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Local Annealing of Ag-TiO₂ Nanocomposite Films with Plasmonic Response by CW UV Laser Scanning [†]

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Abstract: Semiconductor sol–gel films containing plasmonic nanoparticles are being increasingly used in wet analytics (μ -TAS systems) as functional substrates for surface enhanced Raman spectroscopy (SERS), as optical elements, and as 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 TiO₂ thin films structure containing plasmon nanoparticles as a result of laser annealing. The material processing was carried out by scanning with a continuous wave (CW) semiconductor laser at a wavelength of 405 nm and at radiation intensity from 35 to 85 kW/cm². 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/cm². 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 in 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; TiO₂ thin films; laser annealing; plasmon resonance; nanoparticles; phase transformation

1. Introduction

In the last decade, nanocomposite materials based on such transparent matrices as TiO₂, ZnO, and 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 the surface plasmon resonance that influences 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-TiO₂ films. The square fields of interest were obtained by a constant speed line-by-line scanning and different laser intensities for each one. The change in the spectral characteristics depending on the regimes of laser processing was analyzed, and the structures of the modified areas 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 the regimes of laser irradiation are given.

2. Materials and Methods

The mesoporous amorphous titania films used in this study were produced with titanium tetraisopropoxide by the sol-gel technique as previously described in [5]. The thickness of the film deposited on a glass substrate was 180 ± 10 nm. Silver ions are introduced within the mesoporosity by soaking in an aqueous ammoniacal silver nitrate solution (5 M) for 90 min with prior 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 optical absorption of the structure 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-TiO₂ samples. Double-mode irradiation of the laser was focused with the optical system to reach two elliptical spots in the beam with dimensions of $23 \mu\text{m}$ by $10 \mu\text{m}$ located at a distance $11.5 \mu\text{m}$ (Figure 1). The structure modification was carried out by scanning with the laser beam along a major semi-axis with the speed at $100 \mu\text{m/s}$ using a Thorlabs MTS50/M-Z8 motorized three-coordinate table.

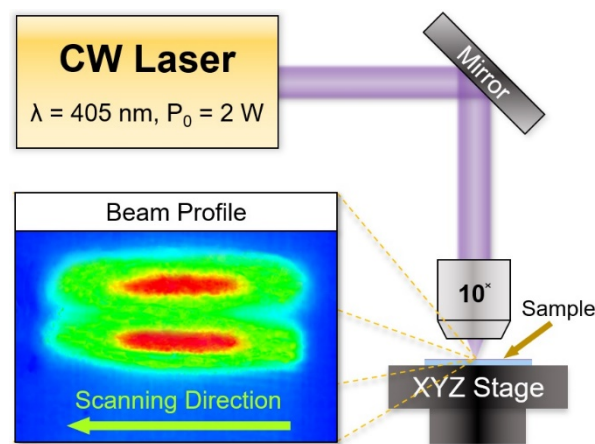


Figure 1. Experimental setup used for laser annealing of Ag-TiO₂ nanocomposite films.

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 $160\times$. Spectral characteristics in the range of 300–900 nm after laser treatment were measured in circular areas of about $200 \mu\text{m}$ in diameter using an MSFU-K microscope spectrophotometer (LOMO). To investigate the resulting structures on the nanoscale, a scanning electron microscope (SEM) of CrossBeam workstation Zeiss AURIGA was used.

3. Results

The laser processing of the samples was accomplished by line-by-line scanning covering the squares with area of $700 \times 700 \mu\text{m}^2$. The distance between two lines was $20 \mu\text{m}$, providing an overlap of laser tracks of 50 lines/mm. The intensity of 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/cm², the color of the square visibly seems pink, and at 55.4 kW/cm², 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 redshift from 435 to 475 nm. It should be noted that the intensity in the minimum is slightly increased with an increase in intensity up to 68.8 kW/cm², but reaching the value of 82.5 kW/cm² leads to a distinguishable increase in the minimum intensity from 0.02 to 0.17.

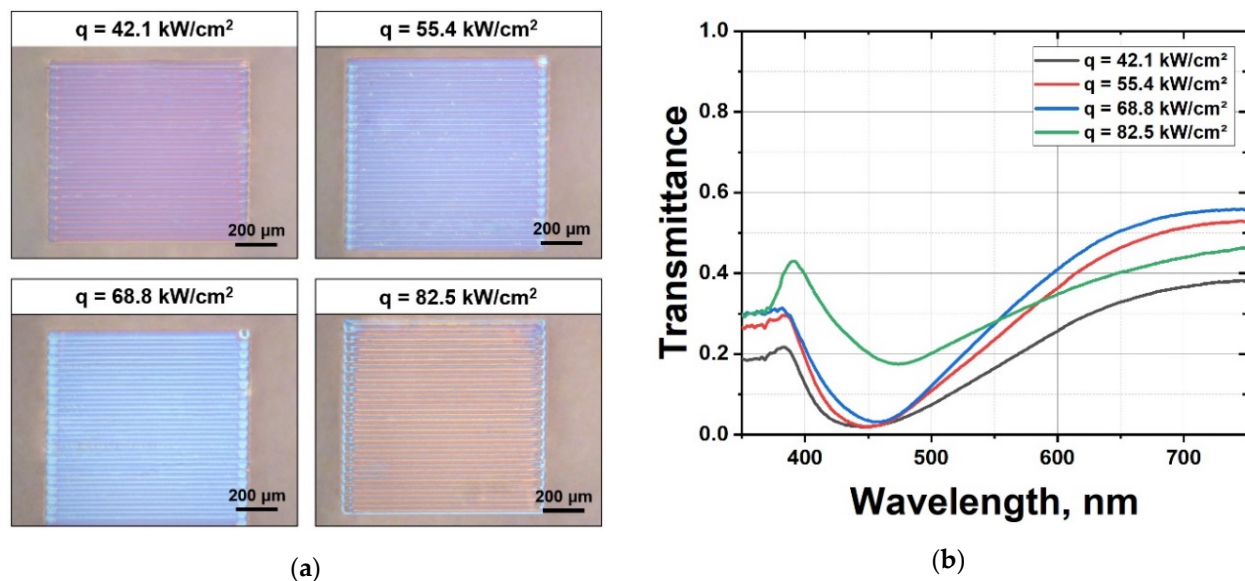


Figure 2. (a) Microphotographs of the squares obtained by the laser annealing in the range of 42.1–82.5 kW/cm². (b) Transmittance spectra of the obtained squares.

The presence of a minimum in transmittance spectra of Ag-TiO₂ films in the 400–500 nm range is due to the plasmon properties of Ag NPs. In our experiments, the laser annealing of the films activated NPs formation, which is demonstrated in the SEM images (Figure 3). The concentration and size of NPs affect the spectral characteristics. In particular, the more NPs there are, the more redshifted the peak is, and the higher the concentration is, the lower the intensity is [6]. Hence, we conclude that the size of NPs was decreased accompanying the concentration decrease as the intensity increased.

As a result of exposure to laser irradiation, the surface of the material changes. Laser annealing causes compaction of Ag-TiO₂ films, which reduces its thickness by 10–20% compared to the thickness of the original film [4,7], which 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.

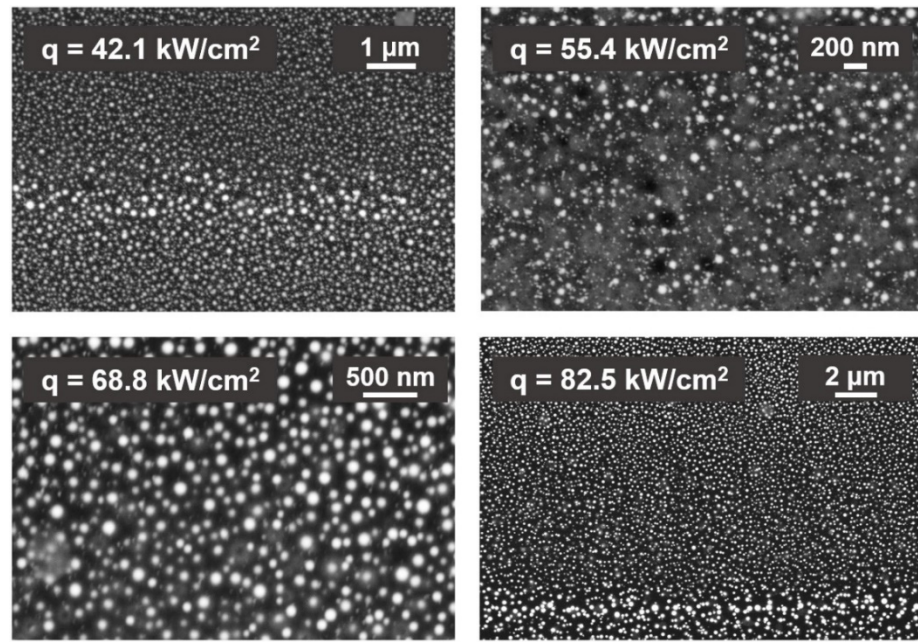


Figure 3. SEM images of the squares obtained by laser annealing in the range of 42.5–82.5 kW/cm².

4. Discussion

The change in optical characteristics is associated with both the formation of NPs and the change in TiO₂ 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 intensity of laser radiation.

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

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

where $t = R^{-1}(2ax_r r/v)^{0.5}$ is the effective time of film heating, δ is the distance between two spots, and $Q(z)$ is the absorbed energy source from a single laser spot. To calculate $Q(z)$, we assumed that the absorptivity 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 Miamoto equations [8] that were extended for the case of a double-mode beam. Within the framework of this work, we present only the formula for calculating temperatures:

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

where $v = 100 \mu\text{m/s}$ is the scanning velocity, τ is the time-dependent variable, $z_r = l_f/(r^2 l_f)^{1/3}$ 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, and l_f is the film half-thickness. The thermal diffusivity a takes into account heat outflow from the irradiated regions 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/cm² 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]. NP 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 characterizes laser annealing is the duration time of annealing. This parameter can be calculated for certain temperature as the ratio of the heating source size and the laser scanning speed of laser. For example, we cross the temperature distribution for the X axis at 200°C and find the cross-section size. At the intensity of 42.1 kW/cm^2 , the size is around $48 \mu\text{m}$. The ratio of the size to the scanning speed ($v = 100 \mu\text{m/s}$) is 48 ms, which is the desired duration time of annealing. For 200°C the annealing time increases from 48 to 81.5 ms in the intensity range $42.1\text{--}82.5 \text{ kW/cm}^2$, respectively. The temperature does not reach 400°C at 42.1 kW/cm^2 , so the duration time changes from 0 up to 32 ms at 400°C .

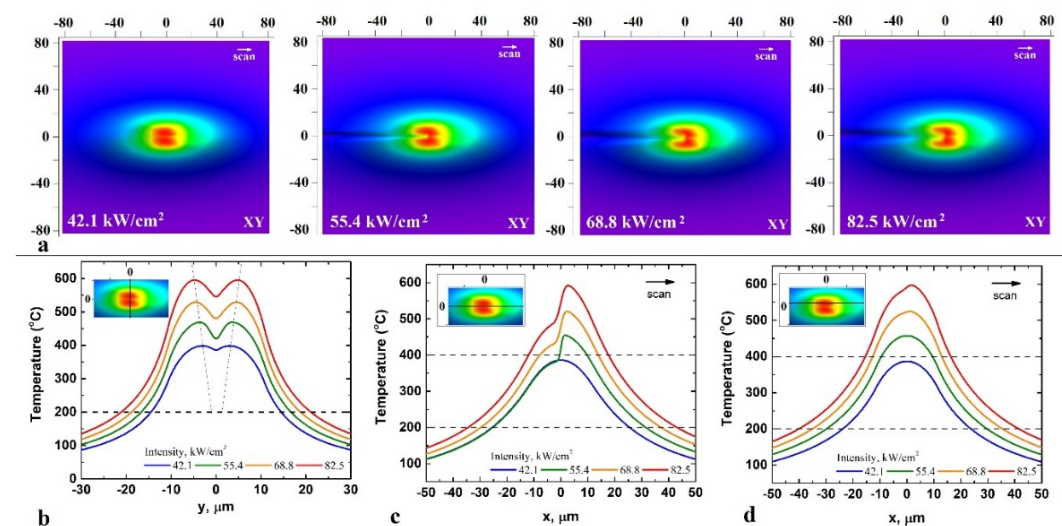


Figure 4. (a) Temperature distribution of the laser heat source on the film surface for different laser intensities. (b) Temperature profiles for different intensities in the middle of the laser heat source and along the Y axis. (c) Temperature profiles for different intensities in the middle of the 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-TiO₂ 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 $700 \times 700 \mu\text{m}^2$ were recorded by line-by-line scanning, which 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 to 82.5 kW/cm^2 led to a change in the spectral transmittance in the region of the plasmon resonance peak from 435 to 475 nm. It was 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.

diation and scanning speed. As a result of the simulation, it was shown that when the intensity was increased from 45.1 to 82.5 kW/cm², the maximum temperature in the irradiated zone changed from 390 to 600 °C. The thermal annealing time at 400 °C in this temperature range varies up to 32 ms.

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References

1. Avayu, O.; Almeida, E.; Prior, Y.; Ellenbogen, T. Composite functional metasurfaces for multispectral achromatic optics. *Nat. Commun.* **2017**, *8*, 14992, doi:10.1038/ncomms14992.
2. Wang, Y.; Yan, C.; Li, C.; Lu, Z.; Ma, C.; Yan, Y.; Zhang, Y. Charge Transfer Tuned by the Surrounding Dielectrics in TiO₂-Ag Composite Arrays. *Nanomaterials* **2018**, *8*, 1019, doi:10.3390/nano8121019.
3. Chibac-Scutaru, A.L.; Podasca, V.; Timpu, D.; Melinte, V. Comparative Study on the Influence of Noble Metal Nanoparticles (Ag, Au, Pd) on the Photocatalytic Activity of ZnO NPs Embedded in Renewable Castor Oil Polymer Matrices. *Materials* **2020**, *13*, 3468, doi:10.3390/ma13163468.
4. Sharma, N.; Vangheluwe, M.; Vocanson, F.; Cazier, A.; Bugnet, M.; Reynaud, S.; Vermeulin, A.; Destouches, N. Laser-driven plasmonic gratings for hiding multiple images. *Mater. Horizons* **2019**, *6*, 978–983, doi:10.1039/c9mh00017h.
5. Nadar, L.; Sayah, R.; Vocanson, F.; Crespo-Monteiro, N.; Boukenter, A.; Joao, S.S.; Destouches, N. Influence of reduction processes on the colour and photochromism of amorphous mesoporous TiO₂ thin films loaded with a silver salt. *Photochem. Photobiol. Sci.* **2011**, *10*, 1810, doi:10.1039/c1pp05172e.
6. Garcia, M.A. Surface plasmons in metallic nanoparticles: Fundamentals and applications. *J. Phys. D: Appl. Phys.* **2011**, *44*, 283001, doi:10.1088/0022-3727/44/28/283001.
7. Liu, Z.; Siegel, J.; Garcia-Lechuga, M.; Epicier, T.; Lefkir, Y.; Reynaud, S.; Bugnet, M.; Vocanson, F.; Solis, J.; Vitrant, G.; et al. Three-Dimensional Self-Organization in Nanocomposite Layered Systems by Ultrafast Laser Pulses. *ACS Nano* **2017**, *11*, 5031–5040, doi:10.1021/acsnano.7b01748.
8. Miyamoto, I. Local Melting of Glass Material and Its Application to Direct Fusion Welding by Ps-laser Pulses. *J. Laser Micro/Nanoeng.* **2007**, *2*, 7–14, doi:10.2961/jlmn.2007.01.0002.
9. Shul'Ga, Y.M.; Kabachkov, E.N.; Matyushenko, D.V.; Kurkin, E.N.; Domashnev, I.A. Thermally stimulated transformations in brookite-containing TiO₂ nanopowders produced by the hydrolysis of TiCl₄. *Tech. Phys.* **2011**, *56*, 97–101, doi:10.1134/s1063784211010233.