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Variation of the Vibration and Electronic States at Ion Irradiation of TiO_2 Nanofilms with Ag and Au Nanoparticles

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The nonmonotonic dependence of the intensities of vibrational lines in the Raman scattering of TiO_2 nanofilms, including Ag and Au nanoparticles, from the irradiation dose D by Ti^+ (140 keV) ions was established. The increase of the intensity in 1.3-1.5 times for TiO_2 films at D = 10^{12} - 10^{13} ions/cm^2 related with improved of films structure at low doses. The enhancement of low-frequency electronic bands with dose increasing was study. It was shown that the effect of plasmon is not a major and the vibrational-electronic interaction plays the main function.

Keywords: TiO_2 Nanofilms, Ion Irradiation, Raman Scattering, Vibration Line, New Electronic Band.

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Titanium dioxide is widely known as a catalyst due to its high chemical stability. The doping of TiO_2 by Ag and Au nanoparticles (~20 nm) was carried out to improve the catalytic activity and shift of photoactivity in the visible region. Anatase TiO_2 nanofilms with thickness of ~ 200 nm on crystalline Si substrate were obtained by the sol-gel method. The Raman spectroscopy (RS) was used to study the changes in the properties of both pure nanofilms TiO_2, and composite systems TiO_2/Ag, Au at ion Ti+ irradiation (with an energy of 140 keV). Raman spectra were obtained using a spectrometer Horbia Jobin Yvon T64000 with a cooled CCD-detector at 488 nm excitation (power 2.1 mW, focusing ~ 1 μm). Radiation doses D were changed from 10^{12} to 5×10^{14} ion/cm2. There is the distinctive and most intense vibrational mode Eg(1) at about v1 = 143 cm^{-1} in the low-frequency Raman spectra for anatase modification of TiO_2. This mode corresponds to vibration of the bridges between TiO_6 octahedron and it's very sensitive to electron states change at ion irradiation and Ag, Au addition. This mode is very weak in rutile as v2 mode in anatase. The vibrational modes of anatase are numbered in ascending order of frequency for the convenience.

The weakening of the fundamental vibrational bands was observed based on the results of spectral studies of TiO_2 nanofilms as well as the emergence and strengthening of new electronic states in the band gap at high ion implantation doses D. Figure 1 shows a selection of induced electronic bands in the Raman spectrum of nanofilms TiO_2 at the highest dose of ion irradiation Dmax = 5×1014 ions/cm^2 and the difference spectrum at doses of 10^{13} ions/cm^2 and Dmax with a negative polarity of the vibrational bands. The overlapping vibrational bands A1g and B1g of anatase denotes a frequency v4, which is superimposed on a very intense vibrational line substrate vSi = 520 cm^{-1}. A similar wideband background is observed in the Raman spectra of composite nanofilms TiO_2/Ag, Au even in the absence of irradiation exposure. This is due to the influence of the plasmonic states of metal nanoparticles and its confirm the electronic nature of the broad bands, that are beginning in the narrow vibrational bands at irradiation.

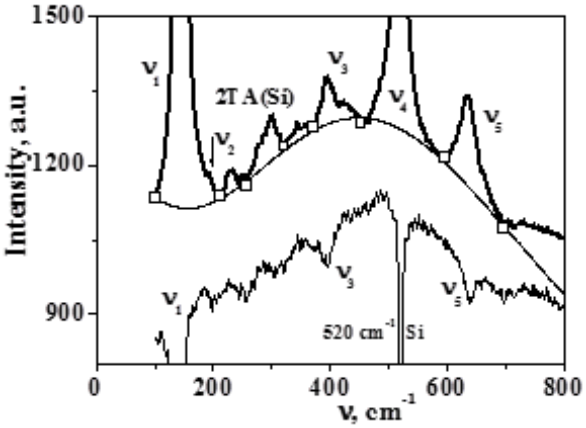

Fig. 1 – The appearance of broad and intense electronic bands in the Raman spectrum of TiO_2 nanofilms with increasing irradiation dose and observation negative polarities of the vibrational bands of anatase in the difference between the observed spectra.

We observed anomalously strong nonmonotonic dependence of the vibrational bands ν_1=143, ν_3=396 and ν_5 = 638 cm^{-1} intensities from the irradiation dose that normalized to the initial value of Ij(D = 0) values shown in Fig.2. The intensity of the bands in the spectrum of TiO_2 increased about 1.5 times at low doses (10^{12}-10^{13} ions/cm^2), and at doses of Ti^+ ions over 10^{14} ions/cm^2 appreciably weaken to less than I(D = 0). Further weakening of bands $\nu_{1,5}$ to (0,2-0,6)I(D = 0) is observed for nanofilms with nanoparticles Au and Ag. This is due to two opposite patterns of change in the collective energy states in radiation effects. The collectivization of the electronic states increases at low doses, which is accompanied by catalytic activity increased, but at high doses Ti^+ ions increases ionic interparticle bonds. The plasmon excitations contribut to increasing collectivization of electronic states at D = 0 in TiO_2 films with Ag and Au nanoparticles, and the irradiation at 10^{13}

ions/cm^2 leads to weakening of the vibrational and electronic bands. This points to different mechanisms of the effects of plasma resonances and ion irradiation. The changing of the maximum intensity of the background of electronic bands I_{Fmax} for all studied systems shown in the inset in Figure 2. Thus, the increase in I_{Fmax} accompanied by a weakening of most vibrational bands. The strengthening of the band $\nu_5 = 637$ cm^{-1} for the composite system TiO_2/Ag at D_{max} is the exception. Its correlates with increased in catalytic activity as the maximum gain bands $\nu_{1,3,5}$ for pure TiO_2 nanofilm with low doses.

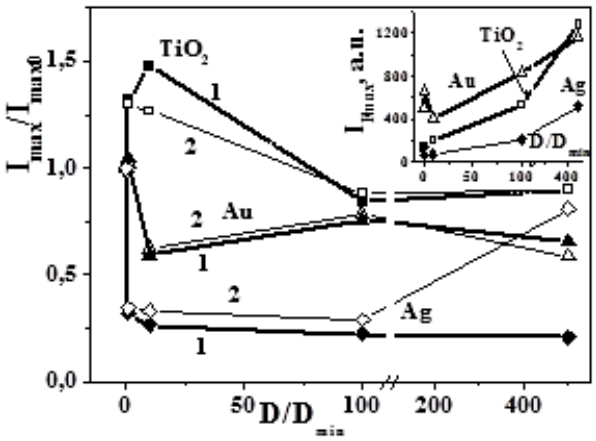

Fig. 2 – Dependence of the normalized peak intensities of vibrational bands ν_1 (1) и ν_5 (2) and the maximum intensity of the electron bands (inset) on the reduced irradiation dose D/D_{min} ($D_{min} = 10^{12}$ ion/cm^2).

An essential feature of the studied catalytic nanostructures is a significant increase in composite vibrational tones ν_4-$\nu_1 \approx 230$ cm^{-1}; ν_4-$\nu_3 \approx 120$ cm^{-1} and overtones $2\nu_1 \approx 280$; $3\nu_1 \approx 420$ cm^{-1} with an increase in dosage irradiation by Ti^+. This point to a strengthening of the vibrational anharmonicity and nonlinear susceptibilities for the interaction of vibrational modes.The strengthening of the role of the higher vibrational states leads to the appearance of strong vibrational-electronic interactions (VEI) [1]. This is due to the approach of the total high-frequency overtones and composite tones to the electronic states and the interaction with them.This leads to a change in the electronic states, which is manifested in the intensity change of the vibration bands and the appearance of a fundamentally new bands in the band gap. The observation of significant intensity broad electronic bands in irradiated by TiO_2 films, shows that the effect of plasmon resonance is not the main one. Their influence is one of the special cases of increased activity of the electronic states. The shift of the maxima of the vibrational bands and changes in their half width $\delta\nu$ with radiation exposure was studied. The parallel in the increase in ν_1, $\delta\nu_1$ and $\delta\nu_5$ with increasing of doses of radiation exposure, regardless of the presence of nanoparticles of Au and Ag, and the linear correlation $\delta\nu_{1,5}$ and I_{Fmax} show that the main role in the phenomenon of radiation environments leads to increased activation of the nonlinear interaction of the vibrational modes and the strong VEI.

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