Studies of Ag/TiO₂ plasmonics structures integrated in side polished optical fiber used as humidity sensor


ᵃ Photonics Research Centre, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
ᵇ Department of Mechanical, Materials and Manufacturing Engineering, University of Nottingham Malaysia Campus, Jalan Broga, 43500 Semenyih, Selangor Darul Ehsan, Malaysia
ᶜ Department of Computer System and Technology, Faculty of Computer Science and Information Technology, University of Malaya, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

In this report, we investigate the effects of Ag/TiO₂ integrated in side polished optical fiber. Several layers of Ag thickness has been deposited on glass substrates using electron beam (e-beam) evaporation technique in order to determine the influence of silver with combination of TiO₂ on final properties of the sensor. Several thicknesses of Ag NPs were sets to 5 nm, 7 nm, 12 nm, and 16 nm. Another layer of metal oxide, specifically titanium oxide (TiO₂) is introduced, covering the Ag layer to study the effect of metal oxides toward the performance of the device. The morphology of the samples was observed using a field-emission scanning electron microscope (FESEM). Raman UV–Vis spectroscopy and Raman photoluminescence (PL) spectroscopy. A CST Microwave used to observe the electric field distribution for all the samples to support the experimental findings. Based on the simulation analysis, two thicknesses of Ag layers (7 nm and 16 nm) were selected to be coated on a side polished optical fiber and tested as a humidity sensor. TiO₂ layer was introduced to see the enhancement in the sensing measurements as a suitable material for trapping the photo generated electrons and avoiding charge recombination. From this observation, it can be conclusively shows that the sensitivity of the sensor is improved with integration of Ag NPs and TiO₂. Based on the experimental results, the sensor of Ag/TiO₂ with 7 nm of Ag layers shows the best characteristics in humidity sensing with good sensitivity and linearity of 0.9201% and 13.4 mW/% RH, respectively.

Introduction

The development of humidity sensors has been an interest especially using fiber optic as sensing probes. In industrial application, humidity measurement is important including food processing, pharmaceutical, semiconductor manufacturing and automobile industries [1]. Comparing with conventional electronic sensors, humidity sensors based on optical fiber offers more effectiveness including higher sensitivity, efficient signal detection, compact in size and potential in remote controls [2]. With rapid growth of humidity fiber based sensor, many compact design of the sensors have been proposed such as side polished optical fiber [3,4], tapered fiber [5] and hetero-core structure fiber [6].

The merging of fiber optics and nanotechnologies specifically plasmonics nanoparticles as a sensor has become a concern. The finding on new materials for plasmonics is an ongoing process in the research field of modern science and technology. Metallic nanoparticles (NPs) have been an interest to the researcher as it possesses a wide range of properties, both in physical and chemical which can be used in many applications. Each noble metal NPs shows different properties and in current research, silver (Ag) are notably to be the interest of researchers due to the strong plasmonics interaction with incident light [7]. This special metal are advantageous in many application because of the behaviour as oxidation catalysts, additives in conductive adhesives and also substrates for bioassays and surface–enhanced Raman spectroscopy (SERS) [8]. It was reported that the uses of metal nanostructures as humidity sensing materials enhanced the performance of humidity measurement [8–10]. Additionally, Ag nanostructures have received much attention are in humidity sensing application due to antibacterial behaviour preventing the growth of microorganisms on the sensing probes [11].

Meanwhile, titanium dioxide (TiO₂) is a materials that being considered because of the well-known properties, such as chemically stable, have a wide band gap and high dielectric constant and also a high refractive index [12]. Thus, TiO₂ is a promising material for optical and sensing applications [13–15] and this material appears in three phases; anatase, rutile and brookite [16]. Among the three phases,
TiO$_2$ with anatase phase showed a good capability in water adsorption [9]. In addition, the size of TiO$_2$ in nanometer scale is important because of small size will result to the absorbance edge shift and the appearance of photoluminescence (PL) intensity peak [17]. TiO$_2$ also has a good adsorption behaviour and this become a strong reason for its application in humidity measurements [18].

In this paper, the study is focused on the effects of the thickness of Ag NPs films and the application on D-shaped fiber as humidity sensor. Ag films were fabricated on glass substrates using electron beam (e-beam) evaporation techniques with four different thicknesses, 5 nm, 7 nm, 12 nm and 16 nm. The technique is highly selected to coat metal films due to the homogeneous and well coated on substrates, formed by this technique. The morphology of Ag NPs including the sizes of particles was then observed using field-effect scanning electron microscope (FESEM).

Table 1
EDX analysis of glass surfaces after deposition of silver nanoparticles at different thickness.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight%</th>
<th>Si (Silicon)</th>
<th>O (Oxygen)</th>
<th>Ag (Silver)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 nm</td>
<td>56.76</td>
<td>41.21</td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td>7 nm</td>
<td>31.23</td>
<td>45.76</td>
<td>2.31</td>
<td></td>
</tr>
<tr>
<td>12 nm</td>
<td>56.63</td>
<td>39.37</td>
<td>4.01</td>
<td></td>
</tr>
<tr>
<td>16 nm</td>
<td>53.9</td>
<td>40.16</td>
<td>5.94</td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Average size of Ag NPs at different thickness of Ag films.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Average size of Ag nanoparticles (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>40.11 ± 5</td>
</tr>
<tr>
<td>7</td>
<td>54.43 ± 8</td>
</tr>
<tr>
<td>12</td>
<td>90.86 ± 32</td>
</tr>
<tr>
<td>16</td>
<td>102.68 ± 44</td>
</tr>
</tbody>
</table>

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Fig. 1. FESEM images of; a) TiO$_2$ at 60,000× magnification, and Ag NPs at 80,000× magnification with thicknesses of b) 5 nm c) 7 nm d) 12 nm and e) 16 nm.

Fig. 2. PL intensity of (a) Ag-NPs (b) Ag-NPs/TiO$_2$ at different thicknesses of 5 nm, 7 nm, 12 nm and 16 nm.
Based on the characterization measurement, two samples were then selected to be coated on D-shaped fiber and were tested as humidity sensors in a controlled environment.

**Experimental section**

Electron beam evaporation technique was used to coat metal nanoparticles on top of the substrates. The glass slides were placed on a stage inside a vacuum chamber and the parameters was set for the deposition to take place. Several values of thicknesses (5 nm, 7 nm, 12 nm, and 16 nm) were as this technique produces a smooth and uniform coating on the substrates. Followed by annealing process, this step involves the exposure of the metal thin layers to a certain temperature at fixed annealing time, depending on the types of metal, to form randomly distributed nanoparticles structures. The annealing temperature to form Ag NPs is undergoes 100 °C for 2 h. The surface morphology of the nanoparticles (TiO_2, Ag and Ag/TiO_2,) was observed using field emission scanning electron microscope (FESEM) images. The optical characterization of the samples was observed through photoluminescence (PL) and Raman UV–Vis measurement. The parameters (FESEM), Raman photoluminescence (PL) spectroscopy and Raman UV–vis spectrometer.

**Fig. 3.** UV–Vis spectra shows absorbance of Ag NPs prepared by e-beam evaporation technique.

**Fig. 4.** UV–Vis spectra shows absorbance of Ag/TiO_2 NPs prepared by e-beam evaporation technique with different thickness of Ag film; a) 5 nm, b) 7 nm, c) 12 nm and d) 16 nm.
for PL measurement were set as; excitation wavelength of 325 nm and focused by 20× UV objective lens. Electric field (E-field) distribution was observed using CST Studio simulation for all the samples.

Results and discussion

Surface morphology of nanoparticles (NPs)

The surface morphology of (a) TiO2-NPs and Ag NPs coated at different thicknesses as (b) 5 nm, (c) 7 nm, (d) 12 nm and (e) 16 nm are shown in Fig. 1, respectively. From Fig. 1(a), it is observed that the TiO2 nanoparticles were coated homogeneously on the glass surface as all nanoparticles were approximately same in size. In Fig. 1((b)–(e)), sizes of Ag NPs were not consistent as big agglomeration of Ag-NPs can be seen on the surface of the glass. The nanoparticle size increases gradually with the increase in film thicknesses as in Fig. 1(c) shows more circular islands are obtained after annealing process, whereas in Fig. 1(d) displays the islands start to merge with condition of 12 nm thickness of thin film. It is observed in Fig. 1(e) that nanoparticles are tending to be more elongated and have a broader distribution of particles that the due to thicker sample. Here, the annealing temperature was assigned to all the thicknesses, resulting to the imperfect formation of Ag-NPs at 16 nm thickness. Similar observations of these thicknesses relation and annealing reported by other groups [19,20].

Based on the EDX analysis as shown in Table 1, the presence of silicon (Si) and oxygen (O) atoms represents the substrate used. The presence of silver (Ag) atoms with different weight proved that Ag nanoparticles had been deposited on glass surface according to their thicknesses. Meanwhile, Table 2 shows the average size of Ag nanoparticles obtained from several measurements. It is noted that the size of Ag nanoparticles were increased as the thickness layer is increased.

Photoluminescence (PL) measurement of NPs

Fig. 2 shows the photoluminescence (PL) spectra of Ag and Ag/TiO2 nanostructures with different coating thicknesses, recorded under identical conditions with the excitation photon energy of 3.815 eV (325 nm laser line). The intensity and band structure of PL spectra is completely relying on the power of excitation source. PL spectra of silver nanoparticles samples at different thicknesses are shown in Fig. 2(a). A highest intensity dip was observed at 1.6531 eV (750 nm) along with minor dip, located at 1.1271 eV (1100 nm). It was observed that the wavelength is totally independent to the thickness of Ag films, however, the luminescence intensities decreases with the increment in thickness of Ag films. After post annealing process, large size of NPs was formed as the thickness of deposited films was increased; which shows decreasing in luminescence intensity. The decline in PL intensity occurred might be due to the capacity of luminescent centre reduced. The position and shaped of luminescence spectra for all samples were similar and stables, and this possibly due to the equilibrium thermal
temperature during annealing process. Meanwhile, the luminescence intensity spectra of Ag/TiO$_2$ were illustrates in Fig. 2(b). It seems that the intensity of the sample with thickest (16 nm) Ag films was at the maximum value. Also, a sharp and broader peaks were observed at 1.1533 eV (1075 nm) and 2.214 eV (560 nm), respectively. The increment in intensity might be occurred from the charge transfer between Ag NPs and conductance band of TiO$_2$ [14]. As Ag NPs were having photoexcitation due to the plasmon effect, the formation of electron-hole pairs occurred which an excited electron from Ag NPs was transferred to the conduction band of TiO$_2$ and simultaneously, a hole left by Ag NPs is filled by a donor electron from the surrounding [21]. Thus, the photocatalytic activity between Ag NPs and TiO$_2$ resulting to the increment of PL intensity.

Theoretically, PL measurement will increase in terms of intensity with the increasing in the number of emitted electrons from the recombination between excited electrons and holes [22,23]. The broad luminescence peak for both TiO$_2$ and Ag NPs are in visible emission band and can be refer to the electron transition from low donor level of the oxygen vacancies in valence band. When UV light is introduced to the TiO$_2$ and Ag NPs thin films, the oxygen vacancies are responsible to

**Fig. 6.** Electric field (E-field) intensity distributions for all samples.

**Fig. 7.** Experimental set-ups for polishing process.
the distance between particles. Fig. 4 illustrates the comparison of absorption spectra between Ag NPs and Ag/TiO2 NPs at all condition. Comparing the absorption spectra of all Ag samples before the deposition of TiO2 layers, the resonance peaks are slightly shifted to red-shift with the significant increment in absorption intensities after drop cast of TiO2 solution. The slight wavelength shifting might be caused by the change of refractive index (RI) of the coating region of Ag NPs after TiO2 was dropped on the Ag layer. Meanwhile, the increasing in absorbance was due to the enhancement in photo excitation efficiency of TiO2.

CST Microwave Studio simulation

This investigation is concerned with the simulation of the electromagnetic field produced by an electric dipole using the electromagnetic simulation software CST.

In this simulation section, the shape and the thickness of Ag structures, shown in Fig. 5 were drawn based on the FESEM images. Fig. 6 is the model of nanoparticles established with CST software. As the model drawn, the closer the distance from the source point is, the larger the mesh density is, so the basis of dividing the mesh is the finite element algorithm based on the frequency domain solver [28]. As mentioned earlier, the size of NPs is totally depends on the thickness of Ag thin films and the simulation was run based on the size of NPs. The shape of Ag NPs are fixed to spherical shapes but differed in sizes, as illustrated in Fig. 6. The sizes of Ag NPs were drawn based on the average measurement, obtained from Table 2. Fig. 7 shows the intensity distribution of E-field for samples at four thicknesses of Ag NPs. The E-field distribution of 7 nm Ag thin layer shows a high intensity and strong coupling effects between the particles, which results to higher LSPR effects on the particles. Contrastingly, a slight absorption of E-field distribution in sample with 16 nm Ag thin layer shows that the NPs exhibit low LSPR characteristics. Although the size of particles for thickness of 16 nm Ag thin layer are bigger compared to others, the simulation shows that thickness of 7 nm Ag thin layer produced an optimum size of particles since E-field distribution shows a high intensity compared to others.

Characterization of humidity sensors

A single mode fiber (SMF-28, Corning) was used to fabricate a D-shaped sensing. The fabrication process starts from a side polished an unclad fiber using polishing film manually and the setup was illustrated in Fig. 7. This process needs several repetitions since the polished fiber is fragile and easily breaks. This polishing process ended after desired polishing depth is determined, by observing a leakage of red light and loss in output power after the process. The polished fiber had about 1.18 dBm loss in power (Fig. 8) and the estimated length of polished fiber had about 1.18 dBm loss in power (Fig. 8) and the estimated length of polished fiber was about 1.18 dBm loss in power (Fig. 8) and the estimated length of polished fiber of 0.5 cm. After polishing process, the polished fiber was placed on a clean glass substrate and then cleaned with de-ionized water before went through coating process using electron beam deposition machine. The sensing probe was characterized using optical white light source as the input and optical power meter as the output. As observed in Fig. 9, the sensor was placed in a small chamber and a reference hygrometer was attached to the chamber. The absolute values of the relative humidity (% RH) were set from 50 to 90% RH with interval of 5% RH. The humidity inside the chamber was varied using saturated salt solution, sodium hydroxide (NaOH) specifically and the experiment was conducted in a controlled room temperature at 25°C.

Firstly, the polished fibres were coated with Ag at thickness of 7 nm and 16 nm, respectively and the samples were then coated with TiO2 NPs. The thickness of Ag films used to coat on the sensing probes was selected based on the photoluminescence (PL) intensity measurement. Ag and TiO2 were selected as external layers, to replace the cladding of the fiber to ensure performance of the sensor is enhanced. Fig. 10(a) illustrates the experimental results of transmittance output power with respect to percentage of relative humidity for all samples. Based on the
Fig. 10. Comparison of transmitted output power with respected to relative humidity (a) Uncoated, TiO$_2$, Ag and Ag/TiO$_2$ at 7 nm and 16 nm thickness, (b) transmitted output power of all samples with respected to relative humidity.
graph, the transmitted power seems to be increased when D-shaped fiber were coated with Ag NPs and TiO$_2$ solution. When the polished fiber was covered with Ag NPs at thickness of 7 nm and 16 nm, the output power at 50% RH increased by 2.82 mW and 1.5 mW, respectively. This signifies the coating of Ag NPs enhanced the performance of humidity detector. When the percentage of humidity changed, the moisture from the surrounding was absorbed by the Ag NPs, thus influence the output power to change. By adding another layer on top of the Ag NPs, in this case TiO$_2$ solution, the power drastically increased from 4.40 mW to 8.93 mW for 7 nm thickness of Ag and from 3.08 mW to 8.05 mW for Ag with 16 nm thickness, at 50% RH.

Since the changes in output power are small for each sample throughout the experiment, Fig. 10(b) shows the transmitted output power with respect to relative humidity for each sample. It was noticed that the output power of uncoated D-shaped fiber is decreased as the humidity increased. The adsorption and condensation of water vapor molecules in the D-shape fiber, the presence of humid air and nitrogen gas flow, variation of refractive index in D-shape fiber with ambient medium or the combination of these factors might influence the optical power drop. This phenomena is similar with a previous report [29]. This situation similarly happened to the sensing probes coated with 16 nm thickness of Ag NPs and when TiO$_2$ solution covered the Ag layer (16 nm). At humid environment, the moisture ions were absorbed by the Ag NPs, causing the electron mobility to be increased in the Ag films, which resulting to the decreasing in output power [9]. On the other hand, the output power increased with the increment in relative humidity for the sensing probes coated with 7 nm thicknesses of Ag NPs and also coated with Ag (7 nm)/TiO$_2$.

Table 3 above illustrates the performance of D-shaped fiber as sensing probes in humidity environment. The resolution of the sensor was obtained from the division of the standard deviation with the sensitivity of the sensor. In the meantime, the linearity of the sensor was obtained from the correlation coefficient, R, which is the calculation of reliability of the linear relationship between the input and output parameters. The good value of the sensor linearity is determined as the value of R is approached 100%. Based on the table, the sensitivity and linearity of the sensing probes were enhanced when coated with Ag and TiO$_2$ NPs. The effect of water moisture in the sensing layers is the reason for the enhancement in the output power. From the observation, sensing probes with Ag (7 nm)/TiO$_2$ coating perform a good criteria as humidity sensor since the sensitivity and linearity are the highest among others, which the values are 0.9201% and 13.4 mW/% RH, respectively. Throughout the experiment, the performance of the sensing probes is enhanced after coated with Ag and TiO$_2$ NPs.

**Table 3**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncoated</th>
<th>Ag (7 nm)</th>
<th>Ag/TiO$_2$ (7 nm)</th>
<th>Ag (16 nm)</th>
<th>Ag/TiO$_2$ (16 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Deviation (mW)</td>
<td>0.01</td>
<td>0.56</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Resolution (% RH)</td>
<td>0.016</td>
<td>0.078</td>
<td>0.062</td>
<td>0.329</td>
<td>0.028</td>
</tr>
<tr>
<td>Linearity</td>
<td>0.814</td>
<td>0.892</td>
<td>0.920</td>
<td>0.854</td>
<td>0.883</td>
</tr>
<tr>
<td>Sensitivity (mW/% RH)</td>
<td>0.693</td>
<td>7.217</td>
<td>13.40</td>
<td>0.730</td>
<td>1.237</td>
</tr>
</tbody>
</table>

Meanwhile, the UV–Vis measurements show the resonance wavelength shift to the longer wavelength as the thickness of Ag layer increases. As the thickness of Ag layer increases, the size of NPs is also increases as the distance between particles decreases, resulting to strong coupling effects between particles. Dropping the TiO$_2$ solution on top of the Ag layer caused the intensity of each Ag samples to increase significantly. Ag films with 7 nm and 16 nm thickness were selected as optimum thickness based on luminescence measurement and used to study the performance of the materials as humidity sensor. D-shaped fiber was used to be coated with the materials, thus act as sensing probes. To see the performance of the humidity sensor, and the presence of this metal oxides show an enhancement the sensing probes. Comparing those sensors, probes coated with Ag (7 nm)/TiO$_2$ exhibit the best performance with sensitivity and linearity of 0.9201% and 13.4 mW/% RH, respectively.

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**References**


