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Photocatalytic properties of NiO – gold plasmonic nanocomposite

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Abstract. This study evaluates the photocatalytic activity of nickel oxide films synthesized by magnetron sputtering before and after thermal annealing. The effect of NiO film activation with gold nanoparticles is also investigated. Sample characterization performed by complementary techniques reveals formation of nanocrystalline cubic NiO and gold nanoparticles embedded into the NiO matrix. The ability of samples to decompose glycerol under ultraviolet (UV) and visible (VIS) light irradiation was tested. NiO films behave as active compound under UV light. Incorporation of gold nanoparticles into the oxide matrix not only enhances its activity under UV, but allows to decompose the model pollutant on the surface under the VIS light irradiation.

Keywords: nanocomposite materials, nickel oxide, gold nanoparticles, decomposition of organic pollutants

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Материалы конференции

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Фотокаталитические свойства плазмонного нанокompозита NiO – золото

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Аннотация. В данном исследовании оценивается фотокаталитическая активность пленок оксида никеля, синтезированных методом магнетронного распыления, и влияние активации наночастицами золота. Исследование свойств образцов с помощью нескольких методов показывает успешное формирование нанокристаллического кубического NiO и встроенных наночастиц золота. Способность образцов разлагать глицерин была проверена при облучении ультрафиолетовым (УФ) и видимым светом.

Пленки NiO ведут себя как активное соединение под ультрафиолетовым светом. Встраивание наночастиц золота в оксидную матрицу не только усиливает ее активность под УФ, но и позволяет разлагать модельный загрязнитель на поверхности при облучении видимым светом.

Ключевые слова: нанокompозитные материалы, оксид никеля, оптическая ширина запрещенной зоны, разложение органических загрязнений

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Introduction

Pollution with complex organic compounds is a problem of modern society. Although clean drinking water is essential for human survival, many of its sources are now heavily polluted. With the growth of the population, the amount of substances that mankind emits into the environment increases dramatically. Most of these emissions are complex organic compounds, so the search for easily accessible ways to decompose pollutants into simple components is an important problem that needs to be solved. One of the possible mechanisms for getting rid of organic pollution is the photodegradation of a substance when it is exposed to sunlight, which is the most accessible source of inducing radiation.

Nanocomposite materials based on metal oxides are actively studied in terms of environmental applications. Transition metal oxides have electrooptical properties that ensure a relatively high efficiency of photodegradation [1]. Various transition metal oxides are being studied as possible catalysts [2–6]. At the same time, methods for applying such coatings have been developed [7]. In most cases, effective photodegradation is achieved using UV light. When sunlight is used, the radiation intensity is greatest in the visible part of the spectrum. For this reason, the development of oxide photocatalysts for the decomposition of complex organic compounds under the action of visible light is promising and of great interest to modern society. In this work, we propose a method for the formation of oxide layers and evaluate the photocatalytic activity of nickel oxide layers activated with gold nanoparticles upon irradiation with ultraviolet and visible light.

Materials and methods

Sample preparation and characterization. Magnetron sputtering was used to form a nickel oxide film on a silicon substrate. Nickel oxide was deposited on a standard vacuum deposition unit (UVN, type URM 3279017). The targets used were 1.2 mm thick and 106 mm in diameter, made of 99.7 H95 nickel. (100) n-type single-crystal silicon wafer was used as a substrate. Reactive magnetron sputtering took place in a mixture of argon and oxygen at a discharge power of 100 W (0.3 A, 330 V). In this mode, the target surface remained completely passivated by oxygen during the entire deposition process. The deposition rate was 1.6 nm/min.

The formation of gold nanoparticles was carried out by thermal annealing of a gold film. The film was deposited by the thermoresistive evaporation. The film thickness was about 3 nm. Annealing was carried out in an air at a temperature of 550 degrees Celsius for an hour.

The crystal structure of thin films and nanocomposites was studied by X-ray diffraction. The spectral characteristics of the optical transmission, reflection, and absorption of the obtained samples were measured to study the optical band gap.

Study of the photoactivity of the material. In a darkened room, a drop of glycerol solution was applied to the surface of the sample. After drying at ambient conditions, a thin film forms on the surface. The transmission through the test sample was evaluated by Fourier-transform IR spectroscopy.

Then, irradiation with green or violet light was carried out for 30, 60, 150 and 300 seconds. After each irradiation, the FTIR spectrum was measured. The data were then normalized to the film thickness. A thin film of residual glycerol was irradiated with a laser beam with a wavelength of 400 nm or 532 nm with a power of 10 mW in continuous mode. All measurements were taken 3 times for each light exposure time and wavelength and averaged to minimize the experimental error.

To assess the effect of irradiation with a given wavelength, an original technique was used, which consists in assessing the change in the intensity of absorption by the glycerol layer, which can be quantitatively expressed using the Bouguer–Lambert law:

$$I(d) = I_0 e^{-k_\lambda d}, \quad (1)$$

where $I(d)$ is the intensity of light passing through a layer of matter with thickness d , I_0 is the light intensity at the entrance to the substance, k_λ is the natural absorption index depending on the wavelength λ . In this case, the thickness of the absorbing layer is equal to

$$d = \frac{\ln(T)}{-k_\lambda}, \quad (2)$$

where d is the thickness of the analytical layer, k_λ is the natural absorption index depending on the wavelength λ , T is the transmittance equal to the ratio $I(d)$ to I_0 .

Results and discussion

The results of X-ray phase analysis of thin films are shown in Fig. 1. On the X-ray patterns of all samples, about 2θ 43° is visible, corresponding to reflections from the (200) planes, characteristic of Fm-3 m nickel oxide with a lattice parameter of 0.417 ± 0.002 nm (bunsenite), well consistent with the reference value of $a = 0.418$ nm (ICDD 00-001-1239). At the same time, it was noted that annealing at 550°C significantly increases the intensity of this peak (see Fig. 1). In the case of samples with gold (not shown), additional peaks appeared in the diffractograms around the $2\theta = 38^\circ$. These peak corresponds to X-ray reflection from the (111) Fm-3m planes of gold with a lattice parameter of 0.408 ± 0.001 nm (ICDD 03-065-2870). Thus, gold nanoparticles have a good crystal plane set parallel to the sample surface.

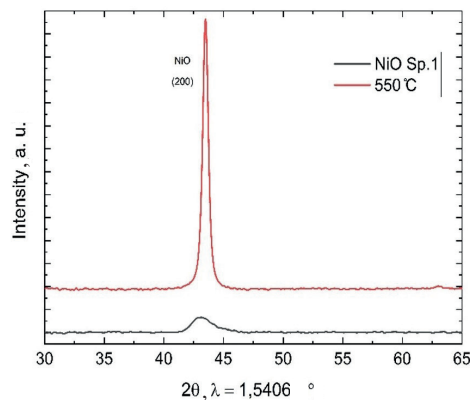


Fig. 1 XRD spectrum of NiO film obtained by RF-magnetron sputtering

Based on the transmission, reflection and absorption spectral characteristics, the optical band gap of nickel oxide was determined as 3.45 eV (see Fig. 2, b). A slight decrease in the optical band gap compared to the electronic band gap is probably due to blurring of the bands due to crystalline imperfection of the material.

During the acquisition of transmission spectra in the IR range, it was noticed that gold nanoparticles have almost no effect on absorption in this range.

Typical FTIR spectra are presented in the Fig 3. The broad band between 1200 cm^{-1} and 2000 cm^{-1} (characteristic vibration of O–H bonds) is due to both intermolecular and intramolecular hydrogen bonds. The spectra of all samples showed characteristic vibrations of OH groups in glycerol (peak with a maximum at about 1651 cm^{-1}) and, probably, fatty acid residues (the

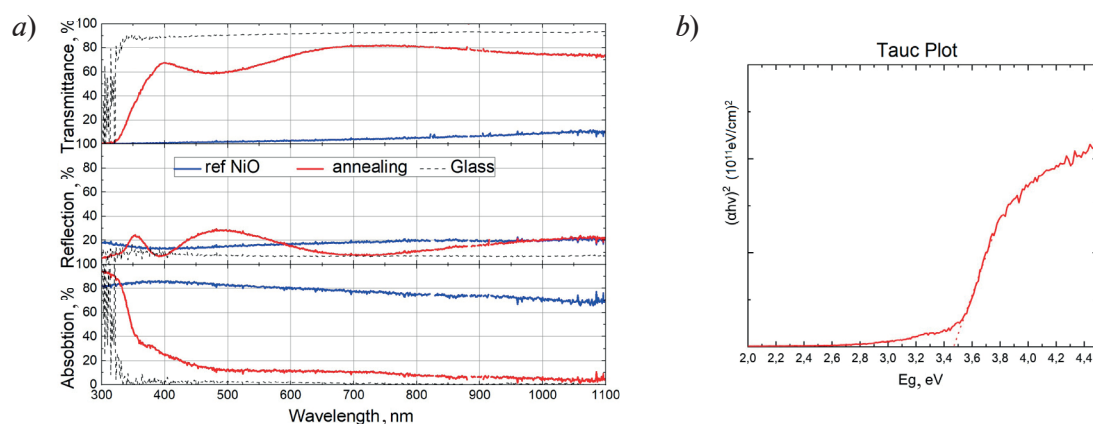


Fig. 2. Transmission, Reflection, and Absorption Spectra (a) and Tauc plot (b) obtained for the samples

intense C=O peak at 1735 cm^{-1}). The long alkyl chain of fatty acids is represented by a peak between 2925 and 2852 cm^{-1} , which corresponds to the axial deformation of CH bonds in the secondary ($-\text{CH}_2-$) and primary ($-\text{CH}_3-$) methyl groups. They are characteristic of many organic substances [8]. The narrow band at 2349 cm^{-1} corresponds to the C–O vibration in CO_2 [9]. The absence of new peaks in the spectrum after irradiation indicates a heterogeneous mechanism of glycerol decomposition on the surface under consideration.

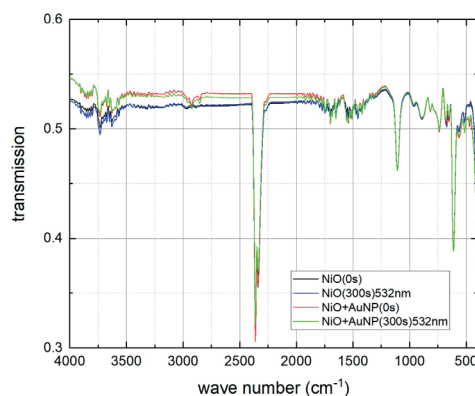


Fig. 3. FTIR spectra of samples irradiated with 532 nm light

The decomposition of the organic compound glycerol was estimated by comparison of the intensities of peaks around 950 , 1450 , and 1550 cm^{-1} before and after light exposure. The decrease in optical density in these wavelengths was recalculated into the thickness of the absorbing layer, as described in Section 2. The ratio of the obtained thickness to the initial one is presented in Fig. 4. Figure 4 shows that decomposition occurs on all substrates under 400 nm light irradiation, which corresponds to a photon energy of 3.2 eV . In this case, the destruction of glycerol on silicon oxide and nickel occurs with the same rate within the experimental error. The most probable mechanism of film destruction in this case is the bond decay under the action of ultraviolet radiation. This is obvious, since the typical binding energy of organic compounds is $\sim 3 \text{ eV}$ [10], so the photon energy is high enough to break some bonds.

As follows from Fig. 4, nickel oxide with embedded gold nanoparticles is able to decompose glycerol much more efficiently. From Fig. 4 one can see that irradiation with 532 nm green light does not affect glycerol deposited on silicon and nickel oxide. Indeed, the photon energy in this case is 2.33 eV , which is not enough to directly break chemical bonds. At the same time, the decomposition of glycerol is clearly manifested on nickel oxide with embedded gold nanoparticles. The effectiveness of green light is inferior to the decomposition under the action of a violet laser. In the case of a nanocomposite material, an additional decay path probably appears due to photoinduced electron–hole exchange between metal nanoparticles and the oxide matrix [11].

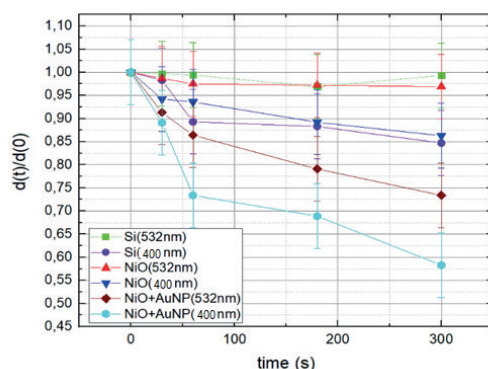


Fig. 4. Degree of the organic layer degradation vs time of irradiation with different wavelength

Conclusion

Nickel oxide films were synthesized by magnetron sputtering. Some films were activated with embedded gold nanoparticles grown by thermal annealing of a thin gold film. The degradation of an organic glycerin film on the nickel oxide surface upon irradiation with 400 and 532 nm light has been studied. The incorporation of gold nanoparticles into the metal oxide matrix significantly increased the efficiency of glycerol destruction under UV irradiation. In addition, it was founded that the nanocomposite system is able to decompose glycerol under the 532 nm green light irradiation, which is not observed on the surface of silicon and pure nickel oxide.

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