B R I E F C O M M U N I C A T I O N S

THE CHANGE IN THE OPTICAL DENSITY OF THIN TITANIUM DIOXIDE FILMS UNDER BOMBARDMENT BY LOW-ENERGY IONS

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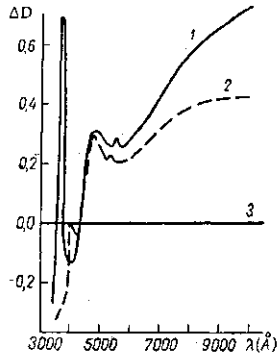
This paper reports a spectral investigation of the effects of low-energy hydrogen and oxygen ions on a TiO_2 film. The method used to obtain hydrogen and oxygen ions with energies of ~10 eV and a flux density of 10^{15} $cm^{-2} \cdot sec^{-1}$ in the plasma of a high-frequency discharge was described in [1,2]. Since the pressure in the experimental setup is 10^{-2} mm Hg during ion bombardment, the ions interact with a specimen surface carrying a damping layer of adsorbed gas atoms and molecules, in which 10-eV ions experience elastic scattering and partial charge transfer. The spectral method makes it possible to observe changes in the state of the surface and the adsorbed layer of the specimen in a vacuum immediately after exposure to the ions, and the relaxation of these changes.

The experimental setup incorporates a vacuum station with an oil diffusion pump and freezeout traps, a gas discharge tube with quartz windows, which accommodates the movable specimen, and an optical system for measurement of the TiO_2 transmission spectra. The maximum vacuum in front of the gas inlet into the discharge space is 10^{-7} mm Hg, and a continuous-flow gas-delivery system ensures a pressure of 10^{-2} mm Hg during bombardment of the film by the ions. The optical system for registration of the spectral transmission coefficients consists of a DMR-4 double monochromator and FEU-39 and FEU-22 photomultipliers to receive the optical system transmitted through the TiO_2 specimen on its quartz support and the quartz windows of the discharge tube.

TiO_2 films a few tenths of a micron thick were sputtered onto a quartz base in a separate vacuum-spray unit with a maximum vacuum of 10^{-5} mm Hg. The specimens have a control area that is free of TiO_2 and can be placed under the sounding light beam by moving the support; this makes it possible to isolate the effect due only to the change in the TiO_2 surface. The manner in which the transmission spectra of the sputtered films vary [1] indicates the absence of any significant interference effects. Travina and Mukhin [3], who used a similar technique to prepare TiO_2 films, also failed to observe any effect of interference extremes on the variation of absorption in the TiO_2 layer as a result of chemical treatment.

The figure shows the spectral characteristics that we obtained; they represent the typical changes ΔD in the optical density of the TiO_2 film in the wavelength range λ = = 3000-10,000 Å ($\Delta D = \Delta(kx)$, where k is the absorption coefficient and x is the thickness of the film). The error of determination of ΔD does not exceed 2%.

As we see (curve 1), a sharp increase in absorption appears around $\lambda \leq 3650$ Å, which is near the limit of the Balmer series of hydrogen, after hydrogen-ion bombardment of the TiO_2 film. This absorption continuum is observed for about 15 minutes after termination of the discharge at 10^{-2} mm Hg in the hydrogen-filled tube, but it vanishes instantly on subsequent admission of oxygen to 760 mm Hg.



Variation of optical density of TiO_2 film as a result of successive exposure to: 1) a 10^{18} cm^{-2} flux of 10-eV hydrogen ions; 2) molecular oxygen at atmospheric pressure for 13 hr; 3) a 10^{18} cm^{-2} flux of 10-eV oxygen ions.

The manner in which the optical density of the TiO_2 film varies after admission of oxygen is a basis for attributing the unstable absorption band at $\lambda \leq 3650$ Å to a change in the composition of the adsorbed gas layer formed on the surface of the film as a result of its bombardment by the hydrogen ions. An adsorbed layer of atomic hydrogen is formed in the discharge because of the high degree of dissociation of the hydrogen molecules (up tp 90% [2]) and in the process of surface recombination of H^+ with the electrons that form the negative surface potential. Since the narrow absorption band bounded above at $\lambda = 3650$ Å can correspond to the photoionization maximum of only the excited ($n = 2$) hydrogen atom, it must be concluded that the adsorbed hydrogen layer is in a partially excited state (for the normal state of hydrogen, absorption is observed in the far ultraviolet at $\lambda \leq 970$ Å [4]). The prolonged existence of this excited layer on the surface after termination of the discharge at 10^{-2} mm Hg indicates the possibility of an isomeric state of the hydrogen; its subsequent interaction with the hydrogen may result in hydration of the TiO_2 and contribute to the absorption at $\lambda = 4200$ Å.

This small absorption maximum that appears on the spectral characteristic of TiO_2 after holding in an oxygen atmosphere for 13 hr (curve 2) can be attributed to a combination of titanium ions with hydrogen peroxide molecules. As was shown in [5], exposure of hydrated metal oxides to ionizing radiation results in the appearance of hydrogen peroxide on the surface, where it forms colored complexes with transition elements. The wavelength of the absorption maximum corresponding to the complex of H_2O_2 and Ti^{+4} is about 4200 Å [6].

The next clear absorption maximum near 4800 Å is stable, and is observed both on the surface after termination of hydrogen-ion bombardment and on subsequent admission of oxygen to 760 mm Hg. A slight decrease in the intensity ΔD around 4800 Å occurs only after further holding of the specimen in oxygen for more than 12 hr (curve 2). A similar ΔD relation was registered for the small absorption maximum in the neighborhood of 500 Å. These two maxima on the optical-density curve of the TiO_2 film are presumably due to the characteristic coloring as a result of chemisorption processes with participation of organic impurities (which are inevitable, primarily because of the presence of oil traces when the films are prepared in the vacuum-deposition unit). There is no question but that the presence of hydrocarbons in the TiO_2 film may result in the formation of carbonium-ion complexes on the surface when it is bombarded with H^+ ions, and the absorption spectra of these ions would be responsible for the color of the titanium dioxide in visible light [7]. The two stable absorption bands in the visible region that are typical for the spectra of carbonium ions and their complexes, the maxima of which are separated by ~1000 Å, were first observed in proton-containing media [8].

The strongest increase in the absorption of the TiO_2 film under hydrogen ion bombardment is observed at $\lambda = 6000$-10,000 Å (curve 1). This maximum of ΔD persists in stable form in hydrogen at 10^{-2} mm Hg after termination of the bombardment, but it gradually weakens under the action of molecular oxygen (curve 2). The absorption at $\lambda = 6000$-10,000 Å apparently characterizes the change in the state of the TiO_2 surface as a result of chemisorption bonds between H^+ and TiO_2, which are stronger than those formed in the simple physical sorption of hydrogen and disturb the stoichiometry of the oxide as a result of reduction of the TiO_2 by the hydrogen ions. A similar absorption maximum was observed in [9] during chemical reduction of titanium dioxide.

After holding in the oxygen atmosphere, the TiO_2 film was bombarded by 10-eV oxygen

ions in an integral flux of 10^{18} cm^{-2}. This eliminated all of the optical-density changes indicated on the figure, and the transmission spectrum of the TiO_2 reverted to its original form before primary bombardment of the film by H^+ ions, which corresponds to the level $\Delta D = 0$ (curve 3). Thus, all of the hypothetical mechanisms behind the optical-density variation of the TiO_2 film with organic purities under the influence of the H^+ of the high-frequency plasma are fully reversible on interaction with ionized oxygen, an effect consistent with their physicochemical nature.

The strong dependence of the optical-density maxima of TiO_2 films on treatment in reducing (hydrogen plasma) and oxidizing (oxygen plasma) media also indicates that these maxima should be regarded as a result of heterogeneous reactions in the interaction of the low-temperature plasma with the TiO_2 surface rather than as interference phenomena in the layer.

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