RADIATION DEFECT CREATION IN SILICON DOPED
BY TRANSITION METALS

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1. INTRODUCTION

It is well known that more than twenty chemical elements of periodical table introduce deep levels into silic­
on forbidden gap. Deep levels are created in the material by the penetrating irradiation too. Electrical levels
and their (acceptor or donor) nature have been well established for many impurity and radiation defect cen­
ters in silicon. However, our knowledge on their detailed structure and behavior of their constituents, includ­
ing self-interstitial (I) atoms and vacancies (V), are still poor. Meanwhile, self-interstitial atoms, vacancies,
as well as uncontrollable impurities participate efficiently in formation of deep levels in silicon at high dop­
ing levels or irradiation doses, significantly affecting on its electrophysical, photoelectrical and recombin­
ation properties.

Gamma-irradiation of the material is particularly useful for reliable study of interaction process of elemental
radiation defects (V and I) with impurities, because it creates only vacancies and self-interstitial atoms. Thus,
this work is aimed at comparative investigation of interaction of V and I, created in n- and p-type Si by
gamma-irradiation, with extensively studied deep level impurities such as Cu, Ni, Rh, Ir, Au and Pt [1-10] to
reveal peculiarities of participation of V and I in formation of impurity-related and radiation defect centers.

2. EXPERIMENTAL PROCEDURES

The Czochralski-grown n- and p-type silicon single crystals with resistivity from 2 to 5 Ohm-cm were used
as the initial material. The impurity doping of these samples was performed by the thermal diffusion tech­
nique in open air during ~5 hrs from the layer of impurity atoms put on the both opposite surfaces of the
samples. Diffusion temperatures were ranged from 1000 to 1150°C for Cu and Ni, from 1000 to 1100°C for
Ir and Rh, from 850 to 930°C for Pt and Au. At these diffusion conditions, as our estimations using corre­
sponding diffusion equations show, all above impurities are distributed practically evenly along whole depth
of the samples. The concentrations of impurity centers (N_{imp}) after diffusion met requirements (N_{imp} \ll
0.1-N_P) for the deep level transient spectroscopy measurements (DLTS) [12].

Post-diffusion cooling of samples was conducted in open air with rate of ~250-300 K/min. Control samples
without above impurities were annealed simultaneously at the same conditions. Hall measurements showed
that resistivity and concentration of charge carriers were practically the same in doped and control samples.
Shottky diodes for DLTS measurements were prepared by fusion of Au and Sb onto the silicon surface.
Temperature dependence of relaxation rate of charge carriers was determined using the time window of t_1 =
0.2-20 ms (t_2 = 2 < t_1) after filling pulse of deep levels by majority charge carriers.

3. RESULTS AND DISCUSSION

Available data in the literature on parameters (electrical levels, diffusion coefficients, solubility etc) of impu­
rities under interest, Cu, Ni, Rh, Ir, Au and Pt, are summarized in Table 1.
Table 1. Parameters of impurities Ni, Cu, Rh, Ir, Pt, Au in Si.

<table>
<thead>
<tr>
<th>Element</th>
<th>Covalence radii (Å)</th>
<th>Solubility at 1100°C (cm³)</th>
<th>Diffusion coefficient at 1100°C (cm² s⁻¹)</th>
<th>Electrical levels (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.17</td>
<td>7.10¹⁷</td>
<td>3.10⁵</td>
<td>E⁺⁻ (0.15 to 0.2); E⁻⁻ (0.36 to 0.47)</td>
<td>1, 11</td>
</tr>
<tr>
<td>Cu</td>
<td>1.25</td>
<td>1.10¹⁸</td>
<td>1.10⁴</td>
<td>E⁺⁻ (0.15 to 0.2); E⁻⁻ (0.41 to 0.46)</td>
<td>1, 11</td>
</tr>
<tr>
<td>Rh</td>
<td>1.27</td>
<td>1.10¹⁶</td>
<td>6.10⁷</td>
<td>E⁺⁻ (0.17 to 0.2); E⁻⁻ (0.32)</td>
<td>2, 4, 11</td>
</tr>
<tr>
<td>Ir</td>
<td>1.28</td>
<td>2.10¹⁶</td>
<td>7.10⁷</td>
<td>E⁺⁻ (0.19 to 0.26); E⁻⁻ (0.31 to 0.36)</td>
<td>3, 4, 11</td>
</tr>
<tr>
<td>Pt</td>
<td>1.30</td>
<td>8.10¹⁵</td>
<td>3.10⁷</td>
<td>E⁺⁻ (0.19 to 0.29); E⁻⁻ (0.30 to 0.42)</td>
<td>5, 7, 11</td>
</tr>
<tr>
<td>Au</td>
<td>1.43</td>
<td>3.10¹⁶</td>
<td>9.10⁶</td>
<td>E⁺⁻ (0.53); E⁻⁻ (0.35)</td>
<td>9, 10, 11</td>
</tr>
</tbody>
</table>

The measurements show that in the DLTS spectra of n-Si<Cu> there are two peaks corresponding to ionization energies of electrical levels of E₀ = E_c -0.17 eV (% = 1.5<10¹⁴ cm²) and E₁ = E_c -0.23±0.02 eV (% = 1.3<10¹⁷ cm²). Copper possesses high diffusion coefficient and is known to be unstable in an isolated interstitial position [1], therefore, the level E₀ with very low concentration (~10¹² cm⁻³) corresponds rather to interstitial copper and possesses donor character.

Although nickel and copper behave similarly in silicon, there is overall difference in their spatial distribution. Nickel has more tend to precipitate than copper and primarily at the surface, which can be related with different elemental sizes of silicides of copper and nickel [1]. In the case of n-Si<Ni> we found two electrical levels of E₂=E_c -0.19±0.02 eV (n=5<10¹⁵ cm²) and E₃=E_c -0.42±0.03 eV (n=8<10¹⁶ cm²), but only after thermal diffusion above 1200°C. The nickel-related centers perhaps are more complex than those of copper and, according to [1], may be caused by microprecipitates. The above levels were observed, though in less concentrations, in control samples too, therefore, we do not tend to attribute them to nickel.

Spectra of electrical levels of Ir (E₄, E₅, E₆), Rh (E₇, E₈), Au (E₉) and Pt (E₁₀, E₁₁) in n-Si and their concentrations for different diffusion temperature are given in Table 2. The observed electrical levels overall are in good correlation with those in the literature [2-10].

The research on accumulation of radiation defects (up to 60Co γ-quanta doses ~2*10⁸ Rad) in n-type samples with different concentrations of copper shows that the concentrations of A-centers (V+O) with the level of E₀=0.18 eV (n=1.5<10¹⁵ cm²) and E₁=0.42±0.03 eV (n=8<10¹⁶ cm²), but only after thermal diffusion above 1200°C. The nickel-related centers perhaps are more complex than those of copper and, according to [1], may be caused by microprecipitates. The above levels were observed, though in less concentrations, in control samples too, therefore, we do not tend to attribute them to nickel.

A-center and copper center with close energy levels were distinguished by their charge capture cross-sections. It should be noted that the formation efficiency of E-centers is significantly lower (from 10 to 100 times, depending on the concentrations of shallow impurities and oxygen) than A-centers, which is in agreement with the literature data [14].

Radiation decay of copper center, E₁, and decrease in efficiency of radiation defect formation can be explained by substitution of impurities in lattice sites by self-interstitial Si atoms by kick-out reaction, as well as by possible formation of electrically neutral oxygen-copper precipitates [15]. The reaction between interstitial Cu and O or vacancy is facilitated by their charge states: Cu is positively charged, but O and vacancy are negatively charged in n-Si. Note concentrations of copper and oxygen are comparable in doped n-Si.
Table 2. Electrical levels, charge capture cross-sections, and concentrations of deep levels in doped silicon versus diffusion temperature.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Diffusion temperature, °C</th>
<th>Electrical levels (eV), charge capture cross-sections (cm^2), and concentrations (cm^3) of deep centers</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Si&lt;P,Cu&gt;</td>
<td>1010 1050 1100 1150</td>
<td>$E_c = 0.23$ $\begin{array}{c} 1.3 \times 10^{11} \ 6.0 \times 10^{11} \ 6.9 \times 10^{11} \ 8.0 \times 10^{11} \ 9.0 \times 10^{11} \end{array}$ $\begin{array}{c} 4 \times 10^{11} \ 1.2 \times 10^{12} \ 1.0 \times 10^{12} \ 8.0 \times 10^{11} \ 7.0 \times 10^{11} \end{array}$ $\begin{array}{c} 1.3 \times 10^{11} \ 2.6 \times 10^{11} \ 1.0 \times 10^{11} \ 1.9 \times 10^{11} \ 9.0 \times 10^{10} \end{array}$ $\begin{array}{c} 2.6 \times 10^{11} \ 8.0 \times 10^{11} \ 8.0 \times 10^{11} \ 7.0 \times 10^{11} \ 6.0 \times 10^{11} \end{array}$</td>
</tr>
<tr>
<td>n-Si&lt;P,Ir&gt;</td>
<td>1000 1050 1100</td>
<td>$E_c = 0.18$ $\begin{array}{c} 1.1 \times 10^{11} \ 6.6 \times 10^{11} \ 1.8 \times 10^{11} \ 3.2 \times 10^{11} \ 2.1 \times 10^{11} \end{array}$ $\begin{array}{c} 4.5 \times 10^{11} \ 4.5 \times 10^{11} \ 3.5 \times 10^{11} \ 4.2 \times 10^{11} \ 3.5 \times 10^{11} \end{array}$ $\begin{array}{c} 1.6 \times 10^{11} \ 1.5 \times 10^{11} \ 1.2 \times 10^{11} \ 4.2 \times 10^{11} \ 3.5 \times 10^{11} \end{array}$ $\begin{array}{c} 1.6 \times 10^{11} \ 1.5 \times 10^{11} \ 1.2 \times 10^{11} \ 4.2 \times 10^{11} \ 3.5 \times 10^{11} \end{array}$</td>
</tr>
<tr>
<td>n-Si&lt;P,Rh&gt;</td>
<td>870 900 930</td>
<td>$E_c = 0.53$ $\begin{array}{c} 2.1 \times 10^{11} \ 4.5 \times 10^{11} \ 8.1 \times 10^{11} \ 6.0 \times 10^{11} \end{array}$ $\begin{array}{c} 1.5 \times 10^{11} \ 1.9 \times 10^{11} \ 4.2 \times 10^{11} \ 3.5 \times 10^{11} \end{array}$ $\begin{array}{c} 1.6 \times 10^{11} \ 1.2 \times 10^{11} \ 3.7 \times 10^{11} \end{array}$ $\begin{array}{c} 1.6 \times 10^{11} \ 1.2 \times 10^{11} \ 3.7 \times 10^{11} \end{array}$</td>
</tr>
</tbody>
</table>

**Figure 1.** Concentration of radiation defects versus that of copper in n-Si<P,Cu> at the gamma-irradiation dose of $D=2\times10^8$ Rad: 1 – A-center; 2 – E-center.

**Figure 2.** Concentration of the center $E_c = 0.23$ eV ($N_{Cu} = 2\times10^{13}$ cm$^{-3}$), attributed to Cu, in n-Si<P,Cu> versus gamma-irradiation dose.
In samples n-Si< Ni> influence of nickel’s concentration on formation of radiation defects was not observed up to irradiation doses $6 \times 10^8$ Rad; the concentrations of radiation defects practically are the same in control and doped samples. This can be explained by larger concentration of oxygen ($\sim 10^{18}$ cm$^{-3}$) as compared to nickel ($\sim 5 \times 10^{17}$ cm$^{-3}$). However note that with increasing radiation dose electrical capacity of n-Si< Ni> samples decreases faster than that in control samples. It may be related with increase in concentration of acceptor center of nickel with level of $E_v + 0.22 \pm 0.02$ eV [1,7], which located in lower part of silicon forbidden gap.

Fig. 3 depicts changes in concentration of centers of iridium, rhodium, platinum, and aurum versus $\gamma$-quanta dose. As seen from the figure, concentrations of centers $E_6$, $E_8$, $E_9$ and $E_{10}$ remain practically unchanged with growing irradiation dose, but concentrations of centers $E_5$, $E_7$ and $E_{11}$ of acceptor nature increase by $20 \pm 30$ % at the dose of $4.5 \times 10^8$ Rad, which enable one to attribute these centers to complexes of interstitial impurities (Ir, Rh and Pt) with vacancies. To support this assumption, changes of concentration of impurity centers were studied depending on annealing temperature. Fig. 4 shows the results for n-Si<P, Pt> as typical example. As seen, concentration of center $E_9$ increases slightly with increasing of annealing temperature, but concentration of center $E_{11}$ decreases starting from $\sim 150^\circ$C, that is the decay of the center occurs in sufficiently low temperatures.

A- and E-centers were found to be main radiation defects in both doped and control n-Si, while in p-Si main radiation defects are divacancy (W), K-centers (W+O+C), and a complex of boron with vacancy (V+B). With increasing irradiation dose the concentration of A-centers (Fig. 5) increases in the samples n-Si<P, Rh>, n-Si<P, Pt>, n-Si<P, Au> (the concentration of E-centers are in limits of sensitivity of the measurement technique ($< 10^{12}$ cm$^{-3}$) in these samples and about $\sim 10^{13}$ cm$^{-3}$ in the control samples). In p-type samples concentration of K-center increases, concentration of divacancy decreases, but concentration of complex (V+B) does not practically change with increase of metal impurity concentration (Fig. 6). Such behavior of radiation defects in p-type Si can be explained by decay of impurity centers, clusters of silicides and SiOn.

![Figure 3](image URL)  
**Figure 3.** The concentration of impurity centers in n-Si<Ir> ($E_5$, $E_6$), n-Si<Rh> ($E_7$, $E_8$), n-Si<Au> ($E_9$) and n-Si<Pt> ($E_{10}$, $E_{11}$) versus $\gamma$-irradiation dose. The concentrations of the centers before irradiation correspond to values for $D=0$.

![Figure 4](image URL)  
**Figure 4.** The concentration of Pt centers in n-type silicon versus annealing temperature: $E_{10} = E_v - 0.24$ eV, $E_{11} = E_v - 0.53$ eV.

Such behaviour of the radiation defects in a doped p-silicon is explained by a decay of impurity centers, clusters, silicides and SiOn–type compositions (see table 1).
Table 1. Quasi chemical reactions of the defect formation in a doped silicon

\[ \begin{array}{c}
\text{Si} + Xs - \rightarrow \text{SiO}_n \\
\text{Si} + C_s - \rightarrow \text{SiC} \\
V + \text{C}_i \rightarrow \text{C}_i \\
\text{C}_s \rightarrow \text{B}_i \\
\text{C}_i \rightarrow \text{C}_i \\
\text{O}_s \rightarrow \text{O}_i \\
\{ \text{OC} \} \rightarrow \{ \text{VV} + \text{Vi} + \text{Ci} \} \\
V + P \rightarrow \{ \text{VP} \} - E \text{ centers} \\
V + B \rightarrow \{ \text{VB} \} \\
V + M_{\text{inactiv}} \rightarrow \{ \text{V+M} \} \rightarrow M_{\text{activ}} \\
V + \text{O}_i \rightarrow \{ \text{V+O} \} - A \text{ centers} \\
\end{array} \]

The concentration of A-centers increases with increasing of covalence radii of impurities (Fig. 5). Because the covalence radii of Rh, Pt, Au are substantially larger than that of silicon (1.17 Å), strained regions around them are of compressed ones and will serve as sinks for vacancies. This decreases probability of mutual annihilation of vacancies and silicon self-interstitials and leads to enhancing concentration of radiation defects. On the other hand, strain fields of the same kind around isolated substitutional impurities also decreases probability of their replacement by silicon atoms by kick-out reaction. This may explain practical independence of number of impurity centers (E6, E8, E9 and E10) on irradiation dose and enables one to attribute these centers to substitutional impurities. Slight increase of their concentration (Fig. 3) supports to some extent this suggestion and attribution of E5, E7 and E10 centers to weakly-bonded vacancy and interstitial impurity pairs too, because such pair not only decays easily, but also can transform into substitutional impurity due to annihilation of its constituents.

Note that in the work [18] the formation efficiency of A- and E-centers was found to increase with increase of the covalent radii of donor impurities (P, As, Sb with concentrations of \( \sim 2 \times 10^{15} \text{ cm}^3 \)) at the gamma-irradiation of Czochralski-grown n-type silicon. Negligibility of E-center concentration in our case can be explained by quite large concentration of deep impurities, which leads to more local inhomogeneity of the material as compared to that containing only shallow impurities and making the meeting of the latter with vacancies less probable.
4. CONCLUSIONS

In summary, we investigated peculiarities of formation of radiation defects (A- and E-centers etc) at the gamma-irradiation in silicon doped by transition metal impurities depending on the parameters (solubility, covalence radii and diffusion coefficient) of impurities (Ni, Cu, Ir, Rh, Pt, Au). This enabled one to reveal relative roles of vacancies, silicon self-interstitials, as well as substitutional and interstitial impurity atoms on the observed centers.

Decay of impurity centers at γ-irradiation was observed only for the center $E_c = 0.23 \pm 0.02$ eV of copper, which we attribute to substitutional copper. Apart from, the concentration of A-centers decrease in the copper doped samples as compared to control samples. Such different behavior of copper as compared to other impurities considered is due to large diffusion coefficient and solubility of copper in silicon and its interaction with both components of Frenkel pairs to be created at γ-irradiation, as well as due to possible formation electrically neutral complexes of copper and oxygen.

5. REFERENCES

3. Physics and materials science of semiconductors with deep levels /Ed. V.I. Fistul (Moskow, Metallurgiya, 1987) [in Russian].


