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Investigation of the Absorption Spectrum of Annealed Zn Nanorods in Oxygen Flux Using Discrete Dipole Approximation Theory

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Abstract

In this work, the discrete dipole approximations (DDA) theory was used to investigate the absorption spectrum of annealed Zn nanorods in oxygen flux. For this purpose, the Zn nanorod was replaced with 1786 dipoles arranged on a rod-shaped structure, and the interaction of these dipoles with polarized light was investigated. In this study, it is found that the extinction spectrum has two absorption peaks, which are related to the plasmonic oscillations, and Zn nanorods annealed in oxygen flux show metallic behavior. Changes in plasmonic oscillations were investigated by changing the deposition angle of nanorods and it was found that the oscillations in the direction perpendicular to the axis of the nanorod are strongly dependent on the angle of deposition and with increasing deposition angle, the number of oscillating dipoles and consequently the intensity of the absorption decreases sharply.

Keywords: ZnO, Nano rod, Optical spectra, extinction spectra, DDA.

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Introduction

In nanoscale, the properties of nanostructures are highly dependent on the shape and size of nanostructures. In this scale by preparing nanostructures from the same material but with different shapes and sizes, different behaviors can be observed. Therefore, by changing the shape and size of the nanoparticles and its properties can be changed to the desired applications [1-7]. Glancing angle deposition and oblique angle deposition methods are interesting methods for preparing of nanostructures with different shapes and sizes. In the glancing angle deposition method, the particle flux descends on the substrate at the scratch angle. In this method, different structures can be prepared by substrate rotating. By controlling the dimensions, shape and porosity of the thin films, the optical properties of the thin films such as transmission, reflection, absorption, refractive index, etc. can be controlled. Using this methods, different helical nanostructures [5, 6], star shapes [7], nanoflowers [8], polygonal structures [9] and etc, with different dimensions have been made and analyzed.

Nano Rods are widely used structures. These structures have many applications in biomedical [10], photovoltaic device improvement [11], nanoelectronics [12-14], field emitter [15, 16], nano optics [17], crystal photonics [18] and gas sensors [19]. The study of the physical and chemical properties of nanorods is very important for understanding the advantages and limitations of these widely used structures. This has led researchers to study their optical and electrical properties [6-9]. Discrete dipole approximation theory (DDA) is an attractive theory to study the Extinction (absorption+ scatting) spectrum of metallic structures. The details of this theory are fully explained in our previous work, [1, 2] and here only a summary of the work process is explained. In this theory, the object is considered as an array of oscillating dipoles. In interaction with the descending electric field ($E_{inc}(r) = E_0\, exp(ik.r)$), each of these dipoles has a dipole moment, which is obtained from the following equation:

$$p_i = \alpha_i . E_{loc}(r_i) \qquad (1)$$

In the above equation, E_{loc} is the electric field at the dipole position. By considering the interaction potential of Aij, E_{loc} is given with the following equation:

$$E_{loc}(r_i) = E_{inc,i} - \sum_{j \neq i} A_{ij} P_j . \qquad (2)$$

$$A_{ij} = \frac{\exp(ikr_{ij})}{r_{ij}} \times \left[k^2 (\hat{r}_{ij}\hat{r}_{ij} - I_3) + \frac{ikr_{ij} - 1}{r_{ij}^2} (3\hat{r}_{ij}\hat{r}_{ij} - I_3) \right], i \neq j \qquad (3)$$

In equation 3, $r_{ij} = r_i - r_j$, $\hat{r}_{ij} = \frac{r_i - r_j}{|r_i - r_j|}$, and I_3 is a 3 × 3 Identity matrix, and α_i is the polarization in r_i and permittivity of ε_i, and is given by the following equation:

$$\alpha_i = \frac{\frac{3d^3}{4\pi}\frac{\varepsilon_i - 1}{\varepsilon_i + 2}}{1 - \frac{2}{3}ik^3\left(\frac{3d^3}{4\pi}\frac{\varepsilon_i - 1}{\varepsilon_i + 2}\right)} \qquad (4)$$

The extinction cross-section (absorption + dispersion) of structures is obtained using the following equation:

$$C_{ext} = \frac{4\pi k}{\left|E_0^2\right|}\sum_{i=1}^{N}\mathrm{Im}(E^*_{inc,i}.P_i) \qquad (5)$$

So far, the extinction spectra of different structures such as Silver Nano Flower [1], Silver Chiral structure [2], manganese helical structure [20], and manganese columnar structures [21] have been investigated using this theory. In this work, using DDA theory, the extinction spectrum of the composite material (surface oxidation of Zn nanorods), was calculated and its changes with the deposition angle were investigated and the cause of these changes were explained.

Experimental

The preparation details of the "annealed Zn nanorod in oxygen flux" and its interaction with light are given in our previous work [22]. In this work, due to the need of experimental results for comparison, those results are briefly explained. Initially, the glass substrates were cleaned with acetone and alcohol in an ultrasonic bath, and pasted to a substrate holder by using the vacuum adhesive. Oblique angle deposition method was used for Zn deposition at different deposition angles of 0˚, 30˚, 45˚ and 60˚ on glass substrates. During the deposition, deposition rate and film thickness were controlled by means of crystal quartz placed near the substrate holder and for all of the deposition angles were considered 2A/s and 80nm respectively. After deposition, the obtained nanorod structures were annealed at oxygen flux of 250 sccm at 340° C for 2 hours. The samples were cooled in the presence of oxygen gas for six hours to bring the samples to room temperature.

Because these structures are inhomogeneous and anisotropic structures, the optical spectra of the structures, including the transmittance and reflectance spectra for p polarization light at 10˚ incident light angle, were obtained by using a spectrophotometer at different deposition angles. Using DDA theory, the extinction spectra of structures at different deposition angles were calculated and their changes were explained by changing the deposition angle.

Results and discussions

Optical results

These results were thoroughly explained in our previous work [22], but because of the need to compare with theoretical results, they are briefly presented here. Figure 1 shows the transmission (T) and reflection (R) spectra of nanorod structures formed at different deposition angles for with p-polarized light at 10˚ incident light angle. It is clear from the figure that the structures formed at the 0˚ deposition angle have less transmission and reflection than the structures formed at other deposition angles. As the deposition angle increases, so do the transmission and reflection.

The reason for the increase in transmission with increasing deposition angle is the increase in porosity of structures with increasing deposition angle. Although with increasing the deposition the transmission increases, but the transmission of structures is less than 10 percent. This indicates that although the structures were annealed in the oxygen flux, they tended to behave like metals.

The absorption spectrum of these structures, calculated from Equation (6), and shown in Figure 2, indicates that the structures have a high absorption intensity, and this indicates the metal behavior of the structures. Because for semiconductor structures, the percentage of transmission, especially in the visible region, is much higher than the absorption of structures, and in fact, semiconductor structures are transparent structures in the visible light region:

$$A=1-(T+R) \qquad (6)$$

It is clear in the figure that the structures formed at the deposition angle of 0˚, due to the lowest porosity, have the highest absorption intensity. The absorption spectrum of this structure has two absorption peaks at wavelengths of 430 nm and 1015 nm. As the deposition angle increases, the absorption of the structures decreases due to the increase in the porosity. Although the structures are oxidized, the absorption peaks are attributed to the plasmonic oscillations. Because (discrete dipoles approximation) DDA is a good theory to study plasmonic oscillations, this method was used to study the absorption spectrum. For this, the extinction spectra of the structures were calculated and compared with experimental results.

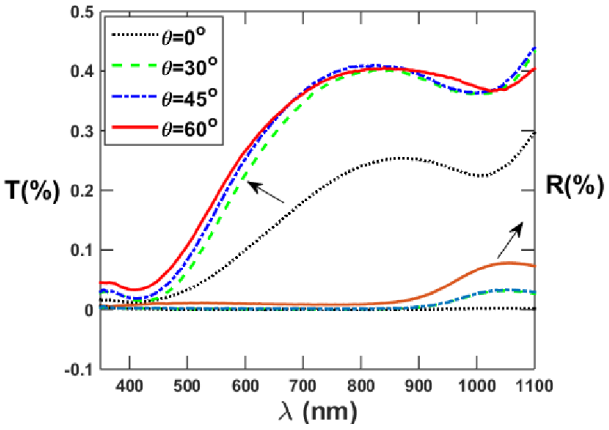

Figure 1. Experimental transmission and reflection spectra of Nano rods deposited at different deposition angle of 0°, 30°, 45° and 60° [22].

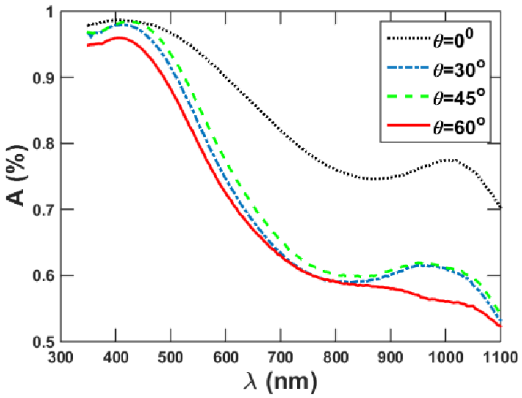

Figure 2. Experimental Absorption spectra of Nano rod structures deposited at different deposition angle of 0°, 30°, 45° and 60° [22].

DDA results

To further investigate the behavior of metalic behavior of oxidized Nano Rods and plasmonic peaks, the extinction spectra of structures were calculated using discrete dipole theory. In this work, nanorods were considered as solid cylindrical columns with a circular cross section with 1786 dipoles. This structure was considered to have a length of 80 nm and diameter of 50 nm. Figure 3 shows a schematic of this structure. The interaction of these dipoles with light was investigated.

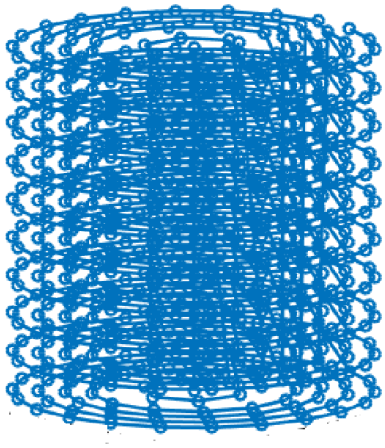

Figure 3. Schematic of dipoles arrangements on Nano rod structure for DDA calculations.

The extinction spectra of the nanorods obtained at different deposition angles for p polarized light (at 10 ° incident light angle), are shown in Figure 4. Due to the small scattering coefficient, the extinction spectrum is considered almost equal to the absorption spectrum. It is clear from the figure that the extinction spectrum of the structure at 0° deposition angle has two oscillation peaks, which are located at wavelengths of 550 nm and 1050 nm.

The peak at a wavelength of 550 nm is due to the electric field component along the axis of the Nano rod, is due to the oscillation of electrons along the axis of the nanorod, and is called the longitudinal mode. The peak at the wavelength of 1050 nm is due to the electrical field component in the direction perpendicular to the axis of the nanorod, and is called transverse mode. Because longitudinal mode is the modes with larger amplitude than the transverse modes, it appears at shorter wavelengths relative to the transverse mode. With increasing deposition angle, due to the reduction of electrical field components along these axes, the intensity of longitudinal and transverse modes decreases and the longitudinal mode shifts toward shorter wavelengths, on the other words, with deposition angle increasing, the amplitude of longitudinal modes increases, so this peak shifts toward shorter wavelengths.

The results also show that with increasing the deposition angle, due to the decrease in the number of oscillating dipoles perpendicular to the axis of the nanorod, the absorption intensity in this direction decreases sharply. These results are in good agreement with the experimental results and show the metalic behavior of the structures. The differences that may exist between the experimental results and the DDA theory are because in the DDA theory only one structure with one size is considered, while the actual film is a combination of non-ideal Nano rods with different sizes.

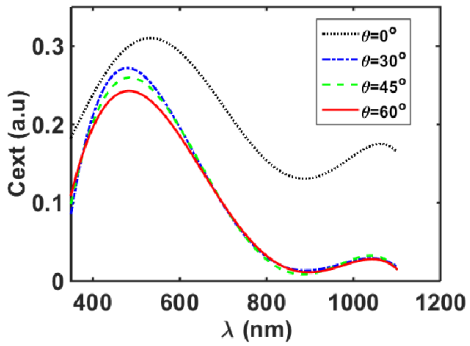

Figure 4. Extinction spectra of Nano rod structures deposited at different deposition angle of 0°, 30°, 45° and 60°.

Conclusions

In this work, the extinction spectra of Zn nanorods deposited at different deposition angles and annealed in oxygen flux were calculated by the discrete dipoles approximation theory and they were compared with experimental results. The results showed that this theory is in good agreement with the experimental results. These results showed that the nanorod annealed in oxygen flux show metalic behavior despite oxidation. DDA theory showed that the absorption spectra of these structures have two absorption peaks, which are related to plasmonic oscillations along the axis of the nanorod and perpendicular to this axis. It was found that the oscillations in the direction perpendicular to the axis of the nanorod are strongly dependent on the angle of accumulation and with increasing the angle of accumulation, the intensity of these fluctuations and consequently their associated absorption that occur at longer wavelengths is greatly reduced.

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