Aging and degradation of transparent copper iodide thin film electrodes for functional electronic devices

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Transparent CuI copper iodide thin-film electrodes are widely used in various optoelectronic devices, such as solar cells, electroluminescent displays, touch screens, multifunctional photoconverters, etc. Their advantages are high transparency, because CuI absorbs light in a limited range of wavelengths, which allows them to transmit visible light, making them ideal for transparent devices, low cost, because copper iodide is an inexpensive material, making it economically viable for mass production, simplicity fabrication, as CuI can be easily deposited on various substrates using simple film deposition techniques such as vacuum deposition and magnetron sputtering. However, transparent CuI type thin-film electrodes are subject to aging and degradation, which can reduce their performance and service life. The main factors affecting the aging and degradation of CuI are the processes of oxidation, diffusion, degradation under the influence of light, and humidity. Despite numerous studies in the direction of obtaining high-quality thin films of copper iodide, today there is a need for a detailed study of the processes of their aging and degradation of properties. Therefore, in this article, we investigated the degradation processes of transparent upper copper iodide electrodes of thin-film multicomponent semiconductor heterostructures. This article shows the features of the use of film copper iodide in multilayer thin-film semiconductor structures. The influence of atmospheric conditions and lighting on the values of the rates of degradation of electrical resistance of copper iodide in semiconductor thin-film structures was studied. It has been found that atmospheric exposure to oxygen, moisture and other factors increases the electrical resistance of the copper iodide top electrode, and the use of Elastosil sealant does not lead to appreciable improvement. Heterostructures in vacuum are minimally affected by external factors, and therefore a significant increase in their CuI upper electrode resistance values indicates the predominant role of aging of copper iodide films, which is not related to atmospheric conditions. It was established that natural sunlight significantly increases the degradation of copper iodide films, which should be taken into account when forming and using the corresponding thin film structures.

Key words: copper iodide, upper electrodes, organic semiconductors, thin films, production methods, phthalocyanines.

Старіння і деградація прозорих тонкоплівкових електродів йодиду міді для функціональних пристроїв електронної техніки

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Старіння і деградація прозорих тонкоплівкових електродів йодиду міді для функціональних пристроїв електронної техніки
Prorozry toksylnizovky elektrordiy puty ioyodu moid Cui широко никаростилося в рiзних оптоелектронних приладах, таких як сонячнi батареi, електролюминесцентнi дисплiй, сенсорнi екрани, балатонфункцiональнi фотометривачi та ін. Їхнi переможцi є висока прозорiсть, оскiльки Cui поглинає свiтло в обмеженому дiапазонi довжинi хвиль, що дозволяє їм пропускати вiдповiдно свiтло, робочий як джерело для пророзьок пристроjв, назва вартiсть, бо ioyodu мiдi є недорогим матерiалом, що робить його економiчно вигодним для масового виробництва, оскiльки Cui можна легко наносити на рiзнi пiдвiдки за допомогою простих методiв нанесення пiвки, таких як вакуумне осадження та магнетронне розпилення. Однак пророзь отокон- лізовковi електроди мiдi схильнi до старiння i деградацiї, що може призвести до зниження їхньої продуктивностi та термiну служби. Основними факторами, що впливають на стiйкiсть i деградацiю Cui є процеси окиснення, дифузiя, деградацiя пiд впливом свiтла, вологiсть. Незважаючи на численнi дослiдження в напрямку виявлення високоякiсних тонких пiовок ioyodu мiдi, на свого- дiнiшнiй день є існують вплив детального вивчення процесiв їхнього старiння i деградaцiї властивостей. Тому в даннiй статтi мi дослiджуємо процеси деградацiї пророзьок верхнiх електродi йойоду мiдi тонкiх iоннiх багатокомпонентних пiвпровадкових гетероструктур. Встановлено, що дiї атмосферних умов, пов'язанi з киснем, вологiстю i тимчасовi факторами оцiнюють значення електричного опoru верхнього електрору йойоду мiдi, а використання гетероструктур мiдi в багатокомпонентних пiвпровадкових структурах. Дослiдження вплив атмосферних умов на стiйкiсть верхнього електрору йойоду мiдi на iоннiх тонкiх iоннiх багатокомпонентних структурах. Встановлено, що дiї атмосферних умов, пов'язанi з киснем, вологiстю i тимчасовi факторами оцiнюють значення електричного опoru верхнього електрору йойоду мiдi, а використання гетероструктур мiдi в багатокомпонентних пiвпровадкових структурах. 

**Introduction**

Transparent CuJ copper iodide thin-film electrodes are widely used in various optoelectronic devices, such as solar cells, electroluminescent displays, touch screens, multifunctional photovaracters, etc. Their advantages are high transparency, as CuJ absorbs light in a limited range of wavelengths, allowing them to transmit visible light, making them ideal for transparent devices, low cost, as CuJ is an inexpensive material, making it cost-effective for mass production, ease of fabrication, as CuJ can be easily deposited on various substrates using simple film deposition methods such as vacuum deposition and magnetron sputtering (Frey & Khan, 2015; Davydenko et al., 2016; Konakov at al., 2021).

However, transparent CuJ type thin-film electrodes are subject to aging and degradation, which can reduce their performance and service life. The main factors affecting the aging and degradation of CuJ are oxidation processes, since CuJ can oxidize in air, which leads to the formation of CuO, which is not conductive and can deteriorate the transparency of the electrode, diffusion, since copper and iodine ions can diffuse from CuJ into other layers of the device, which can lead to short circuits and other problems, light degradation, because CuJ can degrade when exposed to UV light, which can reduce the conductivity and transparency of the electrode, humidity, because CuJ can absorb moisture from the air, which can lead to corrosion and degradation of the electrode. In the processes of aging and degradation of copper iodide thin films, their thickness and topology are also important factors. Thus, in the experiments on the production of CuJ films by iodination, it was established that as the film thickness increased, the size of the grains increased, and the shape of the grains changed from regular hexagonal to triangular, in particular, atomic force microscopy studies showed that the rms roughness of samples of different thicknesses varied from 58.6 nm to 101 nm (Zhang et al., 2016). The mentioned authors investigated the decomposition of iodine indirectly by analyzing the relative intensity of the luminescence peaks of various defects in the photoluminescence spectra. The decomposition of iodine leads to a change in the type and density of defect states in the films, which significantly affects the optoelectronic properties of the films, in particular, the electrical resistance of copper iodide with a thickness of 440 nm increased from 0.078 Ω×cm to 0.165 Ω×cm after decomposition. The results of the experiment show that iodine decomposes more sharply in thick samples. Decreasing the thickness of the films can weaken the decomposition of iodine, but obvious cracks and crystal discontinuities appear in samples with a small thickness. An in-depth analysis of photoluminescence and electrical resistance spectra shows that iodine decomposition can be directly related to surface roughness. By adjusting the film thickness, copper iodide films with structural integrity, good stability, and excellent photovoltaic properties can be obtained.

The authors (Rahman at al., 2019) studied in detail the effect of temperature and liquid phase iodination on the electrical properties of CuJ thin films obtained by centrifugation. Their research using SEM images shows that CuJ thin films are polycrystalline in nature, iodine doping improves the crystal quality, and the surface uniformity of CuJ thin films is increased by iodine doping. Doping with iodine also increases the conductivity, carrier concentration and mobility of the films, which was confirmed by Hall method studies. The temperature-dependent resistivity of CuJ films shows a sharp drop at ~80 °C for undoped films, while this behavior disappears for iodine-doped films. The optical transmittance and band gap of the iodine-doped films also increase, indicating high degeneracy of the films. Such results mean that CuJ thin films doped with iodine are more resistant to aging and degradation processes.

In the research of the authors (Yang et al., 2016) it is shown that the degenerate electrical conductivity of p-type copper iodide thin films is achieved under iodine-enriched growth conditions, which provides record high conductivity values at room temperature – 156 C/sm for deposited CuJ and 283 C/sm for iodine-doped CuJ. At the same time, the films appear clear and exhibit a high transmittance of 60–85 % in the visible spectral range. The implementation of such simultaneously high conductivity and transparency increases the p-type Q factor: its...
value increases from ~200 to ~17000 Ωm⁻¹. Polycrystalline CuJ thin films were deposited at room temperature by jet sputtering. Their electrical and optical properties were studied in comparison with other p-type transparent conductors and it was shown that aging and degradation processes slow down with this method of obtaining CuJ films.

The authors (Viloan et al., 2021) investigated the synthesis of CuJ thin films by low-energy ion bombardment using bipolar and conventional pulsed target configurations in combination with different substrate displacement techniques. For the bipolar method with a substrate at a floating potential, the minimum ion acceleration and the change in film growth were measured as the potential of the substrate holder increased to the level of the applied positive voltage. In contrast, the use of a bipolar method with a substrate at ground potential results in a similar ion current profile with a synchronized pulse offset with the same delay and time as the positive pulse. The observed differences in film growth can be explained not only by ion energy, but also by the type of ions (working gas vs. metal ions) that are accelerated either during the positive pulse or during substrate displacement. Thus, by selecting the technological parameters of production, it is possible to widely adjust both the properties and aging processes of condensates.

The authors (Bae et al., 2023) obtained highly conductive copper iodide films with excellent thermoelectric characteristics using spray printing technology. Compensating for the loss of iodine caused by sublimation or evaporation during the spray printing process, the addition of a small amount (1 at. %) of iodine (J₂) to the CuJ precursor solution was extremely effective in producing CuJ films exhibiting excellent electrical conductivity of 207.6 C×sm⁻¹ and the power factor is 673.3 μW×m⁻²×K⁻². Importantly, the added J₂ played a crucial role in increasing the electrical conductivity by providing iodide to improve the Cu to J stoichiometry in the CuJ films and improve crystallite growth. This efficient and simple approach to the fabrication of solution-processable transparent conductors has potential applications for the development of transparent conductive coatings with improved performance.

Methods to prevent aging and degradation of CuJ are also protective coatings, which applied to CuJ can help prevent oxidation, diffusion and degradation by light, vacuum sealing, since sealing the device can help prevent CuJ from oxidizing and absorbing moisture, adding impurities, since it can help to improve the resistance of CuJ to degradation. Research and development in this area is focused on the development of new materials and methods that can help improve the aging and degradation resistance of CuJ-type transparent thin-film electrodes. It is important to note that the rate of aging and degradation of CuJ depends on a number of factors, such as environmental conditions, material composition and manufacturing method, etc.

The aim of the study

Despite numerous studies in the direction of obtaining high-quality thin films of copper iodide, today there is a need for a detailed study of the processes of their aging and degradation of properties. Therefore, in this article, we investigated the degradation processes of transparent upper copper iodide electrodes of thin-film multicomponent semiconductor heterostructures.

Material and methods

To study the processes of aging and degradation of transparent upper electrodes of copper iodide, we studied multicomponent thin-film heterostructures (HS) of organic semiconductors (OS) with cadmium sulfoselenides (SnO₂/CdsₓSe₁₋ₓ/OS/CuJ), which are promising active elements for multifunctional photoconverters. As OS, pentacene (Pn), lead phthalocyanine (PbPc) and chloroalumnum-chloro phthalocyanine (CIAICIPc) were used. In order to find out the causes of the aging processes, HS was stored in the dark and in a vacuum, in the dark and in the air, under direct sunlight, and also protected from the effects of external factors with the organosilicon sealant Elastosil 137–180, which is characterized by good moisture protection properties due to its high hygroscopicity and transparency in the ultraviolet and visible regions of the spectrum. Protection by elastosil from the influence of gases, in particular oxygen, is less effective than moisture, so it is possible to predict weak doping of CuJ and OS by O₂ molecules that diffuse through the sealant layer. Elastosil was applied to the surface of HS immediately after removal from the vacuum chamber by a simple method of varnishing, and the samples were stored in the dark in the air. The parameters of the samples stored in a vacuum were measured in air, so it is necessary to take into account the partial effect of atmospheric conditions on the properties of HS. HS parameters, which were preserved under direct sunlight, were measured approximately at the time of maximum intensity of sunlight in order to avoid the influence of the effect of partial recovery during the night period. Measurements of the electrical resistance values of the upper R_CuJ copper iodide electrode were performed under illumination alternately from both sides with polychromatic light with an intensity of 750 W×m⁻². At the same time, the resistance of SnO₂/OS/CuJ sandwich structures, which were stored in the dark in air, was also measured. Previous studies have shown that the electrical and photoconductivity of our CdsₓSe₁₋ₓ films under the influence of atmospheric conditions for a long time (more than 1 year) practically do not change. Therefore, the degradation of the CdsₓSe₁₋ₓ layers, which were part of the HS, was not studied separately.

One of the most used methods for depositing semiconductor thin films is thermal vacuum sputtering (Bunshah, 1994; Seshan, 2002; Frey & Khan, 2015; Ghanbari & Salavat-Niasari, 2021). The deposition of multicomponent thin films of chalcogenide semiconductors, linear polycenes, metallophthalocyanines, as well as transparent upper copper iodide electrodes in our research was carried out in serial vacuum sputtering units of previous generations, such as URM 3.279.011 with a steam-oil high-vacuum pump and URM 3.279.047 with a high-vacuum ion-heter pump, as well as in a modern combined installation of vacuum sputtering of thin films manufactured by the company “Torr International” (USA) accord-
ing to previously described methods (Tsizh & Dziamski, 2019, 2020, 2022, 2023). It has been experimentally confirmed that high-quality films of organic semiconductors and copper iodide without heterogeneous inclusions, with properties close to single crystals, are deposited at low sputtering speeds. Therefore, the sputtering rate of OS was 0.5...1.0 nm·s⁻¹. Control of sputtering speed and film thickness was carried out using the KST-1 ionization sensor, the work of which is based on the partial ionization of the material transferred to the substrate by an electron beam, and the measurement of the resulting ion current proportional to the density of the vapor phase, and, accordingly, the speed of film sputtering. For each substance, the sensor was calibrated based on the results of thickness measurements on an interference microscope MII-4.

Glass, quartz, sital and other plates were used for substrates. Substrates were heated using infrared radiation from quartz lamps, the temperature was controlled by chromel-alumelum thermocouples. To improve the quality and adhesion of condensates, chemical, and in some cases also ionization cleaning of substrates was carried out before sputtering. They used technology that allows for quick and effective removal of pollution, including organic nature. After preliminary degreasing with acetone, glass substrates were cleaned by boiling in a solution of hydrogen peroxide in the presence of ammonia, followed by washing in hot deionized water and drying in isopropyl alcohol vapors. For a more effective effect of detergents, ultrasonic excitation was used. In addition, before sputtering, thermal cleaning of the substrates was carried out in a vacuum by heating for half an hour at 623 K.

Control of sputtering speed and film thickness in the process of their growth was carried out by an optical method, which is based on the interference of passing light beams due to reflection from the boundaries of the film with the substrate and vacuum. At the same time, an increase in the physical thickness of the film by an amount equal to a quarter of the wavelength of light corresponds to an increase in the order of the interference extremum. Since in the area of transparency of films, the value of the refractive index is weakly dependent on \( \lambda \), the interference pattern was extracted using an interference filter with a bandwidth of \( \lambda = 774 \pm 15 \text{ nm} \), which increases the accuracy of measurements. In addition, in the area of film transparency, there are no undesirable processes of reducing the intensity of the interference pattern due to absorption. In the installations we use, optical control units are provided, which allow modulation, selection and amplification of the useful light signal, which ensured the measurement of the thickness of condensates with an accuracy of at least 10 nm at the extreme points and 20 nm between them.

In addition to controlling the thickness of the films during the sputtering process, the thickness was measured on an MII-4 interference microscope and on two-beam spectrometers. The Linnyk MII-4 microinterferometer made it possible to measure the height of irregularities in thin films, such as the etched edge, scratches and others from 0.1 to 5 \( \mu \text{m} \) with an accuracy of 6 % due to the use of the phenomenon of interference of pre-separated light beams reflected from the surface of the film and the substrate, which emanate from a single source point. To increase the measurement accuracy, the thickness of films with \( d < 0.5 \mu \text{m} \) was determined in parallel from the values of the difference in optical densities \( D - D_0 \). To do this, a wavelength was chosen on the spectral dependence \( D \) at which \( 0.5 < D < 2.0 \) for films of a given composition with \( 0.1 < d < 0.5 \mu \text{m} \), and the value of \( d \) was specified based on the calibrated dependence \( D(d) \). This made it possible to increase the accuracy of film thickness measurement to 4 % in the thickness range of 0.1...0.5 \( \mu \text{m} \).

Optical absorption spectra of polymer films were obtained using a modified two-beam optical spectrometer Specord M-400 with the following measurement parameters: spectral range: 200...900 nm, slit width: 1 nm, integration time: 1 s, scan step: 1 nm, recording speed: 10 nm/s. Optical beam of the spectrometer passed directly through the film and the substrate, was collimated and perpendicular to the surface of the film. Surface reflection when measuring spectra optical absorption was not taken into account because the relative changes. All measurements were performed at temperature 293 ± 1 K. The analysis of the results was performed using a standard correlation program, in which the relative error in the entire measurement range did not exceed 1.5 %.

**Results and discussions**

The results of the research are presented in Tables 1–3 in the form of time dependences of the ratio of the initial resistance values of the CuJ upper electrode \( R_{CuJ0} \) to their values \( R_{CuJ} \) at the time \( t \) of the measurements. Since the most significant changes occur in the first few tens of hours, the rates of degradation are presented in a semilogarithmic scale. The first measurements were carried out within 1 hour after spraying, and the next ones – after approximately 10, 15, 20, 30, 50, 100, 200, 500, and 1000 hours. For greater reliability of the obtained data, there were at least three HS in each batch. The maximum deviations from the average values did not exceed 10 %.

**Tables 1–3** present the rates of degradation of the resistance of the upper CuJ electrode of SnO₂/CdS₆₅/CuJ/OS/CuJ heterostructures. The following \( R_{CuJ} \) changes are characteristic of all HS. Over time, \( R_{CuJ} \) values first increase sharply and then more slowly, with minimal increases observed in vacuum in the dark, and maximal increases during storage in air under illumination. The rates of degradation of \( R_{CuJ} \) HS values in the dark in air occupy intermediate values. In HS covered with elastosil, the increase in \( R_{CuJ} \) values is almost no different from similar HSs without elastosil, and is not highlighted separately in the tables. It is interesting that the values of \( R_{CuJ} \) of HS, which were stored under sunlight after about 200 hours of exposure and sharp growth, begin to gradually decrease, and over time reach values of \((5–10) \ R_{CuJ0}\), which is better than for HS in the dark, and for HS with pentacene it is better than in a vacuum. Starting from 200 h. exposure, and especially after 500 h. the values of \( R_{CuJ} \) of all HS somehow stabilize at the level of \((5–20) \ R_{CuJ0}\). We observed an increase in \( R_{CuJ} \) above the values of \((50 \ R_{CuJ0})\) only for HS that were stored in the air under sunlight in the time interval of 20–150 h. The maximum increase in \( R_{CuJ} \) of HS data was \(10^3 \ R_{CuJ0}\).
Degradation rates of electrical resistance of the CuJ upper electrode of the SnO$_2$/CdS$_{0.6}$Se$_{0.4}$/pentacene/CuJ heterostructure in the dark in vacuum, in the dark in air, and under sunlight in air

<table>
<thead>
<tr>
<th>$R_{CuJ}(0)$ / $R_{CuJ}(t)$</th>
<th>Exposure time, hours</th>
</tr>
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<tbody>
<tr>
<td>In the dark in a vacuum</td>
<td>0.85 0.68 0.48</td>
</tr>
<tr>
<td>In the dark in the air</td>
<td>0.79 0.54 0.32</td>
</tr>
<tr>
<td>With sunlight in the air</td>
<td>0.64 0.31 0.01</td>
</tr>
</tbody>
</table>

Degradation rates of electrical resistance of the CuJ upper electrode of the SnO$_2$/CdS$_{0.6}$Se$_{0.4}$/lead phthalocyanine/CuJ heterostructure in the dark in vacuum, in the dark in air, and under sunlight in air

<table>
<thead>
<tr>
<th>$R_{CuJ}(0)$ / $R_{CuJ}(t)$</th>
<th>Exposure time, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the dark in a vacuum</td>
<td>0.34 0.82 0.68</td>
</tr>
<tr>
<td>In the dark in the air</td>
<td>0.87 0.68 0.42</td>
</tr>
<tr>
<td>With sunlight in the air</td>
<td>0.74 0.42 0.11</td>
</tr>
</tbody>
</table>

Degradation rates of electrical resistance of the CuJ upper electrode of the SnO$_2$/CdS$_{0.6}$Se$_{0.4}$/chloro-aluminum-chloro phthalocyanine/CuJ heterostructure in the dark in vacuum, in the dark in air, and under sunlight in air

<table>
<thead>
<tr>
<th>$R_{CuJ}(0)$ / $R_{CuJ}(t)$</th>
<th>Exposure time, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the dark in a vacuum</td>
<td>0.86 0.61 0.62</td>
</tr>
<tr>
<td>In the dark in the air</td>
<td>0.75 0.39 0.18</td>
</tr>
<tr>
<td>With sunlight in the air</td>
<td>0.74 0.23 0.08</td>
</tr>
</tbody>
</table>

To explain the peculiarities of the degradation of $R_{CuJ}$ values, the following processes must be taken into account: natural aging of CuJ films, changes in their properties under the influence of light and atmospheric conditions, possible interaction of CuJ with contacting OS. In addition, the topology of multi-layer HS leads to the formation of many folds of the upper layer in the places of the sharp edge of the films, the so-called «steps». At such bends, the thickness of the upper layer decreases, additional mechanical stresses are created, and degradation processes intensify. Therefore, minimal increases in $R_{CuJ}$ values are observed for sandwich structures, in which the number of folds of the upper layer is less than in HS. Comparing the rates of degradation of $R_{CuJ}$ values of HS, which were stored in different conditions, the following conclusions can be drawn. Atmospheric effects due to oxygen, moisture and other factors increase the $R_{CuJ}$ value, and the use of elastosil sealant does not lead to appreciable improvement. HS in vacuum are minimally affected by external factors, and therefore a significant increase in their $R_{CuJ}$ values indicates the predominant role of aging of CuJ films, which is not related to atmospheric conditions. Natural sunlight significantly increases the degradation of CuJ, and after approximately 500 hours of exposure, $R_{CuJ}$ values are partially restored. Local extremes of some degradation rates can be explained by the superposition of different aging mechanisms. For example, the local decrease in $R_{CuJ}$ values of HS SnO$_2$/CdS$_{0.6}$Se$_{0.4}$/ClAIICPC/CuJ in vacuum (Table 3) can be explained by the temporary predominance of the processes of decreasing the $R_{CuJ}$ value over their increase due to iodine desorption.

Thus, the conducted studies show the role of atmospheric conditions and lighting in the processes of degradation of the CuJ upper electrode resistance and indicate the peculiarities of the use of film copper iodide for these purposes.

Conclusions

In this article, it is experimentally confirmed that the processes of aging and degradation of the resistance of the upper CuJ electrode in multicomponent heterostructures play a significant role in the formation of operational parameters of functional units of electronic equipment. Features of the use of film copper iodide in multilayer thin-film semiconductor structures are shown. The influence of atmospheric conditions and lighting on the values of the rates of degradation of electrical resistance of copper iodide in semiconductor thin-film structures was studied. Atmospheric exposure to oxygen, moisture, and other factors has been found to increase the electrical resistance of the CuJ top electrode, and the use of an elastosil sealant does not lead to appreciable improvement. Heterostructures in vacuum are minimally affected by external factors, and therefore a significant increase in their CuJ upper electrode resistance values indicates the predominant role of aging of copper iodide films, which is not related to atmospheric conditions. Natural sunlight significantly increases the degradation of copper iodide films, which should be taken into account when forming and using appropriate thin-film structures.

Prospects for further research. In further research, it is necessary to continue the optimization of methods for obtaining thin-film electrodes of multicomponent struc-
tures of organic and inorganic semiconductors in order to improve their properties.

Conflict of interest
The authors declare that there is no conflict of interest.

References


