

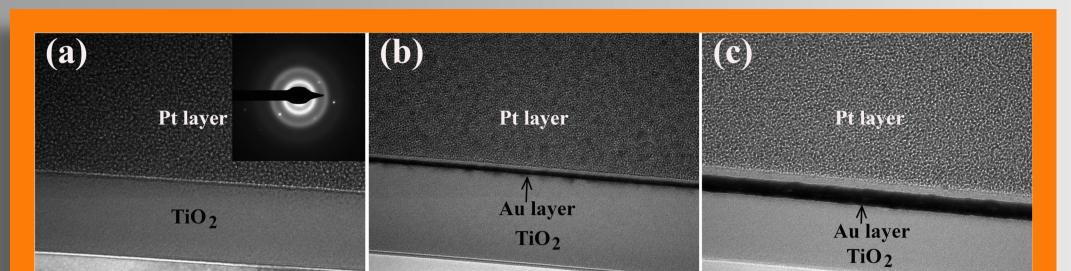
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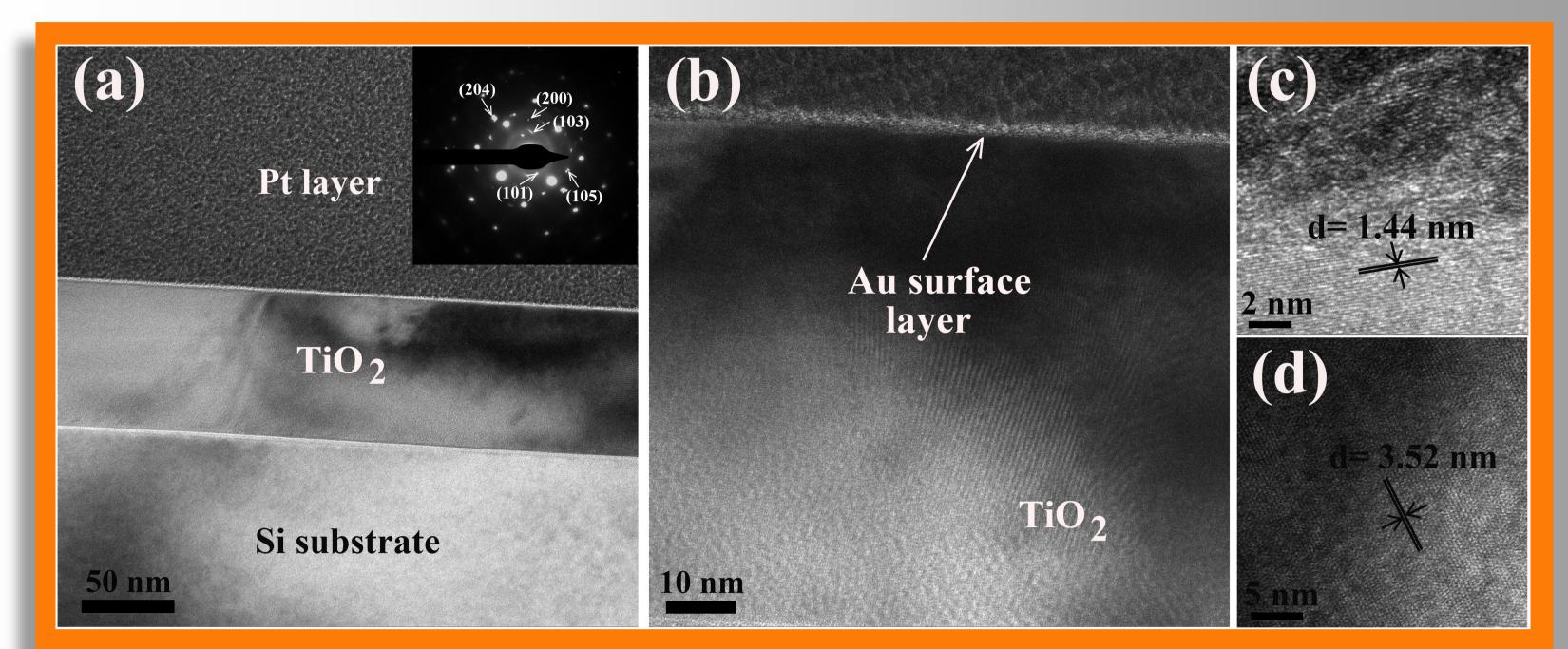
## Influencing on optical properties of buffered TiO<sub>2</sub>-Au thin film systems by deposition and annealing parameters

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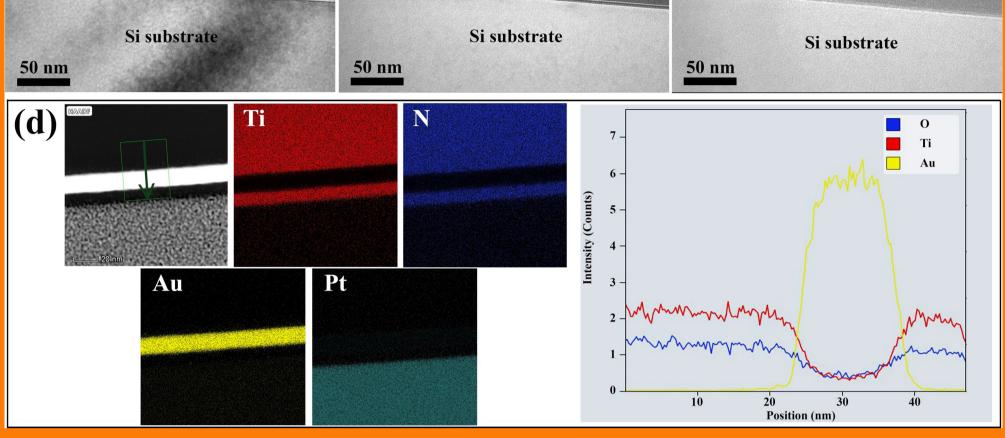
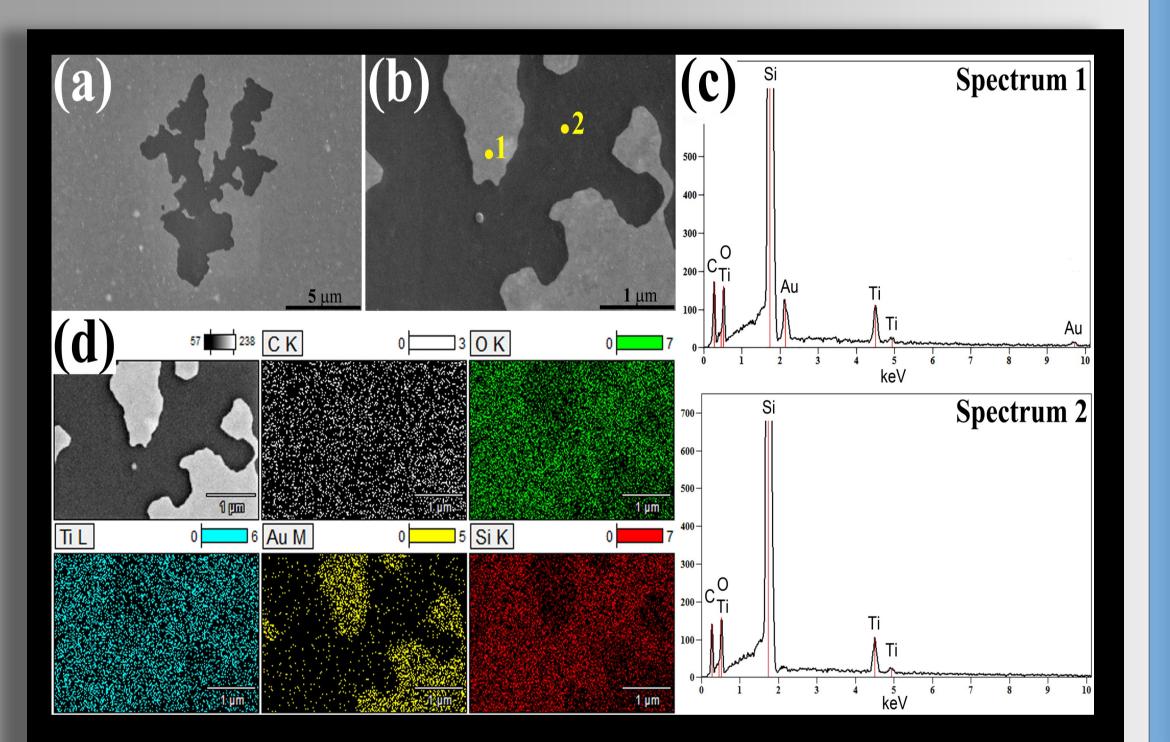


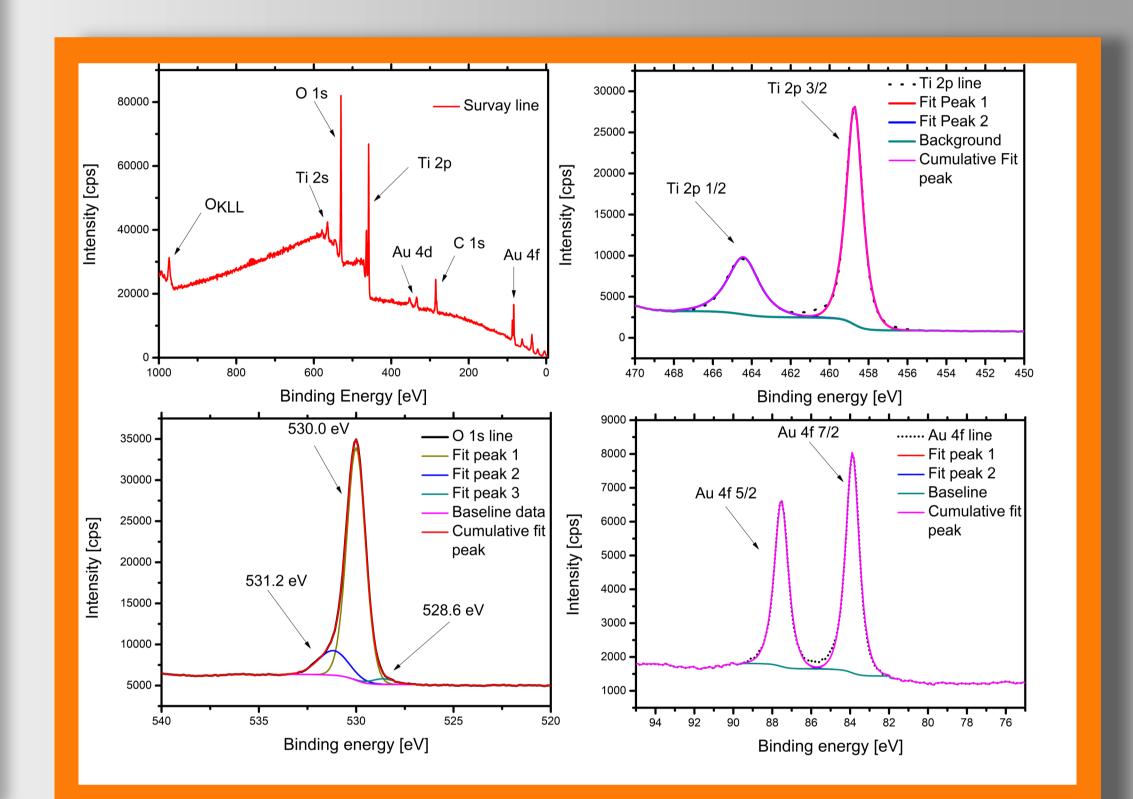
Fig. 1. Low magnification cross-sectional TEM bright-field micrographs of pure TiO<sub>2</sub> thin film with corresponding electron diffraction pattern in the inset (a) and TiO<sub>2</sub> systems with Au buffer layers thicknesses of 5 nm (b) and 15 nm (c), also presenting Si substrate and Pt protective layers at the top of the samples. (d) STEM-HAADF image of TiO<sub>2</sub>-Au sample with the 15 nm thick buffer layer with corresponding EDS maps highlighting the Ti, O, Au and Pt elements (left side) and elemental line profiles taken along the green line as indicated in HAADF image (right side).



## INTRODUCTION

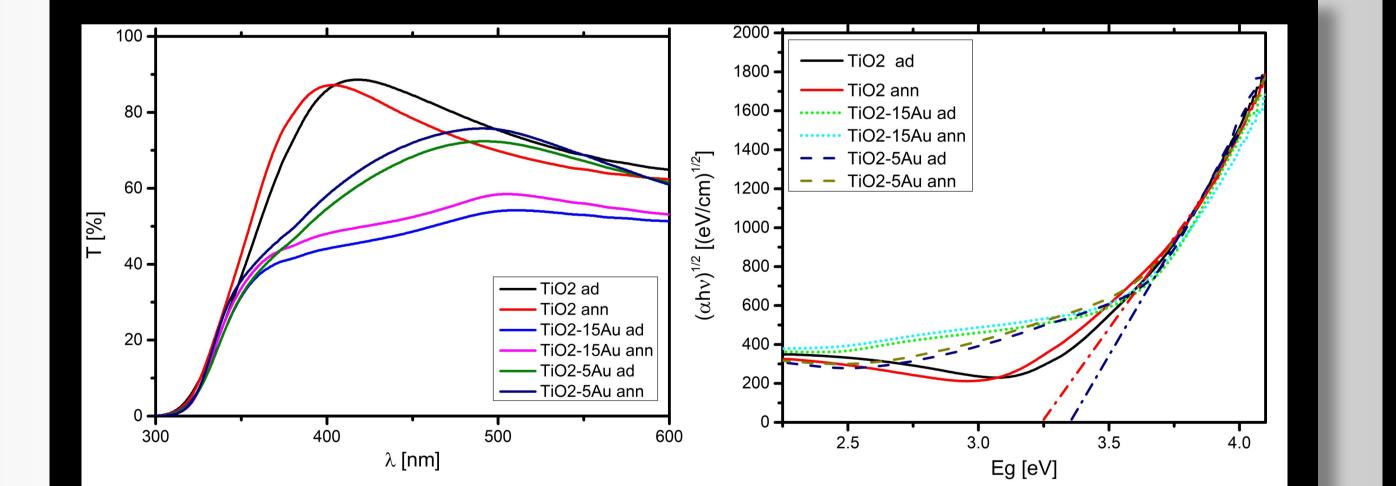
TiO<sub>2</sub> and TiO<sub>2</sub>:Au thin films were obtained by DC magnetron sputtering of Ti target with Ar ions in O<sub>2</sub> atmosphere. Three different systems were deposited for comparison, with different thickness of buffered Au layer. Post deposition annealing for 3h on 400 °C was carried out in nitrogen atmosphere. For structural analyses XRD, XPS, TEM and SEM methods were used, while for optical characterization UV/Vis method was used. The photo-degradation rate was measured using Rhodamine B which simulated pollutant. Post deposition annealing caused diffusion of Au atoms through the layer toward the surface. Structural characterization showed that deposited films have good stoichiometry of TiO<sub>2</sub> in anatase phase and that concentration of Au on the surface can be controlled by sputtering and annealing conditions. By controlling Au concentration on the surface, we can influence on optical properties of deposited TiO<sub>2</sub> thin films.

Fig. 2. TEM analysis of TiO<sub>2</sub>-Au sample with the 15 nm thick buffer layer, after annealing for 3 hours at 400 °C: (a) low magnification bright-field TEM micrograph of the sample presenting TiO<sub>2</sub> layer, Si substrate and Pt protective layer, with SAED pattern given in the inset; (b) high magnification bright-field TEM micrograph of the near-surface region showing a clearly visible interface layer at the sample surface; (c) and (d) HRTEM micrographs of the surface layer and TiO2 layer, respectively, with the measured d-spacings.



FESEM-EDS characterization of TiO2-Au 15 AN sample Fig. 3. surface: (a) and (b) micrographs recorded at different magnifications (10 000 and 50 000 time, respectively); (c) EDS spectra obtained at two different points indicated with yellow dots in image b; (d) corresponding elemental mapping from the whole area shown in FESEM image.

(a)3 µm **Fig. 5.** XPS analysis of TiO<sub>2</sub>-Au 15 sample: (a) survey spectrum; (b) Ti  $2p_{3/2}$  and  $2p_{1/2}$  lines; (c)  $O_{1s}$  line and (d) Au  $4f_{5/2}$  and  $4f_{7/2}$  lines.





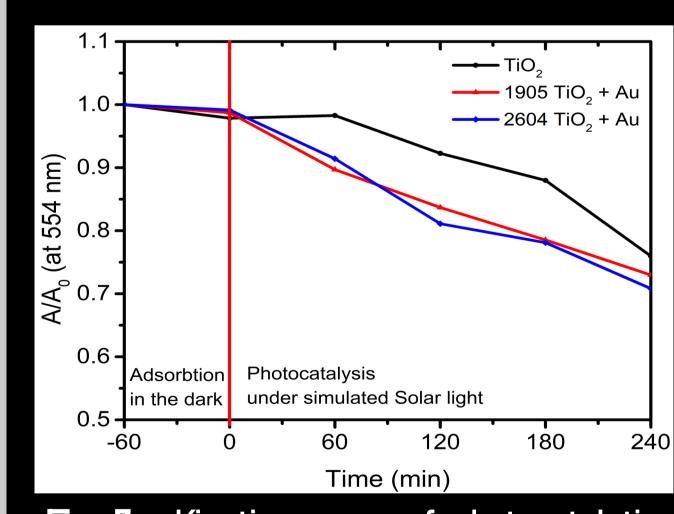


Fig. 4. FESEM topography micrographs of (a) as-deposited TiO<sub>2</sub> thin film and annealed buffered TiO<sub>2</sub>-Au system with: (b) 5 nm and (c) 15 nm thick Au layer.

**Fig. 6.** Transmittance spectra for deposited TiO<sub>2</sub> and TiO<sub>2</sub>-Au thin films and Tauc's plot for determination of energy gap values.

## Fig. 7. Kinetic curves of photocatalytic degradation of Rhodamine B on TiO<sub>2</sub> and TiO<sub>2</sub>-Au samples.

## CONCLUSION

- \* Au buffered TiO<sub>2</sub> thin films were successfully produced by DC sputtering method with Au layers of different thickness placed 5 nm and 10 nm below top  $TiO_2$  layer.
- \* Annealing of thin films induced migration and diffusion of Au atoms into the layer and toward the surface.
- By controlling sputtering deposition parameters, annealing temperature and time of annealing we can produce TiO<sub>2</sub> thin films with desired concentration of Au on the surface, changing its optical properties.
- Photocatalytic properties of TiO<sub>2</sub>-Au thin films were improved compared to pure TiO<sub>2</sub>.
- \* Samples that were subject to additional thermal treatment in a nitrogen atmosphere reduced the values of the contact angle towards both water and organic liquid.

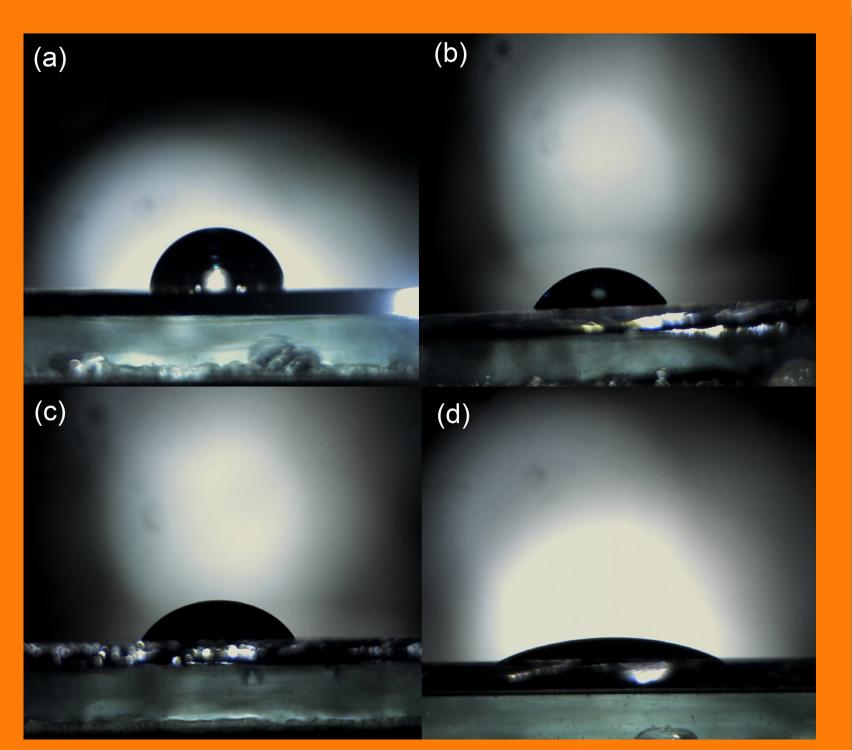


Fig. 8. Side view photographs of water (a and b) and diiodomethane (c and d) droplets on the surface of TiO<sub>2</sub> and TiO<sub>2</sub>-Au 5 samples, before and after annealing, respectively.