

Luminescent down-shifting coatings for UV-responsive CCD image sensors

Streszczenie. Opracowano luminescencyjne powłoki z konwersją promieniowania na bazie kompleksów europu z fluorowanymi β -diketonami do rozszerzenia czułości sensorów CCD w zakresie ultrafioletu bez obniżania innych parametrów (rozdzielczości przestrzennej, czułości). Powłoki naniesiona na światłoczułą powierzchnię krzemowej matrycy CCD zapewniły jej wydajność kwantową w zakresie 220–380 nm do 40% sprawności przy maksymalnej czułości. (Powłoki luminescencyjne z konwersją promieniowania do zwiększenia czułości sensorów CCD w zakresie UV)

Abstract. Luminescent UV radiation down-shifting coatings based on europium complexes with fluorinated β -diketones for extension the range of spectral sensitivity of CCD image sensors into the ultraviolet region without decreasing the other parameters (spatial resolution, sensitivity, etc.) has been developed. Coatings applied to the photosensitive surface of a silicon CCD array ensured their quantum efficiency in the range of 220–380 nm up to 40% efficiency at the maximum spectral sensitivity.

Słowa kluczowe: luminescencyjne powłoki z konwersją promieniowanie w zakresie UV, kompleksy europu.

Keywords: luminescent down-shifting coating for UV region, complexes of europium.

Introduction

The extension of the spectral sensitivity of photodetectors, in particular, silicon charge coupled devices (CCDs) into the ultraviolet (UV) region without decreasing the other parameters (spatial resolution, NIR sensitivity, etc.) is actual problem whose solution makes it possible to considerably increase the potentialities of the spectral and optical devices used. In particular large - format ultraviolet image sensors have been and are actively being developed for a variety of space-borne astronomy missions, science and military applications.

The rapid drop decrease in the sensitivity of silicon photodetectors in the short-wave region of the spectrum is associated with a small penetration depth of UV radiation into silicon. Most of the radiation is absorbed in the polysilicon gate region and very little penetrates into the buried channel region of the sensor to generate a photoelectric signal. Two different approaches to improve this limitation are: structural modifications to the CCD and post processing deposited phosphor coatings. Structural designs such as back-side thinned devices, exhibit good characteristics but require complicated fabrication processes that may be expensive to manufacture.

A universal method for increasing the sensitivity of photodetectors in the UV spectral region is the application to the photosensitive surface of a detector a phosphor absorbing the UV radiation and reemitting it in a longer-wave region. These light converters for CCD image sensors must satisfy several conditions: complete absorption of radiation throughout the UV region in a layer, a few micrometers thick; a high transmission in VIS and NIR spectral range, a high quantum yield of luminescence (up to 90–100%) at high concentrations, quantum yield and spectrum of luminescence should be independent of the excitation wavelength, the luminescence spectrum displaced from the absorption spectrum toward long wavelengths by at least 150 nm, the luminescence spectrum maximum coinciding with the maximum of the photodetector spectral sensitivity and a high thermo- and photo-stability.

Both organic and inorganic phosphor coatings were used [1–6]. Blouke et al. [1] was a first who solved the problem of developing a UV image sensor for the STWF/PC space telescope on the basis of silicon CCD matrices. As a luminescent converter, they used vacuum-deposited 0.05–0.20 μm films of aromatic hydrocarbon — coronene. Upon

excitation by $\lambda < 380\text{nm}$, coronene luminesces in the green spectral region with a maximum at 500 nm. Measurements of the total quantum efficiency of the 800×800 CCD matrix covered with 0.16 μm thick coronene film at $\lambda = 253.7$ nm yielded quantum efficiency only 9%. Compared with inorganic materials [2], organic materials have higher fluorescence conversion efficiency with more uniform coating, so they are more commonly used to make phosphor coating. The inorganic coating also is not completely transparent at wavelengths outside of the absorption spectrum [2]. So a composite organic phosphor coating Metachrome II have been developed by Teledyne Photometrics to improve sensitivity of both front-illuminated and back-illuminated CCDs in blue-visible and UV wavelengths [3].

We have explored the possibility of using complexes of europium with fluorinated β -diketones in UV radiation film converters. The β -diketones consisting of a combination of aromatic and aliphatic substituents are appropriate for preparation of europium(III) complexes exhibiting good luminescence properties at UV excitation. Such organic ligands, have the possibility of sensitizing the Eu(III) ion luminescence by transfer of the electronic excitation energy to the central metal ion ("antenna effect"). Additionally, the β -diketone ligands bearing "hard" donor atoms ensure the formation of stable complexes that are soluble in organic solvents [7].

Luminescence of Europium complexes

Eu(III) β -diketonate complexes due to their narrow $f-f$ emissions bands and high luminescence quantum yield is the one most efficient luminescent emitters in red spectral region at UV excitation [7]. It was investigated the spectral-luminescent properties of tris-complexes of Eu(III) with thenoyltrifluoroacetone (TTA), 2-naphthyltrifluoroacetone (NTA), and their adducts with a number of nitrogen bases: 1,10-phenanthroline (phen), diantipyrylpropylmethane (DAPM), and diantipyrylphenylmethane (DAPhM). As a matrix, we chose polymethylmetacrylate (PMMA). PMMA is transparent in the UV spectral region up to 225 nm, and β -diketonates of europium exhibit in PMMA a fairly good solubility. Upon excitation into the UV absorption bands of ligands intense ${}^5D_0 \rightarrow {}^7F_j$ luminescence of Eu^{3+} is observed (Fig. 1a).

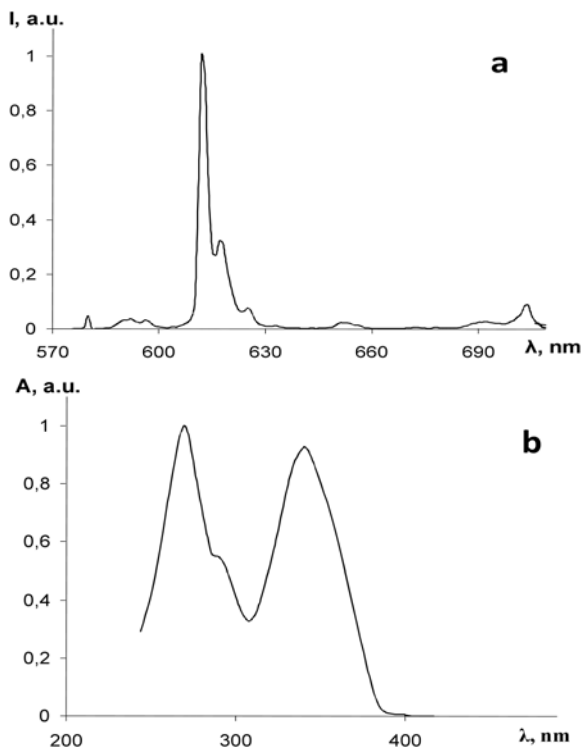


Fig.1. $\text{Eu}(\text{TTA})_3 \cdot \text{DAPM}$ w PMMA film at 25°C: (1a) - luminescence spectrum at $\lambda_{\text{ex}} = 360 \text{ nm}$, (1b) - absorption spectrum

The most intense band in the luminescence spectrum is at 614nm (${}^3D_0 \rightarrow {}^7F_2$ transition; 70% of the total luminescence intensity). The absorption spectrum of adducts of $\text{Eu}(\text{III})$ - β -diketonates with nitrogen bases overlaps practically the entire UV spectral region (Fig.1b)

The value of the absolute quantum yield of luminescence was determined at room temperature with the use of an integrating sphere [8] in order to evaluate the intensity of luminescence emitted by thin film coating on quartz slide in all directions. In table 1 presents the measurement data for the quantum yields φ and lifetimes τ of the ${}^5D_0 \rightarrow {}^7F_j$ fluorescence of a number of investigated europium β -diketonates in PMMA films on quartz slide at 293K and 77K. It is seen that quantum yield of fluorescence at room temperature reaches 0.68 – 0.77 for the investigated complexes. These are likely to be the highest known values of the quantum yield of fluorescence of Eu-chelates at 293K upon excitation into the absorption bands of ligands [7]. The quantum yield of luminescence of europium β -diketonates in thin PMMA films is independent of the exciting wavelength in the 225–370 nm range. In all cases decrease in the temperature leads to an increase in the quantum yield of luminescence - at 77K is close to unity (tab.1).

Table 1. The quantum yield φ and lifetime τ of luminescence of europium complexes in PMMA films at 293K (a) and 77K (b).

Complex	φ^a	φ^b	$\tau^a \mu\text{s}$	$\tau^b \mu\text{s}$
$\text{Eu}(\text{TTA})_3\text{phen}$	0,68	0,87	615	670
$\text{Eu}(\text{TTA})_3\text{DAPhM}$	0,69	0,85	510	530
$\text{Eu}(\text{TTA})_3\text{DAPM}$	0,71	0,98	510	530
$\text{Eu}(\text{NTA})_3\text{phen}$	0,73	0,98	580	650
$\text{Eu}(\text{NTA})_3\text{DAPhM}$	0,75	1,00	500	540
$\text{Eu}(\text{NTA})_3\text{DAPM}$	0,77	1,00	500	550

The results of the spectral-luminescence investigations show that PMMA films activated by $\text{Eu}(\text{III})$ - β -diketonates basically meet the requirements for a luminescent UV radiation down-shifting converter.

Preparation of the luminescent down-shifting coatings.

The concentration of europium chelates introduced into a polymer should be very high ($> 1\text{M}$) in order to provide complete absorption of UV radiation in a thin layer. In this connection, the influence of the concentration of europium β -diketonates on the luminescence lifetimes has been checked. At a concentration of $C=0.3, 1.3,$ and 3.0 M , the fluorescence lifetimes of $\text{Eu}(\text{TTA})_3 \cdot \text{TBPh}$ (where TBPh is tributylphosphate) in PMMA ($\lambda_{\text{ex}} = 266 \text{ nm}$, $\lambda_{\text{det}} = 614 \text{ nm}$) were 575, 575, and 530 μsec , which points to the absence of concentration quenching of ${}^5D_0 \rightarrow {}^7F_j$ luminescence up to concentrations of 1M. Since the extinction coefficient ϵ of $\text{Eu}(\text{III})$ - β -diketonates is $2 \cdot 10^4 \text{ mole}^{-1} \cdot \text{liter} \cdot \text{cm}^{-1}$, at a concentration of 1M and a layer thickness of 2 μm an absorption $A = \epsilon c l = 4.0$ providing complete absorption of incident radiation is attained.

One can obtain 1–5- μm -thick luminescent coatings by the spin-coating, immersion, casting, and other methods. Evaluation of these methods has shown that the most thickness-homogeneous films with the least number of defects are obtained by the spin-coating method. The technological process of creating a luminescent coating involves the preparation of the initial composition representing a polymer and luminophore-activator solution and its application to the prepared surface. To prepare the compositions, we used a solvent reagent-grade toluene, a polymer PMMA, preliminarily purified by the method of precipitation by methanol from the toluene solution, and a $\text{Eu}\beta$ -diketonate complex — the compounds under investigation.

The polymer is first introduced into the solvent and, when heated to 50°C and continuously stirred, it is maintained until it is completely dissolved (about 5 hours). Then $\text{Eu}\beta$ -diketonate is added to the resulting solution and also kept under continuous stirring until complete dissolution. The resulting mixture is filtered under pressure through a filter with a pore diameter of 0.8 μm . At the spin-coating process rotation speed was 2000 rpm and the rotation time was 1 min. After coating, the CCD is dried in an oven at a temperature of 60°C for 30 minutes. The thickness of the resulting luminescent coating is 2 μm . Its microinhomogeneity is less than 0.2 μm .

A test of luminescent coatings deposited on quartz slides by the spin-coating was carried out for heat resistance and frost resistance. When testing for heat resistance, the samples were heated and kept at a temperature of 100°C, and when tested for frost resistance, they were cooled and kept at a temperature of -70°C. After these tests, no changes were found in any parameters of the luminescent coatings.

Comparing the luminescence spectra of polycrystalline Eu complexes and the one of the complexes in toluene and PMMA films showed that the structural uniformity of studied complexes was saved in luminescent coatings. Significantly that homogeneity films stayed unchanged also at low temperatures up 77K.

Characteristics of the silicon photodiode with a UV radiation down-shifting coating

For the silicon photodiode, it was measured the spectral sensitivity curve in units of quantum efficiency Q before and after applying a coating (Fig.2). It is seen that quantum efficiency reaches 65% and 32% respectively at $\lambda = 850 \text{ nm}$ (maximum at the spectral sensitivity) and $\lambda = 614\text{nm}$ (the fluorescence maximum of $\text{Eu}(\text{TTA})_3\text{DAPM}$). Below 400nm the photodiode is practically insensitive (the quantum efficiency is less than 1%).

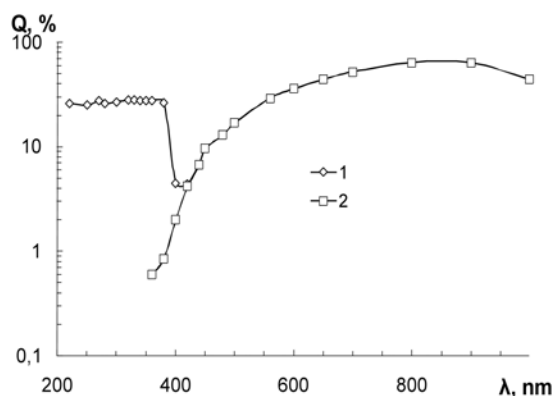


Fig.2. Curves of the spectral sensitivity of the FD-4K photodiode without a luminescent coating (1) and with an $\text{Eu}(\text{TTA})_3\text{DAPM}$ -based film converter (2)

The application of PMMA coating with $\text{Eu}(\text{TTA})_3\text{DAPM}$ to the photosensitive surface of the diode sharply increases the sensitivity in the UV region without decreasing the sensitivity in the visible and IR regions. With increasing concentration of $\text{Eu}(\text{TTA})_3\text{DAPM}$ in PMMA the conversion efficiency increases, especially at the edge of the $\text{Eu}(\text{TTA})_3\text{DAPM}$ absorption band (380–390 nm). At the absorption band maximum ($\lambda = 350$ nm) quantum efficiency reaches 0.26 and 0.27 respectively for $C = 0.28$ M and $C = 0.57$ M. i.e., Q practically remains unchanged. This corroborates the data on the absence of the concentration quenching of Eu - β -diketonate luminescence at least up to $C = 1$ M.

The total quantum efficiency converting UV photons to useful signal electrons in CCD of the combination film-silicon photodetector is determined by the expression

$$(1) \quad Q = (1 - S)(1 - R_1)(1 - R_2)[\varphi_f(1 - F_1)A(\lambda)Q_d - (1 - A(\lambda))Q(\lambda)]$$

$$\text{where } R_1 = \left\{ \frac{n_f - 1}{n_f + 1} \right\}^2, R_2 = \left\{ \frac{n_{Si} - n_f}{n_{Si} + n_f} \right\}^2, F_1 = \frac{1}{2} \left[1 - \frac{(n_f^2 - 1)^{1/2}}{n_f} \right],$$

S is the portion of the incident flux scattered in the film, R_1 and R_2 are the Fresnel reflection coefficients at the air-film and film-silicon surface interfaces, n_f and n_{Si} are the refractive indices of the film and silicon, φ_f is the quantum luminescence yield of the luminophore film, $A(\lambda)$ is the film-absorbed portion of the photon flux, F_1 is the portion of the fluorescent radiation leaving the film, and Q_d and $Q(\lambda)$ is the averaged quantum efficiency of the silicon detector over the luminophore fluorescence spectrum and its efficiency upon irradiation in the UV region [1-2].

Assuming $S = 0$, $n_f = 1.5$ and complete absorption of the UV radiation in the film, we obtain $R_1 = 0.04$, $R_2 = 0$, $F_1 = 0.127$ and

$$(2) \quad Q = 0.84\varphi_f Q_d$$

Formula (1) enables one to evaluate the sensitivity Q of a photodetector with an ideal luminescent converter having a quantum fluorescence yield $\varphi_f = 1$ at coinciding maxima positions of fluorescence and the spectral sensitivity of the photodetector $Q_d = 1$ as well as under the condition of complete absorption of the incident UV radiation. The obtained value of $Q = 0.84$ shows that with the use of a luminescent converter it is possible to attain, in principle, in the UV region a sensitivity equal to 84% of the sensitivity at the maximum of the spectral characteristic.

Assuming that the UV radiation is totally absorbed in the film, we determine by formula (1) the limiting value of Q for the $\text{Eu}(\text{TTA})_3\text{DAPM}$ based converter. The absolute quantum yield of $\text{Eu}(\text{TTA})_3\text{DAPM}$ luminescence is $\varphi_f = 0.71$ and the value of the detector efficiency averaged over the fluorescence yield of europium $Q_d = 0.46$. The calculated $Q = 0.84 \cdot 0.71 \cdot 0.46 = 0.274$ is in excellent agreement with the measured value of $Q = 0.27$. Thus, the quantum efficiency of the silicon photodiode with a luminescent converter in the UV region is 40% of its quantum efficiency $Q = 0.65$ at the maximum of the spectral sensitivity at 850 nm.

Characteristics of the silicon CCD with a UV radiation down-shifting coating

For effective operation of the radiation converter with image detectors it is necessary to provide a high spatial resolution of the whole system. This can only be attained in the case where the luminescent converter thickness is small compared to the dimensions of the sensitive element of the detector (for the CCD matrix it is 10 – 15 μm). Since the elaborated coatings are 2 μm thick, they can be used effectively for these purposes. We have tested a luminescent converter applied to a 1200TsM1 CCD matrix (230×288 elements). Before and after the application of the converting coating in the visible region of the spectrum the light-signal characteristic of the photodetectors was measured, and the image definition, number of transmitted gradations, and background quality were estimated visually on a 0460K test chart.

In the visible spectral region, there is no image degradation after the deposition of a coating.

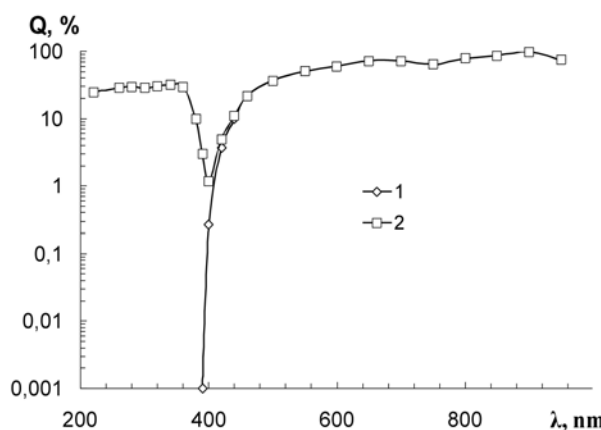


Fig. 3 Curves of the spectral sensitivity of the CCD matrix 1200TsM1 without a luminescent coating (1) and with an $\text{Eu}(\text{TTA})_3\text{DAPM}$ based film converter (2)

To measure the spectral distribution of the CCD matrix sensitivity, the swing of the video signal was registered by means of an S1-81 line-separation oscilloscope. Since the region of CCD matrix linearity is small, the video signal swing in all measurements was maintained by attenuating the light flux.

Figure 3 shows the spectral distribution of the quantum efficiency of the 1200TsM1 CCD matrix before and after the application of the coating. It is seen that the application of the coating leads to an increase in the matrix sensitivity in the 220–390 nm range, reaching 30% of the quantum efficiency in the region of maximum sensitivity at 900nm.

Conclusions

It was demonstrated the use of the europium complexes with fluorinated β -diketones in PMMA to extend the spectral range of a CCD image sensors in the ultraviolet band. The

high emission quantum yield and practically complete absorption UV radiation in 225 - 370 nm spectral regions make them uniquely suited for use as a luminescent down-shifter. The thin (~2 μm thickness) luminescent down-shifting coating can be deposited after assembly of the CCD array using low cost spin-coating techniques. The measured values of the quantum efficiency photodiode and CCD sensor are in good agreement with those calculated by formula (1) using the photophysical characteristics of the studied complexes. However, the achieved UV quantum efficiency values do not reflect the potential capabilities of the developed coatings, since a CCD with a maximum spectral sensitivity at 850nm was used.

For CCD image sensors having maximum spectral sensitivity at 600 – 700 nm developed coating is practically meet the conditions for an ideal UV radiation down-shifting coating. Based on the expression (2) and using luminescent parameters of the most promising Eu(NTA)₃DAPM coating, some additional estimates in this case may be done. Quantum efficiency of CCD UV sensor may receive efficiency up to 65% at the room temperature. Cooling is used to minimize the contribution of thermally generated "dark noise" in the CCD. Sensor temperatures can reach -100°C in the latest generation of thermoelectric cooling science chambers. The quantum yield of luminescence Eu(NTA)₃DAPM increases from 0.9 to 1.0 with decreasing temperature from -100°C to -196°C [9]. Therefore, when using coatings on thermoelectric cooling CCDs, it is possible to achieve the UV quantum efficiency up to 75% in spectral maximum.

The UV radiation down-shifting coatings presented here are a viable alternative to organic and inorganic phosphor coatings [1-5] for use with silicon UV-responsive CCD image sensors.

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