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Growth of metal-oxide semiconductor nanocomposite thin films by a dual-laser, dual target deposition system

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Abstract

Nanocomposite formed by gold nanoparticles embedded in a titanium dioxide matrix thin films have been synthesized by a synchronized two laser system. An ArF* excimer ($\lambda=193$ nm, $\tau_{\text{FWHM}} \sim 12$ ns) laser and a frequency tripled Nd:Yttrium Aluminium Garnet (YAG; $\lambda=355$ nm, $\tau_{\text{FWHM}} \sim 10$ ns) laser were used for the irradiation of titanium dioxide and gold targets. The investigations showed that there exists the possibility for tailoring the optical properties of gold-titanium dioxide nanocomposites by the proper choice of the laser irradiation parameters. The band gap narrowing and additional absorption in the visible spectral region induced by the incorporation of gold in the host TiO₂ matrix allows for the design of nanostructured thin films for new generation of photocatalysts or solar energy converters.

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1. Introduction

Doped transition metal oxide semiconductors, as shown by recent investigations, could represent a new generation of photocatalysts with enhanced photoactivity in the near UV and visible spectral regions [1–3]. Among various transition metal oxide photocatalysts, titanium dioxide received by far the largest attention. Indeed, due to its strong oxidizing power, non-toxicity, photoinduced hydrophilicity, and photostability, it represents an ideal material for photocatalytic applications [4–6]. However, its relatively large band-gap ($E_g \sim 3.2$ eV) limits the optical absorption to the UV spectral range, i.e. only to a small fraction of the solar radiation. Thus, latest investigations focused on possible band gap narrowing, by doping of the host TiO₂ matrix with non-metallic [1,7–9] and metallic [3,10–16] ions.

Different methods have been used for the development of doped TiO₂ thin films, as supersonic cluster beam deposition [8], reactive sputtering [1], liquid phase deposition [10], spin coating [11], dip coating [12], or conventional pulsed laser

deposition [9,13–16]. However, in all mentioned techniques, the precise control of dopant concentration is quite difficult.

We propose a new laser technique for the preparation of Au doped TiO₂ thin films. Two synchronized laser sources are used for the simultaneous irradiation of the TiO₂ and Au targets. The system permits the continuous tuning of the amount of Au in the TiO₂ thin film host material, deposited on the substrate surface, by simply changing the laser fluence value incident on the Au target.

In this article we present a direct correlation between the amount of Au embedded in the TiO₂ host matrix on one side and the structure and optical properties on the other side of the deposited nanostructured thin films. The enhanced absorption in the near UV-visible spectral range allows for the implementation of the synthesized materials in new generation of photocatalysts and solar energy converters.

2. Experimental

The deposition of the Au–TiO₂ nanocomposite thin films was performed inside a stainless steel vacuum chamber, evacuated down to a residual pressure of 7×10^{-4} Pa before each irradiation experiment. UV laser pulses generated by a Lumonics Mo. TE-861T ArF* excimer laser ($\lambda=193$ nm, $\tau_{\text{FWHM}} \sim 12$ ns) were

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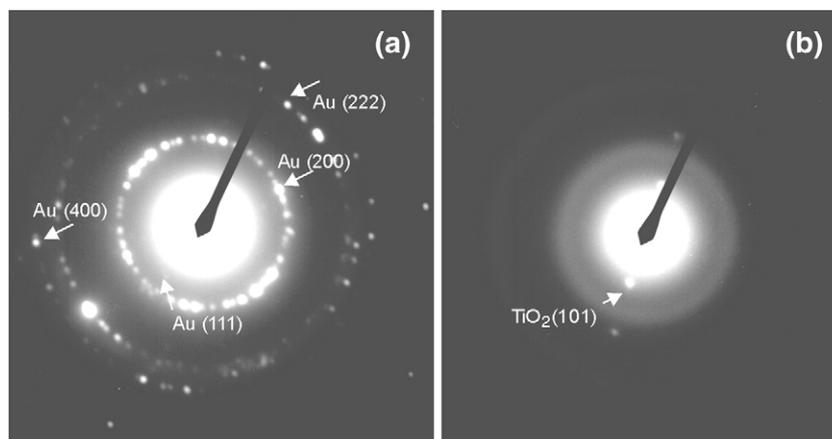


Fig. 1. SAED patterns of a Au doped TiO₂ thin film deposited at 30 Pa oxygen pressure and 300 °C substrate temperature, obtained with 2.3 J/cm² laser fluence applied to the Au target.

applied for the host TiO₂ target ablation. For the simultaneous ablation of the Au targets the pulses of a Quantel Mo. YG851 Nd:YAG laser ($\lambda=355$ nm, $\tau_{FWHM} \sim 10$ ns) were used. The two lasers were synchronized and operated at 10 Hz pulse repetition rate. The beams incidence angle was about 30° with respect to the normal of the targets surfaces.

The targets were placed on a vacuum-compatible computer-controlled XY table to avoid their fast drilling. The SiO₂ (001) substrates were positioned at 40 mm from the targets, at a place where the two ablation plumes intersect each other. The substrates were heated during the thin films growth at 300 °C. The depositions were performed in 30 Pa oxygen pressure. The ArF* laser fluence was estimated at 3 J/cm². The Nd:YAG laser fluence values were selected in the range 1–7 J/cm² range. For the deposition of each film, we applied 21000 laser pulses both to the TiO₂ and Au targets.

The deposited films were investigated by transmission electron microscopy (TEM) with a JEOL 1210 operated at 200 keV. The preparation of the samples for the TEM studies was carried out by the extraction replica method. The thin films crystalline status was studied by the selected area electron diffraction (SAED), micro-Raman spectroscopy, and X-ray diffraction (XRD). The micro-Raman spectra were recorded in backscattering configuration, with a Jobin-Yvon T64000 spectrometer equipped with an optical microscope. For excitation, the 514.5 nm line of the Ar⁺ ion laser was focused with a 50× objective over a 2 μm diameter spot area on the sample surface, with 4 min integrating time per scan. The laser power on the sample was 10 mW. The XRD investigations were performed in θ – 2θ configuration with a Philips MRD diffractometer (CuK α , $\lambda=1.5418$ Å radiation). Optical absorbance measurements were performed with a double beam Perkin Elmer Lambda 19 spectrophotometer in the wavelength range of (200–1000) nm.

3. Results and discussion

The crystalline structure of the synthesized nanostructures was investigated by SAED (Fig. 1a, b) and for a more general insight by micro-Raman spectroscopy (Fig. 2) and XRD (Fig. 3).

Indexing the SAED patterns of selected zones, we find interplanar distances of 0.235, 0.203, 0.117, and 0.101 nm attributed to the (111), (200), (222), and (400) lattice plane reflection of polycrystalline cubic phase of Au (Fig. 1a), as referred in the JC-PDC 04-0784 file [17]. The diffraction rings consist of sharp spots, indicating that the Au nanoparticles are well crystallized. The TiO₂ matrix is formed by nanocrystals with the same growth orientation (Fig. 1b). Indexing the corresponding SAED pattern we obtain an interplanar distance of 0.352 nm assigned to the (101) lattice plane reflection of the tetragonal anatase TiO₂ phase as referred in the JC-PDS 21-1272 file [17].

The micro-Raman spectra of the reference TiO₂ and TiO₂–Au nanostructures are presented in Fig. 2. The micro-Raman spectrum of the SiO₂ quartz substrate is also shown. As can be observed, besides the lines corresponding to the substrate material the micro-Raman spectra of the deposited thin films contain only one line at 143 cm^{–1}, the most intense Raman line of the phase TiO₂. The gradual decrease of the 143 cm^{–1} line intensity with the increase of the Au concentration could be due

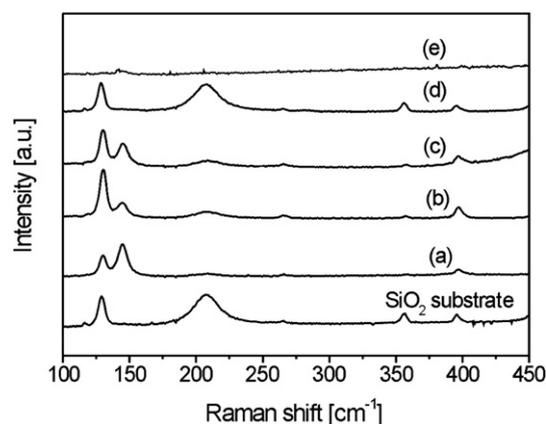


Fig. 2. Micro-Raman spectra of thin films deposited at 30 Pa oxygen pressure, 300 °C substrate temperature (a) reference TiO₂ thin film as well as Au doped TiO₂ thin films obtained with (b) 1, (c) 2.3, (d) 3.2, and (e) 7 J/cm² laser fluence applied to the Au target. The micro-Raman spectrum of the SiO₂ quartz substrate is also represented.

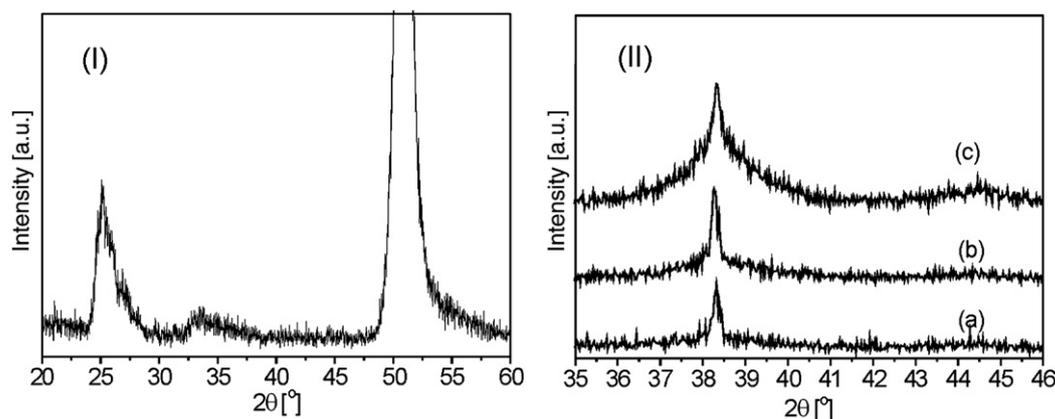


Fig. 3. XRD diffractograms of thin films deposited at 30 Pa oxygen pressure, 300 °C substrate temperature (I) reference TiO₂ thin film and (II) Au doped TiO₂ thin films obtained with (a) 2.3, (b) 3.2, and (c) 7 J/cm² laser fluence incident on the Au targets.

to the absorption of the incident Ar⁺ ion laser radiation used for excitation by the metallic Au.

The diffractograms of the Au–TiO₂ nanostructures obtained with laser fluence below 2 J/cm² used for ablation of the Au targets are similar to that of the reference thin film (Fig. 3I), containing besides the lines of the SiO₂ substrate only one line at 25.3°. This line is attributed to the (101) lattice plane reflection of the tetragonal anatase TiO₂ phase and confirms the preferential growth orientation indicated by the SAED patterns. The diffractogram of the nanostructures obtained with higher laser fluences applied to the Au targets (Fig. 3II) contains a new line at 38.3° corresponding to the (111) lattice plane reflection of the cubic phase Au [17]. For the Au–TiO₂ nanocomposite films obtained with the highest, 7 J/cm² laser fluence a new, weak line appears at 44.5° corresponding to the (200) lattice plane reflection of the cubic phase Au (Fig. 3II, c). The full width at half maximum FWHM of the (111) line remains approximately the same while its intensity increases with the increase of laser fluence, confirming the micro-Raman spectroscopy results.

The optical absorption spectra of the reference TiO₂ thin film and the Au–TiO₂ nanostructures are given in Fig. 4. With the

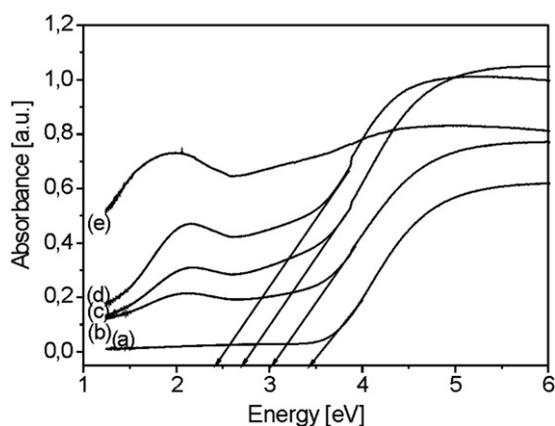


Fig. 4. UV–visible absorbance spectra of thin films deposited at 30 Pa oxygen pressure, 300 °C substrate temperature (a) reference TiO₂ thin film as well as Au doped TiO₂ thin films obtained with (b) 1, (c) 2.3, (d) 3.2, and (e) 7 J/cm² laser fluence applied to the Au target.

increase of the Au coverage the optical characteristics of the TiO₂–Au nanostructures gradually change in the UV–visible spectral range (between 1 and 4 eV photon energy) from transparent (Fig. 3a) in case of the undoped TiO₂ film to highly absorbent, metallic character (Fig. 3e) for the highest Au concentration. In addition, in the Au–TiO₂ nanostructures spectra an absorption maximum appears centered at around 2.2 eV (corresponding to the wavelength of about 550 nm).

The absorption maximum around 550 nm is associated with the surface plasmon resonance (SPR) absorption band of Au nanoparticles [18]. As it is known, the incident photons with this wavelength are converted to surface plasmons as a result of the interaction with the free electron distribution on the Au nanoparticles surface.

The intensity and the width of the SPR band increase with the increase of the laser fluence value incident on the Au target, i.e. the increase of the Au concentration in the deposited films. The gradual broadening and shift of the absorption band maximum towards higher wavelengths in the case of the spectra corresponding to the film with the highest Au concentration (curve e in Fig. 4) could be due to the increase of the Au particles diameter accompanied by their coalescence [19–21].

As can be also observed, the absorption edge of the reference TiO₂ thin film (Fig. 4a) is shifted towards smaller wavelengths as compared to the band gap of bulk TiO₂ (3.2 eV). This shift could be attributed to quantum confinement effect induced by crystallites with relatively low sizes [22]. Residual stress in the films exerted by the substrate could also contribute [23]. The absorption edge is displaced towards lower photon energies with the increase of the Au amount in the deposited Au–TiO₂ nanostructures (Fig. 4b–e), indicating a continuous and significant decrease of the band gap.

The established dependence between the Au concentration and optical absorption features permits the continuous tuning of the optical properties of the Au–TiO₂ nanostructures both in the near UV and visible spectral range. The obtained results are promising for a broad range of applications surpassing the main drawback of TiO₂, namely to absorb only in the UV region, at photon energies exceeding its band gap of 3.2 eV.

4. Conclusion

Nanocomposite thin films formed by Au and anatase phase TiO₂ were grown by pulsed laser deposition on quartz substrates with the aid of a dual-laser, dual-target system. We investigated the influence of the laser irradiation parameters (e.g. laser fluence used for the irradiation of the Au targets) on the optical properties of Au–TiO₂ nanocomposites. There exists the possibility of the controlled tuning of the optical properties of the nanostructure systems in the near-UV and visible spectral regions: in the near-UV through continuous band gap narrowing as compared to the undoped TiO₂ thin films and in the visible spectral range the SPR peak position. These features promise a wide range of future applications, as photocatalysts, or solar energy converters.

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