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STUDY OF ELECTRICAL PROPERTIES OF NANO TiO_2 COATINGS BASED ON THE CHARACTERISTIC MATRIX THEORY AND THE BRUS MODEL[†]

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Electrical properties of Nano TiO_2 coatings as a function of the nanoparticle size have been studied. In addition, this study explores how to calculate the quantum confinement energy of TiO_2. The results confirm the effect of particle size on electrical properties especially when the size becomes close to the exciton Bohr radius. The electrical properties are not effected when the size becomes close to 40nm. The Bohr radius of Nano TiO_2 coatings has been found to be 1.4nm. While the confinement energy was 0.43 eV. The program depends on the Characteristic Matrix Theory and The Brus Model.

Keywords: TiO_2, Nano Coatings, TheBrus model, TheCharacteristic matrix, Quantum confinement

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The study of electrical properties of semiconductors nano coatings has a considerable interest in the field of nanotechnology [1]. The present study focuses on Nano TiO_2 because of its many modern coating applications. Titanium dioxide (TiO_2) belongs to the family of transitional metal oxides [2]. Nowadays, TiO_2 has a great attention in researches and industrial fields. TiO_2 is used as a white pigment in paints, paper and plastics [3]. TiO_2 is used in the solar energy industry and in anti-reflective coatings because of its stability and high absorption capacity, as well as for its strong mechanical properties, and because it has a high refractive index and good transmittance in the visible spectrum region [4]. Titanium dioxide is a semiconductor (N-type) [5]. TiO_2 has three important natural crystalline forms: anatase, brookite, and rutile, and the energy gap of anatase or rutile forms range between 3.0-3.05 eV. Titanium dioxide has a wide energy gap, which makes it suitable for UV or X-rays detection application [6]. The rutile phase is more common and stable than the other phases, while brookite is rare in nature. Brookite is formed when titanium dioxide films are amorphous in depositions at temperatures less than 300°C, while rutile is formed at high temperatures [7]. The nano-material of TiO_2 shows good electronic and optical properties because it is effective in the ultraviolet region and the refractive index is high, and it shows the photocatalytic behavior by generating an electron-hole pair when exposed to sunlight or ultraviolet rays [8].

The aim of this work is to study the electrical properties (dielectric constant, activation energy, concentration of charge carriers) of nano TiO_2 coatings with a change in the size of its nanoparticles within the ultraviolet spectral region (10-400 nm). Also, we present the calculation of confinement energy. The Characteristic Matrix Theory and The Brus Model were used to conduct this study.

THEORY

The Brus model

The Brus Model can be considered as one of the most important models which indicates that the energy gap of quantum dots in semiconductors depends on the nanoparticle size. It has another term which is called the Effective Mass Approximation (EMA). This model takes into account the values of the effective masses of the electrons and holes, which change from one material to another. The change in the energy gap of quantum dots (ΔEg) is given by Brus equation [9]:

$$\Delta E_g = \frac{\hbar^2\pi^2}{2r_{ps}^2}\left[\frac{1}{m_e^*}+\frac{1}{m_h^*}\right] - \frac{1.786\, e^2}{\varepsilon\, r_{ps}} - \frac{0.124 e^4}{h^2\varepsilon^2}\left[\frac{1}{m_e^*}+\frac{1}{m_h^*}\right]^{-1}, \tag{1}$$

where r_{ps} is the particle's radius as aspherical quantum dots. m_e^* represents the effective mass of electrons, m_h^* is the effective mass of holes, ε is the dielectic constant.
Since $\Delta E_g = E_g^{nano}(r_{ps}) - E_g^{bulk}$, eq (1) becomes [10]:

$$E_g^{nano}(r_{ps}) = E_g^{bulk} + \frac{\hbar^2\pi^2}{2r_{ps}^2}\left[\frac{1}{m_e^*}+\frac{1}{m_h^*}\right] - \frac{1.786\, e^2}{\varepsilon\, r_{ps}} - \frac{0.124 e^4}{h^2\varepsilon^2}\left[\frac{1}{m_e^*}+\frac{1}{m_h^*}\right]^{-1}. \tag{2}$$

E_g^{bulk} represents the bulk energy gap and $E_g^{nano}(r_{ps})$ is the effective energy gap. We notice from the second term of Eq 2 that the energy gap inversely related to r_{ps}^2 , which means that the particle size decreases when the energy gap increases.

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The third term in Eq 2 will be ignored because the strenght of Coulombic interaction will increase. we observe that the second and third terms can be neglected due to the smalleness compared to the first, then Eq 2 becomes:

$$E_g^{nano}(r_{ps}) = E_g^{bulk} + \frac{\hbar^2\pi^2}{2r_{ps}^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] \quad (3)$$

Moreover, we could suppose that the energy gap increases as the particle size decreases by reason of the effect of quantum confinement, which has a vital effect when r_{ps} becomes equal to or less than the normal Bohr radius $\alpha_\circ$ of the exciton [11] with

$$\alpha_\circ = \frac{4\pi\varepsilon_\circ\varepsilon_r\hbar^2}{e^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] \quad (4)$$

Where e represents the electron charge, whereas $\varepsilon_r$and $\varepsilon_\circ$ are the dielectric constants for the semiconductor and the vacuum, respectively.

The Characteristic Matrix of Single Thin Films

The Characteristic Matrix combines the continous tangential components for the magnetic and electric fields, which can be written as [12]:

$$\begin{bmatrix} B \\ C \end{bmatrix} = \left\{\prod_{r=1}^{q}\begin{bmatrix} cos\delta_r & i\, sin\delta_r/\eta_r \\ i\eta_r sin\delta_r & cos\delta_r \end{bmatrix}\right\}\begin{bmatrix} 1 \\ \eta_m \end{bmatrix} \quad (5)$$

Since, the phase thickness is: $\delta_r = 2\pi n_r d_r cos\theta_r/\lambda$ here (B,C) are the Matrixs' elements (electric and magnetic fields). η_r is the optical permititivity and η_m is the refractive index of substrate. Figure 1 represents the system of a single thin film on substrate.

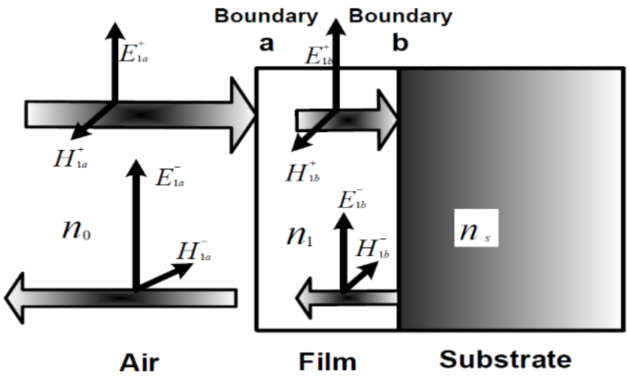

Figure 1. A plane wave incident on a thin film [13]

The equation (4) includes all the information which we need to calculate the reflectivity (R) and transmittance (T) For a single thin film deposited on the substrate's surface. And from Fresnels' equations we can find the reflectivity (R) [14]:

$$R = \left(\frac{\eta_\circ - \eta_1}{\eta_\circ + \eta_1}\right)^2 \quad (6)$$

$\eta_1 and\ \eta_\circ$ are the optical permittivity for the medium transmittance and incidence, respectively.

Quantum confinement

The quantum confinement of electrons occurs when the dimensions of the material are smaller than the distance of liberation of electrons, so it depends on the Bohr radius of the material. The quantum confinement is one of the direct effects of reducing the size of materials to nanoparticle; As the energy levels of the material become discrete, its effect appears through the change in the density of states and the energy gap of the material. Thus, the optical, electronic and electrical properties of materials become dependent on their size. Quantum dots can be defined as a physical system in which electrons are bound in three dimensions, and this electronic confinement is known as quantum confinement. Quantum confinement occurs when the dimensions of the particle structure are equal to or smaller than the de Broglie wavelength of the electron or the gap [15,16].

As an example of quantum confinement, we take a spherical semiconductor particle with a diameter ($D=2r_{ps}$), and which must be smaller than the de Broglie wavelength $\lambda = h/p$ of the electron for the particle to be a quantum dot. The typical electron kinetic energy is given by following formula [17]:

$$E = \left(\frac{2}{3}\right) k_B T = \frac{p^2}{2m_{e,h}} \qquad (7)$$

And when we consider that the effective mass of the electron m_e^* is equal to its mass in free space (9.1×10^{-31}kg) we find that λ≈6 nm at room temperature (300K), and this means that if the spherical crystal diameter is less than 6nm, The electron wave packets or holes are compressed into a smaller space than they should normally be. So, the electron will need more energy to move [18]. The above example does not take into account that the electron mass m_e^* and the hole mass m_h^* are not actually the two masses in free space that we know, but the two effective masses.

Application

In this work, we used MATLAB program version (R2021a) to study the elecrtical properties (Dielectic constant, Activition energy and concentration of charge carriers) of Nano-TiO_2 Coatings on (Ge) substrates as a function of the particle size. Also, we calculated the quantum confinement energy.

Concentration of charge carriers

We studied the concentration of charge carriers by using Brus model. Figure 2 shows the change in the concentration of charge carriers of TiO_2 coatings as a function of the nanoparticle size.

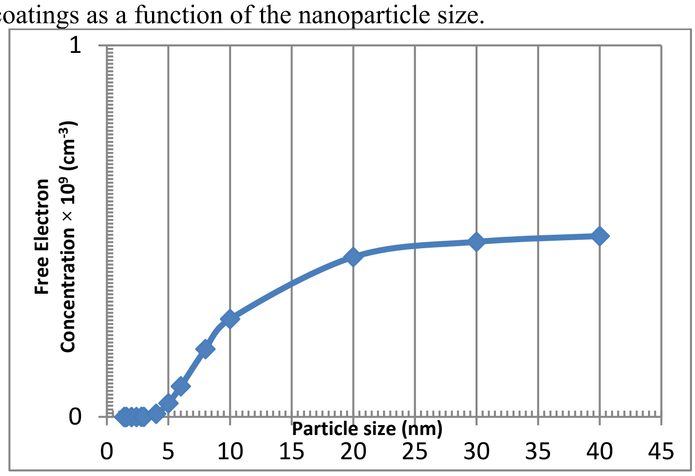

Figure 2. change in concentration of charge carriers of TiO_2 as a function of the nanoparticle size.

We noticed that when the size is very small, the concentration of charge carriers is very small. This is due to the quantum confinement of the electron, as the atoms present on the surface are few. When the nanosize increases, the concentration of charge carriers increases as expected. Indeed, when the nanosize increases, the number of molecules and atoms on the surface increases. This behavior was observed by P. Parameshwari (2012), who pointed that the increase in electrical conductivity could be associated with the decrease in the scattering at the grain boundaries when the size of the grains increases, conducting to an increase in injection and mobility of free charge carriers [19].

From Figure 2, the Bohr radius of TiO_2 was estimated to be not less than 1.4 nm. whereas, the energy gap of TiO_2, was 5.7 eV, and by using the empirical equation to calculate the refractive index of TiO_2, we found 2.2, which is less than the refractive index of the bulk material. The quantum confinement energy was calculated to be 0.43eV.

Activation energy

The activation energy was studied by using the Brus model. Figure 3 shows the change in the value of the activation energy as a function of the nanoparticle size.

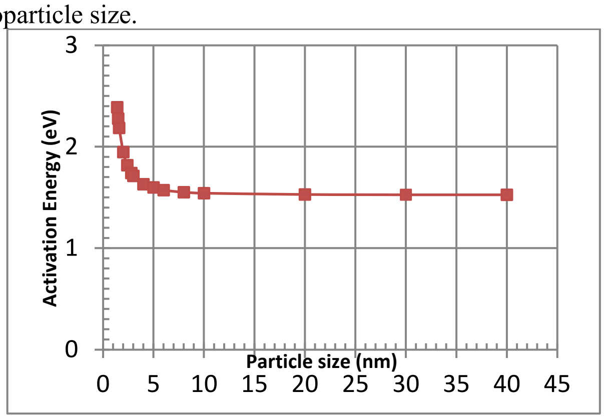

Figure 3. Change in the activition energy of TiO_2 as a function of the nanoparticle size.

From Fig. 3 we observe that at small nanoparticle sizes the values become large, but they decrease when the particle size increases close from to the exciton Bohr radius. The activation energy is at the Fermi level, which is in the middle of the energy gap. That is, the activation energy is equal to half of energy gap. This means that the change in activation energy is exactly corresponding to the change in the energy gap [20]

Generally, it was found from this study that the activation energy depends on the size of the grains and gradually decreases with the grain size. Thus, it is in agreement with previous studies [21].

Dielectric constant

At this stage, the dielectric constant was studied, using the results obtained from the Brus model to extract the dielectric constant value of TiO_2 as a function of the nanoparticle size.

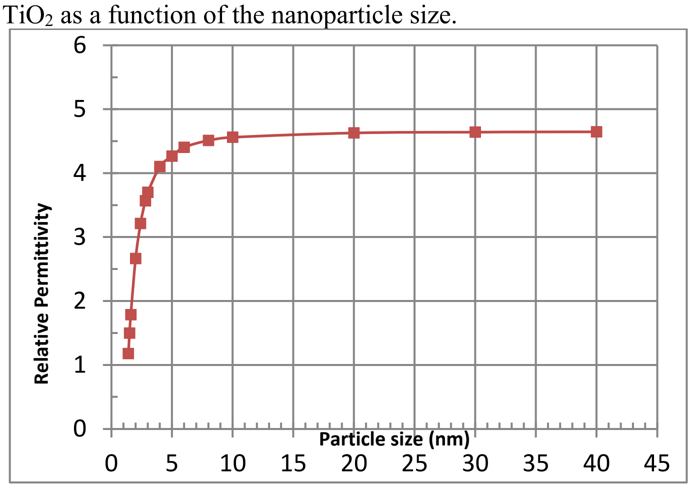

Figure 4. change in the dielectric constant of TiO_2 as a function of the change in nanoparticle size.

We observe from Fig. 4 that the dielectric constant decreases with the decrease in nanoparticle size. To clarify this in the nanoscale range, this can be understood by observing that for small particle sizes, the number of surface atoms is large, while for nanomaterials, the number of atoms per unit volume will decrease because of the quantum confinement, whereas at the nanoscale, the electron orbits causing in the increases of the Coulomb force that supports the force recovery. Thus, the natural angular frequency of electron oscillation, that results in the decreases in the dielectric constant, and this shows that the dielectric constant decreases with the size of the particle's material [22].

CONCLUSION

It has found that the dielectric constant of Nano TiO_2 coatings decreases the nanoparticle size. The values of the activation energy of Nano TiO_2 coatings are inversely related to the particle size. While the concentration of charge carriers for TiO_2 is very small when the size is too small. So no change in the electrical properties of the material can be observed, because it behaves at 40nm size as a bulk material, because the quantum confinement is almost non-existent. The quantum confinement energy was calculated to be 0.43 eV. The Bohr radius of TiO_2 was estimated to be not less than 1.4nm, and the energy gap of TiO_2 was found to be 5.7ev, and we also found the value of the refractive index of TiO_2 to be 2.2, which is less than the refractive index of the bulk material.

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ДОСЛІДЖЕННЯ ЕЛЕКТРИЧНИХ ВЛАСТИВОСТЕЙ ПОКРИТТІВ NANO TiO_2 НА ОСНОВІ ХАРАКТЕРИСТИЧНОЇ МАТРИЧНОЇ ТЕОРІЇ І МОДЕЛІ БРЮСА

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Досліджено електричні властивості нанопокриттів TiO_2 у залежності від розміру наночастинок. Крім того, у дослідженні вивчається, як розрахувати енергію квантового утримання TiO_2. Результати підтверджують вплив розміру частинок на електричні властивості, особливо коли розмір стає близьким до радіусу екситона Бора. Електричні властивості не змінюються, коли розмір стає близьким до 40 нм. Встановлено, що радіус Бора покриттів Nano TiO_2 становить 1,4 нм, тоді як енергія утримання становила 0,43 еВ. Програма залежить від характеристичної матричної теорії та моделі Брюса.

Ключові слова: TiO_2, нанопокриття, модель TheBrus, TheCharacteristic matrix, Quantum confinement