

Photocatalysis by TiO₂ films at structure relaxation

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The crystalline and electron structure of TiO₂ and TiO₂/ZrO₂/SiO₂ coating obtained by sol-gel technique and annealed at 773 K and 873 K has been studied. The film synthesis and further heat treatment result in formation of nano-sized anatase particles with a developed surface and shallow and deep traps within the band gap of titania. Rater localized electron states correspond to these defects, which result in occurrence of some new optical absorption bands. Some of the optical conductivity bands belong to oxygen vacancies which are deep defects, and the other ones are connected with surface defects. The nature of surface defects should be various. The presence of shallow defects deforms the edge of conductive band, tailing it.

Изучены кристаллическая и электронная структура в пределах энергетической щели для пленок TiO₂ и TiO₂/ZrO₂/SiO₂, полученных методом золь-гель синтеза и отожженных при 773 К. При синтезе пленок TiO₂ и их последующей термообработке образуются наноразмерные частицы анатаза с развитой поверхностью и наличием мелких и глубоких дефектов в запрещенной зоне диоксида титана. Этим дефектам соответствуют достаточно локализованные электронные состояния, которые приводят к возникновению ряда полос оптического поглощения. Часть полос оптической проводимости связана с кислородными вакансиями, которые являются глубокими дефектами, а другая часть — с поверхностными дефектами. Природа поверхностных дефектов может быть различной. Наличие мелких дефектов искажает край энергетической зоны проводимости, размывая ее начало.

Titania colloids, powders, and films show a high efficiency in the photooxidation/reduction processes of toxic compounds. However, the practical application thereof requires a further improvement in TiO₂ photocatalytic activity focused on the optimization of charge separation processes, sensitization of TiO₂ to visible light, further enlargement of the surface area, etc. In the last years, numerous synthetic ways to mesoporous materials with high surface area and well-developed porosity have been reported [1–4]. Such materials include binary (TiO₂/ZrO₂, TiO₂/SiO₂), and also ternary (TiO₂/ZrO₂/SiO₂) composite materials. However, physical and chemical nature their photocatalytic activity in redox proc-

esses of toxic impurity destruction is not established even for the main component of these composites, TiO₂. In this connection, it is of importance to study physical properties of those composites in the film form, capable to influence the efficiency of photoreactions. Also, it is necessary to take into account that synthesis of binary or ternary solid solutions is possible only at high temperatures, for example, solid-state reaction between TiO₂ and ZrO₂ proceeds at temperatures above 1700 K. The synthesis at such temperatures results in formation of crystal structures with a poorly developed surface, with low effective photocatalytic properties of the obtained functional materials. Of better prospects is the synthesis of

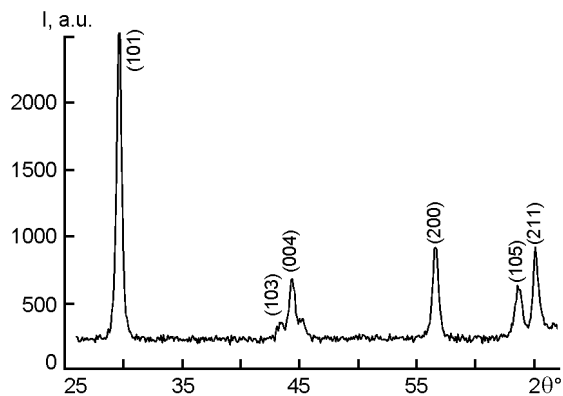


Fig. 1. X-ray diffraction of TiO_2 powder after annealing for $t = 4$ h at 773 K (λCoK_α).

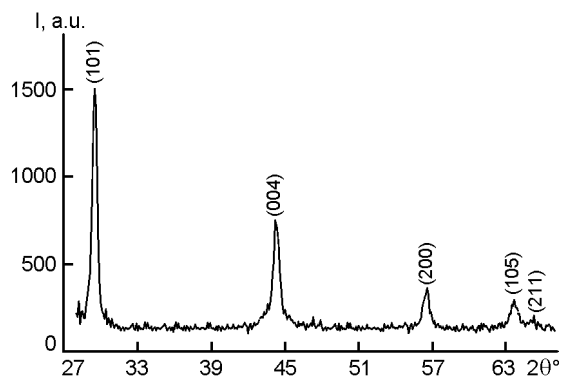


Fig. 2. X-ray diffraction of TiO_2 film after annealing for $t = 4$ h at 773 K (λCoK_α).

composites using the sol-gel method which is carried out at room temperatures. Usually, the composite gel is obtained from the corresponding alkoxides. Its specific feature is the presence both of amorphous phase and nanosized crystals with numerous fragments of $-\text{O}-\text{Si}-\text{O}-\text{Ti}-\text{O}-$, $-\text{O}-\text{Si}-\text{O}-\text{Zr}-\text{O}-$, $-\text{O}-\text{Ti}-\text{O}-\text{Zr}-\text{O}-$ types, etc. Depending on annealing temperature, the crystal structure of phases changes. So, three phases are known for TiO_2 : anatase (tetragonal structure $D_{4h}19$), rutile (tetragonal structure $D_{4h}14$), and brookite (orthorhombic structure). The specific surface area of the samples is well-developed and may exceed that of pure TiO_2 by several times. Such variety of morphology features of crystal structure and amorphous inclusions predetermines their complex influence on vibration spectra, band gap width, electron structure, formation and transport of electron excitations. The study of those properties allows to elucidate mechanisms of photocatalytic activity improvement of TiO_2 composites.

To investigate the crystal structure relaxation and electron energy spectra, sol-gel method of synthesis has been used to prepare powders and films of TiO_2 , $\text{TiO}_2/\text{ZrO}_2$, $\text{TiO}_2/\text{ZrO}_2/\text{SiO}_2$ from appropriate alkoxides using the dip-coating method to prepare the films. The samples were annealed at 773 K and 873 K. The choice of the specified temperatures was defined by necessity to retain the tetragonal phase of anatase. The structure of powders and films was studied using X-ray diffraction. The refractive index n , absorption factor k , as well as the imaginary part of dielectric permeability ϵ_2 and optical conductivity ϵ for the samples obtained with various sources of SiO_2 (TEOS solution, stable SiO_2 colloid or commercial

silica powder Davisil) and heat treatments, were calculated from coefficients of the basic equation, using the spectral ellipsometry method.

In contrast to sol-gel TiO_2 powders (Fig. 1), a TiO_2 film on Si (100) substrate is characterized by reduced size of coherent dispersion blocks and increased lattice parameters. This is confirmed by broadening of diffraction reflections and shift thereof towards smaller interference angles (Fig. 2). The average size of TiO_2 nanoparticles with anatase structure is close to 18.9 nm. In case of ternary composite $\text{TiO}_2/\text{ZrO}_2/\text{SiO}_2$ with molar ratio of components 70:21:9, the structure corresponds mainly to amorphous SiO_2 , although for powders annealed at 773 K for 4 h, a maximum appears in the reflection region of (101) anatase phase. As the annealing temperature and duration increase up to 873 K and 12 h, the half-width of that reflection decreases, its maximum position being unchanged. Its position is shifted towards smaller angles as compared to pure TiO_2 phase (Fig. 3). It is obvious that the specific features of diffraction image evidence a considerable defectness of anatase phase structure and its small nanostructured inclusions. As the annealing temperature and duration increase, the structure defectness changes insignificantly, and the size of TiO_2 particles grows. At a further increase of annealing duration, an improved ideality of anatase crystal structure can be expected as well as increase of photocatalytic activity due to reduction of concentration of traps capturing electron excitations at the photogeneration thereof.

On the other hand, with growth of the nanoparticle size, there is a reduction of the developed surface area that lowers the possibility of the photocatalyst contact with

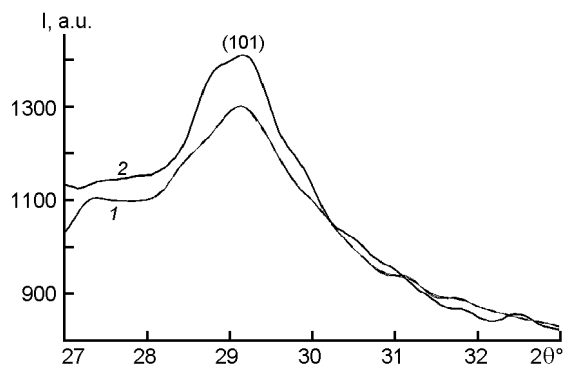


Fig. 3. X-ray diffraction of $\text{TiO}_2/\text{ZrO}_2/\text{SiO}_2$ powders annealed for $t = 4$ h at 773 K (1) and for $t = 12$ h at 873 K (2) (λCoK_α).

surrounding solution as well as forms a Schottky barrier due to heterogeneity of the potential difference between the crystal bulk and its surface. The appearing bend of energy levels reduces the interphase charge transfer and, accordingly, photoinduced catalytic reactions. Synthesis of TiO_2 nanoparticles is accompanied by formation of various crystal structure types including first of all oxygen vacancies and the surface defects connected with adsorbed OH-groups and adsorbed water. The presence of such defects influences considerably the electron energy states within the band gap. This influences both the band gap width and the generation of charges capable to increase the photocatalysis efficiency.

The presence of such defects also influences optical properties of films, in particular, the refractive index, extinction coefficient, the real and imaginary parts of dielectric permeability, thus promoting TiO_2 sensitization to the visible spectral region [6]. Figs. 4 and 5 illustrate the spectral dependences of the refractive index $n(E)$, extinction coefficient $k(E)$, and optical conductivity $\sigma(E)$ (where $\sigma = \varepsilon_0 \omega \varepsilon_2 = 2\varepsilon_0 \omega n k$, ε_0 is dielectric constant, ω is cyclic frequency of incident light) for six-layer titania coatings.

It is to note that the optical properties of TiO_2 films obtained by a sol-gel method differ from those of bulk crystals and films synthesized by other methods [3–7]. The main difference is that there is a number of optical conductivity bands in the visible and near infra-red range, that testifies the presence additional strongly localized electronic levels in the band gap caused by shallow and deep defects [8]. Besides, there is no sharp drop of absorption in the band gap edge area [9, 10]. Spectral curves of optical

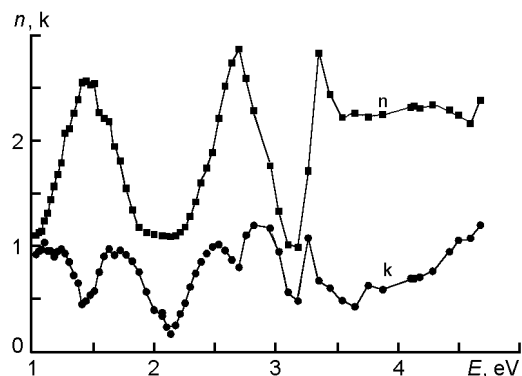


Fig. 4. Spectral dependence of refractive index $n(E)$ and $k(E)$ of TiO_2 film annealed for $t = 4$ h at 773 K (substrate Si(100)).

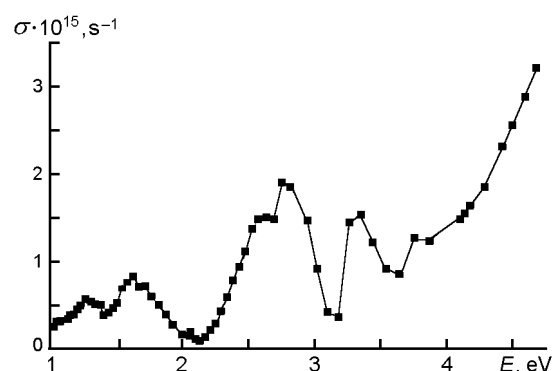


Fig. 5. Spectral dependence of optical conductivity $\sigma(E)$ of TiO_2 film annealed for 4 h at 773 K (substrate Si(100)).

properties testify to an essential role of oxygen desorption which is achieved at TiO_2 film heating. It is known [6] that in this case, a coloration occurs due to oxygen vacancies with optical absorption bands near to 1.17; 2.55 and 2.8 eV. Near to the specified values, optical conductivity bands are observed, that confirms the sensitizing influence of deep defects on photocatalysis; those defects are oxygen vacancies. The highest density of electronic states corresponds to the high-energy bands associated to those defects. Besides of the mentioned bands, other ones are observed. The nature thereof is less obvious, however, it is possible to assume, that the acceptor levels near 1.75 eV are associated with Ti^{3+} ions having absorption band near 2.0 eV. Shift of this band towards lower energy is caused probably by heterogeneity of Ti^{3+} position in TiO_2 matrix, though other defects might also act as acceptors. The absorption in infra-red region is possible also due to electron transitions from energy levels of shal-

low defects that are surface defects of TiO₂ nanocrystals. The presence of such levels is confirmed by increases optical conductivity near to the conductivity band bottom, since in the area close to 3.25 eV, the contribution from Urbach tail because the presence of amorphous phase TiO₂ is not excluded. The absorption near 1.6 eV is structured, thus testifying to a variety of surface defects caused by energetic heterogeneity of TiO₂ surface. No free electron absorption is observed in the energy range between 1.0 and 1.5 eV.

Thus, the presence of defects with various energy positions of electrons in the band gap of nanosized TiO₂ films obtained using the sol-gel technique changes significantly their structure. This promotes a sensitization of the photocatalysts to the visible light, and extends the opportunities of photoinduction and accumulation of the charges being involved in photocatalysis.

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Фотокаталіз плівками TiO₂ при релаксації структури

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Досліджено кристалічну та електронну структуру плівок TiO₂ та TiO₂/ZrO₂/SiO₂, отриманих методом золь-гель синтезу та відпалених при 773 К. При синтезі плівок TiO₂ та їх наступній термообробці утворюються нанорозмірні частинки анатазу з розвинутою поверхнею і наявністю мілких та глибоких дефектів. Цим дефектам відповідають достатньо локалізовані електронні стани, які призводять до виникнення ряду смуг оптичного поглинання. Частина смуг оптичної провідності пов'язана з кисневими вакансіями, які являються глибокими дефектами, а інша частина — з поверхневими дефектами. Природа поверхневих дефектів може бути різноманітною. Наявність мілких дефектів спотворює край енергетичної зони провідності, розмиваючи її початок.