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MECHANISMS OF CURRENT TRANSITION IN HIGH COMPENSATED SILICON SAMPLES WITH ZINC NANOCLUSTERS[†]

Eshkuvat U. Arzikulov*, M. Radzhabova, Sh.J. Quvondiqov, G. Gulyamov
Samarkand State University named after Sharaf Rashidov
140104, University Boulevard 15, Samarkand, Republic of Uzbekistan
**Corresponding Author e-mail: eshkuvata@gmail.com*

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This article presents experimental results on the study of the current-voltage characteristics of strongly compensated n- and p-type silicon samples diffusion-doped with zinc at a temperature of 80 K. The current-voltage characteristics of the studied samples contain both sublinear and superlinear sections. Several (up to eight) characteristic areas were found, the number of which depends on the degree of illumination, temperature, and electrical resistivity of the sample. Under certain conditions, there is an alternation of sections of the current-voltage characteristic with negative differential conductivity of the N- and S-type, behind which current instabilities with an infra-low frequency are observed. The appearance of sections of the current-voltage characteristic with a quadratic dependence is explained by the presence of fast and slow recombination centers associated with zinc nanoclusters, and sublinear sections are explained in terms of the theory of the "injection depletion effect". The formation of nanoclusters with the participation of zinc ions was confirmed by atomic force microscopy studies.

Keywords: *Compensated silicon; Current-voltage characteristic; Current flow; Zinc; Nanocluster; Negative differential conductivity; Sublinearity; Superlinearity*
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1. INTRODUCTION

It is known that the shape of the current-voltage characteristic (CVC) of semiconductors containing deep levels (DL) can have three or more characteristic regions [1]. It has been experimentally established [2] that on many semiconductor materials, usually in the first section of the CVC, a linear dependence of the current on the applied voltage is observed, i.e., Ohm's law is satisfied. In the second section, there is a power-law relationship between current and voltage, i.e., dependence of type $I = U^n$, where n>1. In the third section of the $I(U)$ dependence, starting from certain voltage values, a sharp increase in current is observed. Further, with an increase in the electric field strength, a decrease in current is observed, i.e., there is a region with negative differential conductivity (NDC). Usually the NDC is N- or S-type. Combinations of S- and N-type NDCs are also possible [3]. Under certain conditions, they can replace each other, and it is also possible to transform the S-shaped I–V characteristic into an N-shaped one over time. The statistical characteristic can also have a more complex form. The observation of the CVC in the NDC region is associated with current instabilities, i.e., current or voltage fluctuations with different frequencies and shapes can be observed depending on the experimental conditions [4, 5].

This article presents the experimental results of the dependence of the current density j on the electric field strength E of strongly compensated silicon samples diffusion-doped with zinc with nanoclusters. A study of the surface morphology before and after the diffusion process of samples using AFM atomic force microscopy (Figure 1 and 2) showed that nano-sized periodic structures and pyramid-shaped objects are formed on the surface and near-surface region of diffusion-doped samples, which mainly consist of atoms zinc.

2. EXPERIMENTAL METHODS, RESULTS AND IT'S DISCUSSION

Studies of the I–V characteristics in n–Si<P, Zn> samples were carried out under various background illuminations of integrated light at a temperature of T=80 K measured [15]. The influence of the internal resistance of a constant voltage source on the form of the I–V characteristic has not been investigated by us. However, in all experiments, the operating point was located on a given section of the CVC.

The type of CVC of the studied samples strongly depends on the degree of illumination of the samples. At relatively low illumination (0.05÷0.01 Lx), the CVC of the samples consists of several clearly defined sections (Fig. 3, curve 1): the first section is when the applied electric field in the sample is less than 12.6 V/cm, a dependence of the form $I = U^{0.22}$ is observed, the second section - when E is in the range of values 12.6 $V/cm \leq E \leq 18.9\,V/cm$, a dependence of the form $I = U^{0.77}$ is observed, the third section - when E lies in in the range of 19 $V/cm \leq E \leq 62.9\,V/cm$, an almost quadratic dependence is observed, i.e. $I = U^{1.91}$, the fourth section - when E is in the range of values 62.9 $V/cm \leq E \leq 94.3\,V/cm$, again a dependence close to the second section is observed, i.e. dependence of the form $I = U^{0.71}$. A further increase in E in the range of 94.3 $V/cm \leq E \leq 471.1\,V/cm$ leads to a sharp increase in current. In this case, the dependence $I(U)$ has the following form: $I = U^{4.26}$. When the value of E lies in the range 471.1 $V/cm \leq E \leq 816.1\,V/cm$, a dependence

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of the form $I = U^{1.65}$ is observed. A further increase in E does not lead to noticeable changes in the current values, i.e., there is a weak sublinear dependence of the form $I = U^{0.52}$.

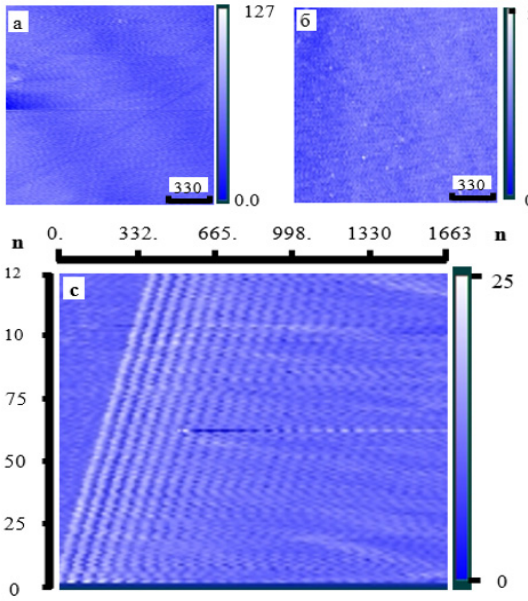


Figure 1. AFM images of the surface of a single-crystal silicon sample (a) - before diffusion zinc atom, (b) - after diffusion at T = 1145°C, (c) - after diffusion at T = 1150°C

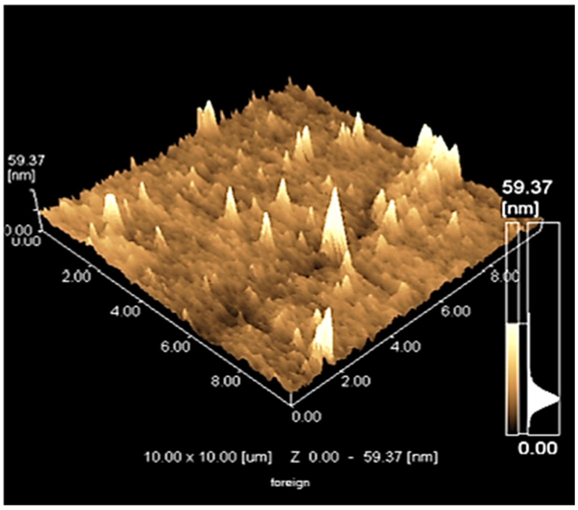
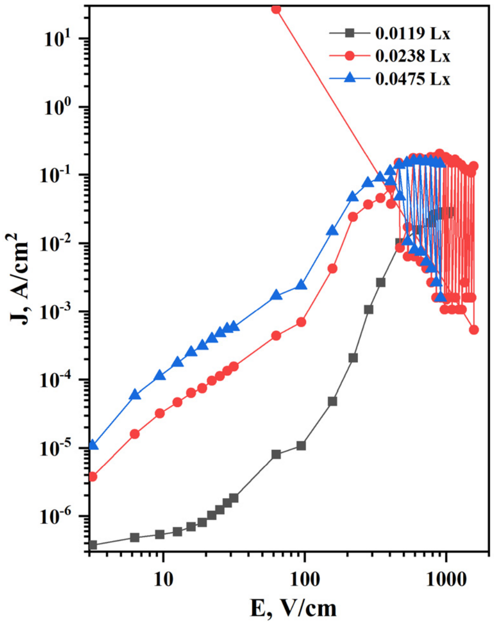


Figure 2. Surface morphology images of n-Si<P,Zn> samples obtained in an atomic microscope (AFM)

An increase in the illumination intensity of the integrated light leads to a noticeable change in both the nature of the $I(U)$ dependence and the region of existence of one or another dependence in electric field strength. So, for example, an increase in the intensity of integral illumination from 0.012 Lx to values of 0.048 Lx leads to a decrease in the number of characteristic sections from 8 to 6, in addition, sections with NDP of both N - and S - types are added to the $I(U)$dependence, alternating with instabilities current (current self-oscillations). At relatively high intensities of the integral light, one dependence of the form $I = U^{0.77}$ is observed in the I(U) dependence in the range $25.2\ V/cm \leq E \leq 42.1\, V/cm$ (Fig. 4).



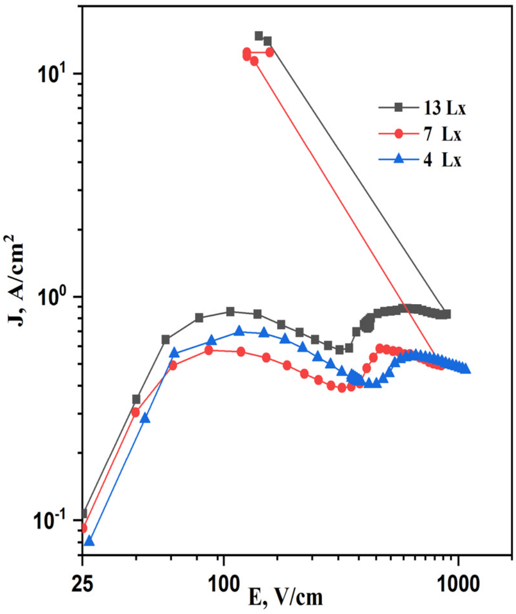


Figure 3. CVC of an n–Si<P, Zn> sample with $\rho = 6.91 \cdot 10^4\, \Omega \cdot cm$ under various background illuminations of integrated light. T=80 K

Figure 4. CVC of an n-Si<P, Zn> sample with $\rho = 7.64 \cdot 10^4\, \Omega \cdot cm$ at relatively high background integral illumination intensities. T=80 K

A further increase in E leads to a decrease in the current growth rate, which, passing through a maximum, begins to decrease, i.e., the NDC region is observed. A further increase in E leads to the second section with NDC. Two consecutive N-shaped sections are in the range of $42.1\ V/cm \leq E_1 \leq 319\, V/cm$ and $320\ V/cm \leq E_2 \leq 751\, V/cm$, respectively.

At the same time, in the first section with NDC, in a certain range of E values, infra-low-frequency current oscillations with deep modulation ~ 99.98 % are observed, which disappears when a certain value of E is reached. In the second section with NDC, also when a certain value of E is reached, quasi-harmonic current oscillations begin, which come from single-cycle spike-shaped to push-pull with modulation coefficients of ~99.98 %, 90.5 %, respectively, with an increase in E. A further increase in E leads to a sharp increase in current at a certain critical value of E, i.e., an S-shaped section of the CVC is observed.

A further increase in E after the end of the second N-shaped section leads to a sharp increase in current. At a certain critical value of E_C, an S-shaped section is observed in the I(U) dependence curve.

The results obtained can be interpreted as how zinc atoms in silicon, under strong compensation, form not only deep levels, but also quantum dots with large charge carrier capture cross sections.

On Figure 4 shows a typical I–V characteristic for one of the n–Si<P, Zn> samples with a specific resistance at room temperature of ~ $7.64 \cdot 10^4\, \Omega \cdot cm$. As can be seen from the figure, the I–V characteristics of the sample under study partially contain characteristic sections of the I–V characteristics corresponding to semiconductors with deep levels, i.e., it contains segments of linear, quadratic, and sharp dependences of the photocurrent density on the applied electric field. In addition, in the studied samples, there are two regions of the N-type NDC and one region of the S-type NDC.

The nonlinearity of the CVC is found not only in many semiconductor devices, in which the main working element is p-n - junctions, but also in many semiconductor materials in which there are no p-n - junctions at all [3]. In semiconductor materials, if we exclude the influence of contacts, it is most often due to the effects of strong fields. It is known that in strong electric fields the dependence of the mobility on the field strength is observed up to velocity saturation, NDP, impact ionization, and breakdown. However, in weak electric fields, the manifestation of the nonlinearity of the CVC is also possible [6].

Studies of the processes of current passage of silicon samples doped with zinc unambiguously showed that the transport of electrons at low electric field strengths (E) obeys Ohm's law, and not too small E is described by the space charge-limited current theory (SCCT) and the capture of electrons to levels located in the band gap of the sample [5].

As is known [4], the reasons for the nonlinear behavior of the CVC in semiconductors have not been unequivocally established. A possible reason for the nonlinearity of the current-voltage characteristics in silicon samples doped with zinc can be the mechanisms known as space charge-limited current and ionization of centers in strong electric fields [6,8]. According to [6] when a voltage is applied to a high-resistance sample, a current arises in the circuit due to the injection of charge carriers from a metal electrode, which is described by a power law in the form $I{\sim}E^2$. The nonlinear section of the CVC in high-resistance crystals containing shallow and deep traps was associated with the implementation of monopolar or double injection [8].

The presence in the Si<P, Zn> HC samples of r − (slow) and s − (fast) recombination centers associated with the centers of zinc atom ions, as well as the t attachment level, suggests that in fields where there is a quadratic dependence of the current strength on the strength electric field ($I{\sim}E^2$) in the I–V characteristics, the trap character of conductivity is realized. The data obtained in the quadratic region of the I–V characteristics show that in the samples of p- and n-type Si<P, Zn>, the transfer of charge carriers in electric fields ($E < 10^2 V/cm$) is mainly due to monopolar injection and is consistent with the Lampert theory [8].

The sublinear segments of the I–V characteristics of the studied samples of the p- and n-type Si<P, Zn> can be satisfactorily explained in terms of the theory of the "injection depletion effect" [8]. Theoretically, the appearance of such a current-voltage characteristic is possible only with opposite directions of ambipolar diffusion of nonequilibrium current carriers and their ambipolar drift, which in our case is mainly determined by injection modulation of the charge of deep levels [10]. Due to the difference in diffusion coefficients, electrons run far ahead, and holes move slowly, as a result of which they are separated in space and an electric field arises between them, which slows down their movement. Reducing their speed causes a decrease in current, i.e., a sublinear portion of the CVC is observed.

An analysis of the obtained experimental data in relatively high fields (at $E > 10^2 V/cm$) shows that the increase in conductivity with an increase in the electric field strength is associated with an increase in the concentration of excess current carriers. This allows us to assume that the presence of a section of a sharper increase in current in the I–V characteristic, where n > 3, can be explained by the fact that in samples of p - and n - type Si<B, Zn> at electric fields $E > 10^2 V/cm$, field devastation (or ionization) of traps.

The phenomenon of thermal quenching of photoconductivity [11] can lead to the appearance of a part of the I–V characteristic with the NDC of the illuminated sample. With an increase in the electric field strength and current density through the sample, the Joule power released in it increases. This also increases the temperature of the sample. An increase in temperature can lead to a sharp decrease in the photoelectron concentration due to the quenching of the phase transition and, due to the following condition (1), also to a change in the sign of the differential conductivity.

$$\sigma = en\mu\left(1 + \frac{dln\mu}{dlnE} + \frac{dlnn}{dlnE}\right) \tag{1}$$

where *e* - is where the value of the charge of the mobile carrier, *n*- and *μ*- are the concentration of charge carriers and their mobility, *E* - electric field strength.

Thus, the differential conductivity becomes negative if either the mobility of charge carriers or the concentration (or both) sharply enough depends on the field strength, decreasing with its increase. It is characteristic of which of these factors plays the main role, we can talk about drift $(\mu = \mu(E))$ or concentration $(n = n(E))$ nonlinearity.

Another mechanism that leads to a strong change in the concentration of charge carriers may be due to a sharp increase in the degree of ionization of shallow donors or acceptors during heating of free carriers. This increase can be associated both with an increase in the impact ionization rate during heating of charge carriers, and with the field dependence of the probability of their capture by like-charged traps. Indeed, the latter probability decreases with increasing carrier energy [3]. Both of these factors lead to the fact that when a certain critical value of the field strength E_c is reached (on the order of several V/cm in germanium and silicon at helium temperatures), a low-temperature breakdown of small impurities occurs. In fields on the order of $10^2 V/cm$, almost complete release of charge carriers from traps occurs, which leads to a sharp superlinearity of the CVC. In compensated samples, in this case, S - shaped sections are observed in the CVC. At present, however, there is still no complete clarity regarding the specific mechanism of the origin of the region corresponding to the NDC [3].

The mechanism of the occurrence of S-shaped I–V characteristics in heavily doped and simultaneously supercritical semiconductors was investigated in [6]. At low temperatures and at relatively high K (K ≥ 0.75, where K is the degree of compensation of the sample), the electrons are in potential wells formed around the NC and the electrical conductivity of such a material is very low. With an increase in E, the “heating” of the electronic subsystem begins and, as a result, the population of states with high electron or hole mobility increases sharply. This, in turn, leads to the appearance of an NDR. If K < 0.75, the CVC will not have an S-shaped form, since the activation energy arises only at high degrees of compensation [10,12]. It should also be added that in this case the critical electric field increases with increasing degree of compensation.

Based on the above, it is possible to explain the presence of N - and S - shaped sections of the CVC in samples of p - and n - type Si<P, Zn> at low temperatures and in the presence of integral illumination. An increase in temperature, of course, in the middle part of the crystal, as a result of Joule heating, causes the effect of thermal quenching of photoconductivity. If the intensity of this process is sufficiently high, then a region of a strong electric field arises near the sample. Then the I–V characteristic of such a sample has a section with NDC [8]. The presence of two sections with NDC can be explained by the presence of two BCs responsible for thermal quenching in the studied samples, the first of which manifests itself at relatively low electric field strengths, and the second at relatively high E.

On the other hand, in order to explain the obtained experimental data, it is also necessary to use the model of a semiconductor with quantum dots (QDs) [13,14]. The presence in the band gap of various traps for charge carriers associated with impurity atoms significantly affects the I–V characteristics of semiconductors. This is especially evident in high-resistance, i.e., compensated semiconductor materials. In this case, instead of the usual Ohm's law, an S- or N-shaped section with a negative resistance appears on the I–V characteristic [15].

Under certain conditions for the time of flight of electrons and holes through the base τ_n and τ_p (where τ_n and τ_p are the time of flight of electrons and holes, respectively), the CVC of the samples consists of several sections - linear (at low electric fields), quadratic, and as well as areas of a sharp increase in the current of an almost vertical nature at $U \approx U_{LFT}$ (where $U \approx U_{LFT}$ is the minimum voltage that leads to complete filling of traps in the material).

Samples of Si<P, Zn> with NCs with a maximum charge state, obtained by the method of high-temperature diffusion, have a sufficiently high electrical resistivity ($\rho \approx 10^3 \div 10^5\ \Omega \cdot cm$. These NCs act as deep traps for electrons and holes. Unlike conventional traps, where electrons are at a fixed energy level, electrons in NCs are not only bound, but can also be at different quantized energy levels with different density of states and capture cross sections. The distribution of electrons over levels depends on the degree of injection; in addition, the process of tunneling between nanocrystals is possible. Therefore, it can be expected that the I–V characteristics in such materials should have their own features, which was experimentally discovered by the samples of Si<P, Zn> studied by us with NCs.

In p-type samples with NC and with $\rho_1 \sim 1.5 \cdot 10^2$; $\rho_2 \sim 1.0 \cdot 10^3$; $\rho_3 \sim 1.0 \cdot 10^4\ \Omega \cdot cm$, uncompensated holes should remain (respectively $p_1=1.8\cdot10^{14}$; $p_2=1.25\cdot10^{13}$ and $p_3=8\cdot10^{12}$ cm-3), which should ensure the appropriate conductivity of the material in the area under study temperatures, taking into account the change in the mobility of holes with a change in temperature. However, at a temperature T=80 K, the resistivity of the samples increases from 3 to 6 orders of magnitude, which means that the hole concentration decreases by the same factor. This conduction behavior can be associated either with the capture of holes and electrons to energy levels lying below the Fermi level at T=300 K, or with the entry of holes into deep potential wells, limiting their participation in conduction. The absence of any energy levels associated with the zinc atom in the lower half of the bandgap in the range $E_V<E\leq E_V+0.3$ eV suggests that both options are not realized [17-19].

Therefore, we assume that holes in the valence band are accumulated between the nearest multiply positively charged NCs of zinc atoms. The depth of potential wells is determined, on the one hand, by the charge multiplicity and the concentration of clusters, and, on the other hand, by the concentration of holes in these wells.

Multicharged clusters act as powerful traps for holes with anomalously large capture cross sections. In the region of low electric fields, the dependence of the current is described as $I=U^n$, and the value of n, depending on the resistivity of the samples, varies in the range n~0.65–1.5, i.e., with a decrease in the resistivity of the samples, the I–V characteristic changes from a sublinear character to a superlinear (quadratic) character. A further increase in the electric field leads to a rather strong ‘change in the current, while the value of n increases with a decrease in the resistivity of the samples and changes in the range n = 2.2–3.2 i.e., current increases faster than quadratic. At higher electric fields, a sharp increase in current is observed, almost vertical, i.e., current increases by several orders of magnitude. This type of current-voltage characteristic allows us to assume that currents limited by the space charge (CLSC) with deep traps take place in the samples under study [20,21].

The values of U_{LFT}, measured in the experiments, increase significantly with the increase in the resistivity of the samples and amount to 15 V, 185 V, and 500 V, respectively. It should also be noted that with a decrease in the resistivity of the samples, the value of n in the vertical section of the CVC also decreases. Knowing the concentrations of charge carriers at a given temperature, we calculated the positions of the Fermi level in these samples at T=80 K, which are F_1=0.15 eV, F_2=0.199 eV and F_3=0.254 eV, respectively. Therefore, it can be assumed that traps with different concentrations and ionization energies operate in these samples, and they are higher than the Fermi level. If we take into account that the samples under study have p-type conductivity, then it should be assumed that the existing traps are located near the top of the valence band [22,23].

Therefore, it can be assumed that the traps responsible for the effect of limiting trap filling in the samples under study are associated with the energy levels of clusters of zinc atoms, and apparently create a whole spectrum of deep energy levels with ionization energies in the range $E=(E_V+0.31) \div (E_V+0.55$ eV) [6,16].

An analysis of these results shows that the active traps in the samples under study have different ionization energies and concentrations. If we take into account that the samples under study contain only NCs with different charge multiplicities, then it can be assumed that the detected energy levels correspond to their different charge states.

3. CONCLUSIONS

Based on the study of the surface morphology using AFM, as well as the photoelectric properties of the synthesized silicon samples diffusion-doped with zinc, the formation of nanosized multiply charged clusters was established, which significantly changes the structure of the energy states of the zinc atom in silicon. As a result, instead of the well-known, two acceptor energy levels corresponding to atomic zinc, a whole spectrum of deep donor energy levels of zinc nanoclusters appears, lying in the range $E=E_V+(0.16\div0.55)$ eV.

It has been established that the I–V characteristics of the studied samples contain sections characteristic of semiconductors, doped with impurities with deep levels.

For the first time, a CVC type containing two N-shaped sections and one S-shaped section in one sample was discovered.

ORCID

Eshkuvat U. Arzikulov, https://orcid.org/0000-0001-9179-3402

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МЕХАНІЗМИ ПЕРЕХІДНОГО СТРУМУ В ВИСОКОКОМПЕНСИРОВАНИХ ЗРАЗКАХ КРЕМНІЮ З НАНОКЛАСТЕРАМИ ЦИНКУ

Ешкуват У. Арзікулов, М. Раджабова, Ш.Й. Кувондиков, Г. Гулямов
Самаркандський державний університет імені Шарафа Рашидова,
140104, Університетський бульвар, 15, Самарканд, Республіка Узбекистан

У статті наведено експериментальні результати дослідження вольт-амперних характеристик сильнокомпенсованих зразків кремнію n- та p-типу, легованих цинком при температурі 80 К. Вольт-амперні характеристики досліджуваних зразків містять як сублінійні, так і надлінійні ділянки. Виявлено декілька (до восьми) характерних ділянок, кількість яких залежить від освітленості, температури та питомого електроопору зразка. За певних умов відбувається чергування ділянок вольт-амперної характеристики з негативною диференціальною провідністю N- і S-типу, за якими спостерігаються нестабільності струму з інфранизькою частотою. Поява ділянок вольт-амперної характеристики з квадратичною залежністю пояснюється наявністю швидких і повільних центрів рекомбінації, пов'язаних з нанокластерами цинку, а сублінійних ділянок пояснюється в рамках теорії «ефекту інжекційного виснаження». Утворення нанокластерів за участю іонів цинку підтверджено дослідженнями атомно-силової мікроскопії.

Ключові слова: *компенсований кремній; вольт-амперна характеристика; протікання струму; цинк; нанокластер; негативна диференціальна провідність; сублінійність; надлінійність*