used. In the measurement, the structures CdS/ZnO/ITO and CdS/TiO\(_2\)/ITO were used as working electrodes (working area was of 1–5 cm\(^2\) for experiment), a platinum net was used as the counter electrode and they were separated by an electrolyte containing 1 M KCl and 0.1 M Na\(_2\)S. The photocurrent was measured on an Auto-Lab Potentiostat PGS-30. A halogen lamp of 400 W with visible filter in the wavelength range of 300–700 nm and illumination power density of 20 mW cm\(^{-2}\) was used as an irradiation source in the laboratory. The PEC cells were also irradiated by sunlight of power density of 100 mW cm\(^{-2}\) in open air. The nanocomposite CdS/ZnO bilayer thin film produced open-circuit photovoltage of 680 mV and photocurrent density of 1.2 and 6.23 mA cm\(^{-2}\) under irradiation by halogen lamp (see figure 15) and sunlight, respectively. The fill-factor of our PEC was 0.31–0.33 and the energy conversion efficiency was 1.3–1.4% (figure 16). It is believed that nanostructured CdS films which effectively sensitize ZnO and/or TiO\(_2\) nanostructure layers can be used in fabricating high-efficiency solar cells.

The novelty of our technology is the fabrication of the nanocomposite ZnO/CdS and/or TiO\(_2\)/CdS film with good homogenous density, high reproducibility and large-scale area by the simple vacuum evaporation method followed by thermal treatment. This method shows great potential for realizing the application in solar cell technology and it was proposed for the ENI AWARD 2012 in the section of Renewable and non-conventional energy.
5. Conclusions

We successfully prepared nanomaterials oriented to fabricating micro- and nanophotonic structures for electro-photonic devices in the visible and near-IR range. Some prototypes of devices such as high sensible bio-chemical sensor, micro-size optical filter, and high efficiency semiconductor-sensitized solar cell are developed from these nanomaterials and composites. The results of investigations on the photonic crystals and up-conversion lasing emission from microcavity laser have received good attention for both their fundamental and application aspects for the exploitation of such things as miniature optical filter, controlling the light propagation, zero threshold laser and photon–atom interaction at room temperature.

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