ON LOW FREQUENCY C-U RELATIONSHIP OF THE IONIZED CLUSTER BEAM, ICB, DEPOSITED Ag/n-Si(111) SCHOTKY DIODES

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Abstract: The low frequency capacitance- voltage, C-U, relationship has been investigated on the basis of the postulated model of the semiconductor energy bands for samples of ionized cluster beam, ICB, deposited Ag/n-Si(111) Schottky diodes for nonzero Ag ions acceleration voltage. In the derivation the fundamental assumption made is the existence, within the Si energy gap, in addition to usual P shallow levels also Ag deep donor and acceptor impurity energy levels which, however, are assumed to be spatially confined to the narrow region at Ag/Si junction, only. The electrical activation of Ag, within this region homogeneous distributed, impurities is biased voltage dependent. The Ag impurity levels are extending up to the maximal penetration length L, which is a function of silver ions acceleration voltage U_a. It is argued, that it is only for small values of L and/or small Ag impurity concentrations, that the C-U relation is expected to exhibit the linear relationship, in accordance with the measurements.

The observed bias dependence of the semiconductor series resistance, at constant temperature, as well as the strong temperature dependency of the I-U measurements as reported previously are, in terms of the proposed model, explained on the phenomenological grounds.

It is argued, that the relationship between the disordered, enriched semiconductor (interface) layer, formed at the metal/semiconductor junction, presumably responsible for the occurrence of the disorder induced gap states (DIGS), and the Fermi level pinning effect, might be most conveniently investigated by carefully controlled and suitably designed ICB experiments in UHV conditions.

O nizkofrekvenčni C-U odvisnosti Ag/n-Si(111) Schottky-jevih diod, nanešenih po metodi curka ioniziranih skupkov, CIS

Ključne besede: Schottky spoj, Schottky diode, C-U karakteristike, , C-U karakteristike nizkofrekvenčne, diode kapacitivne, reže energijske, polprevodniki, ICB nanašanje s curkom skupkov ioniziranih, Ag/n-Si nanosi, napetosti pospeševalne, DIGS stanja energijska nereda v reži energijski, UHV vakuum ultravisoki

Povzetek: Na osnovi modela energijskih pasov v reži polprevodnika za primer po metodi curka ioniziranih skupkov nanešenih Ag/n-Si(111) Schottky-jevih diod za različne vrednosti pospeševalne napetosti Ag ionov, je v limiti nizkih frekvenc raziskana odvisnost kapacitivnosti diod od velikosti zunanje napetosti. Osnovna podmena, ki je bila privzeta v toku izpeljave C-U odvisnosti, zadeva predvideni obstoj omejenega prostorskega področja polprevodnika znotraj katerega se, poleg fosforja, še dodatno nahajajo električno aktivni in nevtralni srebrovi ioni enakomerne koncentracije. Srebrovi atomi se v polprevodniku vedejo kot ali donorji ali akceptorji, njihova električna aktivnost na pripadajočih energijskih nivojih, ki so uvrščeni globoko znotraj energijske reže, pa v splošnem zavisi od zunanje napetosti. Srebrove nečistoče v notranjosti polprevodnika segajo od stika kovina polprevodnik pa vse do največje globine L, ki zavisi od zunanje pospeševalne napetosti, U_a. Na osnovi izvedenih izračunov je pokazano, da je samo v limiti zanemarljivo majhne dolžine L in/ali majhne koncentracije srebra, v splošnem C-U odvisnost lahko linearna, v skladu z opazovanji.

Na osnovi postavljenega modela je v delu podana fenomenološka razlaga odvisnosti serijskega upora od zunanje napetosti, kot tudi temperaturna odvisnost električnega toka in napetosti, I-U, na omenjeni način izvedenih Schottky-jevih diod.

V članku je podan predlog, da je mogoče medsebojno razmerje med neurejeno, z srebrovimi nečistočami obogateno polprevodniško vmesno plastjo ob stiku kovina polprevodnik ter s tem povezanim pojavom nastanka novih elektronskih energijskih stanj (DIGS) v reži polprevodnika in vpetjem Fermijevega nivoja, prikladno proučevati prav z skrbno nadzorovanimi in ustreznimi, v ultra visokem vakuumu, izvedenimi eksperimenti rasti tankih heteroplasti po metodi curka ioniziranih skupkov.

1. Introduction

Formation of thin films of various electric, magnetic, and even organic substances on the suitably chosen substrata is among the other well established methods, also conveniently accomplished by Takagi /1,2/ ionised cluster beam, ICB, vacuum deposition method.

The essential idea of ICB deposition method is illustrated on fig. 1. The material to be deposited is contained in a closed crucible with a small nozzle on top. The vapours, while escaping through the nozzle, undergo adiabatic, supersonic expansion and during this process some of the atoms may reportedly /2/ aggregate in clusters of up to a few dozen atoms. Subsequent

to their formation, through the nozzle ejecting atoms and atomic clusters are the subject of electron impact ionisation and are, on their path towards the substrate, accelerated in the static electric field, U_a. It has been generally observed that ejecting atoms or clusters are singly positively ionised.
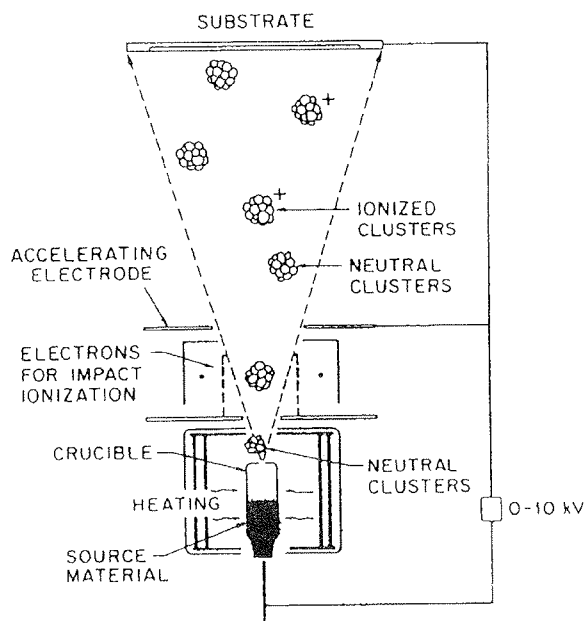

Fig. 1. Schematic drawing of an ion cluster beam, ICB, deposition experiment /1/.

It is rather a well documented fact /2/, that ICB low temperature thin film growth method produces a very good quality thin layers. The reason is attributed to the still unexplained effects which generally accompany this particular ion assisted method of film growth. In addition, there exist at least two additional important features contributing to the quality thin film growth, namely the fact that there are no extra atomic species involved which could contaminate or be incorporated in the growing process, as well as the observation, that the amount of damage on the substrate due to the impinging particles, depending on the experimental condition, might be very small indeed.

The potential barrier height, ϕ_b, of Ag/n-Si(111) Schottky diode when deposited by conventional UHV vacuum deposition methods as derived from I-V measurements /3/, is reported to be 0.78 eV. However, if deposited by ionised cluster beam, ICB, deposition method /1/, depending on the acceleration voltage, U_a, the apparent potential barrier height of the above structure, seemingly could be tailored to vanish. For our purpose it is to be noted, that by the proper choice of U_a, the silver ions possess enough kinetic energy to penetrate the Si substrate.

Since the accelerated Ag+ ions may, for large enough U_a, penetrate the Si wafer a few nm in depth, they might strongly contribute to an additional doping density /4/ within this region. In this respect an attempt /4/ has just

recently been made to analyze the experiment in terms of the theory of thermally assisted tunneling of electrons (thermionic field emission current). This theory /5/ expresses the I-U characteristics in term of a parameter E_{oo} (which is a function of semiconductor doping density) and in certain cases, as evidenced in the literature, could account for the lowering of the **effective** potential junction barrier as a function of increasing semiconductor (homogeneous) doping. From the reverse part of I-U characteristics of our ICB deposited samples the extracted values of the "effective" Schottky barrier height, ϕ_b, the ideality factor, n, (defined as $n = (q/kT)\partial V/\partial(\ln J)$), and the donor doping density, determined separately for each case of the Ag+ ions acceleration voltages, U_a, failed to correctly predict the measured I-U temperature variation of the ICB deposited Ag/Si structures /4/.

The drastic changes as seen in the reverse part of the I-U diagram of ICB deposited Ag/n-Si(111) Schottky junctions, for $U_a = 0$, 300 V and 1 kV, are presented on fig. 2. The details of the deposition and the analyses of the results are thoroughly discussed in ref. /4/. In general, the I-U electrical characteristics of such samples (for U_a nonzero) exhibit, within the small range of the *reverse applied voltage U*, almost linear I-U dependence before the saturation, fig. 2. The interval of almost linear I-U relationship is a monotonic function of U_a, the acceleration voltage of Ag$^+$ ions, however accompanied by the corresponding increase of the (reverse) saturation current, fig. 2. For large enough acceleration voltages (say for $U_a = 6$ kV) the diode rectifying characteristics disappear altogether as thought the effective Schottky barrier height has virtually diminished. The metal/semiconductor structure, in the reverse direction, than effec-
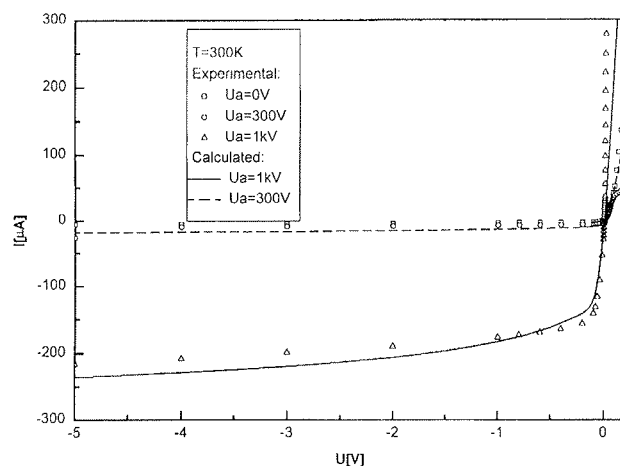

Fig. 2. An example of the room temperature measured reverse I-U characteristics of ionized cluster beam deposited Ag/n-Si(111) Schottky diodes for Ag$^+$ ions acceleration voltages $U_a = 0$, 300 V (these measurements on the drawing coincide) and 1kV, is presented /6/. The circles, squares and the triangles are the calculated values, derived for the case of thermionic-diffusion theory of the majority charge carriers transport taking the Schottky barrier height as a parameter, as described in ref. /6/.

tively behaves as a linear element, however in the forward direction the conditions, due to the experimental difficulties, are presently still not yet determined in details.

In the latter work /6/ it was shown that the distinct features of the reverse I-U temperature dependent measurements (i.e. the appearance of the "knee bend" as well as the large differences of the reverse saturation current densities) of these ICB deposited Schottky junctions could be sufficiently well described in terms of the thermionic-diffusion theory of the charge carrier transport. In the computation the existence of the distinct Ag+ donor additionally enriched region in n-Si sample extending from the Ag/Si junction up to the Ag+ ions maximum penetration length, L, (which is a function of U_a) has been assumed. The doping effect of oxygen, carbon, sulfur and other surface impurities, which are for U_a nonzero also present within Si wafer, have been neglected. The results obtained seem to imply the fact,

that by the ICB deposition method it might be possible directly to modulate the Schottky barrier height.

The measured low frequency capacitance-voltage, C - U, relationship exhibit similar peculiarities, fig. 3. in the sense that for low values of silver ions acceleration voltages the diagram C^{-2} versus applied voltage U (fig. 3) exhibit well defined linear relationship as predicted by the theory /3/, however, say, for acceleration voltages $U_a > 2$ kV, it may soon become nonlinear.

It is a well established fact /7/, that the Si wafer, following the surface preparation, is under normal laboratory atmospheric conditions almost immediately covered by extremely stable (for the period up to one year) dielectric thin film consisting of about 0.7 nm thick native oxide layer on top of which about 0.2 nm thick organic contamination layer is in general also present. Obviously, the extent of the Ag^+ enriched n-Si regions is most conveniently expressed in terms of the penetration lengths, L, which is accessible to Ag^+ ions (at a given value of U_a) within the n-Si wafer. This distances have been correspondingly calculated (including the 1.2 nm thick oxide layer on the Si surface) and have been found to be L=2.4 nm for U_a=300 V, and L=4.0 nm for U_a=1 kV /8/. As it is well known /3/ the impurity silver atoms incorporated within the Si substrate can act either as donors (E_d (Ag) in Si = 0.370 eV above E_V) or as

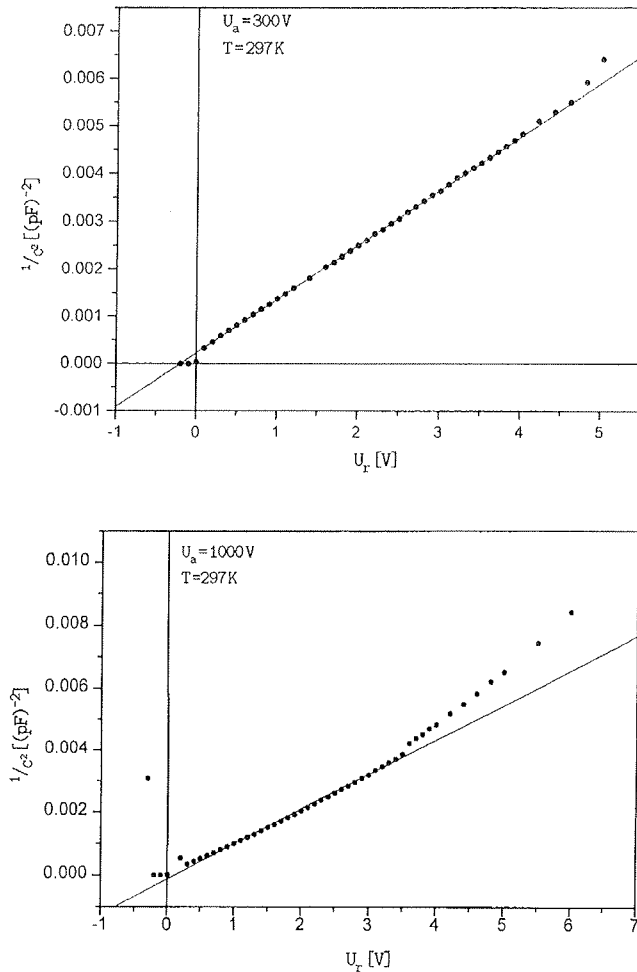

Fig. 3. Two examples of low frequency, ν =2 kHz (the amplitude of the ac measuring signal was set to 10 mV), room temperature measurements of the C-U relationship of ionized cluster beam deposited Ag/n-Si(111) Schottky diodes for Ag^+ ions acceleration voltages of U_a=300 V and 1 kV, are exhibited /13/. The lines are guides to the eyes only.
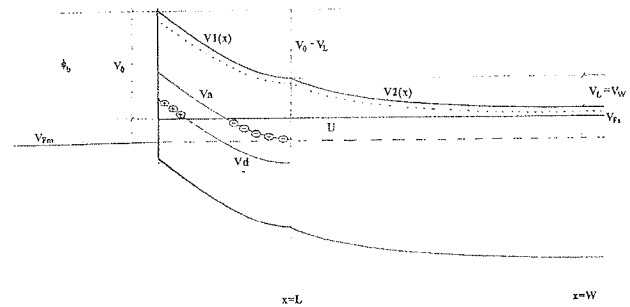

Fig. 4. Schematic drawing (not to scale) of forward biased ionized cluster beam deposited Ag/n-Si(111) metal/semiconductor junction. The region within the semiconductor, up to the abrupt plane at depth L, contains additional (besides electrically activated shallow phosphorous dopant level denoted as dots) deep lying Ag donor and acceptor impurities, which are assumed to be homogeneously distributed. L denotes the maximum penetration range, of silver ions for the given value of the external acceleration voltage, Ua. Within the region 0<x<L the two deep Ag impurities levels explicitly exhibit the activated donor and acceptor ions. Note that the density of electrically activated Ag impurities is (within the certain voltage range) a function of the external DC bias U. The distance L, being a function of the Ag ions acceleration voltage Ua, is usually of the order of a few nm, while the edge of the depletion region, W, is at least an order of magnitude larger.

acceptors (E_a (Ag) in Si = 0.717 eV above E_V). Consequently, these impurity deep-levels lie within the Si energy gap and the expected resulting energy band diagram is schematically depicted on fig. 4.

The present work is an extension of earlier results /10,11/ on the general capacitance voltage, C-U, relationship as applied to the case (of the spatially homogeneous concentration) of the deep-lying impurity atoms in Si wafer confined within the metal/semiconductor junction region. The region in question is of the characteristic length, L, which is expected to be of the order or even smaller than the usual Debye length, L_D, defined as $L_D = \sqrt{\varepsilon_s kT/q^2 N_D}$. Here, N_D is an effective dopant density, k denotes the Boltzman constant, q electronic charge, T the absolute temperature and $\varepsilon_s = \varepsilon\varepsilon_0$. For $N_D = 10^{16}$ cm^{-3} at T = 300 K, the Debye length in Si is about 40 nm and is approximately 3 nm for $N_D = 10^{18}$ cm^{-3} at the same temperature. In this connection one remembers that at thermal equilibrium (and zero applied voltage) depletion layer width, W, is for Si, of the order of $8L_D$. Consequently, depending upon the impurity concen-trations, one expects L to be at most comparable to L_D but it might be smaller. Nevertheless, the excess space charge variation, which is strongly dependent upon the value of an applied external bias U, might be responsible for the unusual features in electrical characteristics of IBC deposited Ag/n-Si Schottky junctions. In this work the effect of the space limited, deep-energy Ag impurity levels confined in the vicinity of metal/semiconductor junction, on low frequency C-U relationship is investigated on a qualitative basis.

It will be shown that these effects might be, under specific conditions, marked.

The notion of the so called disorder induced (semiconductor) gap state spectrum, DIGS, has recently appeared in the literature /9/. It is characterised by the energy E_0, interpreted as Fermi energy of DIGS spectrum at the energy point where the charge neutrality occurs. The DIGS density spectrum consists of bonding (donor-like) and antibonding (acceptor-like) states and E_0 represents the Fermi level location of the DIGS spectrum at the plane within the gap where the charge neutrality is achieved. According to this model, deposition of insulator or metal on semiconductor produces a thin disordered semiconductor layer. This layer is characterised by fluctuations of bond lengths and angles due to stress and due to the interface irregularity and consequently Anderson localisation leads to DIGS continuum in the energy gap whose density depends on degree of the disorder. The unified DIGS model is able to explain the behaviour of the metal/semiconductor interface when formed on the bare or oxide covered metals as well as the various features of the interface state density distribution. According to DIGS model, for cases when the interfacial degree of disorder is high, the Fermi level is firmly pinned at values very close to E_0, effectively resulting in the so called Bardeen limit, according to which the barrier height does not depend on the metal work function. An important feature of the

DIGS model over MIGS model is the fact that the former is able to offer an explanation of the Fermi level pinning on the oxide covered Schottky barriers while the later can not. Since the crucial feature of the DIGS model is the assumption of the presence of a disorder at the interface, a fact which is difficult to characterise experimentally, it is quite evident that by an ICB deposition method one posses-ses the means of an experimentally controlled induce-ment of such type of disorder at the metal/semicon- ductor interface.

DIGS are usually studied by the measurements of the interface state density distributions as for instance provided by the careful interpretation of the frequency dependent C-V measurements in conjunction with the photocapacitance transient spectroscopy.

The ICB deposited samples, among other features, might be of a great potential value for investigation of certain aspects of DIGS model. It is the purpose of this paper to present the basic fundamentals of (low frequency) C-U relationship of such samples which are characterized, as explained earlier, by the coexistence of two adjacent distinct semiconductor doping regions of substantially different spatial extensions.

2. Theoretical outline

As described in the introduction the ICB deposited Ag/n-Si(111) Schottky diodes are characterized, for the ions acceleration voltage $U_a \neq 0$, by the fact that Ag$^+$ ionized clusters as well as ions, depending on the initial kinetic energy imparted to them by the voltage Ua, can penetrate the silicon substrate up to the maximum depth denoted by the distance L. In what follows we assume that the maximum penetration range, L, is attainable to the single ionized Ag$^+$ silver ions, while in general the penetration range of the individual clusters, depending on the number of atoms forming the cluster, is correspondingly shorter. In what follows, for the ease of the computation, we assume that the individual silver ions are uniformly distributed within the penetration range from the Si surface up to the largest range L. As well known /3/ the electrically activated impurity silver atoms incorporated within the Si substrate can act either as donors (E_d (Ag) in Si = 0.370 eV above E_V) or as acceptors (E_a (Ag) in Si= 0.717 eV above E_V). The impurity levels lie within the Si energy gap and the expected energy band diagram is schematically depicted on fig. 4.

Our purpose is to derive an expression for the differential capacitance per unit area, $C = dQ/(SdV_d)$, as a function of the external voltage, U, applied between the metal and the semiconductor, where dQ/dV_d represents the charge increment per infinitesimal change of the diffusion potential and S is the cross section of the Schottky diode (interface) /12/.

For this purpose one starts the derivations by the usual approach using the expressions, $div\mathbf{D} = \rho$, where $\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon_s\mathbf{E}$ and $\varepsilon_s = \varepsilon\varepsilon_0$, but since $\mathbf{E} = -grad\ V$,

(obviously a quasi-static field approximation is adhered to) where V is the electrical (scalar) potential, the Poisson equation in one dimension reads,

$$\frac{d^2V}{dx^2} = -\frac{\rho}{\varepsilon_s} \qquad (1)$$

where $\rho = \rho(x)$ denotes the excess charge density within the semiconductor. The charge density distribution for the described model Schottky diode as a function of x is schematically depicted on Fig. 4. Since in general the electrical potential, V, is a single value function of the coordinate x, from which it follows that the inverse function, $x=x(V)$, also exists, the above expression may be written in a modified form. Namely, observing the following identity,

$$\frac{d}{dx}\left(\frac{dV}{dx}\right)^2 = 2\left(\frac{dV}{dx}\right)\frac{d^2V}{dx^2} \qquad (2)$$

it consequently follows that,

$$\frac{d^2V}{dx^2} = \frac{1}{2}\frac{d}{dV}\left(\frac{dV}{dx}\right)^2 \qquad (3)$$

and after the multiplication by the factor (-1) from which evidently follows that ρ is an even function of the scalar potential V, the following expression is to be solved,

$$d\left[\left(\frac{dV}{dx}\right)^2\right] = \frac{2}{\varepsilon_s}\rho(V)dV. \qquad (4)$$

According to the described model of an ICB deposited Schottky diode, Fig. 4, the excess charge density discontinuously changes at the maximum Ag ions penetration length $x = L$ within the Si substrate. Consequently, the integration of the above expression is to be performed separately within each region such that $\rho = \rho_1(x) \to \rho_1(V)$ for $0 \le x \le L$ and $\rho = \rho_2(x) \to \rho_2(V)$ for $L \le x \le W$, where W is the width of the free carriers depletion range within the semiconductor. As usual we adhere to the approximation that $\rho = 0$ for $W \le x \le \infty$. Integration the expression, eq. (4), within the Ag enriched region of the Si semiconductor gives,

$$\left(\frac{dV}{dx}\right)^2_{x=L} - \left(\frac{dV}{dx}\right)^2_{x=0} = \frac{2}{\varepsilon_s}\int_{V_0}^{V_L}\rho_1(V)dV \qquad (5)$$

from which it follows,

$$\left(\frac{dV}{dx}\right)_{x=0} = -\sqrt{\left(\frac{dV}{dx}\right)^2_{x=L} - \frac{2}{\varepsilon_s}\int_{V_0}^{V_L}\rho_1(V)dV} \qquad (6)$$

and the minus sign is taken on account of potential V decrease with an increasing depth x. At this point it has to be mentioned that at x=L, due to the discontinuity of the excess charge density the electric potential V, while itself continuous, possesses the discontinuous derivatives.

Similarly, the integration of the eq. (4) within the range $L \le x \le W$, results in

$$\left(\frac{dV}{dx}\right)_{x=L} = -\sqrt{\frac{2}{\varepsilon_s}\int_{V_L}^{V_w}\rho_1(V)dV} \qquad (7)$$

since due to potential being flat at the end of the depletion region $(dV/dx)_{x=W} = 0$ and once again the minus sign is taken on account of potential V decrease with an increasing distance x.

From the fig. 4. it is evident that the redistribution of space-charge due to the deep impurities present is expected to occur within the region $0 \le x \le L$ for small applied forward and reverse voltages. Specifically, for large forward U, all deep lying Ag^+ donors will be electrically neutral and the Ag^- acceptor states will be completely populated resulting in an effective decrease of the net positive space charge within this region. And conversely, for larger reverse applied voltages U the acceptor states are empty and the excess positive space charge $\rho_1(x)$ within the same region exceeds that of the normal conditions as provided by the phosphorous doping in n-Si substrate. Obviously, for each value of the silver ions concentrations N_{Ag} within this enriched region there exists an interval of the applied external voltage to which monotonically corresponds the space charge density variations $\rho_1(x)$ for $0 \le x \le L$. For this reason the electron potential energy qV(x), for concentrations of electrically activated silver atoms N_{ag} large enough, may considerably vary for different values of the applied voltage and it is just this variation which presumably might be responsible for the observed C-V behavior of ICB deposited Schottky diodes. In order to compare the experimental I-V characteristics to the predicted ones based upon the model depicted in fig. 4., the detailed numerical evaluation of the electron potential V(x), for $0 \le x \le W$, at each value of the applied external voltage U is required. This, however, is a subject of a future publication /13/. The general characteristics of the differential capaci-tance per unit area, C, of the model diode defined as,

$$C = \frac{\partial Q_d}{\partial V_d} \qquad (8)$$

can be for the above case discussed in the sufficient particulars without adhering to such the detailed numerical procedures. In the eq. (8), the term ∂Q_d represents the infinitesimal change in the total charge per unit area due to all uncompensated electrically active impurities in the depletion region, which is occurring due to the ∂V_d, the infinitesimal change in the so called diffusion potential V_d. The diffusion potential, as well known,

is for an ordinary Schottky diode defined as the difference between the potential at the junction metal/semiconductor interface (i.e. x=0) and the potential evaluated at the edge of the depletion region, x=W, thus $V_d = V(x=0) - V(x=W)$.

In what follows we adhere to the approximation (termed the low frequency approximation) according to which occupations of donor or acceptor energy levels instantaneously respond to the capacitance measuring test small signal (alternating) voltage which is superimposed on an externally applied direct voltage bias.

Viewing fig. 4., the low frequency depletion-layer capacitance C per unit area can be evaluated as a resultant capacitance of two capacitors, C_1, and C_2, connected in series. In order to see this one introduces at x=L two connected, infinitely closely spaced, conducting plates. On account of induced charges appearing on each plate, the charges are equal in magnitude but of opposite signs. Consequently, one may immediately generalize,

$$C_i = \frac{\partial Q_i}{\partial V_{di}} \qquad i = 1,2 \qquad (9)$$

where,

$$V_{d1} = V(x = 0) - V(x = L) \qquad (10)$$

and similarly

$$V_{d2} = V(x = L) - V(x = W), \qquad (11)$$

respectively. From here onwards the following abbreviations; $V(x=0) = V_o$ and $V(x=L) = V_L$ will be adhered to.

The internal electric field in the semiconductor is oriented in the negative direction of x-axis from the edge of the depletion region (where V(x=W)=constant and consequently E=0) towards the metal/semiconductor interface junction. Applying the Gauss's law, $\oint D dS = \rho$, first on the surface of the cylinder placed between x=0 and x=L, and secondly on the surface of the one placed at x=L and x=W one obtains,

$$E_o - E_L = \frac{Q_1}{\varepsilon_s} \qquad (12)$$

where Q1 denotes the excess charge density per unit (junction) area within the first, i.e. Ag enriched, region. Similarly, one obtains

$$E_L = \frac{Q_2}{\varepsilon_s} \qquad (13)$$

yielding the two expressions to be evaluated as,

$$\left(\frac{dV}{dx}\right)_{x=L} - \left(\frac{dV}{dx}\right)_{x=0} = \frac{Q_1}{\varepsilon_s} \qquad (14)$$

$$\left(\frac{dV}{dx}\right)_{x=L} = \frac{Q_2}{\varepsilon_s}. \qquad (15)$$

The excess charge densities for the two regions remains to be defined. In the lowest approximation one writes, noting that the excess charge density per unit area of eq. (12), Q_1, is directly related to ρ_1 of the eq. (7) simply as $Q_1 = \rho_1/S$, and similarly for Q_2, where the net excess charge density in the region (1) is brought about by the electrically activated phosphorous shallow donors (of density N_P^+) in conjunction with the deep lying Ag (donor as well acceptor) impurity atoms of densities N_{Ag}^+ and N_{Ag}^-,

$$\rho_1 = q(N_p^+ + N_{Ag}^+ - N_{Ag}^-) \qquad (16)$$

$$\rho_2 = q(N_p^+ - N_e^-(x=L)). \qquad (17)$$

Here, $N_e^-(x=L)$ denotes the density of the displaced free carriers (i.e. electrons) at the edge of the enriched region, x=L /4/, but the rough estimate shows that this contribution can be, if one is not being interested in the C-V frequency dependence, in the first approximation, neglected. Generally speaking, this contribution also varies (on account of the electrical activation or deactivation of deep lying silver donors and acceptors) with the change of the applied external bias DC voltage. For the exact calculations, the shape of the conduction band in the vicinity around x=L has to be calculated in details. The probability, w(E), for donor or acceptor to be electrically activated is given by /3/,

$$w(E_d) = \frac{N_d^+}{N_d} = \frac{1}{1 + g_d e^{-(E_d - E_F)}} \qquad (18)$$

where, E_d is the donor energy level (as defined with respect to the conduction, E_C, or alternatively valence energy band, E_V, respectively), E_F the Fermi energy in the semiconductor and g_d is the ground state degeneracy of the donor impurity level, equal to $g_d=2$. Obviously the factor $(1-w(E_d))$ is the probability, that the donor is not electrically activated. Similarly, the probability that the acceptor level is electrically active is provided by the expression,

$$w(E_a) = \frac{N_a^-}{N_a} = \frac{1}{1 + g_a e^{-(E_a - E_F)}} \qquad (19)$$

where g_a, the ground state degeneracy factor is equal to $g_a=4$, for acceptor levels of energy E_a.

As schematically indicated on fig. 4, due to the metal/semiconductor junction potential barrier the elec-

tronic potential $V(x)$, or equivalently the conduction band E_C, exhibits relatively strong curvature in the interval $0 \leq x \leq L$, consequently the energy difference of both activated impurities levels is a function of the potential $V(x)$, i.e. the position along the x-axis of the activated impurity within (the silver enriched part of) the semiconductor. Written in terms of the potential $V(x)$, this difference reads,

$$E_d - E_F = q(V_1(x) - V_m) - q\,U - z_d \qquad (20)$$

and similarly,

$$E_a - E_F = q(V_1(x) - V_m) - q\,U - z_a \,, \qquad (21)$$

where, $z_d = 0.75$ eV, and $z_a = 0.40$ eV, for Ag impurity levels within the Si bandgap, and the potential $V(x)$ is now referred with respect to the metal Fermi level characterized by the potential, V_m, and U denotes the externally applied DC bias voltage, see fig. 4. The corresponding transformation for the shallow phosphorous donor level, valid throughout the region $0 \leq x \leq W$ (since, the P donor level never crosses the semiconductor quasifermi level) reads,

$$(E_d - E_F)_p = q(V_i(x) - V_m) - q\,U - z_0, \quad i=1,2 \qquad (22)$$

where $z_0 = 0.05$ eV.

Using the eqs. (6) and (7), the net charge density Q_1 in the region x being between 0 and L as obtained from eq. (14) reads,

$$Q_1 = \sqrt{2\varepsilon_s}\left[\sqrt{\int_{V_W}^{V_L}\rho_2(V)dV + \int_{V_L}^{V_0}\rho_1(V)dV} - \sqrt{\int_{V_W}^{V_L}\rho_2(V)dV}\right]$$

$$(23)$$

and similarly for Q_2, one obtains,

$$Q_2 = \sqrt{2\varepsilon_s\int_{V_L}^{V_W}\rho_2(V)dV}. \qquad (24)$$

These expressions are to be evaluated using the eqs. (16) to (22). After the appropriate transformation of the integral limits, noting the relevant integrals can be easily evaluated, the results are given by,

$$I_1(V_{d1}) = \int_{V_L}^{V_0}\rho_1(v)dV = \int_{V_0}^{V_{d1}}\rho_1(s+V_L)ds =$$

$$= q\left\{N_{d,Ag}\left[V_{d1} - \frac{1}{\beta q}\ln\frac{1+b_1 e^{\beta q V_{d1}}}{1+b_1}\right] + \right.$$

$$N_{d,P}\left[V_{d1} - \frac{1}{\beta q}\ln\frac{1+b_2 e^{\beta q V_{d1}}}{1+b_2}\right] - \qquad (25)$$

$$\left. N_{a,Ag}\left[V_{d1} - \frac{1}{\beta q}\ln\frac{1+b_3 e^{\beta q V_{d1}}}{1+b_3}\right]\right\}$$

where the symbols b_i, $(i=1,3)$ stand for the following functions,

$$b_1 = g_{d,Ag}\, e^{\beta q(U-\phi_b)}\, e^{\beta z_d} \qquad (26)$$

$$b_2 = g_{d,P}\, e^{\beta q(U-\phi_b)}\, e^{\beta z_0} \qquad (27)$$

$$b_3 = g_{a,Ag}\, e^{-\beta q(U-\phi_b)}\, e^{-\beta z_a}. \qquad (28)$$

In the transformations above, the following relation has been used, $V_{d1} = V_0 - V_L = \phi_b - U - V_L$, fig. 4, where ϕ_b, is the Schottky barrier height.
Likewise, the evaluation of the second integral yields,

$$I_2(V_{d2}) = \int_{V_W}^{V_L}\rho_2(V)dV = \int_0^{V_{d2}}\rho_2(s+V_W)ds =$$

$$= qN_{d,P}\left[V_{d2} + \frac{1}{\beta q}\ln\frac{1+b_4 e^{-\beta q V_{d2}}}{1+b_4}\right] \qquad (29)$$

and b_4 is given by,

$$b_4 = g_{d,P}\, e^{-\beta q\xi}\, e^{-\beta z_0} \qquad (30)$$

In the derivation the relation, $V_{d2} = V_L - V_W = V_L - (U+\xi)$, where $\xi = (kT/q)\ln(N_C/N_d)$, and N_C is the effective density of states in the conduction band has been employed.

Finally, performing the indicated operations as suggested by the eq. (9), noting that $Q_1 = Q_1(V_{d1}, V_{d2}, V_d)$, where the diffusion potentials are defined by the eqs. (10), (11), consequently

$$\frac{\partial Q_1}{\partial V_{d1}} = -\frac{\partial Q_1}{\partial V_L} + \frac{\partial Q_1}{\partial V_{d2}} = \frac{\partial Q_1}{\partial V_0} - \frac{\partial Q_1}{\partial V_d} = \text{etc.},$$

the following capacitance's per unit area are derived:

$$C_1 = q\sqrt{\frac{\varepsilon_s}{2}}\frac{\dfrac{N_{d,Ag}}{1+b_1 e^{\beta q V_{d1}}} + \dfrac{N_{d,P}}{1+b_2 e^{\beta q V_{d1}}} - \dfrac{N_{a,Ag}}{1+b_3 e^{-\beta q V_{d1}}}}{\sqrt{I_1(V_{d1}) + I_2(V_{d2})}}$$

$$(31)$$

and similarly,

$$C_2 = q\sqrt{\frac{\varepsilon_s}{2}}\frac{\dfrac{N_{d,P}}{1+b_4 e^{-\beta q V_{d2}}}}{\sqrt{I_2(V_{d2})}}. \qquad (32)$$

The resultant low frequency capacitance, C, of the ICB deposited Ag/n-Si(111) Schottky diode is than obtained as,

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} . \qquad (33)$$

The expressions as given by eqs. (31) and (32) are the central result of the present calculations. One notes that they have been derived without an explicit solution of the Poisson equation, eq. (1). For the interpretation of the I-V measurements, this equation has to be, however, solved explicitly.

3. Results and discussion

On account of complicated expressions as provided by eqs. (31) and (32), it is not self evident in general, that the C^{-2} versus externally applied DC voltage U should yield the straight line. Since the electron potential at x=L, i.e. V_L, is itself an implicit function of the applied bias voltage U, the linear relation obviously is expected to be an exception rather than a rule. However, the above derived results can be simply checked in the limit of very low concentrations of silver impurities in Si substrate as compared to phosphorous concentration doping, i.e. $N_P >> N_{a,Ag}$ and $N_{d,Ag}$. In the lowest approximation (neglecting the Ag impurities in Si substrate), $\rho_1(V) = \rho_2(V) = \rho(V)$, and one therefore obtains from the eq. (23),

$$Q_1 = \sqrt{2\varepsilon_s}\left[\sqrt{\int_{V_W}^{V_0} \rho(V)dV} - \sqrt{\int_{V_W}^{V_L} \rho(V)dV}\right] \qquad (34)$$

and likewise,

$$Q_2 = \sqrt{2\varepsilon_s \int_{V_L}^{V_W} \rho(V)dV}. \qquad (35)$$

In this limit the depletion capacitance of a Schottky diode if evaluated at L = 0, i.e. when $V_L = V_0$, yields $Q_1 \equiv 0$, consequently $C_1 = 0$, and the resulting capacitance is given by,

$$C \equiv C_2 = \sqrt{\frac{q\varepsilon_s N_{d,P}}{2V_d}} \qquad (36)$$

where $V_d = V_0 - V_W$. This is, however, the exact result /3/ for the depletion capacitance of on ordinary Schottky diode, as expected. Setting now the opposite limit, i.e. L=W, hence $V_L = V_W$, only the first term in eq. (34) survives, Q_2, and consequently $C_2 = 0$, and the resulting capacitance C is once again written in terms of the right side of the expression (36), as it should in the presence of only one homogeneously distributed shallow donor in a semiconductor.

On account of the discussion just presented above it is now possible to offer rather an obvious explanation of the experimental observation concerning the low frequency C-U measurements of Schottky diodes deposited for small values of the ionized silver atoms acceleration voltage U_a < 0.6 keV, (say), by the ionized cluster beam, IBC, deposition method. Apparently, as follows from the stopping power calculations, for these small acceleration voltages the penetration range of Ag ions in Si is small, $L \approx 0$, $V_L \approx V_0$, and consequently

$C_1 \approx 0$. The resulting capacitance, C, is then given by the eq. (36) and since,

$$V_d = V_0 - V_W = \Phi_b - U - \xi \qquad (37)$$

where $q\Phi_b = 0.78$ eV, is the Schottky potential barrier height /3/ and $q\xi$ is the energy difference between the semiconductor quasi fermi level and the conduction band, E_C, at the position $x \geq W$, the edge of the depletion region ($q\xi = kT \ln(N_C/N_d)$ and N_C is the effective density of states in the conduction band). Consequently, combining eqs. (36) and (37) the usual linear C^{-2} versus U relationship is obtained, in accordance with the C-U measurements for $U_a = 0$ and 300 V samples, as indicated on fig. 3., respectively. Some relevant examples of the low frequency C-U relationships, calculated for the various values of the deep level impurity concentrations, taking the potential, V_L, as an independent parameter, are explicitly exhibited on figs. 5-7.
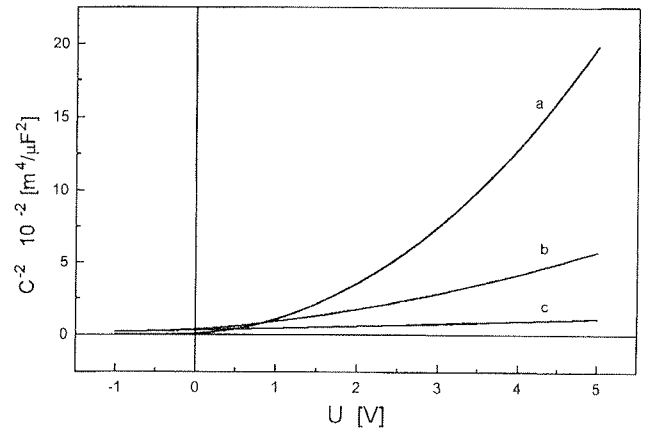

Fig. 5.   The calculated values of the resulting capacitance, $1/C^2$, based on the eq. (33) of the text, versus the external applied DC bias, U, is presented for various values of the parameters. The lines shown are calculated for the following values of parameters expressed in terms of the constant $N_0 = 10^{16}$ cm^{-3}:
line a) $V_L = 0.45$ V, $N_{d,Ag} = 10$ N_0, $N_{d,P} = 1$ N_0, $N_{a,Ag} = 40$ N_0;
line b) $V_L = 0.65$ V, $N_{d,Ag} = 10$ N_0, $N_{d,P} = 1$ N_0, $N_{a,Ag} = 40$ N_0;
line c) $V_L = 0.65$ V, $N_{d,Ag} = 0$, $N_{d,P} = 1$ N_0, $N_{a,Ag} = 0$.
The latter curve represents the usual case of the homogeneously doped metal/Si semiconductor junction.

For the discussion of C-U relationship at large values of Ag ions acceleration voltages, one has to adhere to the full numerical analysis, originating from the exact solution of the Poisson equation /13/.

Nevertheless, the simplified model, as depicted on fig. 4., of ICB deposited Ag/Si diodes might possibly provide a direction towards understanding of the findings presented in ref. /6/, where an unusual feature was reported. Namely, applying the usual I-V evaluation procedure /14/ on the raw experimental data, it was found, quite contrary to the expectations, that the ideal-
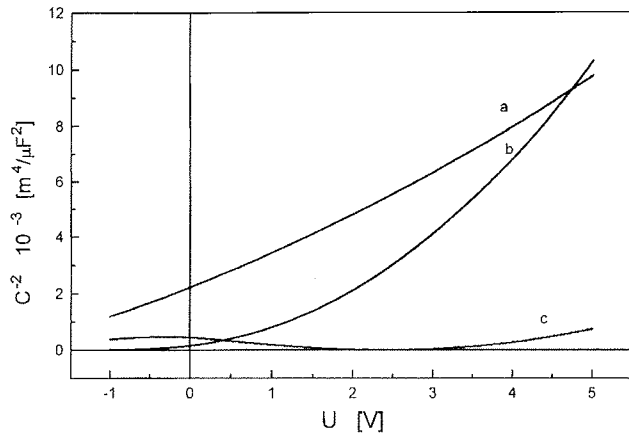
Fig. 6.   The calculated values of the resulting capacitance, $1/C^2$, based on the eq. (33) of the text, versus the external applied DC bias, U, is presented for various values of the parameters. The lines shown are calculated for the following values of parameters, expressed in terms of the constant $N_o=10^{16}$ cm^{-3}: line a) $V_L=0.45$ V, $N_{d,Ag}=0$, $N_{d,P}=1$ N_o, $N_{a,Ag}=0$; (the curve represents the usual case of the homogeneously doped metal/Si semiconductor junction); line b) $V_L=0.45$ V, $N_{d,Ag}=1$ N_o, $N_{d,P}=1$ N_o, $N_{a,Ag}=40$ N_o; line c) $V_L=0.45$ V, $N_{d,Ag}=10$ N_o, $N_{d,P}=1$ N_o, $N_{a,Ag}=100$ N_o.

Fig. 7.   The calculated values of the resulting capacitance, $1/C^2$, based on the eq. (33) of the text, versus the external applied DC bias, U, is presented for various values of the parameters. The lines shown are calculated for the following values of parameters, expressed in terms of the constant $N_o=10^{16}$ cm^{-3}: line a) $V_L=0.45$ V, $N_{d,Ag}=0.3$ N_o, $N_{d,P}=1$ N_o, $N_{a,Ag}=90$ N_o; line b) $V_L=0.45$ V, $N_{d,Ag}=0$, $N_{d,P}=1$ N_o, $N_{a,Ag}=90$ N_o; line c) $V_L=0.45$ V, $N_{d,Ag}=2$ N_o, $N_{d,P}=1$ N_o, $N_{a,Ag}=60$ N_o. Note that the shape of the calculated curves exhibits different curvatures, depending upon the values of parameters.

ity factor, n, as well as the series resistance, R_s, are bias dependent. The results of an alternative, rather involved and more general, analysis /15/ seem to support the above findings. One notes, that the results of ref. /6/, are based upon the assumption, that the n-Si enriched region is characterized by the constant density of electrically activated silver donors throughout the whole interval of bias investigated. Now, according to the model of fig. 4, this assumption is certainly no longer valid; for forward biases, due to the increasing density of activated acceptor silver impurities accompanied by the corresponding density decrease of the Ag^+ donors, the net excess space charge within $0 < x < L$ interval ought to be bias dependent and at all times smaller than if only shallow donor P impurities would have been present. Consequently, the series resistance ought to be bias dependent all the way up to its given upper limit above which the net space charge ought to remain constant. Similar characteristic feature, but in the reversed order, is expected to exists for the case of an applied reverse bias. This behavior would be expected to appear always, providing the enriched range exceeds certain minimal L_{min} and/or certain minimal Ag impurities densities, which are yet to be determined and thoroughly investigated. Strictly speaking, the presented ICB Ag/n-Si structures consequently may not be truly considered to be a typical representative of an ordinary Schottky metal/semiconductor diodes.

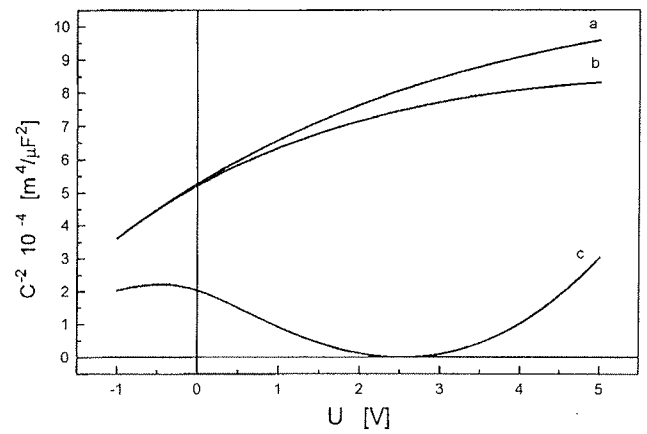The measured strong temperature I-U dependency /4/ of the ICB deposited Ag/n-Si(111) Schottky diodes might now be possible, on the basis of the proposed model exhibited on fig. 4., to assign primarily to the effect of the strong temperature dependent activation of the additional Ag donors and acceptors rather than (in conjunction with the variation of P donors activation) to the direct 1/kT variation itself.

There exists another very important feature which deserves a comment. Namely, as reported in ref. /4/ and /6/ the *effective* Schottky barrier height presumably decreases with an increased silver ions acceleration voltage Ua in clear disagreement with the DIGS model prediction of the strong Fermi level pining at the metal/semiconductor interface for all cases of strong disorders of a semiconductor interface region. Consequently, as DIGS model is generally considered to work well in clear cases of interface disorders, and as an ICB deposition method is certainly expected to produce just such an effect, the question how the effective Schottky barrier is related to the true Schottky barrier height is an important question which still requires to be answered.

4. Conclusions

The low frequency capacitance- voltage, C-U, relationship of ionized cluster beam, ICB, deposited Ag/n-Si(111) Schottky diodes for nonzero acceleration voltage of the silver ions, has been investigated on the basis of the postulated model of the semiconductor energy bands. In the derivation the fundamental assumptions made is the homogenous, spatially limited distribution, laying within the semiconductor energy gap, of the bias voltage dependent activated deep Ag

donor and acceptor impurities energy levels. These are (in addition to the shallow phosphorous donor level throughout the Si sample) spatially confined within the Si region extending up to the maximal silver ions penetration length L, which is a function of the silver acceleration voltage Ua. It is argued, that it is only for small values of L and/or small Ag impurity concentrations, within the described impurity additionally enriched semiconductor region, that the C-U relation is expected to exhibit the linear relationship, in accordance with the measurements.

The previously observed bias dependence of the semiconductor series resistance, at constant temperature, as well as the strong temperature dependency of the previously reported I-U measurements, are being phenomenologically explained in terms of the proposed model.

The effects of the additional, within the Si energy gap placed impurity levels arising on account of surface atoms, like O, C, N and traces of S, to be in the process of the Ag impact also transferred into the semiconductor, have been neglected. These impurities may contribute to the additional space charge within the Ag enriched n-Si region, but very likely their importance, as traps, ought to be taken into account if one is concerned with C-V frequency dependency. However, their possible effect, as microcluster formations, on the Schottky barrier height formation, in a sense as first proposed by Freeouf and Woodall /16/, is not to be neglected.

It is argued, that the relationship of the disordered (due to Ag and surface atoms) enriched semiconductor layer (at small penetration lengths L), on the Fermi level pinning and consequently on the DIGS implications concerning the metal/semiconductor junction, might be most conveniently investigated by carefully controlled and suitably designed ICB experiments in UHV conditions.

Acknowledgment

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