Semiconductor Physics.
Physics of nanostructures

UDC 538.9 + 539.8

EDN RRDAEF
https://www.doi.org/10.33910/2687-153X-2023-4-4-195-202

Peculiarities of the structure and optical properties of amorphous semiconductor plasmon nanocomposites TiO_2<Ag>, prepared by ion plasma co-sputtering

K. Dauithan[1], O. Yu. Prikhodko[1], S. L. Peshaya✉[1], Y. S. Mukhametkarimov[1], S. A. Kozyukhin[2], S. Ya. Maksimova[1], G. A. Ismaylova[1]

[1] NAO al-Farabi Kazakh National University, 71 al-Farabi Ave., Almaty 050040, Kazakhstan
[2] N.S. Kurnakov Institute of General and Inorganic Chemistry of RAS, 31 Leninsky Ave., Moscow 119991, Russia

Authors

Kuanyshbek Dauithan, e-mail: dkuansh@mail.ru

Oleg Yu. Prikhodko, ORCID: 0000-0002-7506-2762, e-mail: prikhodko_o@mail.ru

Svetlana L. Peshaya, ORCID: 0000-0002-1814-7567, e-mail: skysvetik91@mail.ru

Yerzhan S. Mukhametkarimov, ORCID: 0000-0003-1381-4532, e-mail: m.c.erzhan@mail.ru

Sergey A. Kozyukhin, ORCID: 0000-0002-7405-551X, e-mail: kozyukhin59@bk.ru

Suyumbika Ya. Maksimova, ORCID: 0000-0001-7759-0326, e-mail: mak.son.21@mail.ru

Guzal A. Ismaylova, ORCID: 0000-0002-1813-2031, e-mail: guzal_a81@mail.ru

For citation: Dauithan, K., Prikhodko, O. Yu., Peshaya, S. L., Mukhametkarimov, Y. S., Kozyukhin, S. A., Maksimova, S. Ya., Ismaylova, G. A. (2023) Peculiarities of the structure and optical properties of amorphous semiconductor plasmon nanocomposites TiO_2<Ag>, prepared by ion plasma co-sputtering. *Physics of Complex Systems*, 4 (4), 195–202. https://www.doi.org/10.33910/2687-153X-2023-4-4-195-202 EDN RRDAEF

Received 28 June 2023; reviewed 20 September 2023; accepted 20 September 2023.

Funding: This study was supported by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP09258922).

Abstract. Structure and optical properties of amorphous semiconductor nanocomposite TiO_2<Ag> films prepared by ion-plasma RF magnetron co-sputtering of a TiO_2 and Ag target only in the argon atmosphere are studied. Matrix of TiO_2<Ag> films is amorphous with inclusions of isolated 3–4 nm sized silver nanoparticles. The optical transmission spectra have a sharp edge of fundamental absorption band at ~ 300 nm, which is formed by direct and indirect allowed optical transitions. The band gap of the TiO_2<Ag> films increases with the Ag concentration due to some ordering of the matrix. The absorption band is observed in the visible region of the spectrum due to the effect of local surface plasmon resonance absorption (LSPR) on silver nanoparticles. The LSPR intensity increases with the silver concentration, and the maximum of the absorption band, depending on the Ag concentration, is located in the region from 455 to 488 nm.

Keywords: ion-plasma sputtering, amorphous plasmon semiconductor nanocomposites TiO_2<Ag>, silver nanoparticles, structure, optical properties, surface plasmon resonance absorption

Introduction

Titanium dioxide films (TiO_2), a polymorphic wide-gap semiconductor material (anatase, rutile, brookite), are widely used in various fields: from biomedicine to solar energy (Banerjee et al. 2015; Cao et al. 2016; Ghann et al. 2016; Kulkarni et al. 2015; Pakdel et al. 2013). This is due to the generation of high-energy electrons in TiO_2 under the action of near-UV radiation. In recent years, many studies have been aimed to expand of the functional properties of these films by embedding elements of different chemical nature and creating composites on their basis. Special attention is paid to composite films based

on TiO_2 with inclusions of isolated nanoparticles of noble metals such as Ag and Au (Prakash et al. 2016; Wodka et al. 2010; Yu et al. 2017; Zhao et al. 1996). In such wide-gap semiconductor nanocomposite TiO_2<Ag> and TiO_2<Au> films, an absorption band is observed in the visible region of the spectrum due to local surface plasmon resonance (LSPR) on metal nanoparticles. Such films are of significant interest for the physics of plasmon phenomena and have important applied significance, in particular, for improving the photocatalytic and optical properties of TiO_2 films (Bueno-Alejo et al. 2017).

The semiconductor composite TiO_2 films with inclusions of Ag and Au nanoparticles are obtained by various chemical and physical methods. For example, the sol-gel method, PLD, photoreduction treatment, ion doping and magnetron ion-plasma DC/RF co-sputtering (Ghidelli et al. 2020; Navabpour et al. 2014; Ozimek et al. 2016; Pan, Heagy 2019; Usha et al. 2016; Yuan et al. 2017; Zada et al. 2017). Ion-plasma RF magnetron co-sputtering has a number of advantages over other methods. This is due to the possibility of obtaining continuous and homogeneous composite films and the possibility to be well integrated into the planar technology of electronic device manufacturing (Prikhodko et al. 2014). However, in the technology of obtaining TiO_2 films with isolated Ag and Au nanoparticles and with the LSPR effect, the sputtering is carried out in the atmosphere of a mixture of inert gas argon with oxygen and with the obligatory subsequent thermal treatment of the films in air or in the argon and hydrogen mixture (Rodrigues et al. 2018; Torrell et al. 2011), which ultimately complicates the technology of their production.

In this work, we show the possibility of obtaining amorphous semiconductor nanocomposite films TiO_2<Ag> with a brightly pronounced LSPR effect, i. e. plasmon nanocomposites, synthesized by ion-plasma radio-frequency (RF) magnetron co-sputtering only in argon atmosphere, and the peculiarities of their structure and optical properties are studied.

Experimental Technique

Thin nanocomposite TiO_2<Ag> films were obtained by ion-plasma RF (13.56 MHz) magnetron sputtering of a combined TiO_2 and Ag target in an argon atmosphere (99.998%) at a pressure ~ 0.5 Pa. A preliminary high vacuum (~ 10^{-4} Pa) was created by oil-free forevacuum (BocEdwards XDS10) and turbomolecular (BB-150) pumps. The films were deposited on KU-1 fused silica substrates, fresh cleavages of NaCl and KBr crystals, and single-crystal silicon (c-Si) plates that were kept at room temperature. The technological parameters of the sputtering were selected so as to obtain an amorphous TiO_2 matrix with inclusions of isolated silver nanoparticles.

The elemental composition and morphology of the films were monitored by energy dispersive analysis (EDX) using a Quanta 3D 200i SEM with an EDAX. The thickness of the films was measured by scanning a cleavage of the c-Si/TiO_2 and c-Si/TiO_2<Ag> sandwich structures on SEM and ranged from 40 to 50 nm. For these measurements, the films were deposited on c-Si substrates cleaned from the SiO_2 oxide layer. It was found that the composition of TiO_2 films is close to stoichiometric, and the Ag concentration in TiO_2<Ag> films reaches 9.0 at. %.

The structure of TiO_2 and TiO_2<Ag> films was studied by transmission electron microscopy (TEM JEM 2100 JEOL). The optical properties (transmission $T = f(\lambda)$ and reflection spectra $R = f(\lambda)$) of films deposited on quartz substrates were studied on a Shimadzu UV2000 spectrophotometer in the spectral range from 250 to 1100 nm with the recording step—1 nm.

Results and discussion

The structure of TiO_2 and TiO_2<Ag> films

Fig. 1 a-e shows typical TEM images and selected area electron diffraction (SAED) patterns of TiO_2 and TiO_2<Ag> films with silver concentration 9.0 at. %. Figs. 1 b and d show typical SAED patterns of TiO_2 films and the matrix of the TiO_2<Ag> film. The SAED of TiO_2 film (Fig. 1 b) and matrix of the film TiO_2<Ag> (Fig. 1 d) are characterized by a diffuse halo, which is indicative of their amorphous structure. However, in the matrix of TiO_2<Ag> films, the diffuse halo is less blurred, so its structure is more ordered. The decoding of SAED ring reflections (Figs. 1 d and e) is performed using the CrysTBox program (Klinger, Jäger 2015).

 https://www.doi.org/10.33910/2687-153X-2023-4-4-195-202

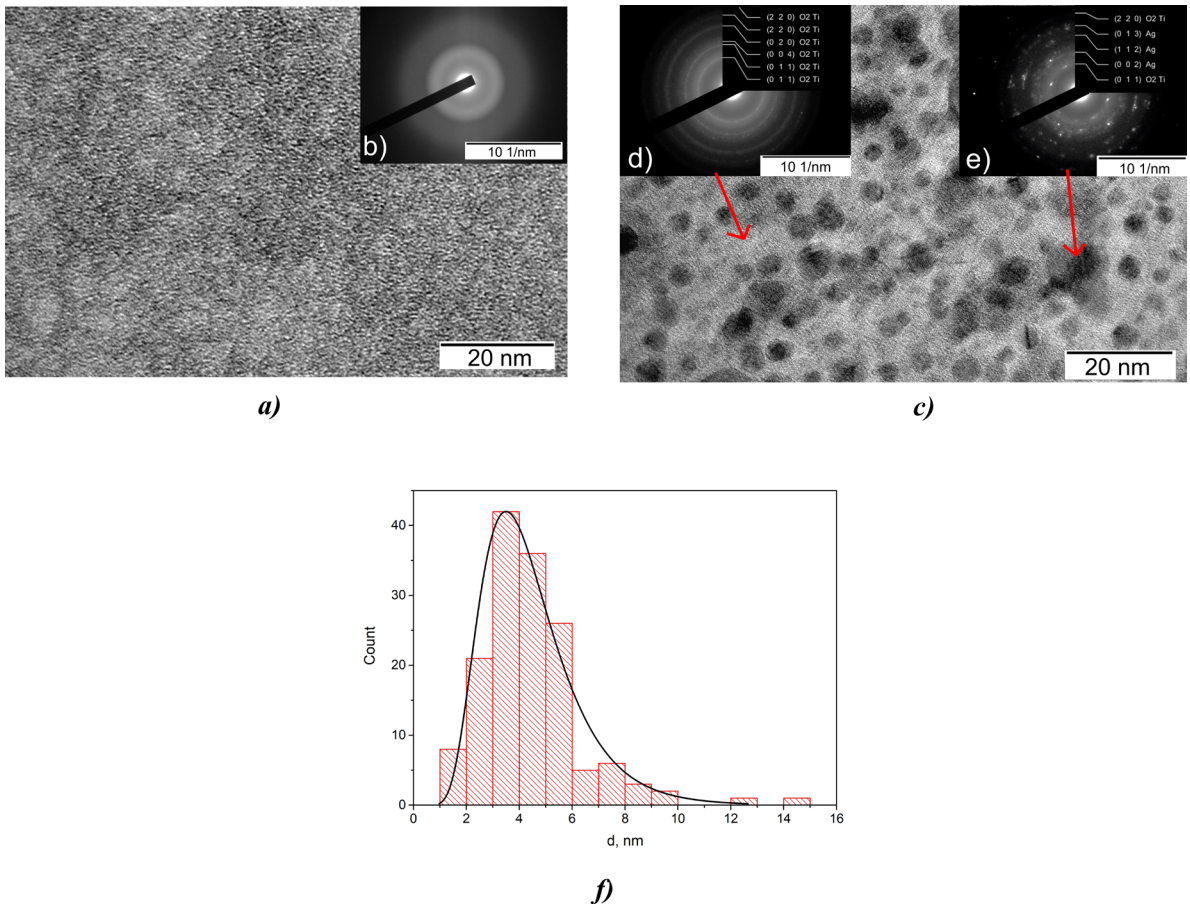

Fig. 1. TEM images (a, c) and SAED patterns (d, e) of TiO_2 (a, b) and TiO_2<9.0 at. % Ag> (c, d, e) films, as well as the size distribution of Ag nanoparticles in TiO_2<9.0 at.% Ag> film (f)

The TiO_2<Ag> film matrix contains isolated nanoparticles (Fig. 1 c). SAED of the nanoparticle (Fig. 1 e) shows clearly pronounced point reflections characteristic of a single-crystal structure. It follows from the interpretation of the SAED that this nanoparticle is silver.

Fig. 1 f shows a histogram of the size distribution of Ag nanoparticles in TiO_2<9.0 at.% Ag> films, obtained as a result of the TEM image processing. We can see that most silver nanoparticles have a diameter ~ 3–4 nm, and the distribution itself is lognormal. The same sizes for silver nanoparticles were obtained for TiO_2<Ag> films with other Ag concentrations. Similar results were obtained for wide-gap semiconductor nanocomposite a-C:H<Ag> films with the LSPR effect, also prepared by ion-plasma co-sputtering (Prikhodko et al. 2016; 2017).

Thus, the nanocomposite TiO_2<Ag> films, obtained by ion-plasma RF magnetron co-sputtering of TiO_2 and Ag in only argon atmosphere, consist of amorphous TiO_2 matrix and isolated crystalline silver nanoparticles.

Optical properties of TiO_2 and TiO_2<Ag> films

Fig. 2 shows the optical transmission spectra of the TiO_2 and TiO_2<Ag> films with different silver concentrations. It can be seen that the spectra of the films are characterized by the sharp transmission band edge (fundamental absorption band edge) in the near UV range from 280 to 320 nm. The slope of the passband edge changes with an increase in the silver concentration in the TiO_2<Ag> films: it increases significantly with the Ag concentration from 0 to 4.9 at. %, and then decreases slightly. The TiO_2 films in the visible and near IR regions (from 400 to 1100 nm) have a sufficiently high transmittance. In contrast, a pronounced absorption band with a maximum in the visible region of the spectrum is observed in TiO_2<Ag> films.

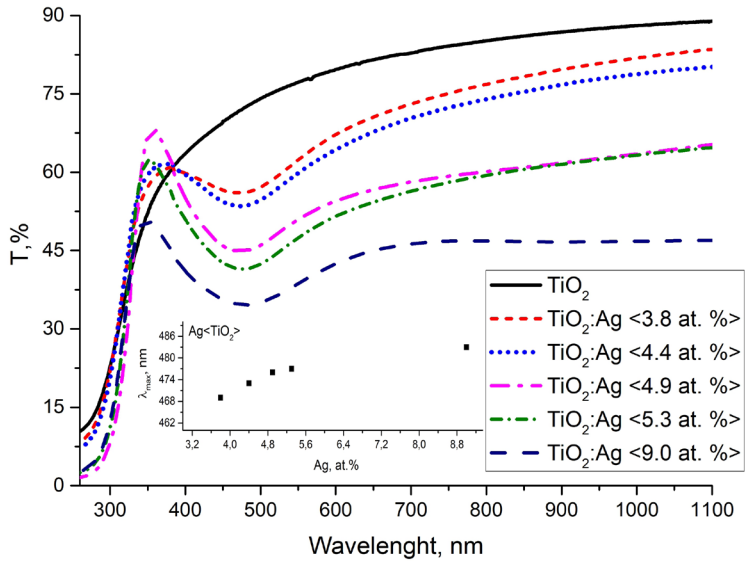

Fig. 2. Transmission spectra of TiO_2 and TiO_2<Ag> films with different concentration of silver

Fig. 2 shows that an increase in the Ag concentration (the volume fraction of Ag nanoparticles) leads to a significant increase in the intensity of this absorption band. The maximum of the absorption band, depending on the Ag concentration, is located in the range from 455 to 488 nm. As the concentration increases, the resonance peak shifts towards longer wavelengths. The main shift of the maximum is observed in the region up to 4.9 at. % Ag.

According to (Manikandan et al. 2003), the observed absorption band in TiO_2<Ag> films is due to the effect of surface plasmon resonance (LSPR) in consequence of resonant absorption of electromagnetic radiation by free surface electrons of isolated silver nanoparticles.

In (Ievlev et al. 2014), it was shown for polycrystalline semiconductor nanosized anatase films that the edge of the fundamental absorption band is formed by both indirect and direct allowed transitions. In this connection, we analyze the features of the fundamental absorption of the studied amorphous semiconductor nanosized TiO_2 and TiO_2<Ag> films.

The optical band gap (E_g) of the films was estimated using the Tauc method (Tauc et al. 1966). According the method, in the fundamental absorption region when the absorption coefficient $\alpha \geq 10^4$ cm^{-1}, the relationship between the light photon energies $h\nu$, α, and E_g is described by the relation

$$\alpha h\nu \sim (h\nu - E_g)^{1/n}, \quad (1)$$

where $n = 1/2$ corresponds to allowed direct-gap optical transitions, $n = 2$—to allowed indirect-gap transitions (quadratic absorption law) (Tauc et al. 1966).

The optical band gap of TiO_2 and TiO_2<Ag> films was determined for both allowed direct-gap and indirect-gap optical transitions. The error in E_g did not exceed ± 0.01 eV. Fig. 3 shows the spectral dependences $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ for nanosized TiO_2 and TiO_2<Ag> films with an Ag concentration of 4.9, 5.3, and 9.0 at. %.

 https://www.doi.org/10.33910/2687-153X-2023-4-4-195-202

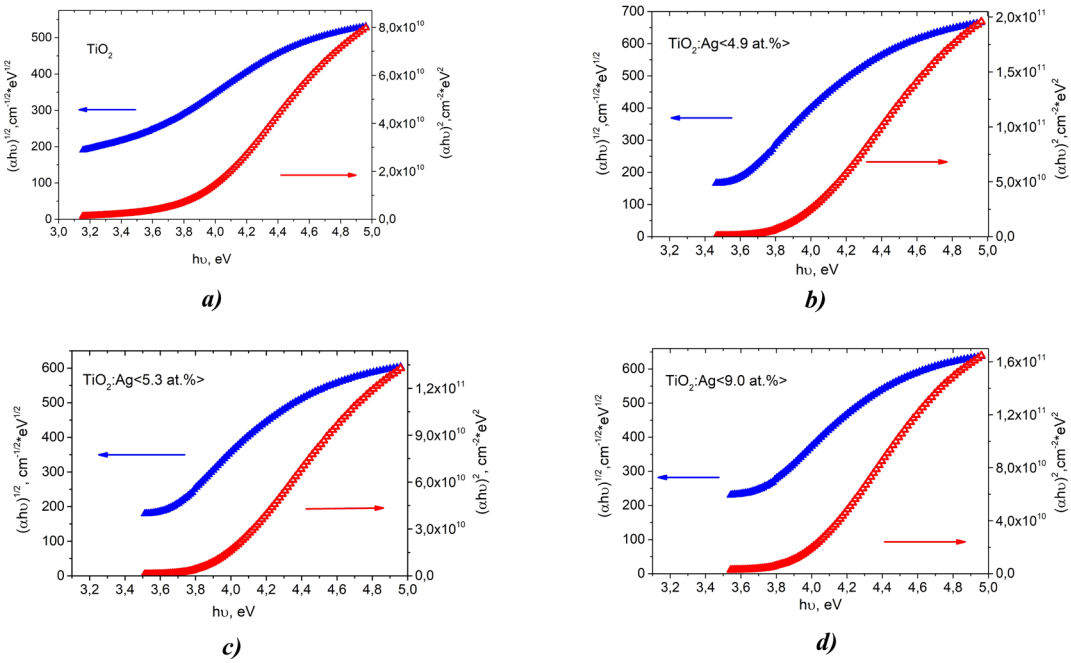

Fig. 3. Spectral dependences $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ for TiO_2 (a) and TiO_2<Ag> (b-d) films

It can be seen that in the TiO_2 and TiO_2<Ag> films spectra there are rather extended characteristic rectilinear sections, and extrapolation of them to the energy axis $h\nu$ gives the values of E_g. However, the detailed analysis shows that the most extended characteristic rectilinear sections are that when n = 2 (quadratic absorption law). It follows that the edge of the fundamental absorption band in the TiO_2 and TiO_2<Ag> films is mainly formed by indirect allowed optical transitions.

Fig. 4 (curves 1 and 2) shows the concentration dependences of TiO_2<Ag> films optical band gap. The E_g values of the films correspond to semiconductor wide-gap materials. Optical band gap for TiO_2 and TiO_2<Ag> films in the case of n = 2 (the quadratic absorption law) are significantly lower than that of n = 1/2. When n = ½, the insignificant rise of E_g with Ag concentration occurs, but when n = 2, the significant increase of E_g takes place in the region of Ag concentration from 0 to 4.9 %, and later on E_g practically is invariable. Note, that the E_g for TiO_2<Ag> films considering both absorption laws with Ag concentration exceeding 3.8 at.% practically coincide with the data (Zhang et al. 2006) for polycrystalline anatase films.

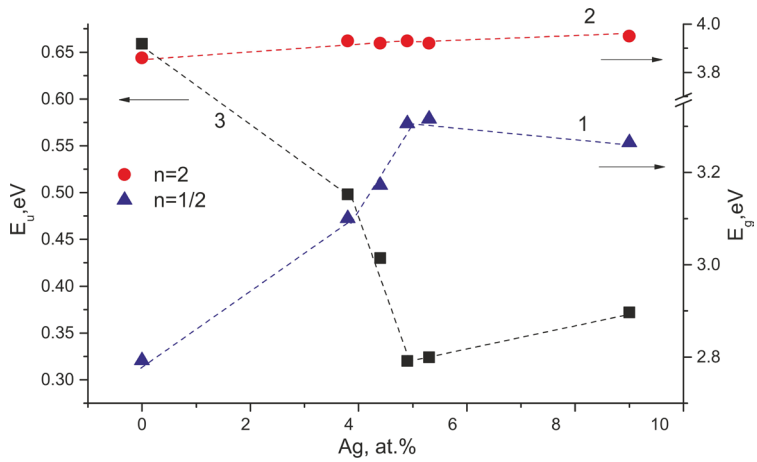

Fig. 4. Concentration dependences of TiO_2<Ag> films E_g for different laws of absorption (curves 1 and 2) and Urbach energy E_u (curve 3)

To explain the increase in the optical band gap in nanocomposite TiO_2<Ag> films, let us consider the variation with the Ag concentration of the Urbach energy (E_u) (Fig. 4, curve 3). According to (Akshay et al. 2019; Urbach et al. 1953), E_u characterizes the degree of semiconductor structure disorder, which determines the tail extension of the density of states at the boundaries of the allowed energy bands E_c and E_v. The relationship between the absorption coefficient α, the energy of the incident photon $h\nu$, and the Urbach energy E_u is given by the following relation (the empirical Urbach's rule)

$$\alpha \sim \exp(h\nu/E_u). \quad (2)$$

The Urbach energy was estimated from the low-energy region of the absorption spectrum. It is seen from Fig. 4 that the Urbach energy significantly decreases in the region from 0 to 4.9 at. % with Ag concentration increase, but the optical band gap of TiO_2<Ag> films significantly rises, in the case of a quadratic absorption mechanism. A further increase in the silver concentration to 9.0 at. % leads to an insignificant increase in the Urbach energy and an insignificant decrease in E_g, i. e., there is a correlation between changes in E_u and E_g when a quadratic absorption law take place. It follows that the increase in the Ag concentration in the TiO_2<Ag> films leads to the decrease of the density of localized states tails extension in the band gap, which is indicative of the ordering of the amorphous TiO_2<Ag> films structure. This is in good agreement with the change in the steepness of the transmission (absorption) band edge founded in this work.

Considering our data on TEM (Peshaya et al. 2022) the ordering of the amorphous structure of TiO_2<Ag> films with an increase in the concentration of Ag from 0 to 4.9 at. %, apparently, is due to a decrease in the porosity of the films because of the filling of pores in them with silver nanoparticles. This, in turn, leads to an increase in the refractive index of the matrix and, as a consequence, to a shift of the resonant peak towards longer wavelengths.

A further increase in the concentration of silver in the films to 9.0 at. % leads to some disordering of the structure as a result of an increase in the amount of silver nanoparticles in the matrix of the films.

It should be noted that an increase in silver volume fraction in the TiO_2<Ag> nanocomposite can also lead, as the theory (Gibson et al. 1982) shows, to a shift of the resonance peak maximum towards longer wavelengths. Apparently, this is the reason for the further shift of the maximum to the red region.

Thus, the optical properties of amorphous semiconductor nanocomposite TiO_2<Ag> films are characterized by a sharp edge of the fundamental absorption band in the near UV region, which is formed mainly by indirect allowed optical transitions. The slope of the absorption band edge and the optical band gap depend on the silver concentration in the films. There is a pronounced LSPR effect in the visible region of the spectrum, the intensity of which increases significantly with the rise of Ag concentration.

Conclusions

Using the ion-plasma RF magnetron sputtering of a combined TiO_2 and Ag target in an atmosphere of only argon without subsequent heat treatment, amorphous semiconductor nanocomposite TiO_2<Ag> films with a thickness from 40 to 50 nm and with a silver concentration of up to 9.0 at. % were obtained.

It was found by TEM that the structure of the films consists of practically amorphous TiO_2 matrix and isolated silver nanoparticles with the diameter ~ 3–4 nm.

The resulting TiO_2<Ag> films are wide-gap semiconductor materials. The optical band gap of the films increases significantly with the silver concentration. The optical properties of TiO_2 and TiO_2<Ag> films are characterized by a sharp fundamental absorption edge at ~ 300 nm, which is due to direct and indirect allowed optical transitions. In the visible region of the spectra of TiO_2<Ag> films, a pronounced surface plasmon resonance absorption is manifested. The LSPR intensity significantly increases with an increase in the silver concentration in the films, and the absorption maximum, depending on the Ag concentration, is located in the region from 455 to 488 nm. The presence of isolated silver nanoparticles and their concentration influences on the degree of the structure order of the amorphous matrix of the TiO_2<Ag> film and, thus, the optical band gap of the films. Amorphous TiO_2<Ag> films, in comparison with TiO_2 films, have a more ordered structure of the amorphous TiO_2 matrix and, as a consequence, higher E_g.

The shown possibility of obtaining amorphous plasmon nanocomposite TiO_2<Ag> films using simpler technology is of significant interest for their application in structures fabricated in a continuous cycle of planar technology.

 https://www.doi.org/10.33910/2687-153X-2023-4-4-195-202

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

The authors have made an equal contribution to the paper.

References

Akshay, V. R., Arun, B., Mandal, G. et al. (2019) Visible range optical absorption, Urbach energy estimation and paramagnetic response in Cr-doped TiO_2 nanocrystals derived by a sol-gel method. *Physical Chemistry Chemical Physics*, 21 (24), 12991–13004. https://doi.org/10.1039/c9cp01351b (In English)

Banerjee, S., Dionysiou, D. D., Pillai, S. C. (2015) Self-cleaning applications of TiO_2 by photo-induced hydrophilicity and photocatalysis. *Applied Catalysis B: Environmental*, 176–177, 396–428. https://doi.org/10.1016/j.apcatb.2015.03.058 (In English)

Bueno-Alejo, C. J., Arca-Ramos, A., Hueso, J. L. (2017) Plasmonics devoted to photocatalytic applications in liquid, gas, and biological environments. In: G. Barbillon (ed.). *Nanoplasmonics—Fundamentals and Applications*. [S. l.]: InTech Publ. [Online]. Available at: https://doi.org/10.5772/intechopen.68812 (15.05.2023). (In English)

Cao, C., Yan, J., Zhang, Y., Zhao, L. (2016) Stability of titania nanotube arrays in aqueous environment and the related factors. *Scientific Reports*, 6 (1), article 23065. https://doi.org/10.1038/srep23065 (In English)

Ghann, W., Rahman, A., Rahman, A., Uddin, J. (2016) Interaction of sensitizing dyes with nanostructured TiO_2 film in dye-sensitized solar cells using terahertz spectroscopy. *Scientific Reports*, 6 (1), article 30140. https://doi.org/10.1038/srep30140 (In English)

Ghidelli, M., Mascaretti, L., Bricchi, B. R. et al. (2020) Light management in TiO_2 thin films integrated with Au plasmonic nanoparticles. *Semiconductor Science and Technology*, 35 (3), article 035016. https://doi.org/10.1088/1361-6641/ab6cea (In English)

Gibson, U. J., Craighead, H. G., Buhrman, R. A. (1982) Topological considerations in the optical properties of granular composite films. *Physical Review B*, 25 (2), 1449–1452. https://doi.org/10.1103/physrevb.25.1449 (In English)

Ievlev, V. M., Kushchev, S. B., Latyshev, A. N., Leonova, L. Yu. (2014) Absorption spectra of TiO_2 thin films synthesized by the reactive radio-frequency magnetron sputtering of titanium. *Semiconductors*, 48 (7), 848–858. https://doi.org/10.1134/S1063782614070094 (In English)

Klinger, M., Jäger, A. (2015) Crystallographic Tool Box (CrysTBox): Automated tools for transmission electron microscopists and crystallographers. *Journal of Applied Crystallography*, 48, 2012–2018. https://doi.org/10.1107/S1600576715017252 (In English)

Kulkarni, M., Mazare, A., Gongadze, E. et al. (2015) Titanium nanostructures for biomedical applications. *Nanotechnology*, 26 (6), article 062002. https://doi.org/10.1088/0957-4484/26/6/062002 (In English)

Manikandan, D., Mohan, S., Nair, K. G. M. (2003) Absorption and luminescence of silver nanocomposite soda-lime glass formed by Ag^+-Na^+ ion-exchange. *Materials Research Bulletin*, 38 (9–10), 1545–1550. https://doi.org/10.1016/S0025-5408(03)00165-X (In English)

Navabpour, P., Ostovarpour, S., Hampshire, J. et al. (2014) The effect of process parameters on the structure, photocatalytic and self-cleaning properties of TiO_2 and Ag-TiO_2 coatings deposited using reactive magnetron sputtering. *Thin Solid Films*, 571-1, 75–83. https://doi.org/10.1016/j.tsf.2014.10.040 (In English)

Ozimek, M., Palewicz, M., Hreniak, A. (2016) Optical properties of TiO_2 nanopowder doped by silver (copper) during synthesis or PVD method. *Acta Physica Polonica A*, 129 (6), 1214–1219. https://doi.org/10.12693/APhysPolA.129.1214 (In English)

Pakdel, E., Daoud, W. A., Wang, X. (2013) Self-cleaning and superhydrophilic wool by TiO_2/SiO_2 nanocomposite. *Applied Surface Science*, 275, 397–402. https://doi.org/10.1016/j.apsusc.2012.10.141 (In English)

Pan, H., Heagy, M. D. (2019) Plasmon-enhanced photocatalysis: Ag/TiO_2 nanocomposite for the photochemical reduction of bicarbonate to formic acid. *MRS Advances*, 4 (7), 425–433. https://doi.org/10.1557/adv.2018.677 (In English)

Peshaya, S. L., Prikhodko, O. Yu., Mukhametkarimov, Ye. S. et al. (2022) Osobennosti opredeleniya opticheskoj shiriny zapreshchennoj zony amorfnykh nanorazmernykh kompozitnykh plenok TiO_2:Ag [Peculiarities of determining the optical band gap of amorphous nanosized TiO_2:Ag composite films]. *Opticheskij zhurnal — Journal of Optical Technology*, 89 (1), 74–81. (In Russian)

Prakash, J., Kumar, P., Harris, R. A. et al. (2016) Synthesis, characterization and multifunctional properties of plasmonic Ag-TiO_2 nanocomposites. *Nanotechnology*, 27 (35), article 355707. https://doi.org/10.1088/0957-4484/27/35/355707 (In English)

Prikhodko, O., Manabayev, N., Guseinov, N. (2014) Plasmon resonance in a-C:H films modified with platinum nanoclusters. *Journal of Nano- and Electronic Physics*, 6 (3), article 03067. (In English)

Prikhodko, O. Yu., Mikhailova, S. L., Mukhametkarimov, E. C. et al. (2016) Optical properties of a-C:H thin films modified by Ti and Ag. *Proceedings of SPIE*, 9929, article 99291G. https://doi.org/10.1117/12.2238455 (In English)

Prikhodko, O. Yu., Mikhailova, S. L., Mukhametkarimov, Ye. S. et al. (2017) Structure and phase composition of thin a-C:H films modified by Ag and Ti. *Optics and Spectroscopy*, 123 (3), 383–387. https://doi.org/10.1134/S0030400X17090260 (In English)

Rodrigues, M. S., Costa, D., Domingues, R. P. et al. (2018) Optimization of nanocomposite Au/TiO_2 thin films towards LSPR optical-sensing. *Applied Surface Science*, 438, 74–83. https://doi.org/10.1016/j.apsusc.2017.09.162 (In English)

Tauc, J., Grigorovici, R., Vancu, A. (1966) Optical Properties and electronic structure of Ge optical properties and electronic structure of amorphous germanium. *Physica Status Solidi b*, 15 (2), 627–637. https://doi.org/10.1002/pssb.19660150224 (In English)

Torrell, M., Kabir, R., Cunha, L. et al. (2011) Tuning of the surface plasmon resonance in TiO_2/Au thin films grown by magnetron sputtering: The effect of thermal annealing. *Journal of Applied Physics*, 109 (7), article 074310. https://doi.org/10.1063/1.3565066 (In English)

Urbach, F. (1953) The long-wavelength edge of photographic sensitivity and of the electronic absorytion of solids. *Physical Review*, 92 (5), 1324–1324. https://doi.org/10.1103/PhysRev.92.1324 (In English)

Usha, K., Kumbhakar, P., Mondal, B. (2016) Effect of Ag-doped TiO_2 thin film passive layers on the performance of photo-anodes for dye-sensitized solar cells. *Materials Science in Semiconductor Processing*, 43, 17–24. https://doi.org/10.1016/j.mssp.2015.11.015 (In English)

Wodka, D., Bielaníska, E., Socha, R. P. et al. (2010) Photocatalytic activity of titanium dioxide modified by silver nanoparticles. *ACS Applied Materials and Interfaces*, 2 (7), 1945–1953. https://doi.org/10.1021/am1002684 (In English)

Yu, Y., Wen, W., Qian, X.-Y. et al. (2017) UV and visible light photocatalytic activity of Au/TiO_2 nanoforests with Anatase/Rutile phase junctions and controlled Au locations. *Scientific Reports*, 7 (1), article 41253. https://doi.org/10.1038/srep41253 (In English)

Yuan, X., Xu, W., Huang, F. et al. (2017) Structural colors of fabric from Ag/TiO_2 composite films prepared by magnetron sputtering deposition. *International Journal of Clothing Science and Technology*, 29 (3), 427–435. https://doi.org/10.1108/IJCST-04-2016-0038 (In English)

Zada, I., Zhang, W., Zheng, W. et al. (2017) The highly efficient photocatalytic and light harvesting property of Ag-TiO_2 with negative nano-holes structure inspired from cicada wings. *Scientific Reports*, 7 (1), article 17277. https://doi.org/10.1038/s41598-017-17479-8 (In English)

Zhang, J., Li, M., Feng, Z. et al. (2006) UV Raman spectroscopic study on TiO_2-I. phase transformation at the surface and in the bulk. *Journal of Physical Chemistry B*, 110 (2), 927–935. https://doi.org/10.1021/jp0552473 (In English)

Zhao, G., Kozuka, H., Yoko, T. (1996) Sol—gel preparation and photoelectrochemical properties of TiO_2 films containing Au and Ag metal particles. *Thin Solid Films*, 277 (1–2), 147–154. https://doi.org/10.1016/0040-6090(95)08006-6 (In English)