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Local Annealing of Ag-TiO_2 Nanocomposite Films with Plasmonic Response by CW UV Laser Scanning †

Pavel Varlamov [1,*], Maksim Sergeev [1], Yaroslava Andreeva [1], Vladislav Gresko [1], Anton Loshachenko [2], Francis Vocanson [3] and Tatiana Itina [1,3]

[1] Faculty of Laser Photonics and Optoelectronics, ITMO University, 197101 Saint Petersburg, Russia; mmsergeev@itmo.ru (M.S.); andreeva.ym@itmo.ru (Y.A.); vrgresko@itmo.ru (V.G.); tatiana.itina@univ-st-etienne.fr (T.I.)
[2] St Petersburg University, 199034 Saint Petersburg, Russia; a.loshachenko@spbu.ru
[3] Laboratoire Hubert Curien, UMR CNRS 5516/UJM/Univ. Lyon, Bat. F, 18 rue du Pr. Benoit Lauras, 42000 Saint-Etienne, France; francis.vocanson@univ-st-etienne.fr
* Correspondence: p.v.varlamov@itmo.ru; Tel.: +7-931-008-07-23

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Abstract: Semiconductor sol-gel films containing plasmonic nanoparticles are increasingly used in wet analytics (μ-TAS systems) as functional substrates for SERS, as optical elements, photovoltaic and photocatalytic devices. A local change in the structure of such materials with predictable properties of the modified region opens up new possibilities for the creation of integrated circuits and multifunctional systems. Here we considered the mechanism of local modification of TiO_2 thin films structure containing plasmon nanoparticles as a result of laser annealing. The material processing was carried out by scanning with a CW semiconductor laser at a wavelength of 405 nm and at radiation intensity from 35 kW/cm^2 to 85 kW/cm^2. The modification region differed in optical characteristics and structural features from the original film. As a result of the laser processing, a heat source was formed that ensured the crystal nucleation and growth of brookite up to an intensity of 55.4 kW/cm^2. A subsequent increase in intensity led to the transformation of brookite into anatase. The crystal phase formation in the obtained track was accompanied by a change in the relief in its cross section and a decrease of the plasmon resonance peak. The density of the film in the modified region increased, which was accompanied by a decrease in its thickness by 20% from the original film thickness. The disappearance of plasmon resonance in the modified region contributed to a decrease in the absorption capacity and, as a consequence, to a sharp decrease in temperature at the central part of the heat source.

Keywords: nanocomposites; TiO_2 thin films; laser annealing; plasmon resonance; nanoparticles; phase transformation

1. Introduction

In the last decade, nanocomposite materials based on such transparent matrices as TiO_2, ZnO, Al doped ZnO with noble nanoparticles (NPs) have become particularly attractive in the emerging fields of photonics [1], catalysis [2,3], and security applications [4]. These materials have unique spectral characteristics because of surface plasmon resonance that have an influence on them.

A number of applications require a local change in optical properties and for this purpose laser irradiation is a good candidate. A laser beam forms a local heat source on the surface of the material, which can be used to carry out local annealing to achieve desired optical properties. However, the effect of laser irradiation parameters on the annealing result is still not fully understood.

In this work, we study the process of local annealing by CW UV laser irradiation of thin Ag-TiO_2 films. Using line-by-line scanning, squares were obtained at a constant scanning speed with different laser intensities. The change in the spectral characteristics depending on the regimes of laser processing is analyzed and the structures of the modified areas are investigated. A model describing a heat source, formed by the laser beam, is proposed, and estimates of the values of temperatures and duration of annealing depending on regimes of laser irradiation are given.

2. Materials and Methods

Mesoporous amorphous titania films used in the study produced with titanium tetraisopropoxide by sol-gel technique previously described in [5]. The thickness of the film deposited on a glass substrate was 180 ± 10 nm. Silver ions are introduced within the mesopority by soaking in an aqueous ammoniacal silver nitrate solution (5 M) for 90 min with a previous thermal treatment of the sample. After rinsing and drying, the sample is exposed to UV light for 10 min to initiate a growth of a high density of Ag NPs which leads to the absorption in range from 400 to 480 nm.

A CW UV semiconductor laser with a wavelength at 405 nm was used for laser annealing of Ag-TiO_2 samples. Double-mode irradiation of the laser was focused with the optical system to reach two elliptical spots in the beam with dimensions of 23 μm by 10 μm located at a distance 11.5 μm (Figure 1). The structure modification was carried out by scanning with the laser beam along a major semi-axis with the speed at 100 μm/s using a Thorlabs MTS50/M-Z8 motorized three-coordinate table.

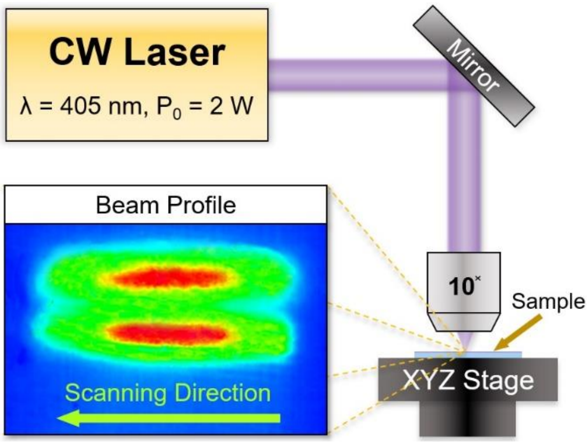


Figure 1. Experimental setup used for laser annealing of Ag-TiO_2 nanocomposite films.

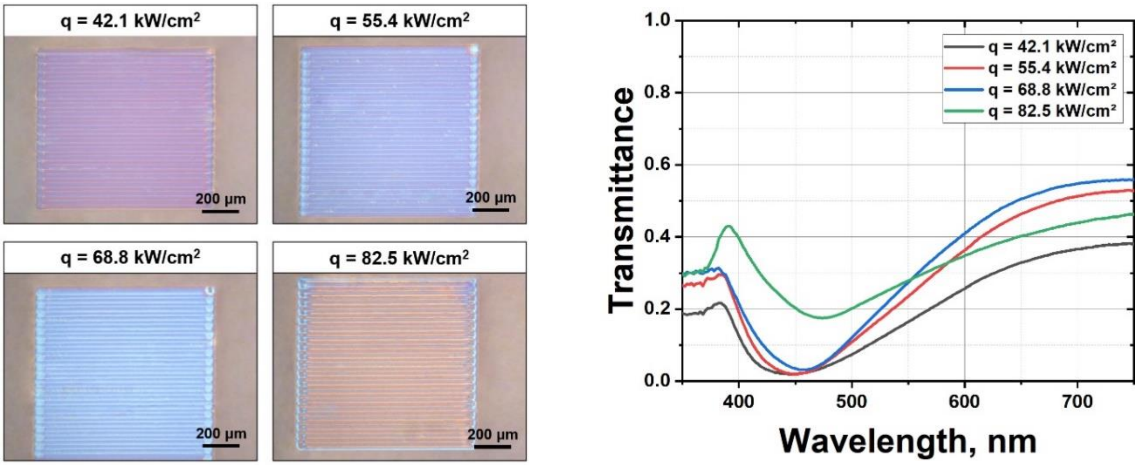
A visual analysis of the sample was applied using an optical microscope Carl Zeiss Axio Imager A1M (Germany). The microscope is equipped with objectives ranging up to 160× Spectral characteristics in the range of 300–900 nm after laser treatment were measured in circular areas of about 200 μm in diameter using an MSFU-K microscope-spectrophotometer (LOMO). To investigate the resulting structures on the nanoscale, a CrossBeam workstation Zeiss AURIGA as a scanning electron microscope (SEM) was used.

3. Results

The laser processing of the samples was accomplished by line-by-line scanning covering the squares with area of 700 × 700 μm^2. The distance between two lines was 20 μm, providing an overlap of laser tracks of 50 lines/mm. Intensity of the laser irradiation was in range from 35 to 85 kW/cm^2.

Figure 2a demonstrates the microphotographs of the squares obtained at four different intensities. One can see the change in color with the change of intensity. In particular, at the intensity of 42.1 kW/cm^2 color of the square visibly seems pink, and at 55.4 kW/cm^2 the obtained square turns to blue. The further increase of intensity up to 68.8 kW/cm² leads to formation of the square with stronger and brighter blue, and at the highest intensity of 82.5 kW/cm² the square seems more like the initial film.

To better understand the change of optical properties, the transmittance spectra were measured for considered squares. Figure 2b shows the presence of the minimum and its red-shift from 435 to 475 nm. It should be noted that the intensity of the minimum is slightly increased with increase of the intensity up to 68.8 kW/cm², but reaching the value of 82.5 kW/cm² leads to a distinguishable increase of the minimum intensity from 0.02 to 0.17.



(**a**) (**b**)

Figure 2. (**a**) Microphotographs of the squares obtained by the laser annealing in the range of 42.1–82.5 kW/cm²; (**b**) Transmittance spectra of the obtained squares.

The presence of a minimum in transmittance spectra of Ag-TiO_2 films in a range 400–500 nm is due to plasmon properties of Ag NPs. In our experiments, the laser annealing of the films activated the NPs formation which is demonstrated by SEM images (Figure 3). The concentration and size of NPs affects on the spectral characteristics. In particular, the more NPs are, the more red-shifted peak is, and the more concentration is, the less intensity is [6]. Hence, we conclude that the size of NPs was decreased accompanying concentration decreasing with intensity increase.

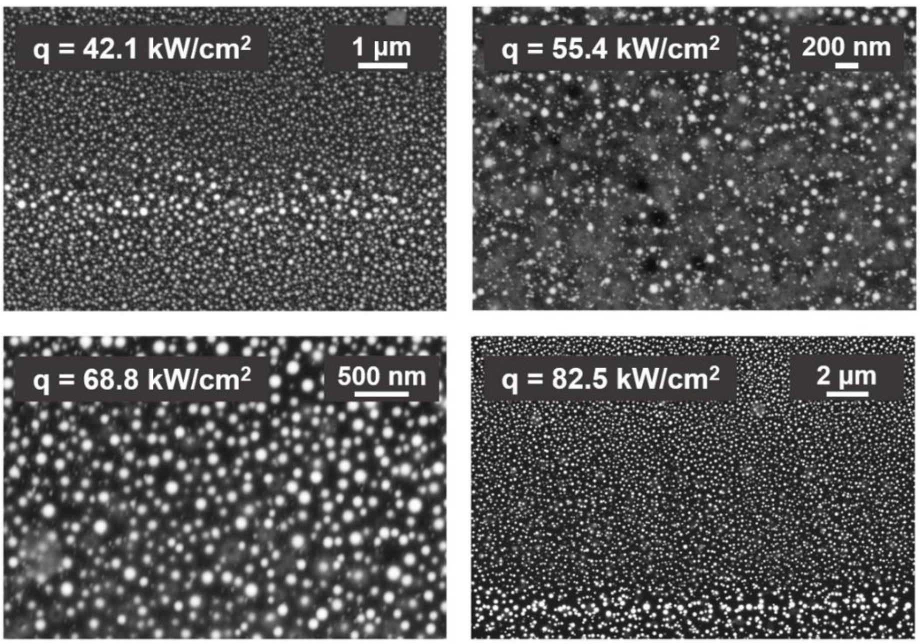


Figure 3. SEM-images of the squares obtained by the laser annealing in the range of 42.5–82.5 kW/cm².

As a result of exposure to laser irradiation, the surface of the material changes. Laser annealing causes compaction of Ag-TiO_2 films, which reduces its thickness by 10–20% compared to the thickness of the original film [4,7], that indicates structural changes in the matrix. Thus, local modification occurs not only due to the formation of NPs, but also due to a change in the structure of the film.

4. Discussion

The change in the optical characteristics is associated with both the formation of NPs and a change in the TiO_2 structure. Both of these processes occur when exposed to laser irradiation, which forms a heat source on the material surface. The characteristics of this source, in turn, are determined by the scanning speed and the intensity of the laser radiation.

To better understand the influence of the parameters of a heat source on optical characteristics, we propose to consider a model of a volume heat source moving at the constant speed. The temperature for such a source formed by double-mode beam is determined as follows:

$$T(x,y,z) = \frac{Q(z)}{2}\left\{\begin{array}{l}\int_0^t \left[dT_x(x,\tau)dT_y(y,\tau,\delta)dT_z(z,\tau)\tau\right]d\tau + \\ + \int_0^t \left[dT_x(x,\tau)dT_y(y,\tau,-\delta)dT_z(z,\tau)\tau\right]d\tau\end{array}\right\}, \quad (1)$$

where $t = R^{-1}(2ax_r r/\upsilon)^{0.5}$ is effective time of film heating, δ is a distance between two spots and $Q(z)$ is absorbed energy source from a single laser spot. To calculate $Q(z)$ we assumed that the absorptivity for of the film consisted of the absorption of the matrix and plasmon resonance from silver NPs, which disappears at a certain intensity or temperature. Calculations of temperatures along the axes were carried out using the Miamoto equations [8], that was extended for the case of a double-mode beam. Within the framework of this work, we present only the formula for calculating temperatures:

$$\begin{bmatrix} dT_x(x,\tau) \\ dT_y(y,\tau,\delta) \\ dT_z(z,\tau) \end{bmatrix} = \begin{bmatrix} erfc\left(\frac{x-x_r r}{x_r R\tau} + \frac{\upsilon R}{4a}\tau\right) - erfc\left(\frac{x+x_r r}{x_r R\tau} + \frac{\upsilon R}{4a}\tau\right) \\ erfc\left(\frac{y-y_r r-\delta}{y_r R\tau}\right) - erfc\left(\frac{y+y_r r-\delta}{y_r R\tau}\right) \\ erfc\left(\frac{z-l_f}{z_r R\tau}\right) - erfc\left(\frac{z-l_f}{z_r R\tau}\right) \end{bmatrix}, \quad (2)$$

where υ = 100 μm/s is the scanning velocity, τ is variable on time, $z_r = l_f/(r^2 l_f)^{1/3}$ is the coefficient of heat source size on the Z coordinate; r is the average radius, x_r and y_r are the proportionality coefficients for the X and Y coordinates; l_f is the film half-thickness. The thermal diffusivity a takes into account heat outflow from the irradiated regions was into air and substrate.

Results of the temperature calculations are presented on Figure 4. One can see that the temperature for intensity of 42.1 kW/cm^2 is in range from 200 to 400 °C along the X and Y axes. Upon reaching these temperatures, crystallization of amorphous titanium dioxide into brookite occurs [9], and the process of formation of NPs is activated. Above 55.4 kW/cm^2, a temperature of 400 °C is reached, which leads to the formation of anatase from brookite [9]. The NPs formation continues due to diffuse growth, that results in a shift in transmission peaks and an increase in their intensity. It should be noted that as the intensity of the temperature distribution increases, it becomes more complex due to the complication of the absorptivity when higher temperatures are reached.

Another important parameter that characterize laser annealing is time duration of annealing. This parameter can be calculated as ratio size of the heat source at the certain temperature along axis to scanning speed of laser. For example, we cross the temperature distribution for X axis at 200 °C and find the cross-section size. At the intensity of 42.1 kW/cm^2 the size is around 48 μm. The ratio of the size to the scanning speed (υ = 100 μm/s) is 48 ms, which is the desired time duration of the annealing. For 200 °C the annealing time increases from 48 to 81.5 ms in the intensity range 42.1–82.5 kW/cm^2 respectively. The temperature does not reach 400 °C at 42.1 kW/cm^2, so the time duration changes from 0 up to 32 ms at 400 °C.

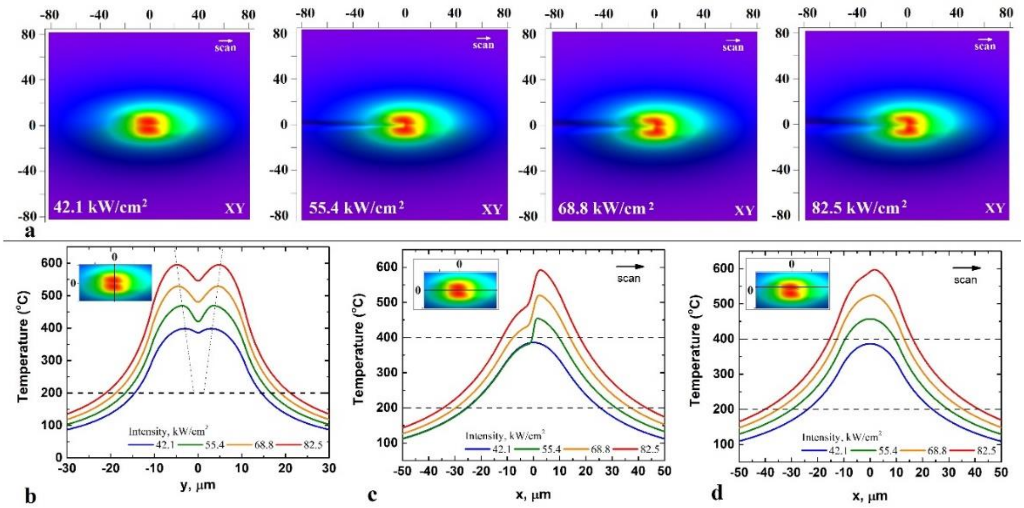


Figure 4. (**a**) Temperature distribution of the laser heat source on the film surface for different laser intensities; (**b**) Temperature profiles for different intensities in the middle of the laser heat source and along the Y axis; (**c**) Temperature profiles for different intensities in the middle of the laser heat source and along the X axis; (**d**) Temperature profiles for different intensities in the middle of one spot and along the X axis.

5. Conclusions

As a result of the work, the process of local annealing of Ag-TiO_2 thin films by CW UV laser radiation has been considered.

The result of the structure modification was a change in the optical characteristics of the material, which manifested itself in the appearance and change of color. Squares with a size of 700 × 700 μm^2 were recorded by line-by-line scanning, that changed their optical properties depending on the intensity of the laser irradiation. As a result, it was shown that an increase in the intensity from 45.1 kW/cm^2 to 82.5 kW/cm^2 led to a change in the spectral transmittance in the region of the plasmon resonance peak from 435 nm to 475 nm. It is shown that a change in the optical characteristics in the plasmon peak region is associated with a change in the size and concentration of NPs in the film, as well as with structural changes in the material.

To describe a heat source formed by laser radiation, a thermophysical model of a volume source moving at a constant velocity was proposed. The range of temperatures and duration of annealing were estimated taking into account the intensity of laser irradiation and scanning speed. As a result of the simulation, it was shown that when the intensity was increased from 45.1 kW/cm^2 to 82.5 kW/cm^2, the maximum temperature in the irradiated zone changed from 390 °C to 600 °C. The thermal annealing time at 400 °C in this temperature range varies up to 32 ms.

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