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 silicon 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 centers in silicon. However, our knowledge on their detailed structure and behavior of their constituents, including 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 doping levels or irradiation doses, significantly affecting on its electrophysical, photoelectrical and recombination 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 resisitivity from 2 to 5 Ohm·cm were used as the initial material. The impurity doping of these samples was performed by the thermal diffusion technique 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 corresponding 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 ($N_{imp} \approx 0.1 \cdot N_P$) 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 мs ($t_2 = 2 \lessdot t_1$) 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 impurities 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.

Element	Covalence radii (Å)	Solubility at 1100°C (cm^{-3})	Diffusion coefficient at 1100°C (cm^2s^{-1})	Electrical levels (eV)	Reference
Ni	1.17	7.10^{17}	3.10^{-5}	E_c - (0.15 to 0.2); E_c - (0.36 to 0.47) E_v + (0.15 to 0.21); E_v +(0.31 to 0.35)	1, 11
Cu	1.25	1.10^{18}	1.10^{-4}	E_c - (0.15 to 0.2); E_c - (0.41 to 0.46) E_v + (0.2 to 0.23); E_v +(0.09 to 0.1)	1, 11
Rh	1.27	1.10^{16}	6.10^{-7}	E_c-0.32; E_c-0.53	2, 4, 11
Ir	1.28	2.10^{16}	7.10^{-7}	E_c-(0.17 to 0.2); E_c-0.33; E_c-0.54	3, 4, 11
Pt	1.30	8.10^{15}	3.10^{-7}	E_c - (0.19 to 0.26); E_c - (0.31 to 0.36) E_v + (0.19 to 0.29); E_v +(0.30 to 0.42)	5-7, 11
Au	1.43	3.10^{16}	9.10^{-6}	E_c-0.53; E_v + 0.35	9-10, 11

The measurements show that in the DLTS spectra of n-Si<Cu> there are two peaks corresponding to ionization energies of electrical levels of $E_0 \sim E_c$-0.17 eV ($\bullet_n$ =1.5$\prec 10^{-14}$ cm^2) and $E_1 = E_c$-0.23±0.02 eV ($\bullet_n$ =1.3$\prec 10^{-17}$ cm^2). Copper possesses high diffusion coefficient and is known to be unstable in an isolated interstitial position [1], therefore, the level E_0 with very low concentration (~10^{12} 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 $E_2=E_c$-0.19±0.02 eV ($\bullet_n$ =5$\prec 10^{-15}$ cm^2) and $E_3=E_c$-0.42±0.03 eV ($\bullet_n$ = 8$\prec 10^{-16}$ cm^2), 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 (E_4, E_5, E_6), Rh (E_7, E_8), Au (E_9) and Pt (E_{10}, E_{11}) 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 ^{60}Co γ-quanta doses ~$2\cdot10^8$ Rad) in n-type samples with different concentrations of copper shows that the concentrations of A-centers (V+O) with the level of E_c-0.18 eV ($\bullet_n$ =1.5$\prec 10^{-15}$ cm^2) and E-centers (V+P) with the level of E_c-0.42 eV ($\bullet_n$ =5$\prec 10^{-15}$ cm^2) decrease with increase of the copper concentration (Fig. 1). The latter is also decreases with increase of gamma-irradiation dose (Fig.2).

A-center and cooper 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, E_1, 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.

Sample type	Diffusion temperature, °C	Electrical levels (eV), charge capture cross-sections (cm^2), and concentrations (cm^{-3}) of deep centers								
		E_i. eV	σ_n, cm^2	N,cm^{-3}	E_i. eV	σ_n, cm^2	N,cm^{-3}	E_i. eV	σ_n, cm^2	N,cm^{-3}
		E_1								
n-Si<P,Cu>	1010 1050 1100 1150	E_c–0.23	$1.3\cdot10^{-17}$	$6\cdot10^{12}$ $6.9\cdot10^{12}$ $8\cdot10^{12}$ $9\cdot10^{12}$						
		E_4			E_5			E_6		
n-Si<P,Ir>	1000 1050 1100	E_c–0.18	$4\cdot10^{-15}$	$9.5\cdot10^{12}$ $1.2\cdot10^{12}$ $1.8\cdot10^{12}$	E_c–0.33	$1.3\cdot10^{-14}$	$2.6\cdot10^{13}$ $1\cdot10^{14}$ $1.9\cdot10^{14}$	E_c–0.52	$8\cdot10^{-16}$	$3.8\cdot10^{13}$ $1.2\cdot10^{14}$ $2.2\cdot10^{14}$
					E_7			E_8		
n-Si<P,Rh>	1000 1050 1100				E_c–0.32	$1.1\cdot10^{-15}$	$6.6\cdot10^{13}$ $1.8\cdot10^{14}$ $3.2\cdot10^{14}$	E_c–0.53	$2\cdot10^{-15}$	$6.1\cdot10^{13}$ $1.6\cdot10^{14}$ $3.1\cdot10^{14}$
		E_9								
n-Si<P,Ir>	870 900 930	E_c–0.53	$4\cdot10^{-16}$	$2\cdot10^{13}$ $4.5\cdot10^{13}$ $8.1\cdot10^{14}$						
					E_{10}			E_{11}		
n-Si<P,Rh>	870 900 930				E_c–0.24	$1.5\cdot10^{-15}$	$1.9\cdot10^{13}$ $4.2\cdot10^{13}$ $3.5\cdot10^{14}$	E_c–0.53	$1.6\cdot10^{-16}$	$1.25\cdot10^{13}$ $3.7\cdot10^{13}$ $6\cdot10^{13}$

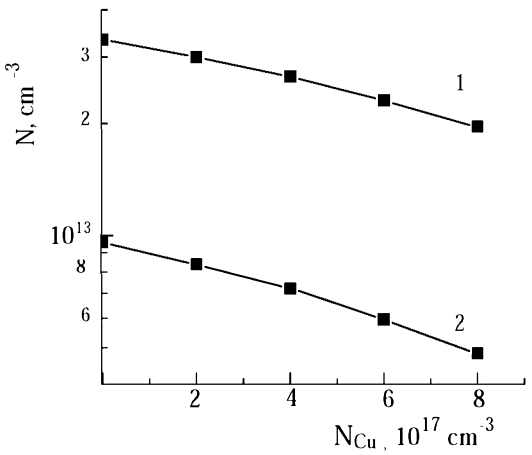


Figure 1. Concentration of radiation defects versus that of copper in n-Si<Cu> at the gamma-irradiation dose of $D=2\cdot10^8$ Rad: 1 – A-center; 2 – E-center.

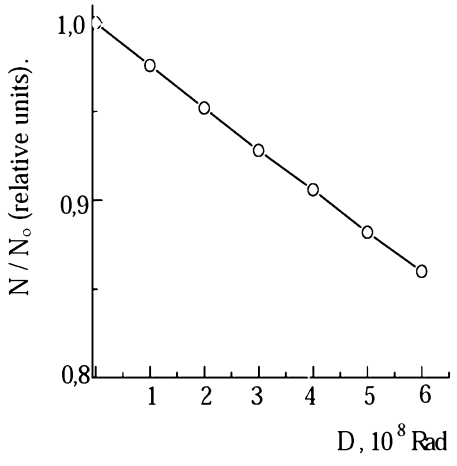


Figure 2. Concentration of the center E_c-0.23 eV ($N_{Cu}\approx2\cdot10^{13}$ cm^{-3}), attributed to Cu, in n-Si<Cu> versus gamma-irradiation dose.

In samples n-Si<Ni> influence of nickel's concentration on formation of radiation defects was not observed up to irradiation doses $6 \cdot 10^8$ 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 ($\sim 5 \cdot 10^{17}$ 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 $E_v+0.22 \pm 0.02$ эВ [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 γ-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÷30 % at the dose of $4.5 \cdot 10^8$ 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 ~150°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 ~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 SiO_n.

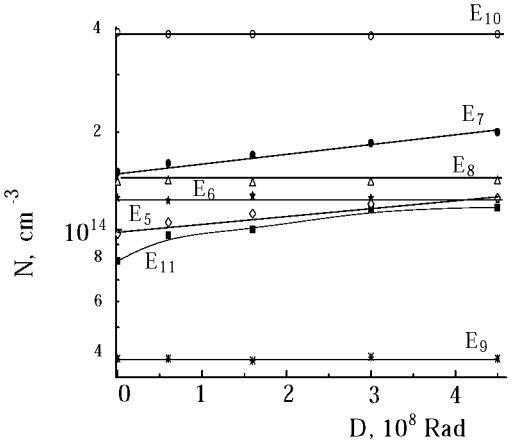


Figure 3. The concentration of impurity centers in n-Si<Ir> (E_5 E_6), n-Si<Rh> (E_7, E_8), n-Si<Au> (E_9) and n-Si<Pt> (E_{10}, E_{11}) versus γ-irradiation dose. The concentrations of the centers before irradiation correspond to values for D=0.

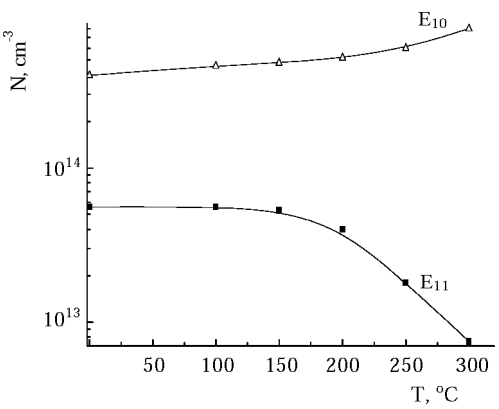
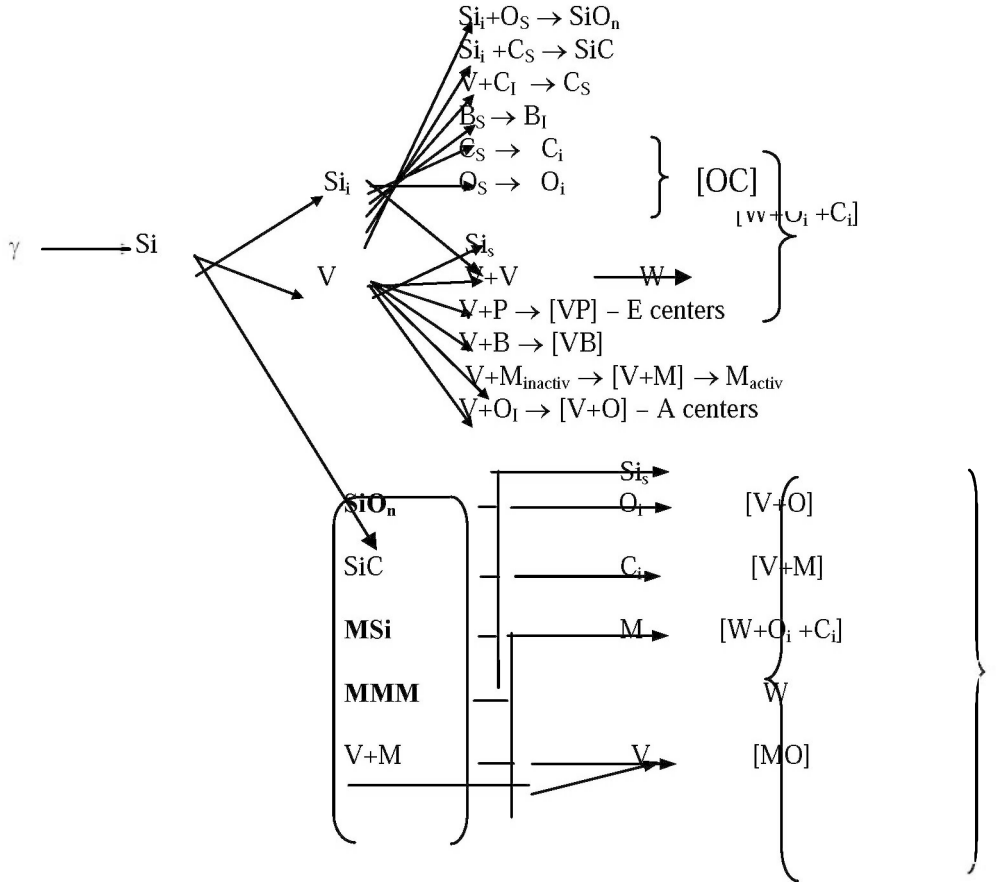


Figure 4. The concentration of Pt centers in n-type silicon versus annealing temperature: E_{10} =E_c-0.24 eV, E_{11} = E_c-0.53 eV.

Such behaviour of the radiation defects in a doped p-silicon is explained by a decay of impurity centers, clusters, silicides and SiO_n -type compositions (see table 1).

Table 1. Quasi chemical reactions of the defect formation in a doped silicon



X_s–, X_i – impurity atoms on site and interstitial position, MMM – clusters
Si_i –, Si_s– silicon atoms on interstitial and substitutional sites, accordingly
W–divacancy, MSi – silicides, M–impurity atoms, [W+O+C] – K-centers

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 (E_6, E_8, E_9 and E_{10}) on irradiation dose and enables one to attribute these centers to substitutional impuritites. Slight increase of their concentration (Fig. 3) supports to some extent this suggestion and attribution of E_5, E_7 and E_{11} 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 ~2.10^{15} 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.

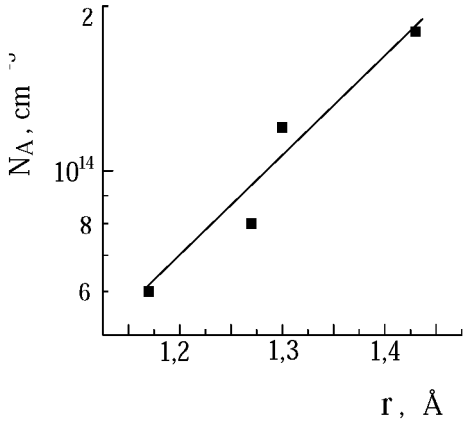


Figure 5. The concentration of A-centers versus covalence radii of metal impurity (Ni, Rh, Pt, Au) at the γ-irradiation dose of $D=2\cdot10^8$ Rad. $N_M=10^{14}$ cm^{-3}.

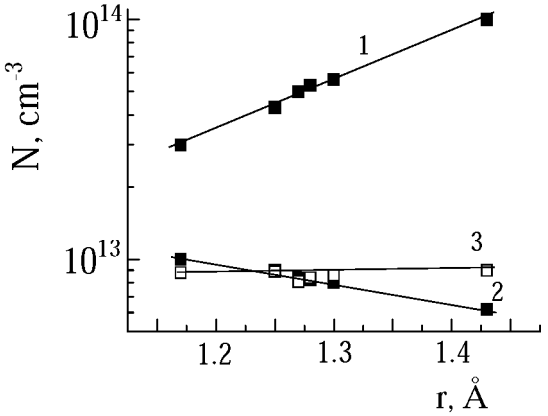


Figure 6. Concentration of radiation defect centers E_v+0.36 eV (1), E_v+0.25 eV (2) and E_v+0.44 eV (3) versus of covalence radii of metal impurity at the γ-irradiation dose of $D=10^9$ Rad. $N_M = 10^{14}$ cm^{-3}, $\rho_{initial}=2$ Ω·cm.

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±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

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