Materials Physics and Mechanics 41 (2019) 15-18 Received: January 31, 2018

ELECTRON TUNNELING TO THE SURFACE STATES AT PHOTOCATALYSIS

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Abstract. Simulation of tunneling electrons excited by the sunlight in TiO_2 to surface states is performed for TiO_2/Si nanostructure. The tunneling transmission coefficient of the surface states created by organic compounds was calculated by phase function method. Dependence of the transmission coefficient of tunneling electrons on potential barrier parameters is explained by interference of transmitted and reflected waves.
Keywords: phase function method, TiO_2/Si nanostructure, transmission, tunneling electron

1. Introduction

Composites with titanium dioxide nanoparticles (nanocomposites) have the widest prevalence in heterogeneous photocatalytic processes of organic compound oxidation [1-5]. Titanium oxide possesses substantial photocatalytic activity in UV range; it is characterized by high resistance to photo-corrosion and absence of toxicity. These features allow applying it as a component of self-purifying surfaces as well as to use it for purification of domestic and industrial waters and air [6]. The TiO_2 photocatalytic properties are connected with the fact that under electromagnetic radiation non-equilibrium electrons and holes are generated in the volume of semiconductor [7,8]. After their separation, they participate in the oxidation of organic compounds on titanium dioxide surface [9,10]. The width of TiO_2 band gap is 3-3.2 eV (it depends on a crystal phase). That is why it displays the significant photocatalytic activity in the UV part of spectrum with the wavelength less than 400 nm.

Titanium dioxide has significant density of unsaturated bonds on a surface that promotes the molecule absorption from the environment. When the non-equilibrium electrons are captured at such levels, dissociation is happened. The sunlight generates the electron-hole pairs in the near-surface area of TiO_2. To eliminate their recombination and to ensure electron transition to the surface states, the pair components must be divided. For this purpose the heterojunctions containing titanium oxide together with silicon are used. The energy diagram of p-Si/n-TiO_2 structure taking into account the TiO_2 surface states is displayed in Fig. 1.

After dividing the holes move to silicon interface, where they recombine, while the electrons move to the surface and participate in tunneling to the surface states. The transfer of generated electrons to the surface states depends on the surface potential relief created by the organic compounds on the TiO_2 surface. A real potential relief has a very complex form and depends on the sunlight intensity. As a result, the photocatalytic activity and oxidation is determined by the sunlight intensity. Therefore, for evaluating and predicting the photocatalytic activity of titanium dioxide surface it is necessary to estimate the spectrum of electrons tunneling to the surface states and its dependence on the sunlight intensity, in particular to determine transmission coefficient of the tunneling electrons.

http://dx.doi.org/10.18720/MPM.4112019_3

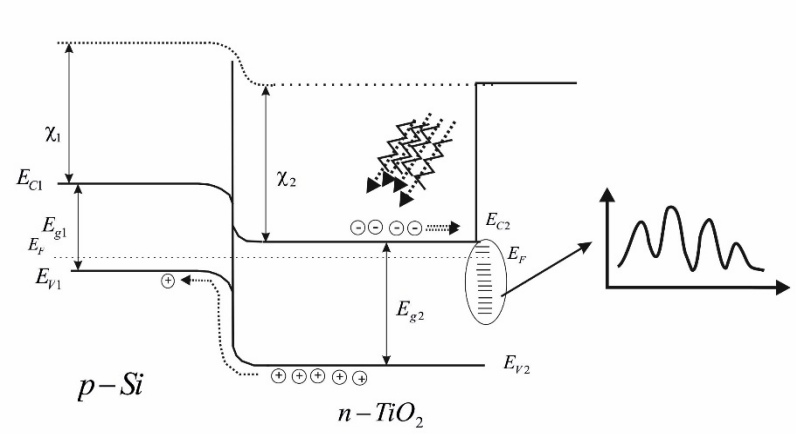

Fig. 1. Potential diagram of the Si/TiO_2 structure with regard to TiO_2 surface states

For this purpose, we have developed the model based on the phase function method [11]. It lets to calculate tunneling transparency for the potential of a complex form. The model takes into account the barrier parameters, the image force potential, and allows including the potential relief at a surface boundary and in a dielectric volume.

The aim of article is modeling the transmission of electrons excited by the sunlight through the barriers generated by the surface states produced due to absorption of impurities and organic compounds.

2. Model

The tunneling transmission coefficient through a barrier of the width *d* which is described by the potential *U(x)* is equal to: [4]

$$D(E) = \exp(\frac{1}{k}\int_0^d U(x)[b(x)\cos(2kx) - a(x)\sin(2kx)]dx), \quad (1)$$

where $k(E) = (8\pi^2 m^* E/h^2)^{1/2}$ is the tunneling electron wave vector, m^* and E are the effective mass and energy of a tunneling electron, h is the Planck constant, d is the tunneling barrier width. Functions *a(x)* and *b(x)* are defined from

$$\frac{da(x)}{dx} = \frac{U(x)}{2k}[-\sin(2kx) - 2b + (a^2 - b^2)\sin(2kx) - 2abcos(2kx)], \quad (2)$$

$$\frac{db(x)}{dx} = \frac{U(x)}{2k}[\cos(2kx) + 2a + (a^2 - b^2)\cos(2kx) - 2absin(2kx)]. \quad (3)$$

The system of equations (2) and (3) allows model tunneling transport taking into account the charge carrier dispersion and the image forces on the potential relief.

To describe the potential barrier *U(x)* the following equation is used:

$$U(x) = \frac{8\pi m^*}{h^2}(U_0 - \frac{q}{\varepsilon\varepsilon_0 x} + A_s \exp\left(\frac{(x-p_0)^2}{\sigma}\right) + \frac{\alpha}{\sqrt{\pi}}\exp[\alpha^2(\mathrm{x} - \Delta)^2]), \quad (4)$$

where U_0 is the maximal height of the TiO_2 surface potential barrier, $\varphi(x)$ is the image force potential, q is the electron charge, ε, ε_0 is the relative dielectric TiO_2 permeability and absolute dielectric vacuum permeability, respectively, A_s, p_0, σ are parameters characterizing imperfection of the potential relief surface. Expression $q/\varepsilon\varepsilon_0 x$ displays counting forces of the mirror images, which smoothed barrier. Expression $\frac{\alpha}{\sqrt{\pi}}\exp[\alpha^2(\mathrm{x} - \Delta)^2])$ describes infinitely high peak placed approximately in the middle of the potential well, where α is a parameter, which influences on the peak width. $N = 2m\frac{x_0^2 kT}{(h/2\pi)^2}$ - coefficient, which has influence on the height and form of the potential barrier, in particular on the height and form of the additional barrier.

The above model was implemented for tunneling electron transmission through an absorbed layer on titanium dioxide surface illuminated by the light in neutral gas environment

with organic compounds. For the generated electron-hole pairs division TiO_2 nanocomposite is positioned on Si substrate.

3. Results and discussion

Consider the electron tunneling through absorbed layers on the titanium oxide surface; it being a part of Si/TiO_2 heterostructure. The surface is illuminated by the light in neutral gas environment, containing organic pollution. Two potential barriers divided by a potential well represent the potential relief. An additional infinitely high barrier is located between the two barriers in the middle of potential well. This barrier indicates the position of an organic molecule. The results of calculation are presented in Figs. 1−4.

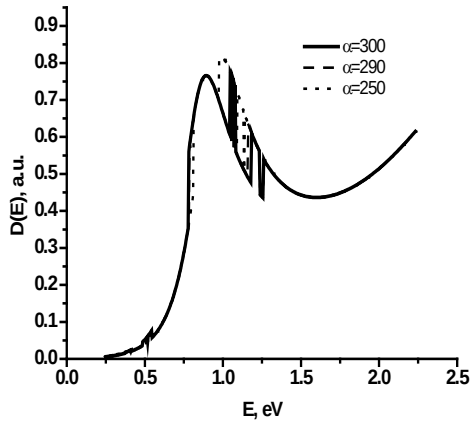

Fig. 1. Dependence of the transmission coefficient on an additional barrier height

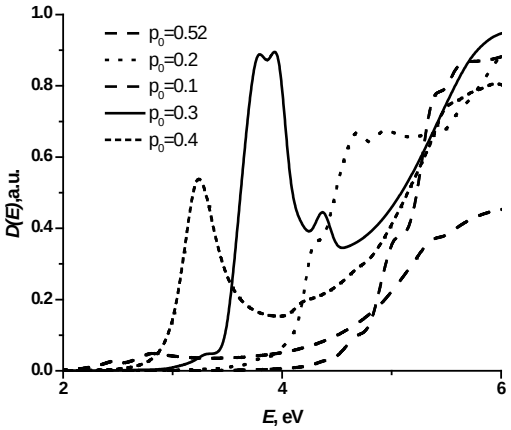

Fig. 2. Dependence of the transmission coefficient on a potential dispersion

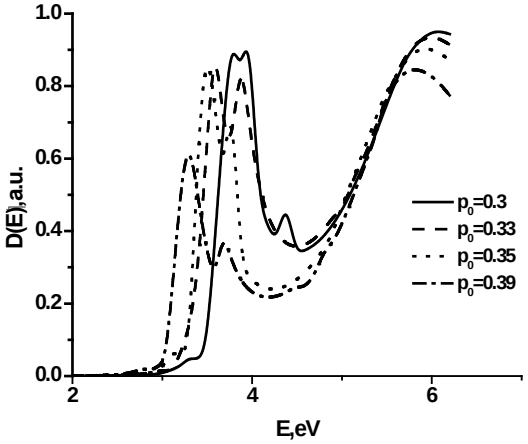

Fig. 3. Dependence of the transmission coefficient on a potential dispersion

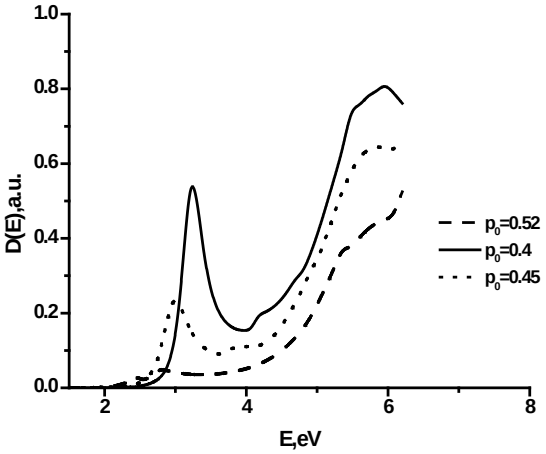

Fig. 4. Dependence of the transmission coefficient on a potential dispersion

The transmission coefficient changes non-monotonically when the additional infinitely high barrier is placed in the potential well middle (Fig. 1). It increases monotonically beginning from E = 0.5 eV. At *E* = 1-2 eV it decreases drastically from 0.8 up to 0.4, after that it continues increasing. At a certain height of the additional barrier, resonance fluctuations appear. The fluctuations become evident at the higher barrier-growth-correction coefficient α. Duration and frequency of changes rise proportionally to the value of α. The highest fluctuation in the form of two sequential additional peaks on *D(E)* curve is observed at

p_0 = 0.3-0.4 (Fig. 3). When the potential dispersion parameter p_0 = 0, the transmission coefficient changes monotonically without peaks and fluctuations. The maximal value of the transmission coefficient is reached at p_0 = 0.3, but at further increasing up to p_0 = 0.4-0.52 the peak height decreases and the transmission coefficient change, depending on the dispersion potential parameter, becomes monotonic again (Fig. 4, p_0 = 0.52).

4. Conclusion

Calculations of electron tunneling to the surface states, which are created by organic compounds on titanium dioxide surface under the light illumination, are performed. It is found that forming potential barrier on the titanium oxide surface, which contains organic compounds, leads to non-monotonic energy dependence of the transmission electron coefficient at the surface states (N-type). At the maximal transmission coefficient, additional peaks with fluctuations are appeared. Such features of the tunneling electrons transmission coefficient are explained by interference of transmitted and reflected waves.

Acknowledgements. *No external funding was received for this study.*

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