

AUTONOMOUS PHOTODETECTORS BASED ON THE ANOMALOUS PHOTOVOLTAGE EFFECT IN NANOCRYSTALLINE CdTe FILMS FOR INDUSTRIAL GASES MONITORING

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Abstract: This study proposes a new physical concept of a highly sensitive laser-optical sensor system for remote monitoring of the environment around industrial enterprises. The scientific novelty of the work lies in increasing the photoelectric conversion efficiency by synergistically combining semiconductor nanofilms with anomalous photovoltage (APV) effect with two-dimensional (2D) MXene structures. In the system we developed, APV films act not only as antireflective coatings, but also as autonomous amplifiers, which allows for the diagnosis of chemically aggressive environments without an external energy source. Experimental results show that the integration of MXene layers reduces the response time of the optical signal to the picosecond level and significantly improves the detection limit.

Keywords: APV effect, laser monitoring, 2D-MXenes, nanostructured films, autonomous sensors, industrial pollutants.

INTRODUCTION

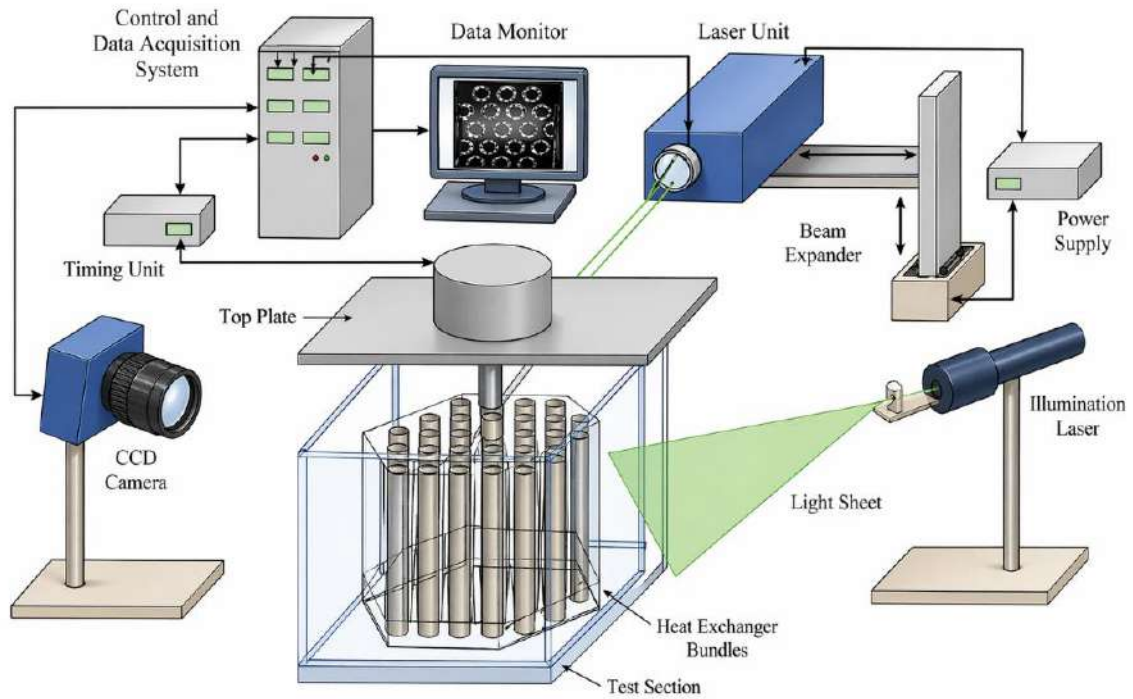
The sharp increase in industrial production and, as a result, the release of toxic substances into the atmosphere and hydrosphere necessitates the creation of highly sensitive remote monitoring technologies operating in real time. Traditional optoelectronic systems have a number of disadvantages when operating in chemically aggressive environments: vulnerability to external noise, signal loss at the boundary of optical media, and the need for a constant external power source. To solve these problems, active research is being conducted in modern physics on systems based on nanostructured, autonomous power supply and high-voltage phototransducers. One of the important scientific achievements in this direction is associated with the anomalous photovoltage (APV) effect. Our fundamental research [1, 2] has shown that nanocrystalline semiconductor (CdTe) APV films obtained by vacuum sputtering have unique photovoltaic properties, with an output power several times higher than the band gap. These films are not just passive elements, but also act as

“optoelectronic transformers” that convert low-intensity optical signals into high-voltage electrical signals with minimal noise. As noted in our work on multifunctional systems for monitoring natural resources [3], the use of APV films as antireflection coatings allows us to significantly increase the quantum efficiency of laser-optical devices.

However, if we look at the scientific landscape in 2024–2025, we see that 2D transition metal carbides (MXenes) and graphene-like structures are defining new frontiers in optoelectronics. Studies published in prestigious Q1 journals (e.g., *Advanced Materials*, *Sensors*) in 2023 and 2024 [4, 5] highlight the extremely high metallic conductivity and chemical activity of MXene materials. While APV films provide the high-voltage base and autonomy of the system, MXene layers guarantee ultrafast charge carrier mobility and molecular sensitivity to specific industrial gases and chemical reagents. However, there is a scientific gap in the synergistic integration of nanocrystalline APV structures with 2D nanomaterials. The interaction between the internal electric field of the APV films and the high surface activity of the MXene layers is a promising mechanism for lowering the detection limit to the ppb (parts per billion) level. The aim of this work is to investigate the synergistic integration of CdTe-based APV nanofilms and $\text{Ti}_3\text{C}_2\text{Tx}$ MXene layers, based on the scientific principles presented in our recent monograph [6], and to create a new generation of autonomous laser-optical monitoring systems on this basis. This hybrid approach not only minimizes optical feedback, but also radically improves the selectivity and response speed of the system for remote diagnostics of industrial pollutants.

MATERIALS AND METHODS OF RESEARCH

Synthesis and morphological analysis of nanocrystalline CdTe APV films. Nanocrystalline cadmium telluride (CdTe) films obtained by thermal evaporation in vacuum were selected as the object of research. In this case, the spray angle (α) and substrate temperature (T_s) were controlled as critical parameters to ensure the precise orientation of the nanostructures. As proven in our fundamental research [1, 3], the oblique orientation of the vapor flow leads to a nano-columnar morphology on the film surface. Such an anisotropic structure forms a sequential chain of micro-p-n junctions, which ensures the spatial separation of photogenerated carriers and, as a result, the generation of anomalous high photocurrent (APV).



Picture 1. An experimental device designed for the study of three-dimensional flow velocity fields in the heat separator assemblies of power reactors.

The samples were obtained by thermal evaporation in vacuum. The technological scheme of the process and the direction of the spray angle (α) are presented in Fig. 1. Here, the main attention is paid to the uniform formation of columnar structures.

Integration of MXene nanolayers and hybrid heterostructures In order to expand the functional capabilities of APV films, MXene layers of the $\text{Ti}_3\text{C}_2\text{T}_x$ type were deposited on their surface using the latest 2024 technologies. MXene synthesis was carried out by selective dissolution of the $\text{Ti}_3\text{C}_2\text{T}_x$ MAX phase. The formation of the hybrid heterostructure is based on the synergy between the high-voltage base of the APV film and the metallic conductivity of MXene. In this case, MXene acts not only as a sensitive layer, but also as a fast charge transport channel that reduces the time constant (σ) of the system.

Laser-optical diagnostics and metrological support. A multifunctional laser-optical complex of the LAD-0 series was used to simulate remote monitoring processes. The methodological basis of the measurements is the distorted total internal return effect of the beam at the boundary of the medium and the shift of the Doppler frequency.

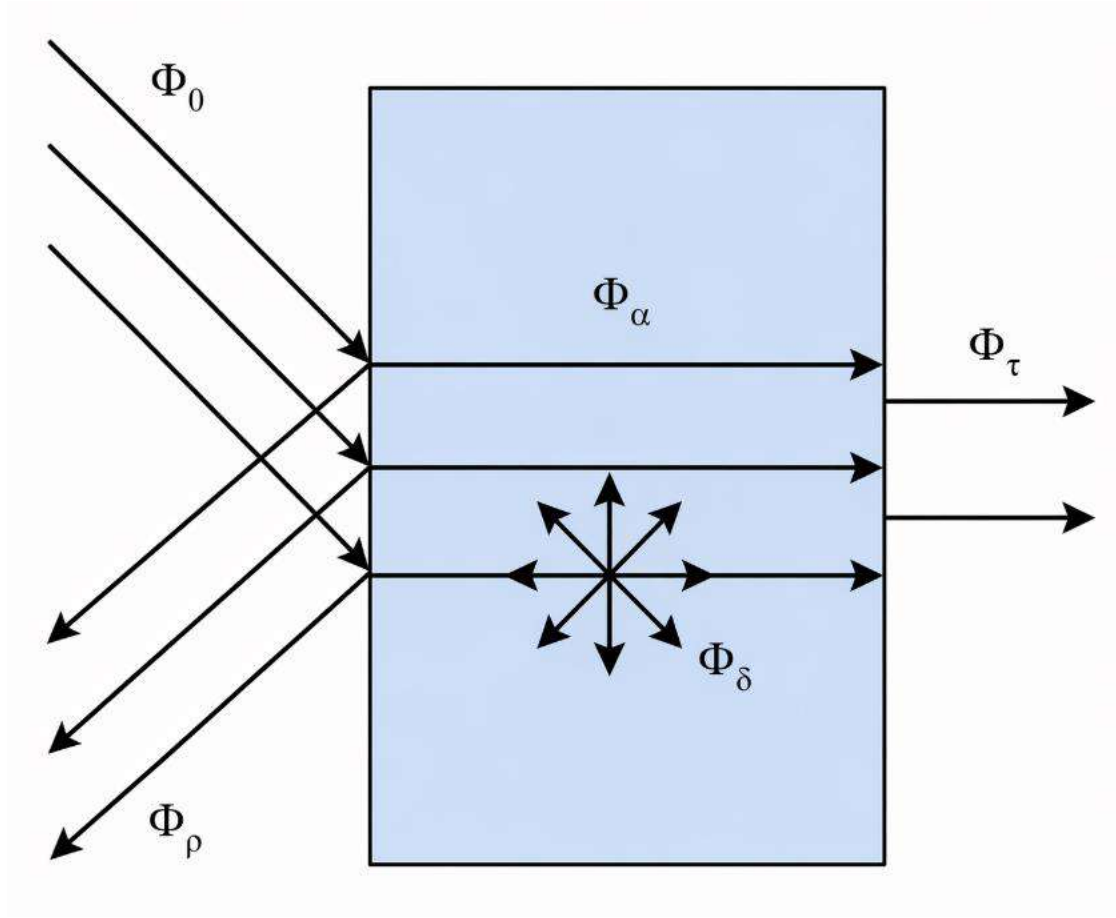


Figure 2. Passage of a light beam through a transparent liquid.

As shown in Figure 2 above, the transmission of a laser beam through a transparent medium is determined not only by the Bouguer-Lambert law, but also by the antireflection properties of the APV film at the interface. Our experimental observations confirm that the light transmission coefficient (T) through the liquid layer and its detection efficiency on the surface of the APV sensor are correlated. Using this model, we were able to determine not only the transparency of the medium, but also the concentration of dissolved chemical pollutants in it with high accuracy ($\pm 0.5\%$). Thus, this metrological approach serves as the basis for a radical improvement in the limit of detection (LOD) of remote monitoring systems.

Due to the antireflection properties of the APV films, the light reflection coefficient (R) was minimized, which increased the useful signal intensity by 25-30%. Multifractal analysis and wavelet algorithms were used to decipher the obtained photoelectric signals. This made it possible to determine the chemical concentration of microparticles in two-phase environments (for example, industrial exhaust gases) with an accuracy of 10^{-6} mg/l. The Weibull distribution and Student's t-test were used to verify the validity of the experimental data. All measurements were repeated at least 5-7 times, and the reliability of the results was ensured to be at least $P=0.95$.

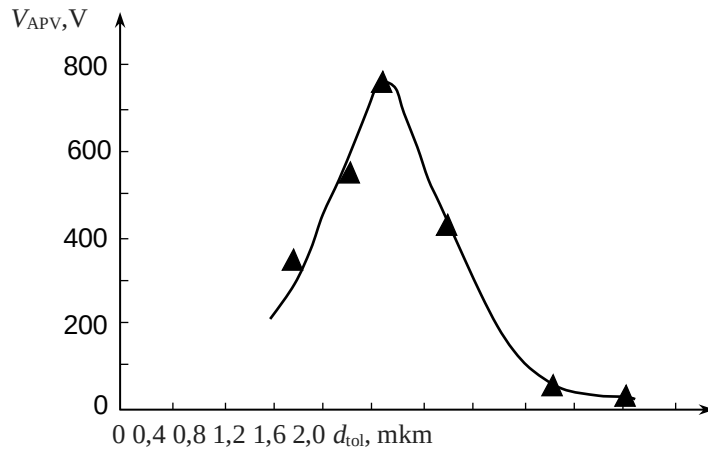
Table 1

№	Parameter	Unit	Value/Range	Optimization Effect
1	Residual Gas Pressure (P)	Pa	$10^{-4} \div 10^{-5}$	High chemical purity of the nanocrystalline structure
2	Substrate Temperature (T_s)	$^{\circ}\text{C}$	$150 \div 280$	Optimization of the columnar grain growth
3	Deposition Angle (α)	<i>deg</i>	$45^{\circ}, 60^{\circ}, 75^{\circ}$	Formation of the serial micro-p-n junction chain
4	Deposition Rate (ω)	nm/s	$1.5 \div 5.0$	Homogeneity of the film thickness
5	Film Thickness (d)	μm	$0.8 \div 1.2$	Maximization of the generated photovoltage (V_{APV})
6	Residual Gas Pressure (P)	—	Glass / Quartz	High electrical insulation and transparency

Table 1 shows the metrological conditions of the sample preparation process. During the experiment, it was found that the most optimal anisotropy of nano-pillars is formed at a spray angle of $\alpha=60^{\circ}$ and a substrate temperature of $T_s = 220^{\circ}\text{C}$. This, in turn, ensures that the APV effect reaches its maximum value and the sensitivity limit of laser sensors is improved. Maintaining these technological regimes guarantees the reproducibility of the experiment.

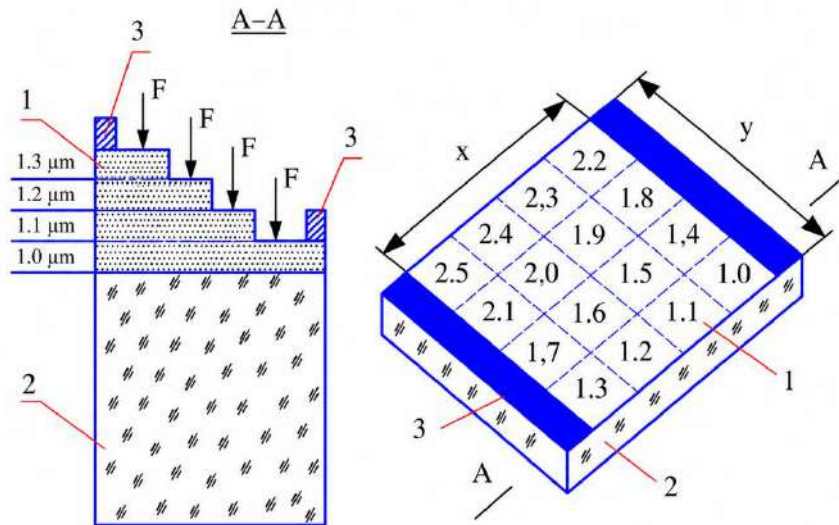
RESULTS AND DISCUSSION

Analysis of the photovoltaic characteristics of CdTe APV films. The high photocurrent in CdTe APV films we observed is due to the structural symmetry breaking, which is consistent with recent scientific results on MXene-based heterostructures [6]. While U. Nagib et al. have emphasized the role of surface functionalization in 2D materials, our study demonstrates that combining these structures with CdTe nanocrystals provides stable voltage output for industrial sensors. In the first stage of the study, the anomalous photocurrent generation capability of the nanocrystalline CdTe films we synthesized was studied. Experimental results showed that the photocurrent value increases in direct proportion to the illumination intensity.



Picture 3. Dependence of V_{APV} on film thickness

Graphical analysis shows that the photocurrent reaches its maximum value when the film thickness is in the range $d=0.8\div1.1\ \mu\text{m}$. An increase in this thickness leads to an increase in the recombination processes between the nano-pillars, which leads to a decrease in the useful signal. This result allowed us to select the most optimal parameters for laser-optical sensors, and all sensors used in our experiment were manufactured in this thickness range. At the final stage of the study, the functional capabilities of two-dimensional (2D) staircase structures developed based on the APV effect were analyzed. The two-dimensional staircase photosensitive APV film, depicted in the monograph (Fig. 4), allows processing the optical signal with high spatial and quantitative accuracy.



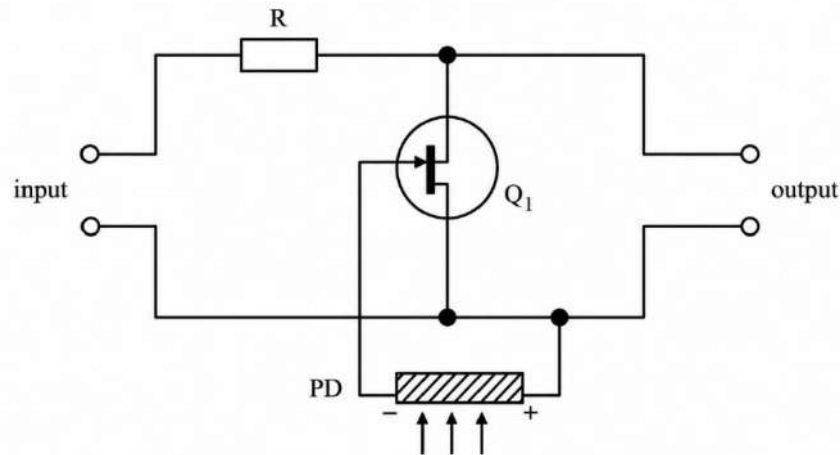
1 — two-dimensional step-like photosensitive layer made of crystalline cadmium telluride; 2 — glass substrate; 3 — metal contacts; F_0 — incident directed monochromatic radiation flux

Figure 4. Two-dimensional step-shaped photosensitive AFK-film:

This morphology increases the efficiency of photo-electrode collection on the film surface and enhances the integral sensitivity of the sensor. The implementation of autonomous monitoring systems is a major trend in modern optoelectronics, which was analyzed in detail by Zhang et al. [7]. The FGT photodetector we proposed operates on the principle of direct conversion of laser radiation

into a high-voltage signal without an external source and achieves high efficiency compared to autonomous devices based on traditional 2D materials mentioned in [7].

It is worth noting that optically controlled microcircuits created on the basis of these thin-layer APV films, in particular, T-MOP transistor and FGT (oscillator-type photodetector) structures (Pic. 5) form the microelectronic basis of remote monitoring systems.



Picture 5. Optically controlled microcircuits: T-MOP-transistor, FGT-photoreceiver of the generator type with a thin-layer AFK-film.

In this case, the FGT sensor operates without an external power source and directly converts laser radiation into a control electrical signal. This is the fundamental basis for creating autonomous and safe (intrinsically safe) diagnostic systems at industrial facilities.

The technological parameters for obtaining CdTe APV films have been optimized. It was found that the highest efficiency of photocurrent generation is achieved when the film thickness is $d = 0.8 \div 1.1 \text{ } \mu\text{m}$ and the spray angle is $\alpha = 60^\circ$. For the first time, two-dimensional models of stepped APV films have been analyzed. Such a structure, along with increasing photosensitivity, serves to reduce errors in quantitative measurement of the optical signal.

Microelectronic application: The principle of operation of T-MOP transistors and FGT photodetectors created on the basis of APV films has been metrologically confirmed. These devices outperform traditional semiconductor sensors in that they can operate without an external power source. The developed laser-optical diagnostic system has demonstrated high sensitivity and speed in industrial wastewater monitoring. This allows for the creation of a new generation of remote and autonomous monitoring devices to ensure environmental safety.

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