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Photochemical Method of Silver Deposition on a Quartz Surface Modified by Polybutoxytitanium

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Abstract—The results of silver photochemical deposition on a surface of titanium-containing coatings are presented. The formation of the particles occurs in a near-surface layer with a direct involvement of the coating which gains an anatase structure under the action of UV light. The deposition of silver begins with the formation of low-atomic clusters which reach particle sizes of 300 nm in diameter and 35–40 nm in thickness under long irradiation. The quantum yield of the reduction of Ag(I) ions is 0.001.

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Semiconductor materials containing nanoparticles of noble metals have become a subject of steadfast attention of researchers owing to unique properties and a wide spectrum of possible applications in such fields as optronics [1], catalysis [2], and medicine [3]. Coatings containing silver nanoparticles can exemplify such nanocomposite materials.

Silver nanoparticles possess both properties characteristic of all noble metals (chemical stability, high electric and heat conduction) and a number of specific properties characteristic of nanoparticles (catalytic and optical activity [4] and bactericidal properties [5], which are widely used at present [6–12]).

Presently a number of methods for obtaining composite materials containing silver nanoparticles has been developed: magnetron spraying [13], electro-deless metal plating [14], chemical [15, 16], photochemical [17–22], and radiation reduction [23–25], and also photocatalytic precipitation of silver nanoparticles on titanium dioxide films [26–28].

Composite materials consisting of titanium dioxide films and silver nanoparticles precipitated on them are characterized by a stronger fixation of silver nanoparticles on various surfaces and by increased photocatalytic activity of titanium dioxide [2]. This is because metal particles promote a more effective separation of electrons and "holes" formed as a result of a photoexcitation [29–31]. The use of titanium dioxide films as substrates allows obtaining stable silver films on glass [26].

Titanium dioxide films are obtained by physical methods (spraying [32], ion-beam deposition [33], pulsing laser deposition [34], and deposition from a gas phase [35]) and by chemical methods (sol-gel method [36–38] and electrochemical deposition [39]). The both physical and chemical methods of obtaining titanium dioxide films have their own advantages and disadvantages. For example, physical methods are characterized by a high energy consumption and the necessity to use vacuum instrumentation. Chemical methods are not so high energy-consuming and do not require so complicated instrumentation, but many of them are characterized by a multiple treatment of a substrate by a reaction mixture for obtaining titanium dioxide films of a sufficient thickness. As the photo-catalytic activity of titanium dioxide films in many respects depends on their structure, structural defects, and also on the size of particles forming thedm [40, 41], and these factors are very difficult to control at multiple repetition of any operation. Thus, the use of chemical methods hampers obtaining titanium dioxide films of a required quality.

The aim of this work was to determine a role of polybutoxytitanium as a modificator of a quartz surface in the formation of silver particles and to study physico-chemical properties of the deposited metal plating.

Preliminary experiments have shown that the radiation treatment of a quartz slide in contact with a silver nitrate aqueous solution by light with an excitation wavelength of 254 nm does not result in a precipitation of silver on its surface, whereas the exposure of a quartz slide covered by a polybutoxytitanium layer results in the precipitation of a gray-brown film of colloid silver. This fact points to the participation of polybutoxytitanium in the metal precipitation.

Absorption spectra of polybutoxytitanium films deposited on quartz from solutions in hexane and 2-propanol are presented in Fig. 1. It is seen from the figure that the absorption spectra of the films contain a band with a maximum at 254 nm. It points to the fact that light with the excitation wavelength of 254 nm is actinic for the polybutoxytitanium layers. The absence of absorption from the visible spectral region makes it convenient to apply polybutoxytitanium for recording absorption spectra of colloid silver, which is characterized by the presence of a plasmon band in the range 380–500 nm. The similarity in the shapes of spectra of the films precipitated from these solvents points to the chemical identity of the coatings. Low optical densities of the films precipitated from hexane are caused by cracking of the coating as a result of a high volatility of the solvent as compared with 2-propanol and by a non-uniform drying of the layer while plotting. Therefore we carried out all subsequent experiments using 2-propanol.

According to the electron microscopy data, the thickness of a single-deposited polybutoxytitanium layer is 70–100 nm. It is inexpedient to obtain thicker films by using more concentrated solutions (5–7 wt %) of the modificator owing to their cracking because of non-uniform drying. Therefore the increase in the thickness of the modifying coating was reached by multiple coating a polybutoxytitanium solution with subsequent drying. Such procedure allows smooth homogeneous films to be formed. According to the atomic-powered micro-scopy, the profile of coatings on selected surface sections (1000×1000 nm) was from 2 up to 3.2 nm for single-layer coatings and from 26.5 up to 27.2 nm for ten-layer coatings. The increase in the number of de-posited polybutoxytitanium layers results in a propor-tional increase in the intensity of the band at 254 nm in the absorption spectrum.

The irradiation of coatings in an argon atmosphere within 30 min does not cause changes in the topology of their surface. However it is evident from the IR spectra presented in Fig. 2 that the intensity of the bands at 1005–1205 cm^{-1} (stretching C–O vibrations), 951, 1463 cm^{-1} (bending vibrations), 2863, 2933, 2968 cm^{-1} (stretching C–H vibrations), and also 819 cm^{-1} (characteristic for vibrations of butoxy groups) decreases in the course of the irradiation, and the bands at 500–670 and 1560 cm^{-1} characteristic of Ti–O bond vibrations appear. Simultaneously with the change in the chemical composition of titanium-containing

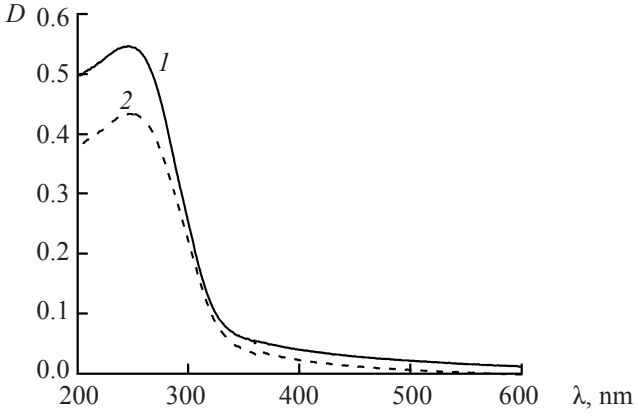

Fig. 1. Absorption spectra of coatings precipitated on quartz from 2% polybutoxytitanium solutions in (*1*) 2-propanol and (*2*) hexane.

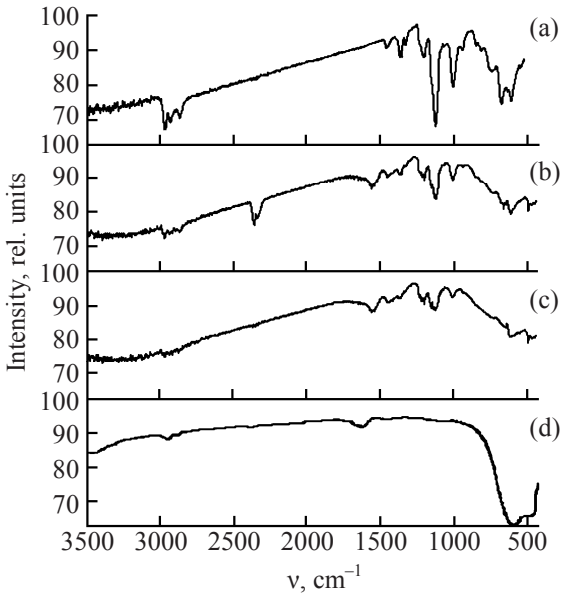

Fig. 2. Variation in the IR spectrum of a single-layer coating on quartz precipitated from 2% polybutoxytitanium solutions in 2-propanol in the course of UV light irradiation within: (a) 0; (b) 10; (c) 30 min; and (d) IR spectrum of anatase.

coatings a hydrophylity of the surface increases, which is seen from the rise of the band in the range 3100–3500 cm^{-1} corresponding to the O–H stretching vibrations. The latter fact can be caused by the detachment of a non-polar organic fragment of polybutoxytitanium and by the formation of OH groups on the coating surfaces.

It follows from the IR spectroscopy data that the UV irradiation results in the detachment of C_4H_9 and/or OC_4H_9 groups and in the formation of the TiO_2 structure. The IR spectrum recorded after a 30 min irradiation of a titanium-containing coating (Fig. 2) approaches the IR spectrum of anatase [42]. It is seen from Fig. 2 that the bands at 500, 600–670, and 1560–1650 cm^{-1} corresponding to this TiO_2 modification appear in the spectrum. The last band arises even at a 5 min exposure.

When slides with a polybutoxytitanium layer preliminarily irradiated within 30 min are dipped into a 0.01 M aqueous solution of silver nitrate and then are irradiated by UV light within 1 min (Fig. 3), a band with a maximum at 325 nm characteristic of small silver clusters Ag_9^+ arises in the spectrum [23, 24]. The irradiation within 25 min results in a decrease in its intensity. At the same time, starting from a 10 min exposure, a plasmon band with a maximum at 550 nm corresponding to the formation of colloid silver particles arises in the spectrum. The subsequent irradiation within 60 min does not cause essential changes in the absorption spectrum.

Attained optical densities of the films (no more than 0.1 relative unit) points to low quantum yields of photochemical processes involving titanium-containing coatings and yielding products, which reduce silver ions. In fact, the calculated quantum yield of silver ions reduction appeared to be 0.001. It can be connected with the existence of a limited number of active polybutoxytitanium surface centers sorbing silver particles. This assumption was checked up by a variation of silver nitrate concentration in the photolyte.

Irradiation of a slide with a polybutoxytitanium layer dipped into an 1×10^{-5} M $AgNO_3$ solution for 15 min results in the appearance of a wide plasmon absorption spectral band of silver particles with a maximum at 410 nm (Fig. 4). When the concentration of silver nitrate increases up to 6.0×10^{-4} M optical density of colloid silver in the spectrum increases and its maximum is shifted up to 560 nm that points to an increase in the number of metal particles in the film and to their integration. The further strengthening of silver nitrate up to 1×10^{-2} M leads alongside with

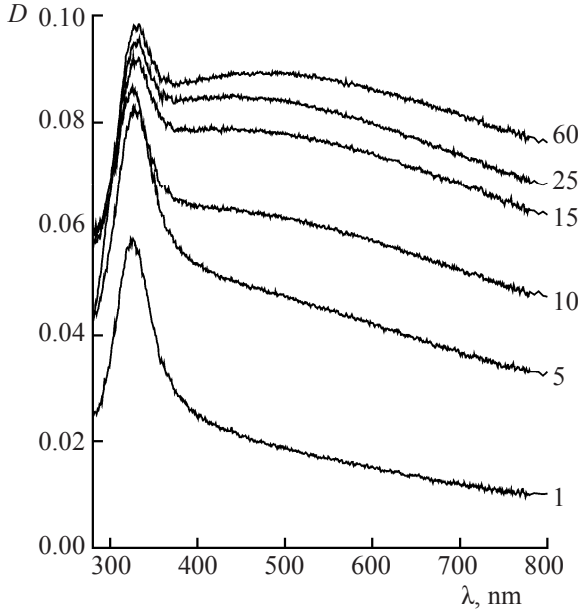

Fig. 3. Absorption spectra of colloid silver precipitated on quartz modified by polybutoxytitanium from 0.01 M aqueous solution of $AgNO_3$ under UV irradiation. Digits at the curves corresponds to the irradiation time, min.

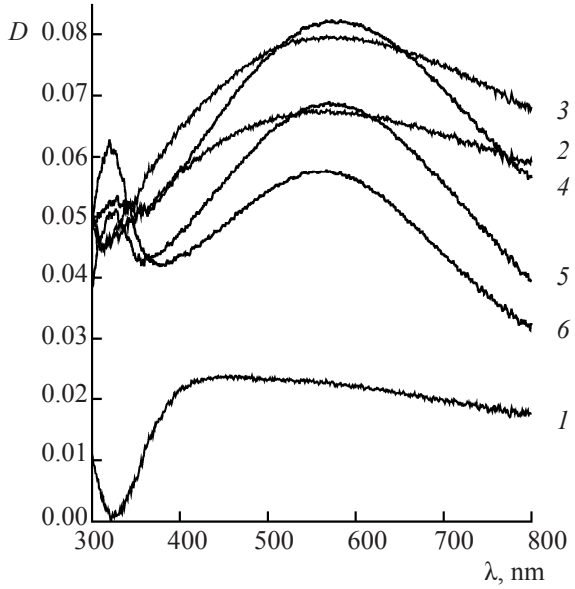

Fig. 4. Absorption spectra of colloid silver precipitated under UV irradiation from aqueous $AgNO_3$ solutions of various concentrations on quartz modified by polybutoxytitanium. $AgNO_3$ concentration: (*1*) 1.0×10^{-5}, (*2*) 6.0×10^{-4}, (*3*) 2.5×10^{-3}, (*4*) 1.0×10^{-2}, (*5*) 2.0×10^{-2}, and (*6*) 4.0×10^{-2} M. Irradiation time 15 min.

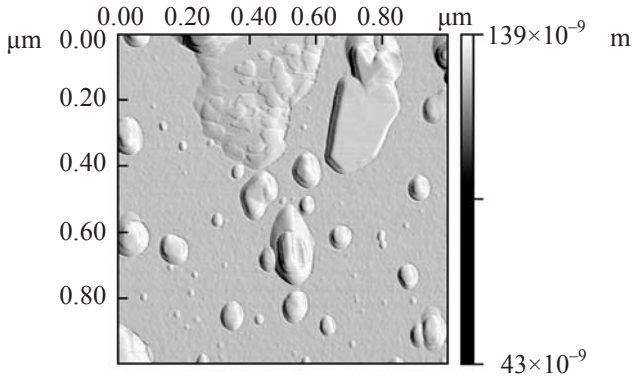

Fig. 5. Microphotograph of titanium-containing coating with silver nanoparticle precipitated photochemically from 0.01 M aqueous solution of $AgNO_3$. Irradiation time 60 min.

increasing optical density to the appearance of a maximum at 325 nm in the spectrum, its intensity increasing with increasing concentration. Optical density (D) of silver particle coatings does not exceed 0.1 units. For comparison, films precipitated on a quartz surface from dimethyl formamide solutions with $AgNO_3$ concentration of 1×10^{-2} M are characterized by optical densities higher than 2 units [43]. Starting from $AgNO_3$ concentration 6.0×10^{-4} M, the position of the plasmon absorption maximum do not vary, being fixed at 560 nm, that points to the formation of particles of a stable size. The decrease in the optical density of the films, beginning with the silver nitrate concentration of 1×10^{-2} M, is attributable to the oxidizing action of Ag(I) ions (E^0 0.799 V) on forming low-atomic silver clusters. The spectral analysis of the photolyte has shown the absence of the absorptions characteristic for silver particles even after a 60 min irradiation, i.e. silver particles are formed only on the surface of a titanium-containing coating. This experimental fact suggests that the reduction of silver ions and the formation of metal nanoparticles occur only with the participation of a titanium-containing coating with the anatase structure.

The energy of the exciting light of 254 nm (~4.88 eV) exceeds the energy of the electron transition from a valence band into a conduction band in anatase (~3.20 eV). Therefore, the irradiation can result in the formation of electron-"hole" pairs in a TiO_2 molecule. Such transition seems to weaken the oxygen-titanium bond due to displacement of electron density and thus promotes silver fixation on the surface due to formation of the Ag–O–Ti≡ bond. Later on silver particles are formed on the appearing centers. In this case the titanium-containing coating plays the roles of a substrate for silver particles and of a photocatalyst in their formation.

According to the electron microscopy data, the size of silver particles precipitated for 1 min is 20 nm, whereas the irradiation for 15 min yields particles with a 100–120 nm diameter and thickness of 35–40 nm. The irradiation for 60 min results in the increase in particle diameter up to 300 nm (Fig. 5) without change in their thickness. Thus obtained materials are stable and save their optical properties within 1 year.

Ten-fold increase in the thickness of a titanium-containing coating (deposition of ten-layer coatings on quartz) does not result in essential variations in the kinetics of silver nanoparticles formation. It points to the fact that silver reduction occurs due to near-surface processes in TiO_2.

The exposure of slides dipped in $AgNO_3$ aqueous solutions with polybutoxytitanium coatings not irradiated preliminarily also results in the formation of a plasmon absorption of silver particles in the spectrum. However their amount and precipitation rate, all other conditions being equal, are twice as little as for preliminarily irradiated titanium-containing coatings. Probably photosensitive TiO_2 structures are not formed owing to a contact of titanium-containing coatings with water during the irradiation.

Thus, silver particles can be photochemically precipitated on surfaces modified with polybutoxytitanium from aqueous solutions. The variation of the time of a preliminary exposure of the modificator provides a possibility of obtaining functional metal images on dielectric surfaces.

EXPERIMENTAL

We prepared modifying 2% solutions of $Ti(OC_4H_9)_n$ on the basis of 2-propanol and hexane. In connection with a high inclination of polybutoxytitanium to hydrolysis all operations with it were carried out in argon atmosphere, and high-purity anhydrous solvents were used for the preparation of solutions. Polybutoxytitanium (1 ml, ρ 1 g ml^{-1}, Aldrich, 99.9%) was dissolved in 75 ml of hexane (Aldrich, 99.9%, ρ 0.655 g ml^{-1}) or 62.4 ml of 2-propanol (Aldrich, 99.9%, 0.785 g ml^{-1}). The resulting solutions were applied on quartz slides (25×10 mm, Chemglass) and dried. The thickness of coatings was regulated by sequential application of equal volumes of a polybutoxytitanium solution with a subsequent drying. As model metal-

lating solutions we used aqueous solutions of silver nitrate $AgNO_3$ (Aldrich, 99.99%) prepared by dissolving a corresponding amount of silver nitrate in a necessary amount of twice distilled water. The range of silver nitrate concentrations was 1×10^{-5}–1×10^{-1} M.

The irradiation was carried out by monochromatic light of an ENF-280C Spectroline lamp with an excitation wavelength of 254 nm. The intensity of a luminous flux was 3.3×10^{16} quantum cm^{-2} s^{-1}. Absorption spectra were recorded on a Shimadzu UV-2401 PC spectrometer. For recording the spectrum of colloid silver deposited on the surface of a polybutoxytitanium film we used a quartz slide with a deposited film as a standard. The IR spectra of coatings were recorded on a MIDAC Grams/32 IR spectrometer. The topography of coating surfaces was studied by means of atomic force microscopy on a Vega II LMU scanning electron microscope. The X-ray-spectral microanalysis was carried out on a JEOL 6380LA scanning electron microscope equipped with an EDX detector. Samples were analyzed when plotted on a silicon support.

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