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To cite this article: A N Ramazanov et al 2018 J. Phys.: Conf. Ser. 1038 012098

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Modification of the CCD photodetectors for the suppression of interference in their internal structure

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Abstract. In this work the reasons leading to the occurrence of interference in the internal structure of the common CCD photodetectors are discussed, that result in degradation of the metrological characteristics of the spectrometers based on them. Methods of removing a protective glass of the photodetector are shown. Possibility of modification of the CCD photodetectors for suppressing the interference by applying the surface phosphor layer is analyzed. It is experimentally confirmed that the proposed method allows achieving almost complete suppression of interference and also increasing the sensitivity of the detector to the radiation in the UV part of the spectral range.

1. Introduction

Photodetectors, based on the charge coupled device (CCD) technology, use the properties of metal–oxide–semiconductor structure (MOS) to accumulate minority charge carriers in the potential wells at the boundary of the semiconductor and oxide [1]. During the generation process under the influence of the incident radiation in the individual cells of the accumulation section charge occurs, depending on the area of the element, the registered radiation intensity and the accumulation time [2].

The most common “standard” (not back-thinned) CCD design is schematically shown in figure 1. On the surface of the CCD photodetector there is a thin layer of a natural oxide. Further, depending on the type of photodetector, the polysilicon electrodes and dielectric system silicon oxide–silicon nitride, situated between the electrodes and the substrate, are located.

![Figure 1. Scheme of the CCD internal structure.](image1)

![Figure 2. Path of a light beam.](image2)

In the shown structure each layer is characterized by its own thickness and refractive index. The refractive index, in turn, has a real part \( n \) and the extinction coefficient \( k \) (imaginary part), which is associated with the absorption coefficient \( \alpha \) by the following relationship [3]: \( \alpha = 4\pi k/\lambda \).
2. Reasons leading to the occurrence of interference in the CCD structure

Let us assume that onto the surface layer with thickness \( d \) a light beam \( E_0 \) falls (figure 2) and consider the interference from the primary beam \( E_0 \) and the two-times reflection from the boundaries of a film \( E_2 \). From the theory of interference it is known that in the presence of two radiation sources with equal amplitudes, the amplitude at the point of observation is equal to:

\[
S = 2a^2 \cos\left(2\pi\left(L_1 - L_2\right)/\lambda + \varphi/2\right),
\]

where \( a \) – amplitude of the primary beam \( E_0 \); \( L_1 \) – path traversed by the first beam \( E_1 \); \( L_2 \) – distance travelled by the second beam \((E_1 + E_2 + E_3)\); \( \lambda \) – wavelength; \( \varphi \) – initial phase difference.

For the case of coherent waves the initial phase difference is constant, the difference \( (L_1 - L_2) \) is also constant and, therefore, the difference in intensity of radiation depends only on the wavelength.

The phase difference resulting from the path difference of the waves is defined as

\[
\Psi = 2\pi(L_1 - L_2)/\lambda.
\]

The path difference can be expressed through the wavelength \( \Delta = L_1 - L_2 = m\lambda \), where \( m \) – any integer or a fractional number. Then the phase difference will be equal to \( \Psi = 2\pi m \). The intensity of the two interfering waves (without consideration of the amplitudes and under the condition of equality of the initial phases) can be written in the form

\[
I - A^2 = 2a^2 \cos\left(2\pi(L_1 - L_2)/\lambda\right) = a^2 \cos^2\left(\pi m\right).
\]

Integer values \( m \) correspond to the difference in the phase by \( 2\pi m \), and the intensity is proportional to \( a^2 \). When \( m \) is half-integer the phase of the emerging waves is opposite and the intensity is zero (for equal amplitudes). In general case assuming the inequality of the amplitudes \( a_1 \) and \( a_2 \) we have:

\[
I - A^2 = a_1^2 + a_2^2 + 2a_1a_2 \cos^2\left(2\pi m\right).
\]

For integer \( m \) we will have maxima \( A^2 = (a_1 + a_2)^2 \), and for half-integer – minima \( A^2 = (a_1 - a_2)^2 \).

Knowing the parameters of the photodetector layers it is possible to calculate the transmittance \( T \), defined as the ratio of radiation power passed into the substrate to the radiation power incident on the first boundary. At a fixed layer thickness dependence of the transmittance from the wavelength has a periodical character for the presented system air–oxide–polysilicon–nitride–oxide–silicon.

The surface oxide film does not affect the waveform of a signal in the case of a non-monochromatic radiation. However, in the optical scheme of the spectrometer [4] each pixel of the sensor is exposed to an almost monochromatic light. As a result, at the interface of two media with different refractive indices the interference occurs. In each pixel the level of interference will be unique, because the wavelength of the incident radiation is continuously changing over the photodetector length. This interference causes a redistribution of the signal amplitude, which leads to a significant alteration of the measurement results [5]. For example, during registration of signals from the sources of radiation with a continuous spectrum the signal at the output of a standard CCD will have an obvious modulation (figure 3).

The location of this oscillation extrema is determined by thickness and refractive index of the oxide film on the photodetector surface and the detected spectral range [6]. The depth of the signal modulation depends on the spectral resolution of the device in which the photodetector is installed.

In the spectrometer with TCD1304 CCD photodetector the modulation depth of the spectral signal shown in figure 3 is 38.35 % at amplitude of 99.04 % in the selected local maximum of the signal with the maximum modulation depth. As a result the normalized modulation depth is 39 % at a wavelength of 603 nm. The photodetector has a signal-to-noise ratio of 300, which gives the amplitude of the noise approximately 0.3 % of the maximum signal. The amplitude of the noise can be considered the same for both the maximum and the minimum of the interference oscillations. Thus, for the minimum of the interference oscillations comparing to the neighborhood maximum the signal-to-noise ratio worsens by 39 % to 180. The best solution to this problem is the use of a back-thinned CCD. The absorption in the silicon layer prevents interference at short wavelengths, however, in NIR range the interference is still possible, particularly for substrates having a thickness of several micrometers. It should be noted that the cost of a linear CCD of this type is quite high, that prevents their use in the low-cost mass
production spectral instruments. In order to get rid of the wavy modulation of the signal in the most common CCD photodetectors a correction of their spectral sensitivity is required [7–9].

3. Suppression of interference by applying the surface phosphor layer

One of the possible ways of suppressing interference is deposition on the irradiated surface of MOS structure of a thin layer of material with strong scattering [10]. As a result, the surface of the accumulation section will be irradiated not by coherent radiation, but by diffuse radiation, resulting in occurrence of interference only for a small fraction of the input luminous flux. When passing through the diffusing surface light has two components: diffuse and directed, whose influence must be reduced to a minimum. As such a surface we will consider a film containing scattering centers on the surface, that are spherical particles which dimensions are small compared with wavelength (figure 4). The most suitable material for such modification of the detector is phosphor. A phosphor layer coated on the surface of the accumulation section can also increase the UV sensitivity of the photodetector, although this will reduce its overall sensitivity due to the partial absorption of the radiation in the phosphor layer. Therefore, the transparency of the phosphor over the whole operating spectral range should be high enough.

Phosphor in condition that it is properly applied on the CCD surface is a parallel layer of light-scattering medium. We can assume that each elementary area, equal to an area of one pixel, is exposed to a monochromatic radiation. Therefore, to solve the given problem, let us consider a flat layer, which is uniformly and diffusely irradiated from one side with monochromatic light (detailed consideration of this problem is given in [10]). Characteristics of the phosphor layer very strongly dependent on the distribution of particle size. The grain size of the phosphor affects the quality of its fixing on the surface of the CCD. Moreover, the strength of fixing of the phosphor increases with decreasing grain size; however, it simultaneously decreases the efficiency of excitation of the phosphor by increasing the reflection coefficient of the exciting radiation. The size of the particles affects the scattering index $s$. Let us view a phosphor as a set of particles with diameter $d$ and the number of particles per unit volume $z$. Then the cross sectional area of all particles $S$ per unit volume has the form

$$S = 0.25\pi d^2 z.$$  \hspace{1cm} (1)

For the dense packing $z$ is inversely proportional to the particle volume:

$$z \sim \frac{1}{V} = \frac{6}{\pi d^3}.$$  \hspace{1cm} (2)

The scattering index $s$ is directly proportional to the cross sectional area of particles per unit volume, then taking into account (1) and (2) it can be written as

$$s \sim S \sim \frac{1}{d}.$$  \hspace{1cm} (3)

From (3) follows, that with increasing in the phosphor of fine particles quantity $s$ also increases, which in turn leads to an increase of the reflection coefficient of the layer $\rho$, and as a result to a decrease in the efficiency of converting radiation into luminescence. Proceeding from the above, it is possible to formulate main requirements to phosphor for the modification of the CCD photodetectors:

- high efficiency of excitation (high quantum yield);
• high transmittance of visible radiation;
• line of emission of the phosphor should match the maximum quantum efficiency of a CCD;
• high stability in the process of operation of the device;
• afterglow time of the phosphor must be coordinated with a clock frequency of CCD.

Due to the fact that the greatest interest from the point of view of increasing the sensitivity of the device causes the UV region, special attention must be paid to the efficiency of excitation at wavelengths from 200 to 400 nm when choosing a type of phosphor. It is desirable that the wavelength of phosphor luminescence coincides with the maximum quantum efficiency of radiation absorption in the CCD. At a present time sufficiently efficient phosphors are produced; for example, Phosphor Technology offers phosphors, which have an excitation wavelength of 254 or 365 nm. In addition, the line of radiation is in the red region, which corresponds to the maximum quantum efficiency of radiation absorption of most spectral instruments built using CCD photodetectors.

4. Results and discussion

Surface modification of the CCD photodetector is impossible without direct access to the crystal (MOS structure) which, as a rule, is sealed by a protective glass. Without such glass a crystal of the photodetector can be easily damaged even with a slight mechanical action. There are companies, such as Framos and Eureca that offer services to remove the glass from almost any CCD photodetectors, however, without revealing the technological features of the process. The cost of such services is quite high, and the probability of failure of the sensor is about 10%. Meanwhile it is stated that after years of use of the CCD photodetectors with removed glass their parameters practically do not change.

For the removal of this glass the heating of the device can be used, followed by a long exposure at sufficiently high temperature [11]. As a result of the temperature exposure adhesive, with which the protective glass is attached to the casing of the sensor, is destroyed and the glass can be removed. This method, however, cannot be applied to all multi-element photodetectors. Experiments carried out with a popular CCD sensor of TCD1304 type showed that its glue does not undergo significant changes in mechanical properties even after prolonged exposure to a temperature of 300 °C. Further increase in temperature allowed to remove the glass, but led to the CCD photodetector damage. For the removal or at least softening of the adhesive, as which epoxy compounds are usually used, it is possible to use a special solvent – dichloromethane (methylene chloride) or dimethylformamide. The process of removing glue lasts up to a month, and solvents themselves are quite toxic. In addition, manufacturers of CCD photodetectors use various types of glues and one universal solvent for all of them simply does not exist.

Another method of the glass removal, which is practically independent of the type of the photodetector casing and used glue is the mechanical “cut” of the glass piece that do not have direct adhesive contact with the shell. This method also does not guarantee the safety of the detector, since during the mechanical destructive effect on the glass, the small fragments fall into the casing and at high speed bombard the surface of the photodetector, causing its damage (figure 5(a)).

![Figure 5. CCD photodetector during the process of removing part of the glass.](image-url)

To prevent the damage of the sensor the following technology of glass removal was designed. At the first phase in the glass at the farthest point from the photodetector a minimized cut is made to gain access to the internal volume of the casing. Then under the glass a fluid, not harmful to the photodetector, for
example, alcohol, is pumped. The next step is a basic procedure for removal of glass using a diamond cutting wheel (figure 5(b)). Liquid, due to a sufficiently high density, prevents glass shards to reach the surface of the CCD sensor at speeds enough to its damaging. After removal of the glass the sensor is released from the liquid and small pieces, after which the surface can be modified. The results of the glass removal from a CCD photodetector TCD1304 using two different ways are shown in figure 6.

![Figure 6. CCD photodetector TCD1304 with removed glass.](image)

A photodetector with glass, for comparison, is shown in figure 6(c). Minimal destruction of the casing was obtained using the thermal method (figure 6(a)), however, during the process the sensor itself was damaged. Results of the glass removal by the mechanical means (figure 6(b), a fragment with notches is shown in figure 6(d)) are acceptable from the point of view of yield of the devices because the number of faulty sensors does not exceed 10 %.

The most common method of applying the phosphor coating is deposition from the aqueous suspensions [12]. Before the beginning of the process, the phosphor powder is sifted: only particles with diameter less than 12 μm are left. Then a suspension of phosphor in the distilled water is made, sometimes with addition of potassium silicate. After that with the help of ultrasonic treatment, the resulting suspension is mixed. Depending on at what point in time to put the substrate under the deposited stream particles of a certain faction would be precipitated. To control the thickness of the applied layer the phosphor is also simultaneously deposited on a control sample, which is weighed before and after the operation. Later the resulting coating is dried.

In this way samples of phosphors were deposited on the surface of the CCD. The experiment gave a positive result, and the technology of deposition phosphors from the aqueous suspensions does not worsen the properties of the photodetector. For the improvement of CCD parameters two phosphors were investigated: K-77 with the specific gravity of 0.77, 0.82, 1.12 and 2.06 mg/cm$^2$ and FK-6 with the specific gravity 1.21 and 2.27 mg/cm$^2$, each of them been deposited on a separate photodetector. The phosphor K-77 is a cathode phosphor with composition Y$_2$O$_3$:Eu, maximum diameter of selected fractions was 4 μm. The luminescence spectra of the phosphor K-77 has a red color and is excited by radiation in the range 210...280 nm. The maximum brightness of the phosphor was observed at the excitation wavelength of 250 nm. The phosphor FK-6 is a phosphorus-containing photoluminescent phosphor. The maximum diameter of the selected fractions does not exceed 4 μm. The phosphor has a red-orange color of luminescence. The exciting radiation lies in a wide interval of wavelengths from UV to visible: 250...512 nm. The maximum brightness was observed at excitation wavelength equal to 400 nm. The luminescence intensity of the phosphor with a specific gravity 2.27 mg/cm$^2$ was higher than for a thinner phosphor with a specific gravity 1.21 mg/cm$^2$.

The luminescence spectrum of the K-77 phosphor has a maximum coincidence with the maximum spectral sensitivity of the CCD photodetector. The luminescence spectrum of the FK-6 phosphor lies in a rather wide interval of wavelengths from 550 to 750 nm and does not have a pronounced maximum. The transmittance of phosphor K-77 is 5–10 %, and weakly depends from the specific gravity. A maximum transmittance has a K-77 phosphor with a specific gravity 0.82 mg/cm$^2$. The transmittance of phosphor
FK-6 varies in the range of 8–50%, intensively depending on the specific gravity of the phosphor and the wavelength. The highest transmittance has FK-6 phosphor with a specific gravity of 1.21 mg/cm². The K-77 phosphor with a specific gravity of 1.12 mg/cm² was deposited on the surface of the accumulation section of the TCD1304AP photodetector manufactured by Toshiba. The application of the phosphor layer does not affect the resolution of the spectrometer – in both cases (with and without phosphor) it was ~3 nm. The application of the phosphor layer completely eliminated the wavy modulation of the spectral characteristic of the spectrometer (figure 7).

Comparing the spectra of the incandescent lamp, obtained using a spectrometer having a CCD without the phosphor coating and with it, it can be concluded that wavy modulation has been completely suppressed. The noise arising on the spectrum is due to the presence of foreign particles in the deposited phosphor layer. These deviations are stationary in time and can be further eliminated by improving the technology of the phosphor deposition.

5. Conclusions
The method of modifying a CCD photodetector considered in this paper, that includes the stages of removing the protective glass and applying a layer of phosphor on MOS structure allows to obtain a sensor for spectrometric applications with metrological characteristics close enough to much more expensive models. However, it should be noted that the photodetector with a removed glass is almost not protected from mechanical damage and requires very careful handling.

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