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Malovychko H., ORCID ID: https://orcid.org/0009-0005-3697-5920
Machulianskyi O., ORCID ID: https://orcid.org/0000-0003-0057-9844
National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine

OPTICALLY SELECTIVE STRUCTURES BASED ON NANOSCALE CHROMIUM CONDENSATES FOR PHOTOTERMAL ENERGY CONVERTERS

The results of the formation of optically selective structures with an optical selectivity ratio of up to 11.4 are presented. These structures are based on nanoscale two-phase chromium–chromium oxide condensates developed via vacuum deposition on copper substrates. A comprehensive experimental study was conducted to evaluate the composition, structure and selective optical parameters (integral, absorptance, thermal emittance, and selectivity ratio) of the test samples. The analysis of the influence of deposition process parameters for nanoscale chromium layers and substrate surface roughness on the properties of optically selective structures is provided. It was established that increasing the substrate roughness contributes to an increase in the integral emittance of the selective structures up to 0.32, which consequently reduced the optical selectivity ratio to 2.8. The results of the investigation into the stability of the selective optical parameters under elevated temperatures and ultraviolet radiation allow for the recommendation of these structures for application in photothermal converters at temperatures up to 500 K under vacuum conditions (1 Pa).
Keywords: *metal-dielectric optically selective structures, nanoscale films, chromium condensates, integral solar absorptance, thermal emittance, selectivity ratio*

Problem statement. An important role in addressing the efficiency of energy resource utilization through renewable energy sources, specifically solar radiation, is occupied by the development of photothermal energy converters alongside photovoltaic systems [1]. The characteristics of such converters are significantly influenced by the optical properties of the radiation-absorbing surface.

For effective solar energy conversion, the surface of a photothermal converter must possess the highest possible absorption coefficient in the solar spectral range (0.3–2.0 μm) and the lowest possible emittance in the infrared range (2–30 μm), which corresponds to its own thermal re-radiation. The conflicting requirement of creating an efficient absorber that is simultaneously a weak emitter can be satisfied by using a surface with optical selectivity. A surface with ideal spectral selectivity should exhibit a transition between regions of low and high reflectance at a wavelength of approximately 2 μm [2, 3].

Most selective absorbing surfaces for photothermal converters are formed on a metallic base. The use of metals in photothermal solar energy converters is dictated by their high reflectance in the infrared range, which ensures a low thermal emittance. High-conductivity metals, such as copper and aluminum, exhibit emittance values in the range of 0.02–0.04 at temperatures up to 300 °C. To increase the absorptance of metals in the solar spectral region, it is necessary to apply a coating that strongly absorbs solar radiation [4, 5].

It should be noted that, in addition to spectral selectivity, optically selective structures must possess high parameter stability under operational conditions and at elevated temperatures. It is noted in [6, 7] that the mechanical and chemical strength, as well as the UV stability of silver and copper materials in multilayer structures, can be enhanced by using nanoscale titanium, chromium, or chromium oxide films as intermediate layers. Coatings consisting of nanodispersed metallic inclusions distributed within a dielectric medium, or island films, are considered more promising [8, 9]. Structures containing transition metal nanoparticles are of particular interest for increasing absorptance in the visible spectral range [10]. However, the correlation between the optically selective characteristics of such metal-dielectric structures and their actual structural parameters has not been sufficiently investigated [11, 12].

Research aim and key objectives. The present work is dedicated to studying the optical properties of selective structures based on nanoscale chromium condensates and their dependence on the technological conditions of the vacuum deposition process and substrate surface roughness.

Results and Discussion. The optical and electrical properties of nanoscale condensates depend on numerous factors, including film thickness, structural morphology, grain size, and substrate characteristics. These factors are determined by the deposition method and the specific process parameters used during formation.

To obtain experimental samples, a modernized vacuum deposition system based on the УВН-15 unit was employed. The system is equipped with sources for thermal evaporation, magnetron sputtering, and arc discharge. This setup enabled the deposition of chromium condensates using various vacuum methods to compare their features in forming nanoscale structures.

Chromium condensates produced by vacuum thermal evaporation utilized a starting material with 99.99% purity at a residual gas pressure of $(3\div7)\times10^{-4}$ Pa. Film deposition was performed after stabilizing the substrate temperature, which was set discretely within the range of 100÷200°C. Following additional thermal treatment at 300 °C in a vacuum (10^{-4} Pa) and subsequent cooling to room temperature, the samples were exposed to air. Heating and cooling in the vacuum chamber were conducted at a rate of 5 °C/min.

For the magnetron reactive sputtering method, a chromium target (99.99% purity) was used. The process parameters were varied as follows: base pressure of 10^{-4} Pa, operating pressure of $(3\div8)\times10^{-1}$ Pa, discharge power from 100 to 500 W, and a magnetic induction at the target surface of 0.04 T. Typical parameters of the chromium samples relative to their deposition conditions are summarized in Table 1.

Copper plates with a thickness of 2 mm and roughness parameters *Ra* of 2.0 and 0.125 µm were used as substrates. Different surface micro-reliefs were created by mechanical polishing with abrasive powders. The mass thickness of the films and the deposition rate were monitored using the quartz crystal microbalance (QCM) method. To evaluate the phase composition and structure, films were simultaneously deposited onto copper grids with a graphite underlayer and onto silicon substrates.

The microstructure of the films was investigated via electron microscopy. Electron microscopic analysis revealed that nanoscale chromium condensates with a mass thickness of approximately 2 nm possess a granular (discontinuous) structure. A continuous structure was observed with a further increase in mass thickness, correlating with data reported in [13].

The phase composition was qualitatively assessed using Infrared (IR) spectroscopy. Analysis of the IR spectra showed that chromium condensates obtained at p = 10^{-1} Pa consist of chromium oxide Cr_2O_3, whereas those obtained at p = 10^{-4} Pa consist of metallic chromium. These studies suggest that the resulting chromium condensates on copper substrates are nanodispersed structures, in which metallic chromium particles are embedded within a dielectric chromium oxide matrix.

Spectral studies of nanodispersed copper, nickel, and chromium films on quartz substrates were conducted in the 0.2 ÷ 1.1 nm range using an СФ-16 spectrophotometer. Reflectance was measured using a П30-1 specular reflection attachment at a near-normal angle of incidence. Reflectance spectra in the *0.8–2.5* µm range were recorded using an ІКС-14 spectrophotometer, while the 2.5–25 µm range was measured using a SPECORD-75IR spectrophotometer. The measurement error for the reflectance coefficient did not exceed ±3%. Figures 1 and 2 illustrate the spectral dependence of the reflectance coefficient for structures based on nanoscale chromium condensates of varying thicknesses on polished copper substrates *Ra* = 0.125 µm formed via thermal evaporation and magnetron sputtering.

The efficiency of photothermal energy converters is evaluated using integral selective parameters: the integral solar absorptance *A*, the integral thermal emittance (degree of blackness, *E*), and the selectivity ratio η at a temperature of T = 300K.

The integral solar absorptance is determined by the following relation:

$$A = \frac{\int_0^{\infty}[1-R_\lambda]P_\lambda(\lambda)d\lambda}{\int_0^{\infty}P_\lambda(\lambda)d\lambda}, \quad (1)$$

where R_λ is the spectral reflectance characteristic of the structure, and P_λ is the spectral distribution of solar radiation intensity.

The integral thermal emittance (degree of blackness) at a temperature of T = 300 K is determined by the following relation:

$$E = \frac{\int_1^{10}[1-R_\lambda]W_B(\lambda,T_B)d\lambda}{\int_1^{10}W_B(\lambda,T_B)d\lambda}, \quad (2)$$

where $W_B(\lambda, T_B)$ is the spectral energy distribution of a blackbody at temperature T_B (with T_B = 300K).

The selectivity ratio is defined by the following expression:

$$\eta = \frac{A}{E}. \quad (3)$$

The integral selective parameters A, E, and η for the photothermal energy converter structures were determined based on the measured spectral reflectance at a normal angle of incidence for experimental samples of nanoscale chromium condensates on copper substrates.

The parameters of the resulting coatings, denoted as A_N, E_N, and η, were calculated according to the proposed algorithm using the reflectance coefficients measured at a normal angle of incidence. Examples of the developed selective structures based on chromium condensates on copper substrates, along with their corresponding optical, selective, and technological parameters, are presented in Table 1.

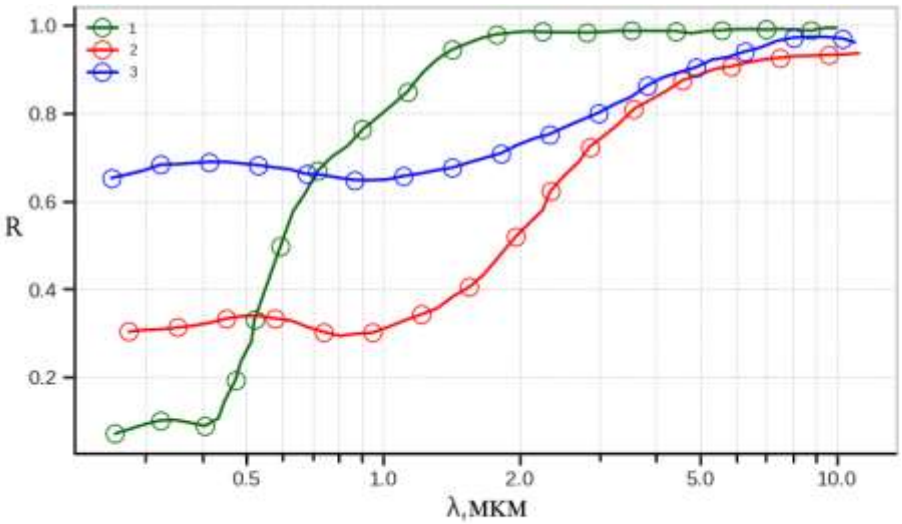

Figure 1 - Spectral reflectance of structures based on nanoscale chromium condensates on copper substrates with a roughness parameter Ra = 0.125$ μm, formed by vacuum thermal evaporation with different mass thicknesses: 1 – 4.0 nm; 2 – 22.0 nm; 3 – for a model structure with bulk chromium properties according to the data from [14]

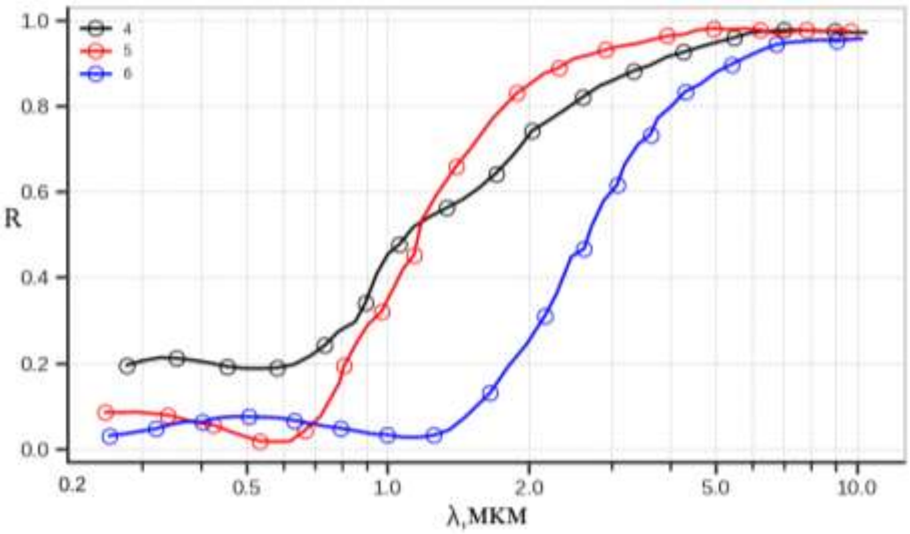

Figure 2 - Spectral reflectance of structures based on nanoscale chromium condensates on copper substrates with a roughness parameter Ra = 0.125 μm, formed by magnetron sputtering with different mass thicknesses: 1 – 7.5 nm; 2 – 14.0 nm; 3 – 53.0 nm

The variation in the mass thickness of the films from 4 to 53 nm leads to a redshift of the absorption edge toward the long-wavelength region, shifting from 0.5 μm to 2 μm for the selective structures. Consequently, for the specified film thicknesses, the integral solar absorptance increases from 0.52 to 0.91, respectively. At the same time, the thermal emittance remains low, maintaining a value of approximately 0.04.

Table 1 – Technological and optical selectivity parameters of structures based on nanoscale chromium condensates on copper substrates.

Mass thickness, nm.	Deposition parameters			Substrate roughness R_a, мкм	*A*	*E*	*η*
	Operating pressure, *Па*	Discharge power, Вт	Substrate temperature, ^0C				
2.0	10^{-4}	–	200	0.125	0.51	0.04	12.7
4.0	10^{-4}	–	100	0.125	0.52	0.04	13
6.0	$7\cdot10^{-1}$	100	100	0.125	0.61	0.06	10.2
8,0	$5\cdot10^{-1}$	200	100	0.125	0.64	0.06	10.7
14,0	$7\cdot 10^{-1}$	250	100	0.125	0.76	0.05	15.2
22,0	10^{-4}	–	200	0.125	0.89	0.07	12.7
53,0	$8\cdot10^{-1}$	100	200	0.125	0.91	0.08	11.4
4.0	10^{-4}	–	100	2.0	0.90	0.31	2.9
8.0	$5\cdot10^{-1}$	200	100	2.0	0.93	0.32	2.9
14,0	$7\cdot10^{-1}$	250	100	2.0	0.93	0.32	2.9
53,0	$8\cdot10^{-1}$	100	200	2.0	0.93	0.30	2.8

At the same time, the influence of vacuum deposition conditions on the optical properties of chromium condensates can be observed. For films with a thickness of up to 10 nm, no significant dependence of the solar absorptance on the deposition parameters was found. However, for thicknesses ranging from 10 to 53 nm and above, the integral absorptance values are lower for structures formed by vacuum thermal evaporation at $p = 10^{-4}$ Pa. Evidently, the observed variations in integral absorptance are caused by the formation of a continuous metallic chromium film, which is consistent with the results of structural and phase analyses. This is further evidenced by the increased reflectance of such films in the visible range, approaching the reflectance values of bulk metallic chromium as the thickness increases. The spectral reflectance of bulk chromium was calculated based on its optical constants reported in [14].

As is well known, the optical properties of a surface are determined by its micro-relief. Therefore, an assessment of the influence of the substrate micro-relief scale on the selective optical parameters of the coatings was conducted. As the substrate roughness parameter *Ra* increased from 0.125 µm to 2.0 µm, the integral absorptance showed only a slight increase. Conversely, the thermal emittance increased significantly, reaching 0.32. The research results indicate that the emittance of the investigated selective structures is independent of film thickness (within the studied range) and is entirely determined by the substrate micro-relief. This is likely explained by the fact that thin films replicate the morphology of the substrate micro-relief [13].

The application of optically selective structures in photothermal converters involves exposure to factors such as elevated temperatures and ultraviolet (UV) radiation. Consequently, the stability of the selective parameters under these conditions was investigated. The results showed that the selective parameters of the formed structures remained unchanged after exposure to temperatures up to 560 K for 8 hours followed by cooling to 300 K under vacuum (p = 1 Pa). Exposure to higher temperatures led to a degradation of the optical characteristics (a decrease in A_N and an increase in E_N). Furthermore, investigations into the effect of UV radiation showed that irradiating the samples in air with a mercury-quartz UV lamp had no impact on their optical properties.

Conclusion. This work presents the results of the formation and investigation of metal-dielectric optically selective structures based on nanoscale chromium condensates on copper substrates, achieving an optical selectivity ratio of up to 11.4. Nanoscale chromium condensates were deposited onto copper substrates with varying degrees of surface roughness using vacuum thermal evaporation and magnetron reactive sputtering. The deposition process involved the systematic variation of key technological parameters, including operating pressure, discharge power, and substrate temperature.

The phase composition, structure, and optical parameters of the fabricated test samples were analyzed using infrared spectroscopy, electron microscopy, and optical spectrophotometry. Based on the optical characterization results, the integral selective parameters – solar absorptance, thermal emittance, and the selectivity ratio – were determined. Comprehensive experimental investigations established the significant influence of deposition parameters on the composition, morphology, and spectral-optical characteristics of the resulting metal-dielectric structures.

It was found that increasing the thickness of the chromium condensates up to 50 nm results in a redshift of the absorption edge in the selective structures. For structures formed on substrates with a roughness of 0.125 μm, the optical selectivity ratio increased to 11.4. Conversely, increasing the substrate roughness parameter to 2.0 μm led to a negligible increase in integral absorptance, while the thermal emittance rose to 0.32, consequently reducing the selectivity ratio to 2.8.

The stability tests of the selective parameters under elevated temperatures and ultraviolet radiation allow for the recommendation of these structures for use in photothermal converters at temperatures up to 500 K under vacuum conditions (1 Pa). These findings provide a foundation for the development and optimization of deposition technologies and further research into nanoscale optically selective structures with tailored spectral characteristics. Future research in this direction may focus on enhancing the environmental stability of such structures, particularly through the application of additional nanoscale protective layers.

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Маловичко Г. С., Мачулянський О. В.
Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського» м. Київ, Україна

ОПТИЧНО СЕЛЕКТИВНІ СТРУКТУРИ НА ОСНОВІ НАНОРОЗМІРНИХ КОНДЕНСАТІВ ХРОМА ДЛЯ ФОТОТЕРМІЧНИХ ПЕРЕТВОРЮВАЧІВ ЕНЕРГІЇ

Представлено результати формування металодіелектричних оптично селективних структур з значенням критерію оптичної селективності до 11,4 на основі нанорозмірних двофазних конденсатів хром-оксид хрому методоми вакуумного осадження на підкладці із міді. Проведено комплексне експериментальне дослідження складу, структури, спектральних характеристик коефіцієнта відбивання та селективно-оптичних параметрів (поглинаючої здатності, тепловипромінюючої здатності та критерій селективної) тестових зразків. Наведені результати аналізу впливу параметрів технологічних режимів осадження нанорозмірних шарів хрому та шорсткості поверхні підкладок на властивості оптично селективних структур. Встановлено, що збільшення шорсткості підкладки сприяє збільшенню значень інтегральної випромінюючої здатності селективних структур до 0.32, що зменшувало значення критерію оптичної селективності до 2,8. Результати досліджень змін оптично селективних параметрів одержаних структур до впливу підвищеної температури і ультрафіолетового випромінювання дозволяють рекомендувати їх для застосування в фототермічних перетворювачах до температури 500 о К в умовах вакууму (1 Па).

Ключові слова: *металодіелектричні оптично селективні структури, нанорозмірні плівки, конденсати хрому, інтегральна поглинаюча здатність, ступінь чорноти, параметр селективності.*

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