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Spectral Ellipsometry as a Method of Investigation of Influence of Rapid Thermal Processing of Silicon Wafers on their Optical Characteristics

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Abstract

One of the possible ways of improvement of the surface properties of silicon is the solid phase recrystallization of the surface silicon layer after the chemical-mechanical polishing with application of the rapid thermal treatment with the pulses of second duration. The purpose of the given paper is investigation of influence of the rapid thermal treatment of the initial silicon wafers of the various doping level and reticular density on their optical characteristics by means of the spectral ellipsometry method.

The investigation results are presented by means of the spectral ellipsometry method of the rapid thermal processing influence on the initial silicon wafers (KDB12 orientation <100>, KDB10 orientation <111> and KDB0.005 orientation <100>) of the various level of doping and reticular density influence on their optical characteristics: refraction and absorption ratios. Influence was confirmed of the silicon reticular density on its optical characteristics before and after the rapid thermal processing. It was shown, that reduction of the refraction and absorption ratios in the center of the Brillouin zone for the silicon samples with the high Boron concentration after the rapid thermal processing as compared with the low doped silicon. In the area of the maximum absorption peak, corresponding to the energy of the electron exit from the silicon surface (4.34 eV) the refraction indicator of the high doped silicon becomes higher, than of the low doped silicon, which is determined by the high concentration of the vacant charge carriers on the silicon surface in this spectral range.

It was established, that the spectral area 3.59–4.67 eV, corresponding to the work of the electrons, exiting the silicon surface, the most informative way shows the difference of the 3 optical parameters of silicon of the different orientation, and for evaluation of influence of the silicon doping level on its optical characteristics the most informative is the spectral range of 3.32–4.34 eV.

Keywords: rapid thermal processing, absorption ratio; refraction ratio.

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Спектральная эллипсометрия как метод изучения влияния быстрой термообработки кремниевых пластин на их оптические характеристики

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Одним из возможных путей улучшения поверхностных свойств кремния является твердофазная рекристаллизация поверхностного слоя кремния после химико-механической полировки с использованием быстрой термической обработки импульсами секундной длительности. Целью данной работы являлось исследование влияния быстрой термической обработки исходных кремниевых пластин различного уровня легирования и ретикулярной плотности на их оптические характеристики методом спектральной эллипсометрии.

Приведены результаты исследования методом спектральной эллипсометрии влияния быстрой термообработки исходных кремниевых пластин (КДБ-12 ориентации <100>, КДБ-10 ориентации <111> и КДБ-0,005 ориентации <100>) различного уровня легирования и ретикулярной плотности на их оптические характеристики: коэффициенты преломления, поглощения. Подтверждено влияние ретикулярной плотности кремния на его оптические характеристики до и после быстрой термообработки. Установлено уменьшение коэффициентов преломления и поглощения в центре зоны Бриллюэна для образцов кремния с высокой концентрацией бора после быстрой термообработки по сравнению с низколегированным кремнием. В области пика максимума поглощения, соответствующего энергии выхода электрона с поверхности кремния (4.34 эВ) показатель преломления высоколегированного кремния становится выше, чем у низколегированного кремния, что обусловлено высокой концентрацией свободных носителей заряда на поверхности кремния в этом спектральном диапазоне.

Установлено, что спектральная область 3.59–4.67 эВ, соответствующая работе выхода электронов с поверхности кремния, наиболее информативно показывает различие оптических параметров кремния различной ориентации, а для оценки влияния уровня легирования кремния на его оптические характеристики наиболее информативен спектральный диапазон 3.32–4.34 эВ.

Ключевые слова: быстрая термическая обработка, коэффициент поглощения, коэффициент преломления.

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Introduction

The main factor, influencing the quality and reliability of the modern integrated circuits is the surface condition of the initial silicon wafers. In view of this, a great attention is paid to the aspects of the silicon surface preparation. As it is known, one of the possible ways of improving the surface properties of silicon is the solid phase recrystallization of the silicon surface layer after the chemical-mechanical polishing with application of the rapid thermal processing (RTP) with the pulses one second long [1, 2]. The important parameters, bearing information about the surface condition of the silicon wafer are in its optical characteristics, and, namely, the ratios of refraction, absorption and reflection, which are most sensitive to presence of the disrupted layer, available on the surface of the silicon wafers after the chemical-mechanical polishing [3]. However no references in publications have been found which are dedicated to reviewing the dependence of optical properties of silicon wafers upon its orientation and the level of doping in broad spectral range, that is from visible light to deep ultraviolet prior to RTP and after that.

The purpose of the given paper was investigation of influence of the rapid thermal treatment of the initial silicon wafers of the various doping level and reticular density on their optical characteristics by means of the spectral ellipsometry method.

Procedure of the experiment

As one of the most sensitive control methods of the optical characteristics of the silicon surface layers is the method of ellipsometry, based on the analysis of the characteristics of the reflected polarized irradiation, the given method was used during performance of the given investigations. Taking into consideration, that the ellipsometrical analysis should be performed in the wide spectral range, as the equipment for the investigations, the use was made of the spectral ellipsometer UVISEL 2, that ensures operation in the spectral range from 2100 to 200 nm (0.6–6.0 eV) and to obtain the results of high accuracy, resolution and the excellent ratio of signal/noise.

As the samples we used the wafers of the initial silicon with the diameter of 100 mm, in particular, of KDB12 orientation <100> (hereinafter – KDB12<100>), KDB10 orientation <111> (hereinafter – KDB10<111>) and KDB0.005 orientation <100> (hereinafter – KDB0.005<100>), that passed the standard chemical-mechanical polishing.

Measurements of the refraction ratio and the absorption ratio of the initial samples were performed on the spectral ellipsometer UVISEL 2 (made by the company Horiba Scientific, France, in the spectral range from 0.6–6.0 eV (2100–200 nm.)). The angle of arrival of the light beam on the sample constituted 70°. Treatment of the spectra and their visualization were performed with application of the software UVISEL 2.

Further, the given samples were subjected to the rapid thermal processing with irradiation by means of the light pulse from the non-operational side of the wafer for 7 s in the medium of Ar (the annealing temperature of 1100 °C). After completion of the process of the rapid thermal processing the initial samples were repeatedly subjected to control of the optical parameters.

Analysis of the initial silicon wafers before rapid thermal processing

As silicon in the infrared zone is transparent, the predominant interest lies in the investigation results of the optical characteristics of the silicon surface in the ultraviolet and visible range of the spectrum of 1.6–6 eV (760–200 nm). Analysis of the given results showed, that in the spectral range from 1.6 to 3.33 eV for the silicon samples of the various orientation and the doping concentration one can observe the “normal dispersion”, i. e. there’s increase of the silicon refraction ratio with reduction of the irradiation wave length. During transition into the ultraviolet zone of the spectrum there takes place the abrupt reduction of the refraction ratio, i. e. in evidence is the “anomalous dispersion” of the refraction ratio. Usually it is observed in the areas of the frequencies, corresponding to the bands of the intensive light absorption in the given medium, which is present in the given case. This is determined by the fact, that during influence of the ultraviolet irradiation there’s concentration rise of the charge carriers because of bond ruptures of Si-Si (bond energy of Si-Si is equal to 2.3 eV). As a result of this, in the spectral zone from 3.33 to 6 eV there takes place the “anomalous dispersion” of the silicon refraction ratio close to the maximum absorption points (see Figures 1, 3), corresponding to:

– G-point (Van Hove singularity point M1) of the Brillouin zone center with the energy of 3.46–3.48 eV (the energy of the direct transition of 3.43 eV) (see Figures 1, 3, point 2, curves *c*, *d*, *h*);

– maximum absorption, that corresponds to the energy of the electrons, exiting the silicon surface of 4.34 eV (exit work of electron for Si is equal to 3.59–4.67 eV) (see Figures 1, 3, point 4, curves *c*, *d*, *h*);

– maximum absorption, corresponding to the energy of the electrons, exiting the natural oxide surface due to rupture of the bonds Si-O about 5.42 eV (the bond energy of Si-O is equal to 4.79 eV).

The spectral dependence of the reflection ratio *R*, as a rule, hardly depends on the photon energy, and the spectral changes in the intensity of the reflected beam are related mainly to alterations of the absorption ratio. Thus, the spectral dependence of the reflection ratio *R* has the similar expression of the absorption ration dependence. Meanwhile, it is specific with the spikes of the maximum reflection in the area of 3.42 eV (when adjacent to the G-point of the Brillouin zone center) (see Figures 2, 4, point 5, curves *i*, *f*, *e*), 4.6 eV (corresponding to the electron exit work from the silicon surface) (see Figures 2, 4, point 6, curves *i*, *f*, *e*) and about 5.75 eV (corresponding to the energy rupture of the bonds Si-O) (see Figures 2, 4) [4, 5].

The comparative analysis of the optical parameters of the silicon samples KDB12<100> and KDB10<111> with the different orientation of the surface revealed (see Figures 1, 2), that in the region of the refraction ratio maxima, corresponding to the energy of 3.33–3.34 eV (see Figure 1, point 1, curves *a*, *b*), 4.1 eV (see Figure 1, point 3, curves *a*, *b*), as well as in the region of the maximum absorption, corresponding to the energy of the electrons, exiting the silicon surface with the value of 4.34 eV (see Figure 1, point 4, curves *c*, *d*) for the silicon orientation <111> the ratios of absorption, refraction and reflection are greater than for the silicon with orientation <100>. In the absorption maximum of the G-point (Van Hove singularity point M1) of the Brillouin zone center (see Figure 1, point 2, curves *c*, *d*) the absorption ratio for the silicon with orientation <111> is greater than for the silicon with orientation <100> by $\Delta k = 0.03$, but in a different way behaves the refraction indicator with the difference $\Delta n = 0.065$. It is explained by the fact, that in the plane {111} the atoms packs are of the maximum density, i. e. the silicon of orientation <111> possesses the higher reticular density [6, 7].

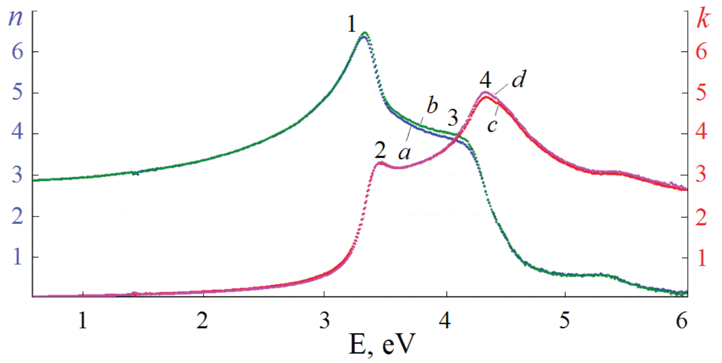

Figure 1 – Spectral dependence of the absorption *k* and refraction *n* ratios of the initial silicon KDB12<100> and KDB10<111> before rapid thermal processing: *a* – *n* KDB12<100>; *b* – *n* KDB10<111>; *c* – *k* KDB12<100>; *d* – *k* KDB10<111>

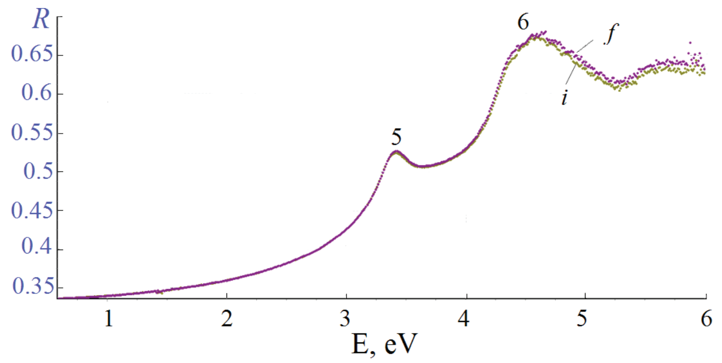

Figure 2 – Spectral dependence of reflection *R* ratios of the initial silicon KDB12<100> (*i*) and KDB10<111> (*f*) before rapid thermal processing

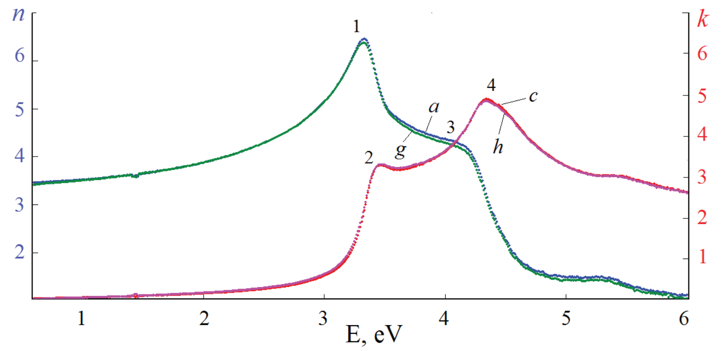

Figure 3 – Spectral dependence of the absorption *k* and refraction *n* ratios of the initial silicon KDB12<100> and KDB0.005<100> before rapid thermal processing: *a* – *n* KDB12<100>; *c* – *k* KDB12<100>; *g* – *n* KDB0.005<100>; *h* – *k* KDB0.005<100>

Meanwhile, for the spectral region nearby the maximum point of the refraction ratio with the energy of 4.1 eV one can observe the greatest difference of $\Delta n = 0.126$, and in the maximum of absorption with the energy of 4.34 eV (see Figure 1, point 4, curves *c*, *d*) the absorption ratio of the silicon with orientation <111> is higher by $\Delta k = 0.118$ than for the silicon with orientation <100>. The given result can be explained by influence of the higher concentration of the vacant charge carriers on the silicon surface with orientation <111> in this spectral range.

From this it ensues, that the spectral region 3.59–4.67 eV, determined by the electrons work, exiting the silicon surface, is more informative in demonstration of the difference of the optical parameters of the silicon of the different orientation.

Investigation of the silicon doping level influence on its optical characteristics on the samples KDB12<100> and KDB0.005<100>, possessing the same orientation and the different doping degree, revealed (see Figures 3, 4), that the maxima of the refraction ratios in the region of energy of 3.33 eV (see Figure 3, point 1, curves *a*, *g*) and 4.1 eV (see Figure 3, point 3, curves *a*, *g*), as well as in the maximum of the absorption ratio of the G-point (Van Hove singularity point M1) of Brillouin zone center (see Figure 3, point 2, curves *c*, *h*) for the silicon with the high concentration of Boron KDB0.005<100> the higher values of the absorption ratios are observed, but the lower values of the refraction indicators than for the silicon KDB12<100> with the difference $\Delta n = 0.082$, $\Delta k = 0.081$, 0.014, 0.016. The given result is determined by step-up in deformation of the silicon crystal lattice with the higher doses of its doping and with the significant content of the point defectswith the higher concentration of the Boron admixture in silicon. And, consequently, in the region of the absorption maximum, corresponding to the exit energy of the electrons from the silicon surface of 4.34 eV (see Figure 3, point 4, curves *c*, *h*) resulting in the additional appearance of the vacant charge carriers on the silicon surface, which is confirmed by the lower value of by refraction ratio by $\Delta n = 0.084$, of the absorption ratio by $\Delta k = 0.056$, than in case of the low alloy silicon. The given circumstance is explained, as it is shown in [8], by dependence of the silicon optical characteristics on concentration of the vacant charge carriers on the silicon surface.

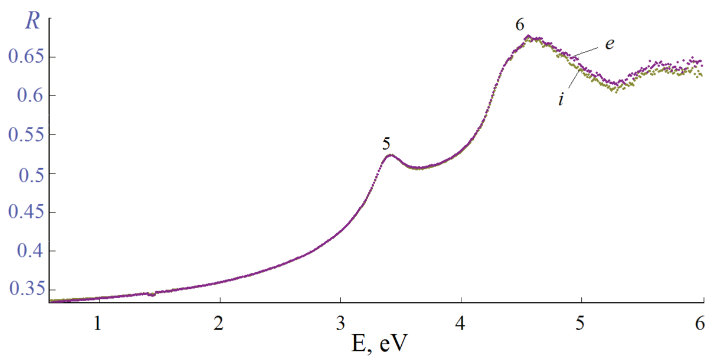

Figure 4 – Spectral dependence of the reflection *R* ratios of the initial silicon KDB12<100> (*i*) and KDB0.005<100> (*e*) before rapid thermal processing

On the basis of this it follows, that for assessment of the silicon doping level influence on its optical characteristics the most informative range is the spectral range of 3.32–4.34 eV.

Analysis of the initial silicon wafers after the rapid thermal processing

Analysis of dependences of the ratios of refraction, absorption and reflection in the spectral range of 0.6–6 eV after RTP showed (see Figure 5), that they are of the same nature as prior to treatment.

The comparative analysis of the optical parameters of the silicon samples KDB12<100> and KDB10<111> with the different orientation of the surface, i. e. possessing the different reticular density, revealed (see Table 1), that after RTP in the region of maxima of the refraction ratio, corresponding to the energy of 3.33–3.34 eV (see Table 1, point 1), 4.1 eV (see Table 1, point 3), as well as in the region of the absorption maxima, corresponding to the G-point (Van Hove singularity point M1) of Brillouin zone center (see Table 1, point 2) and the exit energy of the electrons from the silicon surface of 4.34 eV (see Table 1, point 4) for the silicon of orientation <111> the ratios of absorption, refraction and reflection were greater than for the silicon of orientation <100>.

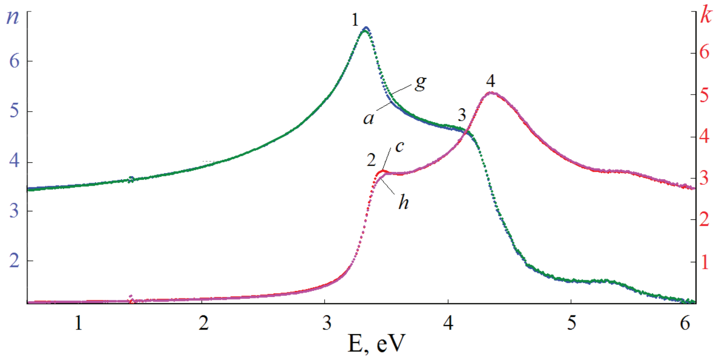

Figure 5 – Spectral dependence of the absorption *k* and refraction *n* ratios of the initial silicon KDB12<100> and KDB0.005<100> after the rapid thermal treatment: a – *n* KDB12<100>; *c* – *k* KDB12<100>; *g* – KDB0.005<100> *n*; *h* – *k* KDB0.005<100>

This has the analogous explanation, as in the case of the initial samples: the planes {111} possess the maximum density of the atoms packing, i. e. the silicon of orientation <111> possesses the higher reticular density [6, 7], and, consequently, in the result of the solid phase recrystallization of the disrupted layer after RTP the smaller deformation potential and the denser natural oxide.

In the absorption maximum with the energy of 4.34 eV the refraction indicator of the silicon of orientation <100> is slightly greater by $\Delta n = 0.004$, than for the silicon with orientation <111>. The given result can be explained by influence of the higher concentration of the vacant charge carriers on the silicon surface in this spectral range [8].

Meanwhile, for the spectral area nearby the maximum point of the refraction ratio with the energy of 4.1 eV one can observe the significant difference of $\Delta n = 0.098$, and in the absorption maximum with the energy of 4.34 eV the difference by the absorption ratio also rises and constitutes $\Delta k = 0.077$. On the basis of this it ensues, that the spectral area of 3.59–4.67 eV, determined by the exit work of the electron from the silicon surface, is more informative in demonstration of the difference in the optical parameters of silicon of the different orientation [6].

Investigation of the silicon doping level influence on its optical characteristics on the samples KDB12<100> and KDB0.005<100>, possessing the same orientation and the different doping degree, showed (see Table 2), that in the region of the absorption maxima, corresponding to the G-point (Van Hove singularity point M1) of Brillouin zone center (see Table 2, point 2) and the exit energy of the electrons from the silicon surface of 4.34 eV (see Table 2, point 4) for the silicon with the high concentration of Boron KDB0.005<100> one can observe the lower va-lues of the optical parameters, than for the silicon KDB12<100>. Just like indicated above, in the region of the refraction ration maximum point, corresponding to the energy of 3.32–3.33 eV (see Table 2, point 1).

For the lightly doped silicon KDB12<100> this can be explained by depletion of the surface layer with Boronbecause of its diffusion to the surface and the subsequent escape into the surrounding environment at the high temperatures of RTP. In case of silicon with the high admixture concentration, despite depletion of the surface layer, deformation of the crystal lattice will be higher, as there's a significant content of the point defects, and, consequently, the optical parameters turn out to be lower, than with the lightly doped silicon.

Table 1

Measurement results of the optical parameters of the silicon wafers after the rapid thermal processing

After RTP		KDB12<100>	KDB10<111>	Δ
1	*R*	0.508	0.511	0.003
	k	1.972	2.043	0.071
	n	6.669	6.722	0.053
	E(eV)	3.33	3.34	0.01
2 (G-point of the conductivity zone)	*R*	0.517	0.519	0.002
	k	3.168	3.193	0.025
	n	5.495	5.549	0.054
	E(eV)	3.48	3.48	0
3	*R*	0.544	0.545	0.001
	k	3.886	3.907	0.021
	n	4.611	4.709	0.098
	E(eV)	4.1	4.1	0
4 (exit energy of electrons from the silicon surface)	*R*	0.631	0.636	0.005
	k	5.053	5.13	0.077
	n	3.502	3.498	-0.004
	E(eV)	4.34	4.34	0

Table 2

Measurement results of the optical parameters of the silicon wafers after the rapid thermal processing

After RTP		KDB12<100>	KDB0.005 <100>	Δ
1	*R*	0.508	0.502	-0.006
	k	1.972	1.829	-0.143
	n	6.669	6.597	-0.072
	E(eV)	3.33	3.32	-0.001
2 (G-point of the conductivity zone)	*R*	0.517	0.514	-0.003
	k	3.168	3.102	-0.066
	n	5.495	5.454	-0.041
	E(eV)	3.48	3.51	0.03
3	*R*	0.544	0.545	0.001
	k	3.886	3.908	0.022
	n	4.611	4.665	0.054
	E(eV)	4.1	4.1	0
4 (exit energy of electrons from the silicon surface)	*R*	0.631	0.629	-0.002
	k	5.053	5.042	-0.011
	n	3.502	3.545	0.043
	E(eV)	4.34	4.34	0

The growth concentration of the ionized acceptors of the heavily doped silicon KDB0.005<100> at the high temperatures of RTP results in the increase and the effect of widening absorption in the region of the G-point of the conductivity zone, which explains the peak shift of the G-point to the value of 3.51 eV (see Figure 5, point 2, curves *c*, *h*) [9].

It should be also noted, that in the region of the refraction ration maximum point with the energy of 4.1 eV for silicon with the high Boron concentration KDB0.005<100> one can observe the higher values of the optical parameters, than for silicon KDB12<100>. Thus, in the absorption maximum point with the energy of 4.34 eV (see Table 2, point 4) the refraction indicator of the heavily doped silicon is greater by $\Delta n = 0.043$, than with KDB12<100>. The obtained result can be explained by the fact, that in the given spectral range there's a higher concentration of the vacant charge carriers on the silicon surface, resulting in its diffusion into the surrounding environment at the high temperatures of heating. This means, that after RTP the surface layer is depleted with the vacant charge carriers, and, consequently, in compliance with [8, 10] there should be the rise in the optical characteristics of silicon.

For the spectral area near the refraction ration maximum point with the energy of 3.32–3.33 eV one can observe the following alteration of the optical characteristics: $\Delta k = 0.143$, $\Delta n = 0.072$, $\Delta R = 0.006$. At the same time in the maximum of absorption with the energy of 4.48–3.51 eV the difference by the absorption ratio is more significant ($\Delta k = 0.066$), than with the energy value of 4.34 eV.

This means, that for evaluation of influence of the silicon doping level on its optical characteristics the most informative is the spectral range of 3.32–4.34 eV.

Conclusion

By means of the spectral ellipsometry method under investigation was influence of the rapid thermal treatment of the initial silicon wafers of the various doping level and reticular density on their optical characteristics.

Thus, influence was confirmed of the reticular density of silicon of the different orientation on its optical characteristics before and after rapid thermal processing. The significant reduction was established of the ratios of refraction and absorption in the center of Brillouin zone for the silicon samples with the high concentration of Boron after rapid thermal processing as compared with the low alloy silicon because of the more considerable depletion of the silicon surface with Boron in the first case as a result of the diffusion processes on the boundary of silicon-silicon dioxide. In the area of the absorption maximum peak, corresponding to the exit energy of the electron from the silicon surface, with the energy of 4.34 eV the refraction indicator of the heavily doped silicon becomes higher than in case of the low alloy silicon, which is determined by the high concentration of the vacant charge carriers on the silicon surface in this spectral range, resultant in the Boron diffusion into the sounding environment at the high temperatures of heating.

It has been ascertained that the spectral area 3.59–4.67 eV, corresponding to the electrons work function from silicon surface more exhaustively demonstrates the difference between the optical parameters of silicon with various orientation, and for estimation of the impact produced by the level of silicon doping at its optical characteristics the spectral range 3.32–4.34 eV happens to be more descriptive.

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