ФИЗИКА

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ANTIREFLECTION AND PASSIVATING COATINGS ON THE BASIS OF RARE EARTH ELEMENT OXIDES FOR SILICON DEVICES

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In this research the optical properties of Rare Earth Elements' (REE) Oxide films, the antireflection effect on silicon surfaces and photoelectric transducers covered by these films, and the recombination properties of silicon, passivated by REE oxide films are studied. The investigations show that the deposition of a REE oxide film onto silicon surface decreases the spectral light reflection index from the surface of silicon down to 0.01–1.2%, increasing the spectral value of short-circuit photocurrent in a silicon photoelectric transducer more than by 50%. It is found out that after a deposition of a rare earth element oxide film the effective life-time of the non-equilibrium charge carriers, measured by means of photoconductivity relaxation method, increases 2–3 times. The surface recombination rate values for the interface silicon-rare earth element oxide are determined. For different REE oxides they are equal to 290–730 cm·sec^{-1}.

Introduction

Among the materials that are prospective for the application as antireflection coatings on silicon photoelectric devices, the REE oxides are distinguished by their advantage of being highly transparent in the working spectrum range, they are characterized by high chemical and thermal stability, and by an optimal for these purposes value of the refraction index [1, 2, 3]. The possibility to obtain an interface with the semiconductor with low recombination losses is an important requirement for optical coatings of semiconductor devices. However the recombination characteristics of the system silicon-REE oxide (that influence the electric losses in silicon devices) were not studied so far. The optical properties of REE oxide films, the antireflection effect with these materials on

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silicon surfaces and photoelectric transducers, and the recombination properties of silicon passivated by REE oxide films were the subject of this research.

1. Experimental details

The REE oxide films were fabricated on crystal and polished silicon substrates by thermal oxidation in air at 500 °C of the previously deposited rare earth metal layer. The REE film was deposited by thermal sputtering of a rare earth metal from a molybdenum vessel at 10^{-5} torr vacuum level on an installation of VUP–4 or VUP–5 types. As long as the maximum antireflection effect for the photoelectric transducers working in space appears at the wave length of 600 nm, and the refraction index of various REE oxides belongs mainly to the range 1.927–2.18, the thickness of the film deposited onto the silicon substrate was chosen equal to 75 nm. The investigation of the properties of anti-reflection REE oxide coatings on silicon surface were conducted on silicon $n^+ - p - p^+$ structures with the $n^+ - p$ interface lying at 0,4–0,5 μm. The value of the specific resistivity of the p-type base area was 10 $\Omega \cdot cm$. The layer of p^+- conductivity type with the impurity concentration of $8{\cdot}10^{-19}$cm^{-3} was formed by ion implantation of boron at 30 keV voltage and current density 2 mC·sec^{-1}·cm^{-2}. n^+- type area was formed by the diffusion of phosphor atoms from PCl_3 at a temperature 860–9000 °C. The impurity concentration on the n^+- layer surface was equal to $6{\cdot}10^{19}$cm^{-3}. The plow contact to n^+- layer was made by thermal evaporation in vacuum through a mask as a stripe of aluminium film.

The spectral dependences of light transmission for REE oxide films were studied on a spectrophotometer of CF–26 or CF–8 types with the compensation of the absorbed radiation in a crystal substrate. The reflection spectrum of the REE oxide films on crystal substrates was studied on CF–4A spectrophotometer. The spectral characteristics of the light reflection index from a silicon surface and from the systems anti-reflection REE oxide coating-silicon were studied at FO–1 photometer. The anti-reflection properties of the REE oxide films on silicon surface were analysed based on the measurements of spectral characteristics of short-circuit photocurrent in $n^+ - p - p^+$ structures, half-covered by an anti-reflection oxide layer. Short-circuit photocurrents during light irradiation of the surface in the structure with the coating and without it were recorded by a potentiometer KSP–4 and compared between each other.

In the presented paper the effective life-time and the surface recombination rate of the non-equilibrium charge carriers in silicon wafers, passivated by the films of some Rare Earth Element Oxide (REEO), are investigated. The samples for the tests were cut out of the polished single-crystal silicon wafers of KEF–20 type with the orientation (100), the size was $10{\times}5{\times}0,34$ mm. Before the REEO film fabrication the silicon wafers were chemically cleaned in order to remove the natural oxide layer. The procedure was started by etching in

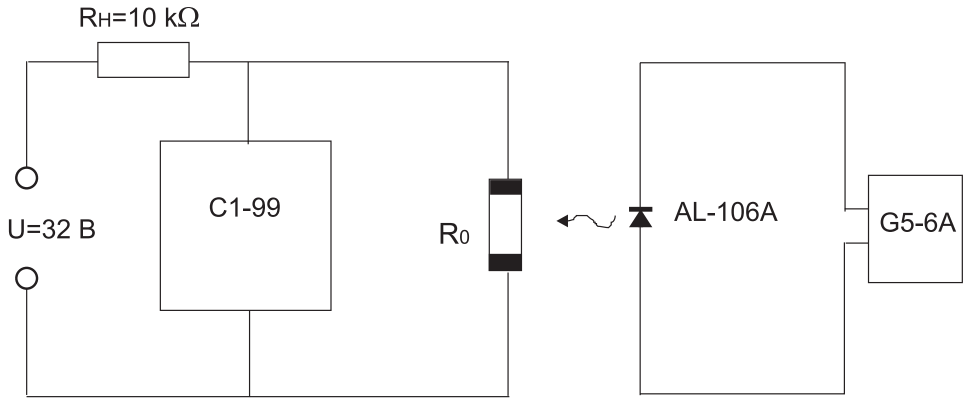


Fig. 1. Block-diagram of the installation for effective life-time measurements

a water solution of hydrofluoric acid $HF : H_2O$ (1:10). After that some of the samples were boiled in ammonia peroxide solution of the following composition: $NH_4OH : H_2O_2 : H_2O$ (1:1:3). After each chemical treatment the samples were several times washed in bi-distilled water and dried on a filter. The films of cerium, europium, dysprosium and gadolinium oxides were formed at both surfaces of the silicon wafer by thermal oxidation of the rare earth metal layer in air at a temperature of 400 °C for 30 minutes. The rare earth metal film was sputtered by thermal sputtering technique from a molybdenum vessel at 10^{-5} torr vacuum at VUP–4 installation. Dysprosium and aluminium layers, sequentially deposited onto the silicon samples through a stencil by thermal sputtering technique in vacuum, were used as ohm contacts. The voltage distribution along the sample measurements have proved that the contacts were linear.

For the effective life-time measurements a widely utilised photoconductivity relaxation method when the sample is irradiated by rectangular light pulses was used [4]. The block-diagram of the measuring installation is presented at fig.1. The light source was a gallium phosphide LED of AL–106A type, exposed by rectangular current pulses with the repetition frequency of 1 kHz from a generator G6–26. The voltage kinetics on the sample R_0 was measured by an oscillograph of C1–99 type. The temperature dependences of the effective life-time were measured in the temperature range 563–683 °C at 0,1 torr vacuum.

2. Results and discussion

2.1. Optical properties of REE oxide films

Figures 2, 3 and 4 present the transmission spectrum of REEO films on crystal substrate, when the radiation passing through a clean crystal plate was taken as 100%, and the reflectance spectrum of silicon surface and the system REEO film-silicon. As it can be seen, high values of the transmission factor

T=92–100% of the films in the maximums in the range 400–1200 nm prove that they are highly transparent in the wave length working range of silicon photoelectric transducers. The variation of the light transmission factor in the transparency range 400–1200 nm of the films depending on the wave length of the radiation is linked with interference effects in the REEO film. Strong light absorption in the short-wave spectrum range, corresponding to high values of quant energies, is explained by band-to-band transitions. The high transparency of the films in the visible spectrum range and the abrupt edge of the bandgap absorption prove that the composition of the oxide films is close to stoichiometric.

Table 1 presents the maximum and minimum values of the reflection factor R and the transmission factor T for the system REE oxide film on a crystal substrate with the refraction index $n = 1.5$, calculated theoretically taking into account the multi-ray interference. The same table also presents the difference between the empirical minimum values of light transmission T_e min adjusted by the radiation loss from the outer surface of the crystal plate and the theoretically calculated value $T_{\text{th min}}$:

$$\frac{\Delta T_{\text{min}}}{T_{\text{th min}}} = \frac{T_{\text{e min}} - T_{\text{th min}}}{T_{\text{th min}}} \tag{2.1}$$

As it can be seen from the table, the experimental values of the transmission factor in the investigated systems co-inside with the theoretical values within the limits of the experiment accuracy.

Minor deviations from the theoretical values are linked with the transparency difference between the areas of the crystal substrate with the REE oxide film and without it, and also by weak radiation absorption in these materials. This result proves that the REEO films are highly transparent in the wave-length range of 400–1200 nm, that do not practically absorb any light radiation. This result is verified by the calculation of the absorption factors of the films in the transparency region: their values were equal to 140–650 cm^{-1}, and by some other works [1, 2].

The typical dependences of the reflection factor from the wave length for silicon and for the system REEO film-silicon are presented at fig. 2 and table 2. It can be seen, that the anti-reflection REEO film deposited onto the silicon surface reduces the reflection of monochromatic light from 34.7–37% for the clean silicon surface down to 0.01–1.2% and practically eliminates light reflection from the semiconductor surface. It was detected, that dysprosium oxide film has the best anti-reflection properties, decreasing the spectral reflection index down to 0.01%. The integral light reflection figure for the silicon systems in the wave lengths range from 400 to 1000 nm was decreasing from 34,2% to 7,5–10% for different REE oxides.

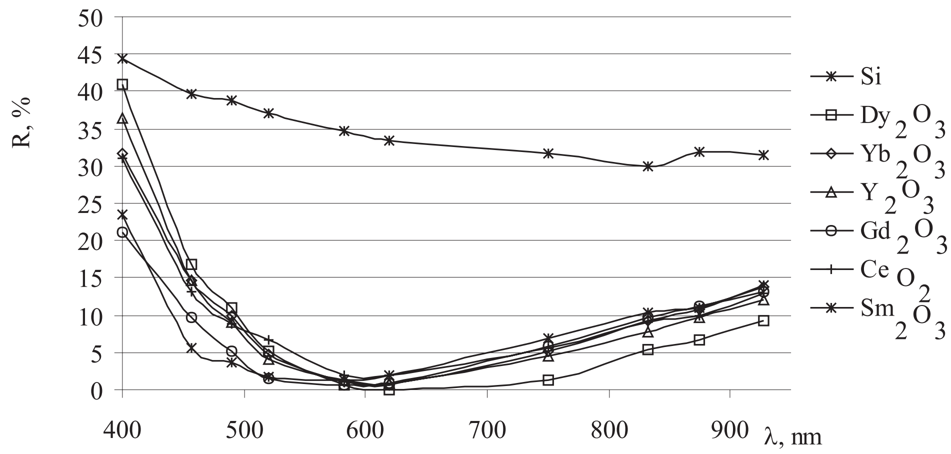


Fig. 2. Light reflection from a silicon surface and a REEO film on a silicon substrate

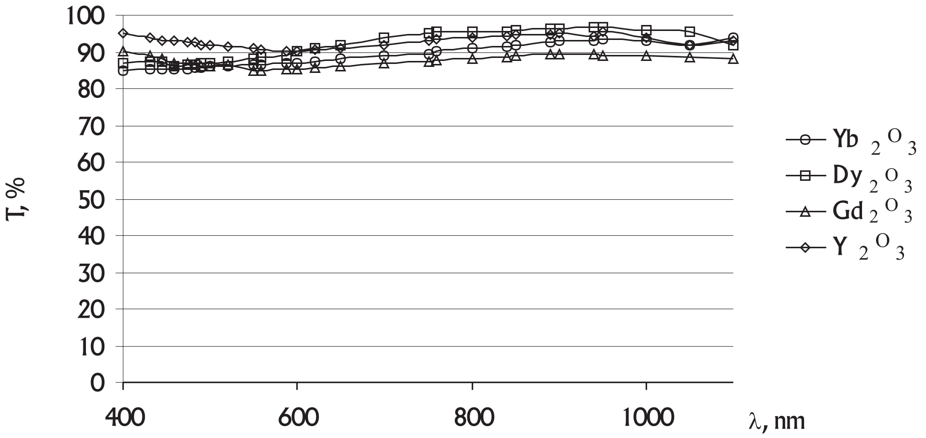
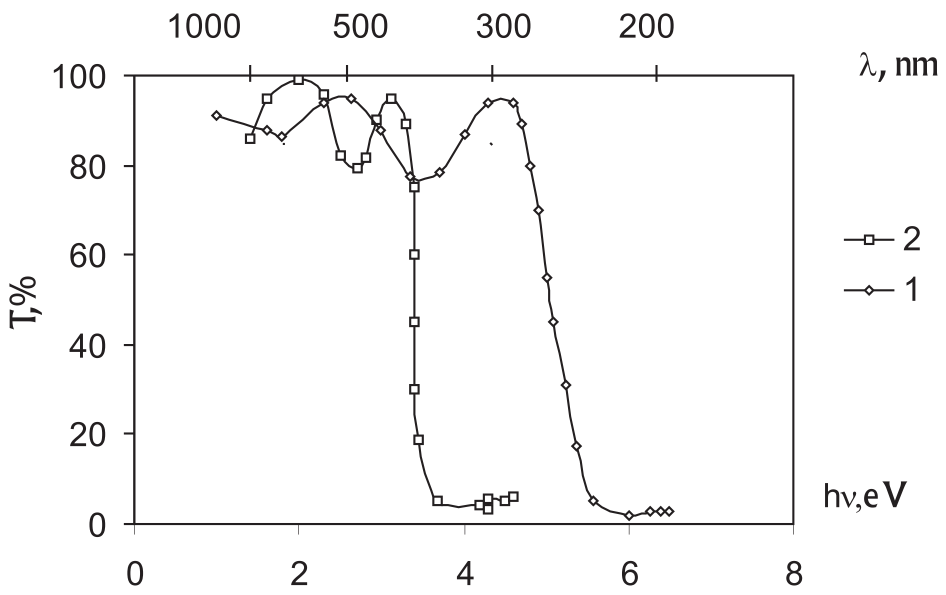


Fig. 3. Spectral dependences of the transmission factor of REE oxide films on crystal substrates



1–Sm_2O_3, thickness 170 nm; 2–CeO_2, thickness 210 nm
Fig. 4. Spectral dependences light transmission for samarium and cerium oxide films

Table 1

Theoretically calculated maximum and minimum values of light reflection and transmission indexes for the system REEO film–crystal substrate

Oxide	Gd_2O_3	Dy_2O_3	Yb_2O_3	Y_2O_3
R_{min}	4,0	4,0	4,0	4,0
R_{max}	19,8	19,7	18,7	12,4
T_{min}	80,2	80,3	81,3	87,6
T_{max}	96,0	96,0	96,0	96,0
$\frac{\Delta T_{min}}{T_{min}}$	+1,3	+2,3	+1,1	-1,7

Table 2

The light reflection factor values from the surface of silicon and REEO films on silicon substrate for different wave lengths of radiation

λ, μ*m* material	400	457	490	520	583	620	750	832	874	927
Si	44,3	39,7	38,8	37,0	34,7	33,4	31,7	30,0	31,8	31,4
Y_2O_3	36,4	14,6	9,1	4,2	1,4	0,9	4,6	7,7	9,6	12,05
Gd_2O_3	21,15	9,8	5,1	1,6	0,7	0,9	5,8	9,7	11,3	13,1
Dy_2O_3	40,98	16,8	11,0	5,2	0,7	0,01	1,2	5,3	6,6	9,25
Yb_2O_3	31,7	14,6	10,0	4,8	1,0	0,7	5,1	9,2	10,7	13,8
CeO_2	31,0	13,1	8,9	6,6	1,9	1,9	5,7	9,0	10,0	13,0
Sm_2O_3	23,5	5,6	3,6	1,8	1,2	2,0	6,9	10,4	11,0	14,0

2.2. The recombination properties of the interface silicon — REEO film

An other important criteria of the quality of optical anti-reflection coatings for semiconductor photoelectric devices is that the deposited film does not impair the recombination properties of both the surface and the bulk of the semiconductor transducer structure. The low temperatures of REEO formation together with their good physical and chemical properties [3] give us the right to assume that the studied materials comply to this requirement. In this respect the recombination parameters of the silicon wafer after the deposition of a REEO film were investigated.

It is known [5], that the value of the effective life-time is influenced by the common impact of the recombination and trapping processes in the bulk and on the surface of the semiconductor. The presence of the traps for charge carriers may have a significant bearing on the characteristic time of photoconductivity decay, measured by this method. Consequently the obtained life-time of the carriers is higher than it really is. In order to investigate the role of trapping processes on the photoconductivity relaxation, the temperature dependences of the characteristic time of photoconductivity decay, presented in fig. 5, were analysed.

As it can be seen from the graph, the effective life-time of the samples without REEO film (curve 1) with temperature increase first decreases and starts to increase after 613 °C. This kind of dependence is typical for a real silicon surface [6], the descending branch conditioned by the trapping processes, and the branch of ascending effective life-time is conditioned by the recombination of charge carriers on silicon surface. For the silicon samples covered by REEO film (curve 2, fig. 5) the monotone growth of, caused by surface recombination, with temperature increase, is observed. These results

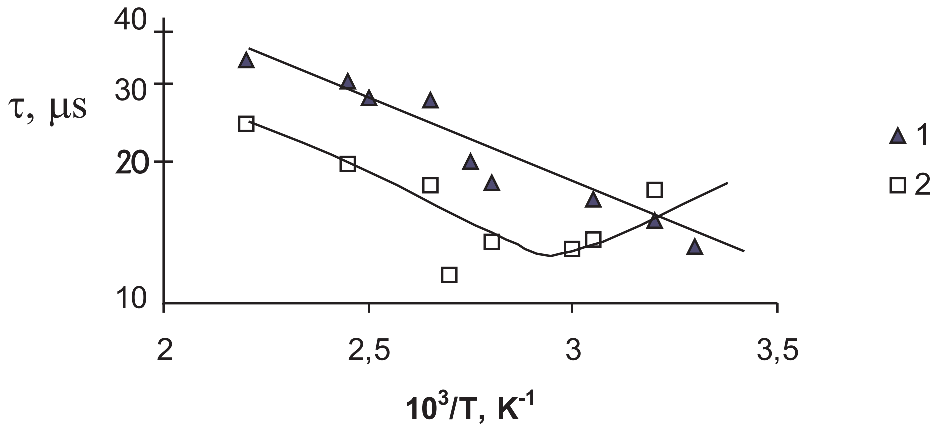


Fig. 5. The temperature dependence of the effective life-time of non-equilibrium charge carriers in silicon without coating (1) and with REEO film (2)

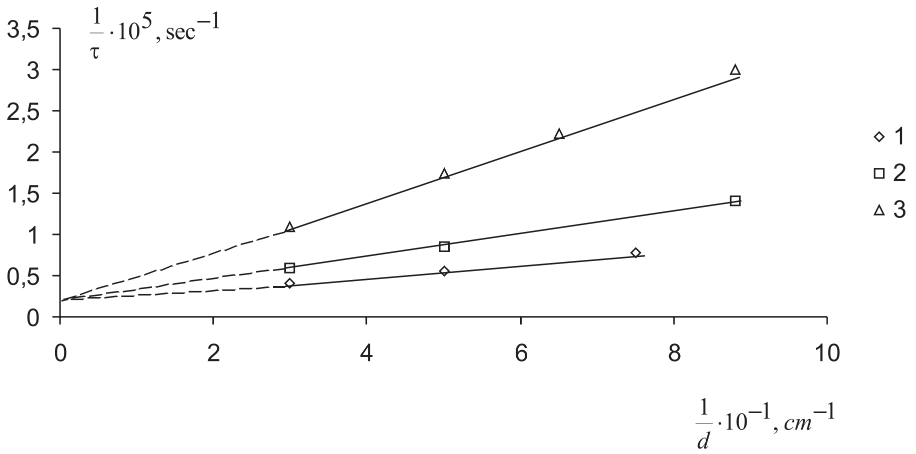
prove, that at high temperature measurements t $\geqslant$ 97 °C for all the studied samples the attachment effect may be neglected. In this case for the effective life-time of thin samples at comparatively low rates of surface recombination the following expression is valid [6]:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{2S}{d} \tag{2.2}$$

where τ and τ_0 — the effective life-time and life-time of non-equilibrium charge carriers in the bulk of the semiconductor respectively; d — semiconductor thickness; S — surface recombination rate. This formula allows to calculate the surface recombination rate if the bulk life-time is known.

The dependence of the effective life-time on the thickness of the semiconductor sample was used for the determination of the bulk life-time. Fig. 6 presents the mentioned dependences, obtained from the measurements of for the samples with different thickness, that were fabricated by silicon etching in the etchant, composed by nitric and hydrofluoric acids in proportion 3:1. The experimental values fit to a straight line in the $\frac{1}{\tau}$ vs $\frac{1}{d}$. This result proves, that the surface recombination rate is constant independently from the samples' thickness. This was expected, because the surfaces have passed through the same treatment during their preparation. The bulk life-time estimation, obtained on the basis of the measurements gives $\tau_i \geqslant 250$ μs for all the studied samples.

Table 3 presents the results of effective life-time measurements at room temperatures for silicon samples, that have passed through different chemical treatment, before (τ^{ini}) and after the film deposition(τ^{aft}). As table 3 shows,



1 — the real surface of silicon; 2 — Sm_2O_3; 3 — CeO_2.
Fig. 6. Effective life-time dependence on the silicon substrate thickness for the real and passivated by REEO film surface

after the deposition of a REEO film a regular growth of τ takes place. The life-time reaches its maximum for the samples, that have passed through ammonia peroxide treatment. Its is typical, that after annealing of the sample without a film in the air at 400 °C for 30 minutes does not change. The surface recombination rate was determined out of effective life-time measurements at 100 °C, because, as it was explained before, the charge carriers' trapping effects can be neglected at temperatures t $\geqslant$ 97 °C.

As long as the measured values of effective life-time did not exceed 50 μsec, and the following equation was true $\frac{1}{\tau} \gg \frac{1}{\tau_0}$, in the equation for surface recombination $\frac{1}{\tau_0}$ was neglected. Table 4 presents the values of surface recombination rate for silicon samples before and after REEO film deposition.

The comparison of these recombination characteristics shows, that the surface recombination rate in the system Si– REE oxide is 1-2 orders of degree lower than it is for the widely used in semiconductor electronics $Si-SiO_2$ and $Si-SiO_2-Si_3N_4$ structures [5, 7].

2.3. REE oxide films application as anti-reflection and passivating coatings for silicon devices

The investigation of the spectral dependences of short-circuit currents in silicon n^+-p-p^+ structures with anti-reflection layers of REE oxides and without them proves, that anti-reflection and passivation effects on silicon surface really take place. The spectral characteristics of photocurrent (fig. 7) are bell-shaped, that is typical for silicon photoelectric devices with $p-n$ junction. Photocurrent maximum is observed for radiation wave lengths close to 800–900 nm and

Table 3

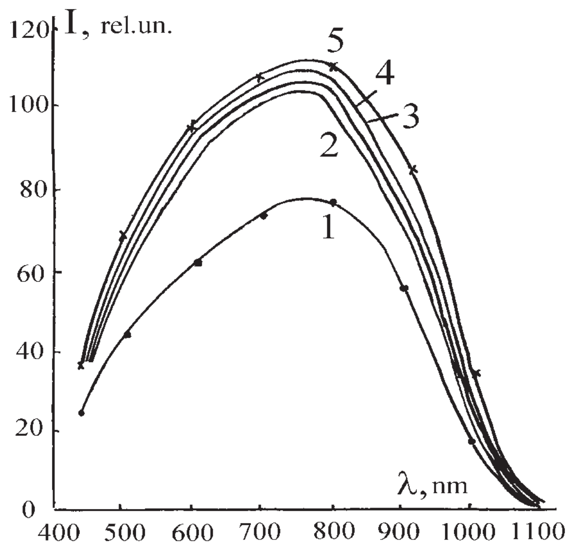
Effective life-time values for silicon samples before τ^{ini} and after the REEO film deposition τ^{aft} at 20 °C

Film material	Type of silicon surface treatment	τ^{ini}, μsec	τ^{aft}, μsec
Y_2O_3	$HF:H_2O$	11	31
Sm_2O_3	$HF:H_2O$	9	13–17
Y_2O_3	$HF:H_2O+APS$	19	23
Dy_2O_3	$HF:H_2O+APS$	18	31
CeO_2	$HF:H_2O$	11,3	25,3
Eu_2O_3	$HF:H_2O$	9	13
Dy_2O_3	$HF:H_2O$	8,5	11,9
Gd_2O_3	$HF:H_2O$	9	18,3
CeO_2	$HF:H_2O+APS$	16	34-36
Dy_2O_3	$HF:H_2O+APS$	18-19	31-34

Table 4

Effective life-time and surface recombination rates in silicon at 120 °C

Film material	Type of silicon surface treatment	τ, μsec	S, $\frac{cm}{sec}$
Without film	$HF:H_2O$	18,5	920
Yb_2O_3	$HF:H_2O+APS$	58	290
Y_2O_3	$HF:H_2O+APS$	30	520
Yb_2O_3	$HF:H_2O$	54	310
CeO_2	$HF:H_2O$	24	720
Dy_2O_3	$HF:H_2O+APS$	50	340
Gd_2O_3	$HF:H_2O$	23	730
Gd_2O_3	$HF:H_2O+APS$	54	330



1 — without coating; 2 — Lu_2O_3; 3 — Gd_2O_3; 4 - Yb_2O_3; 5 — Dy_2O_3

Fig. 7. Spectral dependences of short-circuit photocurrent for a silicon $n^+ - p - p^+$ structure without coating and with REE oxide film

the deposition of REE oxide coatings leads to photosensitivity increase for the samples in the wave lengths range from 400 to 1100 nm.

The values of relative increase of short-circuit photocurrent calculated from these experimental spectral characteristics, are determined by equation:

$$K = \frac{I_{ph} - I_{ph0}}{I_{ph0}} \tag{2.3}$$

where I_{ph} and I_{ph0} — short-circuit photocurrents in $n^+ - p - p^+$ structure with an anti-reflection coating and without it respectively, show, that the application of REE oxide films permits to increase the spectral value of short-circuit photocurrent in silicon photoelectric transducers by more than 50%. The maximum anti-reflection effect was observed for dysprosium oxide layers, that increased photocurrent by 59,4% at wave length 600 nm. This result is validated by the investigation of spectral dependences of the reflection factor, that shows, that the minimum reflection from a silicon system takes place just for this very film. The application of dysprosium oxide antireflection film permits to increase the integral short-circuit photocurrent value for silicon photoelectric transducers in the wave-length range of 400 to 1000 nm by 55.7%. Analysis shows that the observed sensitivity increase for silicon $n^+ - p - p^+$ structures when the dysprosium oxide film is used, is 10% higher than it could be expected considering only the surface anti-reflection effect. This result is explained by the passivating effect of dysprosium oxide film, that decreases the surface recombination rate of charge photocarriers on silicon surface.

Conclusions

The research has revealed, that the deposition of REE oxide film onto silicon surface permits to decrease the spectral reflection factor for silicon surface down to 0,01–1,2% and to increase the spectral value of short-circuit photocurrent in the silicon photoelectric transducer by more than 50%.

It was determined, that after the deposition of a rare earth metal oxide film, the effective life-time of non-equilibrium charge carriers, measured by photoconductivity relaxation method, increases up to 2–3 times. The surface recombination rate values for the interface silicon - rare earth metal oxide were determined. For different samples they were equal to 290–730 cm·sec^{-1}.

The combination of a high optical transparency of the studied materials and low recombination losses in silicon, covered by a rare earth oxide film, makes us recommend the application of rare earth element oxides as optical anti-reflection and passivating coatings for silicon photoelectric devices.

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