Red shift of absorption spectra of metal-doped TiO₂ coatings

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Abstract. The effect of metal elements doping (Cu, Fe, Ni, V, Cr) on the shift of the absorption spectra of the titanium dioxide composite coatings was studied experimentally. It is shown that the most significant effect on the red shift of the absorption spectra (up to 470 nm) is observed for Fe-TiO₂ coatings with Fe doping level up to 20 at. %. Fe-TiO₂ and Ni-TiO₂ coatings with doping levels of 15 at. % also have an extended absorption in the visible region (410÷420 nm).

1. Introduction
Titanium dioxide coatings have been the subject of active research for many years due to their high photocatalytic activity. They have potential applications in many applied fields, including water and air purification from organic contaminants, photocatalytic sterilization in medical and food industries, and solving of environmental problems [1-6]. In process of oxidation, no dangerous carcinogenic, mutagenic and aromatic compounds are formed, because the carbon dioxide and water are the main products of decomposition in the case of organic compounds oxidation. The choice of titanium dioxide as a photocatalyst is related to its nontoxicity, relatively low production cost, chemical and biological inertness.

It is known that the band gap energy of titanium dioxide is about 3.0-3.2 eV, which corresponds to the near-ultraviolet wavelengths [7]. The use of photocatalytic coatings that can be activated only under UV irradiation limits the areas and conditions for their applications. A significant efforts have been made over the last years to develop modified titanium dioxide that is active under visible-light wavelengths (λ>400 nm). For today it is known that the extended absorption is possible due to the doping of titanium dioxide by certain elements, the most promising of which are Fe, Ni, V, Cr, Mo, Pt [8-11]. The doping can be realized by standard sol-gel methods, ion implantation or micro-plasma oxidation [12-14].

In this work, a plasma method on the base of plasma source with external electron injection and sectioned sputtered cathode was used to obtain a titanium dioxide composite films. This plasma source allows to form composite coatings with precise regulation of the elements from sputtering targets in argon and oxygen atmosphere [15].

2. Experimental setup
The experimental scheme for the deposition of metal-doped TiO₂ coatings is shown in figure 1.
A vacuum chamber made of stainless steel with a volume of 0.2 m$^3$ was pumped out with a turbomolecular pump to a residual pressure of 5·10$^{-5}$ Torr. The bulk plasma source 1 is based on high-current DC glow discharge with electron injection. The injected electrons are additionally accelerated near the surface of the sputtering electrode 2 to an energy corresponding to the cathode potential drop (300–500 eV) of the DC glow discharge. In the vacuum chamber these electrons efficiently ionize the operating gas (argon/oxygen mixture). The sputtering targets are located in the region of maximum plasma density. The system of sputtered targets consisted of six flat trapezoidal metal targets with a total area of 650 cm$^2$ mounted on water-cooled holders. Targets were electrically isolated from each other and located around the axis of the plasma source. In order to more uniformly mix the flow of sputtered material, the sections from different metals alternated with each other. The adjustment of negative potential bias on each metal target independently makes it possible to change the fraction of each material in the sputtered flow to the substrate. The argon gas was fed into the hollow cathode of the plasma source 1. The oxygen was filled into the region of electron injection near the sputtered targets 2. The operating pressure during the deposition of coatings after the application of a mixture of operating gases was (2÷3)·10$^{-3}$ Torr. The anode of glow discharge with sputtered targets was grounded as well as the vacuum chambers walls. The detailed design and operating principle of the plasma source with sputtering targets are described in [16].

The distance from the end of the plasma source to the sample holder was 25 cm. Quartz samples (KU-1) were used as substrates. Samples were placed on the carousel holder 4. All the samples were deposited in a single vacuum cycle. Screen 3 was used to protect neighboring samples from unwanted deposition. Before the coating deposition, the samples were subjected to ion etching in argon plasma for 10 min ($j_{ion}$=1 mA/cm$^2$). The coating deposition time for a sample was 60 minutes. The results of preliminary experiments showed that the optimum conditions for the formation of anatase structure in the coating are observed when the quartz substrates were heated to a temperature of 673 K, followed by an annealing in an oxygen atmosphere for 30 min. During the deposition, the all parameters of the plasma source and the gas flow were kept constant. The variable parameter in the experiments was only the each target bias potential, which regulates the proportion of metal components (Cu, Fe, Ni, V, Cr) in the composite coating.

A study of the elemental and percentage composition of composite coating samples was carried out using the Lab Center XRF-1800 sequential X-ray fluorescence spectrometer (Tomsk Materials Science Center of Tomsk State University). The absorption spectra were measured using an optical spectrometer Ocean Optics-2000 (250÷850 nm) in the Absorption mode. The source of radiation was a deuterium and
halogen lamp. The elemental and percentage composition analysis of the composite coating samples was carried out using the Lab Center XRF-1800 sequential X-ray fluorescence spectrometer.

**Figure 2.** Absorption spectra of doped Me-TiO$_2$ composite coatings with low doping level (1 at.%).

**Figure 3.** Absorption spectra of doped Cu-TiO$_2$ composite coatings.

**Figure 4.** Absorption spectra of doped Ni-TiO$_2$ composite coatings.

**Figure 5.** Absorption spectra of doped Fe-TiO$_2$ composite coatings.
3. Results of experiments

The experimental program consisted of two parts. In the first, the oxide composite coatings Me-TiO$_2$ type (where Me is doping metal) with doping level of 1 at. % was investigated. This value was chosen on the basis of the study of literature data related to the processes of doped photocatalytic coatings formation by sol-gel [1, 2] and ion implantation method [3]. As a doped metal, Fe, Ni, Cr, and V were used. Absorption spectra of composite coatings based on titanium dioxide with a low doping level are shown in figure 2. It should be noted that the boundary of the absorption region of coatings based on pure titanium dioxide is on the order of 360–380 nm.

The results of the experiments showed that the content of doped element at 1 at. % does not significantly affect the red shift of the absorption spectra of titanium dioxide composite coatings. In the next series of samples, the doping was increased up to 10-20 at.%. As doped metals, Fe, Ni, and Cu were used. The absorption spectra are shown in figures 3-5.

4. Conclusion

The experimental results show that an increase in the percentage content of metal components (Fe, Ni, Cr, V) in Me-TiO$_2$ coatings to a level of 15–20 at. % provides a notable red shift of the absorption spectra (>400 nm). At that, the maximal shift is provided Ni and Fe doping. The obtained modified Me-TiO$_2$ coatings with extended absorption spectra have a doping percentage that is an order of magnitude higher than the doping content in the photocatalytic Me-TiO$_2$ coatings obtained earlier by other methods (sol-gel and ion implantation, for example).

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