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The thermodefect formation in silicon doped by Sm, Gd, Er and Tm

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ABSTRACT: An influence of heat treatment on electrophysical properties of *n*-type silicon doped by *Sm*, *Gd*, *Er and Tm* under growing has been explored. It is shown that under thermal annealing in the temperature interval of 900 - 1200 ^{0}C during 1-2 hours in air or vacuum followed by hardening or slow cooling, the presence of *Sm*, *Gd*, *Er and Tm* in silicon lead to the suppression of high-temperature defects.

KEYWORDS: silicon, heat treatment, thermal defects, electrophysical properties, rare earth elements, getter action, the electrical conductivity, reduction of defect in silicon.

I. INTRODUCTION

Recently, silicon doped with rare-earth elements (*REE*) has attracted increasing attention of researchers as a promising material for optoelectronics. This is due to the prospect of using *Si*<*REE*> structures in silicon optoelectronics as light sources. As is known, the effectiveness of *REE* impurities in silicon and the manifestation of the optical properties of structures depend both on the spectrum of optically and electrically active centers containing *REE*s, their total concentration, and their interaction with uncontrolled impurities, as well as with thermal defects in the bulk of the material [1-7].

II. DESCIPTION AND RESULTS OF THE RESEARCH

Below are the results of studies on the effect of rare earth elements: samarium (Sm), gadolinium (*Gd*), erbium (*Er*) and thulium (*Tm*) on the thermal defect formation (*TD*) of silicon. The studies were carried out using neutron activation analysis (NAA), electrical conductivity; IR spectroscopy, isothermal relaxation of capacitance (IRE) [2-4], as well as studying the distribution of photo-e.m.f.

To study the deep levels (*DL*) located in the lower half of the *n-Si* band gap [3,4], optical recharging was used. We studied samples of *n*-type silicon single crystals doped with *Sm, Gd, Er and Tm* grown by the Czochralski method with specific resistivities of 10 ÷ 20 $\Omega \cdot cm$. Samples were cut from the washer in the form of parallelepipeds with dimensions 12 x 12 x 0.4 mm^3. Also used were control silicon samples with the same resistivities, grown without the admixtures of rare-earth elements under the same conditions.

The concentrations of *Sm*, *Gd*, *Er*, and *Tm* impurities in silicon, determined by the direct method of labeled atoms (using the direct radioactive-tracer method – DRTM [6,8-12]) and neutron activation analysis (NAA) [7-12] were: $N_{ree} = 5 \cdot 10^{15} \div 5 \cdot 10^{19}$ cm^{-3}. Using IR microscopy in the samples revealed the formation of dislocations . It was established that, at concentrations of the studied rare-earth elements in silicon $N_{ree} \geq 10^{16}$ cm^{-3}, the precipitation of the second hase begins.

The results of electrical measurements show that *Sm*, *Gd*, *Er and Tm* in silicon in the initial state are in an electrically inactive state. Studies of the effect of thermal treatments (900-1200 ^0C) for 1-2 hours in air and in evacuated ampoules followed by quenching or slow cooling show that oxygen precipitation occurs less in *Si*<*REE*> than in control samples.

Studying the results of isothermal relaxation shows that *Sm*, *Gd*, *Er and Tm* in silicon act as a getter for uncontrolled

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impurities and structural defects in heat treatments. It was found that the concentrations of deep levels of the E_v - 0.17 eV, the E_v - 0.2 eV, the E_v - 0.32 eV, the E_v - 0.41 eV, the E_v + 0.4 eV in the *Si*<*REE*> samples are much lower than in control samples that have passed the corresponding stages of heat treatments.

Thermal treatments (*TT*) in the temperature range 1373 ÷ 1473 *K*, for 2 hours, followed by oil quenching or slow cooling, compensated all *Si*<*REE*> samples, as a result of which the *IRE* method in all studied samples in the recharge temperature range 77–300 K no centers were found ($N_d < 5{\cdot}10^{11}$ cm^{-3}), i.e. the measured capacitance of Schottky barriers fabricated on the basis of *Si*<*REE*> with *REE* concentration in silicon $N_{рзэ} \geq 5{\cdot}10^{16}$ cm^{-3} did not depend on the applied voltage to temperatures of ~ 80 *K* and for samples with *REE* concentration in silicon ≥ 10^{17} cm^{-3} up to 100 *K*, i.e. $C_b \sim C_h$, and the degree of compensation in rapidly cooled samples was high.

Heat treatment at 1173 *K* and more leads to a decrease in the concentration of ionized centers in silicon samples doped with the studied *REE* impurities from $3{\cdot}10^{14}$ cm^{-3} to $2.6{\cdot}10^{14}$ cm^{-3}. However, the formation of deepid level (*DL*s) in the band gap of silicon associated specifically with rare-earth elements was not detected. Although, their indirect influence extended to the concentration of most of the observed *GI*s.

Therefore, it can be assumed that the rare-earth elements *Sm*, *Gd*, *Er and Tm* form a shallow acceptor level in the lower half of the silicon band gap, which confirms their acceptor nature. In the case of control (without *REE*) samples after *TT* (1173 ÷ 1473 *K*), the following Gls were detected: (E_c - 0.17 ÷ 0.22) *eV*, (E_c - 0.4) eV, (E_c - 0.54) eV, (E_v + 0.2) eV, (E_v + 0.4) eV, whose parameters coincide with the known literature data [1-5]. The concentration of all these thermal centers did not exceed ~ $5 \cdot 10^{13}$ cm^{-3}.

In the case of heat treatment of *n-Si*<*REE*> samples in pumped quartz ampoules, in contrast to thermally annealed in air, all *DL*s observed in *n-Si* samples without *REE* (control) are found. But their concentration in *n-Si*<*REE*> usually does not exceed the values of ~ $(2 \div 3){\cdot}10^{13}$ cm^{-3}, with the exception of the center with the *DL*s E_v + 0.4 eV, the capture cross section for electrons of which is $\sigma_n \sim 10^{-14}$ cm^{-2}, its concentration in the control samples reaches (3 ÷ 4) $\cdot 10^{14}$ cm^{-3}, and in silicon-doped *REE*s it is ~ $1{\cdot}10^{14}$ cm^{-3}.

As you know, this donor deep level is associated with iron (*Fe*) [**7**]. Thus, it should be noted that the *REE Sm*, *Gd*, *Er and Tm* suppress the formation of both *DL*s associated with rapidly diffusing uncontrolled impurities of gold (*Au*) and iron (*Fe*) [1,2], as well as other thermal centers with E_c - 0.17 *eV* levels (Fig. 1) and E_c-0.4 *eV* levels (Fig. 2) the concentration values of which depend both on the temperature of the treatments and on the presence of *REE* in silicon.

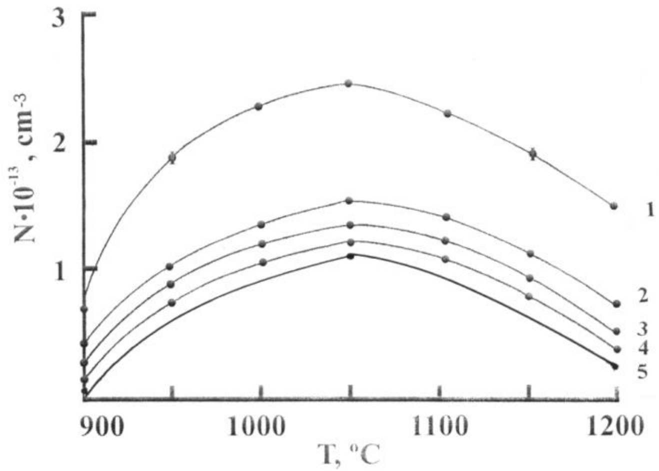

Fig. 1. Dependence of the concentration of thermal centers with a deep level E_c-0.17 *eV* in *n-Si* and *n-Si*<*REE*> from the temperature of the treatments.
1 - *n-Si*. 2 - *n-Si*<Sm>. 3 - *n-Si*<*Gd*>. 4 - *n-Si*<*Er*>. 5 - *n-Si*<*Tm*>. $N_{REE}=3{\cdot}10^{18}$ cm^{-3}.

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It was found that *REE Sm*, *Gd*, *Er*, and *Tm* reduce the concentration of these thermal centers by a factor of 2 ÷ 4. Thus, the presence of *Sm*, *Gd*, *Er*, and *Tm* in silicon leads to the suppression of high temperature APs. The higher the *REE* concentration in silicon, the greater the degree of compensation of the samples and the degree of suppression of thermodefekts (*TD)*.

The results of measurements of the τ_n time in silicon doped with *Sm*, *Gd*, *Er*, and *Tm* impurities during growth show that the presence of all these *REE*s increases the resistance of the samples to thermal treatments (*TT*), thereby increasing their τ_p relative to the control, unalloyed, by 3 ÷ 5 times.

III. CONCLUSION

It was found that *REE Sm*, *Gd*, *Er*, and *Tm*, reduce the concentration of these thermal centers by a factor of 2 ÷ 4. Thus, the presence of *Sm*, *Gd*, *Er*, and *Tm* in silicon leads to the suppression of high temperature APs. The higher the *REE* concentration in silicon, the greater the degree of compensation of the samples and the degree of suppression of thermodefekts (*TD)*.

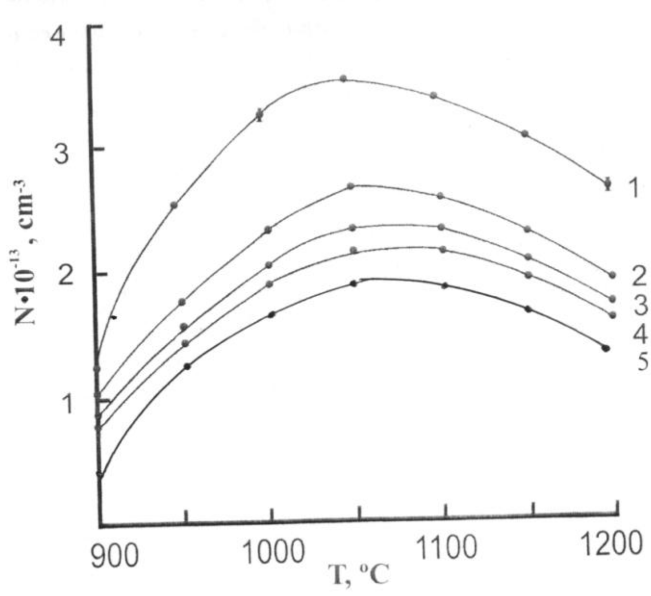

Fig. 2. Dependence of the concentration of thermal centers with a deep level E_c-0.4 *eV* in *n-Si* and *n-Si*<*REE*> from the temperature of the treatments.
1 - *n-Si*. 2 - *n-Si*<Sm>. 3 - *n-Si*<*Gd*>. 4 - *n-Si*<*Er*>. 5 - *n-Si*<*Tm*>. $N_{REE}=3 \cdot 10^{18}$ cm^{-3}.

The results of measurements of the τ_n time in silicon doped with *Sm*, *Gd*, *Er* and *Tm*, impurities during growth show that the presence of all these *REE*s increases the resistance of the samples to thermal treatments (*TT*), thereby increasing their τ_p relative to the control, unalloyed, by 3 ÷ 5 times.

The suppression of *TD* can be due to the purification of the silicon volume from uncontrolled rapidly diffusing impurities - by their gettering with *Sm*, *Gd*, *Er*, and *Tm*, impurities or the formation of <*REE + defect*> complexes of an acceptor nature, as well as the active interaction of *REE* with oxygen in silicon.

The results of studies of *IR* - absorption in *Si* - *REE* show that the effective interaction of *REE* with oxygen in silicon

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begins with concentrations of *REE* - $N_{REE} \geq 5 \cdot 10^{17}$ cm^{-3}, which may indicate the presence in the volume of silicon of inclusions of the second phase of *REE*, as well as *REE* silicides, acting as effluents for uncontrolled and process impurities.

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