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Surface Plasmons and Optical Properties of $TiO_2/X(X = Au$ and $Ag)$ Nanostructure Thin Films *

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$TiO_2/X(X = Au$ and $Ag)$ nanolayers are fabricated by depositing TiO_2 films using rf magnetron sputtering on thin quartz substrates embedded with Au and Ag nanoparticles. Enhancement of light absorption of the nanostructural layers is observed. These plasmonic and non-plasmonic materials are ordered in geometric arrangements with dimensions that are fractions of the wavelength of light. The light absorption enhancement of synthesized structure in comparison to TiO_2 is originated from near-field enhancement caused by the plasmonic effect of metallic nanoparticles, which can be demonstrated by the optical absorption spectra. We show that plasmon modes can exist for the infrared region of the optical spectrum. Also, we analyze the optical properties of the metal-insulator films, in order to clarify the role of metal inclusions in the TiO_2 dielectric matrix. Optical band gaps of the nanolayer films are calculated by using Tauc's relation, and the n values of optical band gaps with the variation composition are found from 1.80 to 3.69 eV. Band gap narrowing and absorption in the visible spectral region induced by the incorporation of $TiO_2/X(X$=Au and Ag) nanolayers enable the design of nanostructured thin films to be achieved for photocatalysts and solar energy converters.

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Our material platform is a sandwich-like construction with nano-spheres layers. It consists of an insulating sheet of a TiO_2 film topped by a film of gold and silver. The compositions of insulators and metals that are ordered in arrangements with dimensions that are fractions of the wavelength of light are called the plasmonic materials. Many research groups have experimented with a variety of dimensions and geometric approaches which are light induced packets of electrical charges that collectively oscillate at the surfaces of metals at infrared or visible frequencies. The surface plasmon polaritons (SPPs) ripple along the metal dielectric interface. In comparison with the incident light that triggers the transformation, the SPPs can be much shorter in wavelength.[1,2] The critical dimension is the thickness of the layers of these nanostructures, which together are only a fraction of the wavelength of blue and green light. Incident light couples with the undulating charges normally on the surface of metals. The waves are confined to the interface between metal and insulator. The interaction of photon-plasmon results in SPPs that generate localized optical fields.[3−5] The surface plasmon hybridization is also thought to play an important role in the strong localized field enhancement.[6] For sensing applications with a perfect absorber, see a model of coupling between the localized surface plasmon within nanoparticles and the propagating surface plasmon along the planar metal layer.[7]

The experimental layers will be made using a variety of fabrication methods, including multilayer thin-film deposition, focused-ion-beam milling, and self-assembly.[8,9] Both the past theoretical and experimental studies revealed that the properties of surface plasmons depend on multiple parameters, including shape, size, and composition of metal nanostructures, and dielectric constant of the media surrounding metal nanostructures.

Recently, we have calculated and simulated sandwich-like layers consisting of an insulating sheet of TiO_2, ZnS, SiO_2 and ZnO nano-spheres topped by films of Au, Ag and Al nano-spheres.[11] We found that the imaginary part of the dielectric function of the metal has a dominant effect on the relative contribution and the real part of the metal dielectric function plays a key role in the response of the SPR wavelength to the refractive index change of the medium. Interestingly, our result shows that the plasmon resonance sensitivity does not change with the metal composition selection. We also found that the chosen metals determine the wavelength dependence dispersion of the real dielectric function of metal.

In this Letter, the main goal is thus to prepare $TiO_2/X(X = Au$ and $Ag)$ nanolayer coatings and to extend the above-mentioned studies to the processing of metal-insulator plasmonics nanostructures. We report structural and optical properties of the formed nanostructures.

The TiO_2-Au and Ag nanostructural layers were obtained by depositing TiO_2 films (10 nm in thickness) on the surface of the as-implanted quartz substrates using an rf helicon magnetron sputtering sys-

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tem (Fig. 1). Only one electrode was powered, composed of a titanium target (99.9% purity), with metallic pellets (with a 40 mm^2 surface area and approximately 2 mm thickness), symmetrically encrusted in its preferential eroded zone.

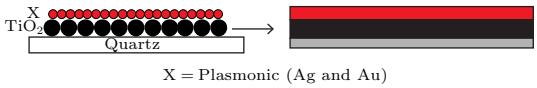

Fig. 1. (Color online) Schematic view of the system under study.

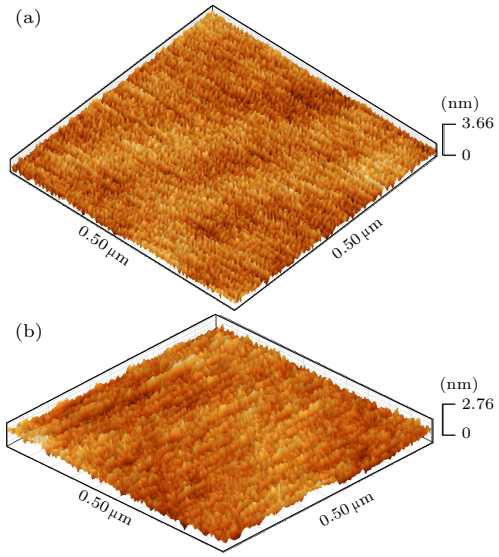

Fig. 2. (Color online) AFM image of (a) TiO_2/Au and (b) TiO_2/Ag nanolayers after annealing, at room temperature.

A constant rf power of 500 W was applied and the target-to-substrate distance was 12 cm. A mixture of argon and oxygen was injected with constant fluxes of 60 sccm and 10 sccm, corresponding to partial pressures of 0.3 Pa and 0.08 Pa, respectively. The final working pressure (∼0.38 Pa) was kept approximately to be constant during the entire coating deposition process. The deposition temperature was close to 200℃. Samples were placed in a rotating substrate holder (7 rpm) under the grounded condition. All the samples were heat treated through annealing experiments, in vacuum, after film deposition. Annealing treatments were carried out in a secondary vacuum furnace, after its evacuation to about 10^{-4} Pa.

The samples were cooled down freely in vacuum before their removal to room conditions. The obtained films were implanted by Ag ions at 40 kV to 1×10^{17} ions/cm^2 using a metal vapor vacuum arc ion source implanter. The prepared nanolayers were characterized by ultraviolet-visible (UV-vis) spectroscopy, x-ray diffraction (XRD) and atomic force microscopy (AFM) techniques.

In order to check for clear evidence of any (micro)structural changes, which could then be used to correlate with the overall coatings behavior, an extensive set of XRD experiments were carried out. All coatings were characterized by XRD using a Philips Xṕert, equipped with a PW3710 MPD diffractometer control unit, operating in a Bragg–Brentano configuration. The crystal phase of the prepared nanostructures is determined by Cu Kα radiation, with $\lambda = 1.54056$ Å, and a nickel monochromator filtering the wave, in the theta two theta mode, in the region of 2θ, from 30° to 100°, with steps of 0.02° and the time of 2 s per step at a tube voltage of 40 kV and tube current of 30 mA. The mean diameter of crystallite size D is estimated by using the Scherrer formula $D = K\lambda/\beta_{\rm cor}\cos\theta$ with $\beta_{\rm cor} = (\beta^2{}_{\rm sample} - \beta^2{}_{\rm ref})^{1/2}$, where $\beta_{\rm cor}$ is the full width at half maximum (FWHM) in radians, and $\beta^2{}_{\rm sample}$ and $\beta^2{}_{\rm ref}$ are the FWHM of the reference and sample peaks, respectively. K is constant ($K = 0.94$), θ is the diffraction angle and λ is the x-ray wavelength ($\lambda = 1.54056$ Å).

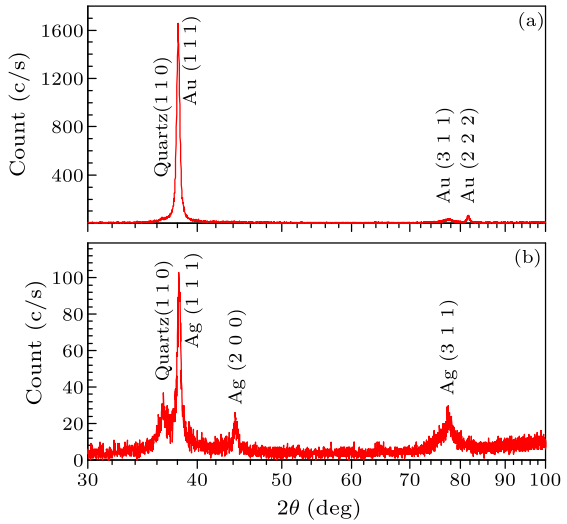

Fig. 3. (Color online) (a) The semi-logarithm XRD scans for sample (Au deposited on TiO_2. (b) The semi-logarithm XRD results of TiO_2/Ag nanostructure.

Any contributions to broadening due to non-uniform stress were ignored and the instrumental line width in the XRD apparatus was subtracted. The optical absorption spectra of all the samples were measured using a UV-vis-NIR dual-beam spectrometer (Shimadzu UV 2550) with wavelengths from 200 to 900 nm.

The surface roughness of the films was measured by an AFM over the area of 0.5×0.5 μm. Figure 2 shows the AFM results of the nanolayers. The TiO_2/Au and TiO_2/Ag nanolayers show roughnesses of 0.54 nm and 0.33 nm, respectively.

In order to obtain a complete view, the crystalline structure of the synthesized thin films was also investigated by XRD. Figure 3 shows the XRD patterns of Au/TiO_2 and Ag/TiO_2 nanostructures films. No peaks are observed for the as-deposited TiO_2/X(X = Au and Ag) films, indicating that they

are amorphous. Usually, the anatase phase of TiO_2 thin films is formed at a calcination temperature above 250℃ and transformed into the rutile phase between 700 and 900℃.[9] Furthermore, a careful observation of the XRD patterns also shows that the initial broad Ag and Au (111) peak, which starts to be detected at an annealing temperature of 300℃, becomes sharper with the annealing treatments. As is known, the metallic clusters grow in size as the annealing temperature increases, which is followed by some crystallization of the remaining amorphous TiO_2 matrix.[9]

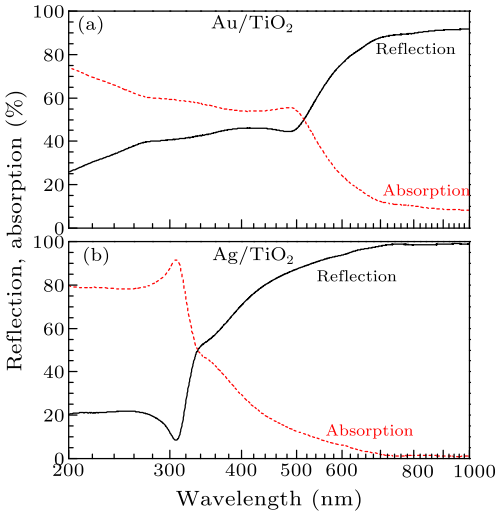

Fig. 4. (Color online) The semi-logarithm absorption/reflection spectra of TiO_2/Au and TiO_2/Ag nanolayers after annealing, at room temperature.

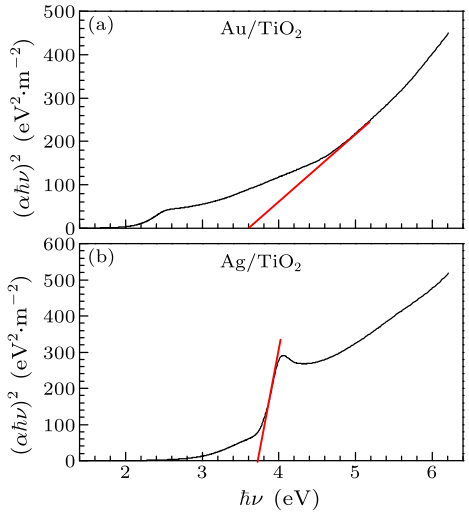

Fig. 5. (Color online) Variation of $(\alpha h\nu)^{1/2}$ as a function of excitation energy ($h\nu$) for Au/TiO_2 and Ag/TiO_2 nanostructure thin film to identify direct transitions.

The Au and Ag particles are confined on the nanoscale, with its growth led by the diffusion of the metallic atoms promoted by the annealing procedure. The surface plasmonic resonance (SPR) and the related changes on the optical properties are directly affected by growth and annealing procedure. The results illustrate that the increase of the metallic particle size is continuous in this range of annealing process. At temperatures below 300℃ no important SPR activity has been found, where the size of metallic clusters are too small to be considered as a phase crystal structure dispersed on the TiO_2. The SPR activity starts to develop for temperatures above 300℃ and becomes higher at higher temperatures.[10] The dielectric constant of titanium oxide matrix presents a different dielectric constant for each annealing temperature modifying the energy of the SPR absorption, located at larger wavelengths for more crystalline matrixes. The influence of the Au and Ag clusters? size embedded within the TiO_2 on the SPR activity was accessed by reflectivity and absorbance measurements. The main SPR activity has been reported between 400℃–600℃, where the increase of the Au particles? size is continuous in the range of increasing temperature.[9]

The samples show a minimum of reflection close to about 483(308) nm for TiO_2/Au(TiO_2/Ag), followed by a progressive increase of the reflection intensity in the highest wavelength of the visible region of the electromagnetic spectrum. In order to enhance the SPR, which should be related to the optical changes described above, absorbance measurements were also carried out for the samples. SPR is manifested as a distinct peak in the absorbance spectrum and has been reported through the localization of an absorbance band on the visible wavelength range.[12] Figure 4 shows the absorbance behavior of the nanostructure films. The peak red shift of the TiO_2/X(X=Au and Ag) samples has to be ascribed, the growth of the nanoparticles and the variance in the dielectric constant of TiO_2 that exist as different ratios of amorphous/anatase phases due to different annealing procedures.[12] Thus, different dielectric constants for each annealing temperature modify the energy of the SPR absorption. The absorption peaks are broad, especially at low temperatures.

Determination of band gap energy is often necessary to develop the electronic band structure of thin film materials. The measurement of the "band gap" of materials is important in the nanolayers. It refers to the energy difference between the top of the valence band and the bottom of the conduction band, where electrons are able to jump from one band to another. In this study, the band gap is determined by the UV-visible absorption spectra using the Tauc relation[13]

$$(\alpha h\nu)^{1/n} = A(\alpha\nu - E_g), \tag{1}$$

where α is the absorption coefficient, A is a constant E_g is the optical band gap of the film, and n has four numeric values (1/2 for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions). The band gap ener-

gies for indirect allowed transitions are evaluated from $(\alpha h\nu)^{1/2}$ versus energy plots. In Figs. 5 and 6, we analyze the $(\alpha h\nu)^{1/2}$ as a function of excitation energy $(h\nu)$ for Au/TiO_2 and Ag/TiO_2 nanostructure thin film to identify direct and indirect transitions.

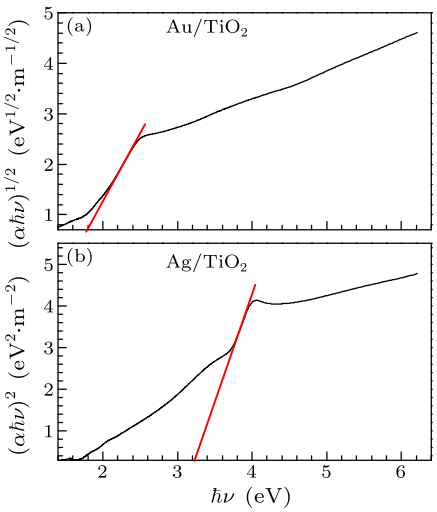

Fig. 6. (Color online) Variation of $(\alpha h\nu)^{1/2}$ as a function of excitation energy $(h\nu)$ for Au/TiO_2 and Ag/TiO_2 nanostructure thin film to identify indirect transitions.

Table 1. The direct/indirect band gap energies of Au/TiO_2 and Ag/TiO_2 nanolayers in eV.

Sample	Au/TiO_2	Ag/TiO_2
Direct	3.56	3.69
Indirect	1.80	3.32

The band gap energies of the films were obtained: a tangent line was obtained by extrapolating the curve and this tangent line was extended to intersect with the x-axis; then the band gap energy was obtained at $(\alpha h\nu)^{1/2} = 0$ according to Eq. (1). The direct (indirect) band gap energy E_g was calculated using Tauc Eq. (1), for $n = 1/2$ (2), from the intersections of the straight line with the energy axis. The results have been listed in Table 1. It should be noted that the direct and indirect band gap energies for the highest absorbance are given in Table 1 and other direct and indirect transitions show lower energy gaps.

The scientific literature reported values of band gap for TiO_2 thin films prepared by magnetron sputtering are 3.60–3.75 eV for the direct band gap and 3.05–3.20 eV for the indirect band gap, respectively.[13]

In summary, we have prepared TiO_2/X(X = Au and Ag) nanolayers fabricated by depositing TiO_2 films using dc magnetron sputtering on glass substrates embedded with Au and Ag nanoparticles, and studied their structural and optical properties. The optical properties of the TiO_2/metal nanolayers are related to the microstructure and crystallographic structure that can be changed by heat treatment. The optical properties also strongly depend on the metal nanolayers. Band gap narrowing and absorption in the visible spectral region are induced by the incorporation of TiO_2/X(X = Au and Ag) nanolayers. Optical band gaps of the nanolayers' films are also calculated by using Tauc's relation, which are found from 1.80 to 3.69 eV. The formed nanostructured thin films can be applied to design photocatalysts and solar energy converters.

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