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Studying the Charging State of Zinc Atoms in Silicon

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ABSTRACT: Lead mixture in silicon is a two-electron acceptor, as shown by the messaging spectroscopy method (^{67}Zn). Here are the cases of the two-electron lead center determined by the correlation energy sign.

KEYWORDS: Isotope, Spectroscopy, Acceptor, Primes, Intrinsic Zone, Energy Efficiency, Correlation Energy.

I. INTRODUCTION

The introduction of impurities into silicon makes it possible to control the parameters of silicon. An admixture of zinc in silicon is an acceptor and forms two deep energy levels {1, 2} in the band gap, and the concentration of electrically active zinc coincides with the total concentration of zinc {1}. It is believed that impurity zinc atoms form two-electron acceptor centers in silicon with ionization energies E_1 ~ 0.31 eV {process (0 / -)} and E_2 ~ 0.55 eV {process (- / - -)} {2}, so that zinc, depending on the position of the Fermi level, can stabilize in three charge states: neutral $\{Zn\}^0$, once {Zn) - and twice {Zn} = ionized.

The first attempts to detect the EPR spectrum of paramagnetic centers {Zn} - in silicon were not successful {3}. The authors of {4} attributed to such centers the EPR spectrum of silicon samples doped with zinc and under uniaxial compression. Later, the authors of {5} reported the existence of two EPR spectra in silicon doped with zinc, which appear only in the process of illuminating high-resistance hole samples with white light. One of these spectra was associated with the centers {Zn} - with orthorhombic symmetry {6}. In connection with this behavior of the EPR spectra, it was suggested that the two-electron acceptor center of zinc in silicon has a negative correlation energy U: the sequence of its levels is inverted; the centers {Zn} =, {Zn} - and $\{Zn\}^0$ are in different positions of the silicon lattice (they are substitution centers, but are displaced relative to the unperturbed site); due to the negative sign of U, the center {Zn} - turns out to be unstable and spontaneously decays by the reaction 2 {Zn} - → $\{Zn\}^0$ + {Zn} = {6}.

II. RELATED WORKS

To choose between two possible models of the acceptor zinc impurity in silicon (U> 0 {2} or U <0 {6}), the identification of the $\{Zn\}^0$ and {Zn} = centers, the determination of the symmetry of their local environment, and the experimental determination of the ratio concentrations depending on the position of the Fermi level. In this regard, it seems relevant to study the behavior of zinc impurity atoms in silicon by Mössbauer emission spectroscopy using the ^{67}Ga (^{67} Zn) isotope: the diffusion introduction of the ^{67}Ga isotope into silicon ensures the stabilization of both the parent ^{67}Ga and ^{67} Zn daughter atoms in the substitution position; varying the concentration of carriers in the initial silicon samples makes it possible to control the position of the Fermi level and obtain a material with a controlled ratio of the concentration of charge states of zinc; The parameters of the ^{67}Zn Mössbauer spectra allow reliable determination of the charge (electronic) state of zinc atoms, the symmetry of their local environment, and the concentration ratio between different charge states of zinc.

Silicon was doped with ^{67}Ga gallium by diffusion in evacuated quartz ampoules from the gas phase at 1320^0 C for 5 h (penetration depth was ~ 1.5 μm, the surface concentration of gallium did not exceed 5 • 10^{14} cm $^{-3}$) Three samples A and B were obtained, and C:

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A - the initial sample was hole (the background impurity was boron, ($p = 2 \cdot 10^{16} cm^{-3}$); after diffusion doping with gallium, the conductivity type and concentration of current carriers did not change; according to {2}, the Fermi level is fixed near the top of the valence band and all centers zinc are in the state $\{Zn\}^0$;

B — the initial sample was electronic (background impurity — phosphorus, $n = 2 \cdot 10^{16} cm^{-3}$); after diffusion doping with gallium, the type of conductivity and concentration of current carriers have not changed; according to {2}, the Fermi level is fixed near the bottom of the conduction band and all zinc centers are in the state {Zn} =;

III. ALGORTHMS USED

The C initial sample was electronic (the background impurity was phosphorus, $n = 2 \cdot 10^{16} cm^{-3}$); First, diffusion doping of the sample with zinc was carried out (in vacuum quartz ampoules from the gas phase at $10,80^0$ C for 60 hours, followed by removal of ~ 100 μm from the surface of the layer, the zinc concentration in the sample was $1.5 \cdot 10^{16} cm^{-3}$ {2}), so that the low-resistance initial sample (~0.3 Ohm • cm) became high-resistance (~10^4 Ohm • cm) without changing the type of conductivity; then diffusion doping with gallium was carried out, after which the type of conductivity and concentration of current carriers did not change; according to {2}, the Fermi level is fixed near the level $E_1 = 0.55$ eV, so that zinc centers are present mainly in the {Zn} - state; the Fermi level is fixed between the levels E1 = 0.316 eV and $E_2 = 0.167$ eV and the zinc centers are present in the form $\{Zn\}^0$ and {Zn} =

The Mössbauer spectra of ^{67}Ga (^{67}Zn) were measured at 4.2 K with a ^{67}ZnS absorber. The spectra of samples A (spectrum A) and B (spectrum B) were single lines, and the transition from a hole to an electron sample leads to a shift in the center of gravity of spectrum S to the region of positive velocities (Figure 1). Obviously, spectrum A corresponds to neutral centers $\{^{67}Zn\}^0$, and spectrum B corresponds to doubly ionized $\{^{67}Zn\}$ =. If the measurement temperature of the spectra is equal, S is determined

$$S = - (9/16) (k \Delta\theta / Mc2) + \alpha\Delta\rho (0)$$

Where k is the Boltzmann constant, M is the mass of the probe nucleus, c is the speed of light in vacuum, Δθ is the temperature difference Debye of the two samples, α is the calibration constant, Δρ (0) is the difference in the relativistic electron charge densities at ^{67}Zn nuclei in two samples.

IV. RESULTS

The first term in this expression describes the effect of the second-order Doppler shift in the Debye approximation, and since both spectra belong to impurity zinc atoms in the silicon matrix, this term can be neglected. The second term is an isomeric shift due to the difference in electron density at ^{67}Zn nuclei in two samples. An increase in S upon going from $\{Zn\}^0$ to [Zn] = indicates an increase in the electron density on ^{67}Zn nuclei and, therefore, on the localization of two electrons at the Mössbauer center.

The spectrum of sample C (spectrum C) is an overlay of spectra A and B (see Figure I). Figure II, III shows the expected forms of the Mössbauer spectra of ^{67}Zn for the cases U <0 and U> 0. The technique for constructing such spectra is described using electron density calculations for various electronic zinc configurations {7}. A comparison of the experimental (Fig. I) and calculated (Fig. II, III) Mössbauer spectra clearly indicates that U <0 for two-electron zinc centers in silicon.

It should be noted that the spectra corresponding to the {Zn} 0 and {Zn} = centers are attenuated (for the 67Cu (67Ga) spectrum) with a ZnS absorber, the width of the spectral line at half maximum Γ = 2.6 (3) μm • s-1 (8), while for the spectra in Fig. I we obtained Γ = 5.0 (5) μm • s-1. Such a significant broadening of the spectra indicates that the local symmetry of the impurity zinc atoms differs from the cubic one and can be interpreted as evidence of the “off-center” nature of the zinc centers in the silicon lattice.

V. CONCLUSION

Thus, it was shown that impurity zinc atoms in silicon are two-electron acceptor centers with negative correlation energy, and the local symmetry of the $\{Zn\}^0$ and {Zn} = centers is not cubic.

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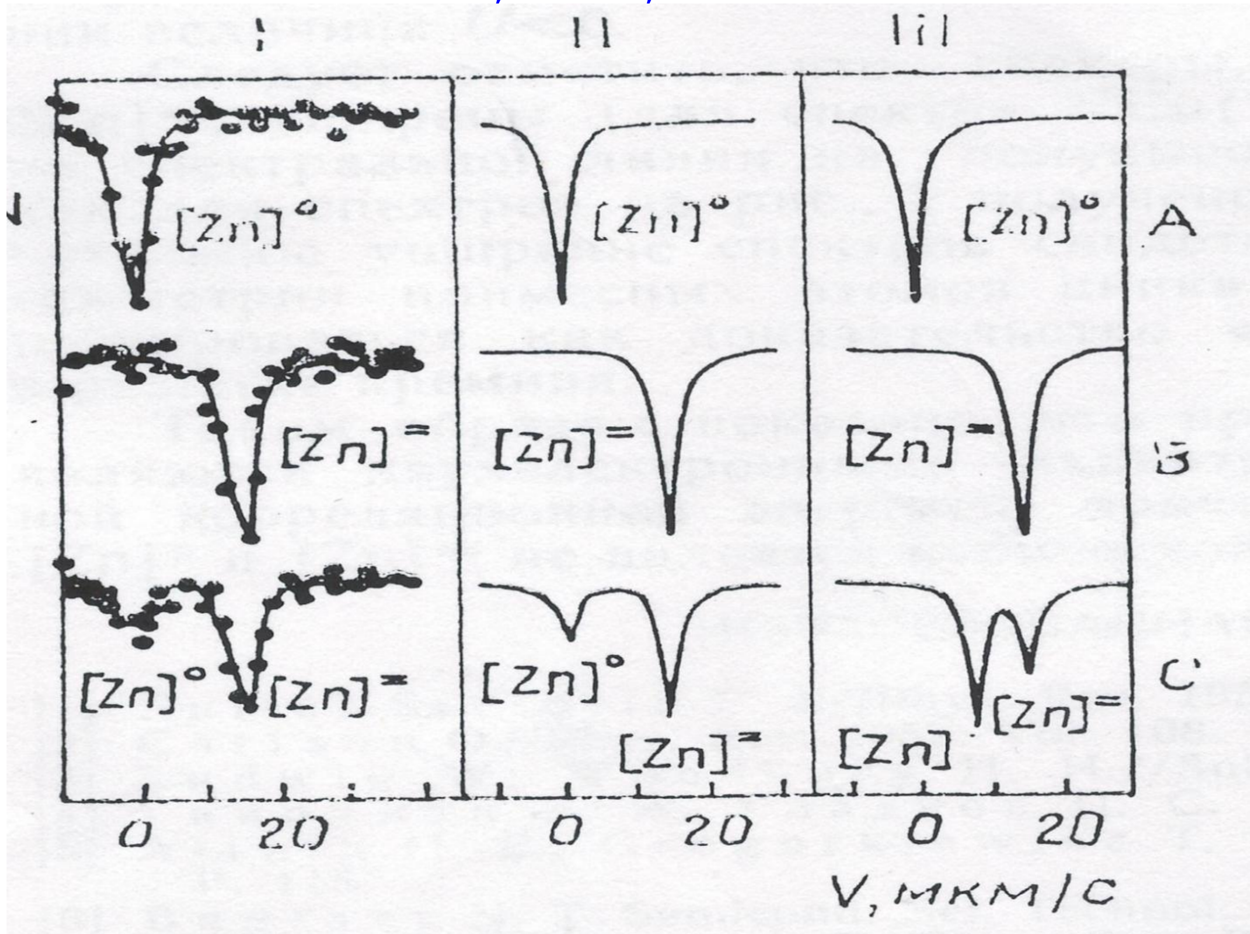

I. Emission Mossbauer spectra of ^{67} Ga (^{67}Zn) impurity atoms in silicon at 4.2 K for samples A (the spectrum corresponds to the [Zn]^{0} centers), B (the spectrum corresponds to the [Zn] = centers) and C (the spectrum corresponds to the presence) [Zn =] and [Zn]^{0}

II. The calculated Mossbauer spectra of ^{67}Zn for samples A, B, and C at U_1<0. The positions of the spectra of the centers [Zn]^{0} and [Zn =] are shown.

III. The calculated Mossbauer spectra of ^{67}Zn for samples A, B, and C at U > 0. The positions of the spectra of the centers [Zn]^{0}, [Zn] - and [Zn] = are shown. The speed scale of all spectra is given relative to the spectrum of sample A.

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