Concerning the mechanism of formation of the diode effect in silicon under the influence of an individual dislocation

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We investigated in detail the current-voltage characteristics of a junction of a tungsten microprobe with *n*-Si at the point where a 60-degree dislocation emerges to the surface, as well as the dependence of these characteristics on the temperature, on the degree of doping of the sample, on the diameter and material of the microprobe, and on the load on the microprobe. It is shown that the main characteristics of the diode effect are due to the influence of the electrostatic potential around the charged dislocation. The experimental data are used to estimate the potential at the dislocation and to calculate the position of the dislocation acceptor level and its occupation coefficient. An anomalous behavior of the potential is observed near the dislocation and a possible explanation is proposed for this phenomenon.

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Rectifying properties of a microscopic junction of a metal with n-type silicon were recently observed[1,2] at the point of emergence of a single 60-degree dislocation to the surface. The study of this phenomenon is promising both for the analysis of the changes of the spectrum of electronic states of a semiconductor under the influence of dislocations, and for an assessment of its efficient technical utilization. We present in this paper the results of further investigations of the current-voltage characteristics of a junction of a tungsten microprobe with the surface of n-Si at the point where the surface crosses a 60-degree dislocation. We determine the dependences of the forward and reverse current on the voltage, temperature, doping-impurity content of the n-Si, and pressure of the microprobe against the crystal surface. We study the variation of the electrostatic potential near the dislocation. We determine the dimensions of the region in which a diode effect is produced under the influence of the dislocation. The possible mechanism of the onset of this effect is discussed on the basis of the obtained data.

EXPERIMENTAL PROCEDURE

Unless specially stipulated, the measurements were made on n-Si samples with resistivity 150 Ω-cm, doped with phosphorus as they were grown by the Czochralski method. Single dislocations were introduced by the method of four-point flexure[3] about the ⟨112⟩ direction at 600°C in such a way that the ends of the dislocation half-loops emerged from the {111} surface. After the deformation, the samples were chemically polished in a 1HF : 7HNO_3 solutions. The dislocations were revealed with a chrome etchant. The sample was then etched for a minute in the acid mixture 1HF : 3hNO_3 : 3HCOOH. After treatment in each solution, the crystal was washed with distilled water. Control experiments have shown that, as a result of such a treatment, a junction of the tungsten microprobe with a dislocation-free surface (Fig. 1, curve 2) does not rectify (i.e., the reverse current differs little from the forward current—by not more than one order of magnitude).

The microprobes were prepared by a previously described procedure.[2] The ohmic contacts were welded to the dislocation-free surface. They were made of gold wire of 0.1 mm diameter. It is known[4] that the form of the characteristic of a point-contact diode depends strongly on the pressure on the contact and on the state of the surface. The procedure used earlier[1,2] did not make it possible to vary the clamping force of the microprobe in controlled fashion. In the present study, to produce a specified contact pressure, we used a device constructed similar to a microhardness meter[5] with a freely falling indentor. The minimum weight of the holder with the microprobe was 0.3 g. Most of the results reported in this article was obtained at this load on the contact. With the aid of special additional small loads we could vary the weight of the holder, and this enabled us to study the dependence of the current-voltage characteristic of the junction at the point of emergence of the 60-degree dislocation as a function of the microprobe pressure. The microprobe was placed in the dislocation etch pit under an optical microscope.

Control experiments have shown that if the measurements are made in the interval between 3 and 180 minutes after the chemical treatment of the samples, the results hardly differ. When the time of exposure of the crystals to air after the chemical treatment is increased, the inverse currents begin to decrease, and this decrease is faster on the surface than on the dislocation. In the course of the investigations we therefore compared successively the current-voltage characteristic of a dislocation diode and the junction with the dislocation-free surface. In all cases, measurements were made only on those samples whose dislocation-free surface did not produce rectification.

The current voltage characteristics (CVC) were plotted point by point or else with "characteriograph" in the voltage range U ~ 0.01—100 V. In our experiments, the error of each individual measurement, due to the instability of the characteristic, did not exceed 10%. When plotting different CVC, however, the currents did not differ by more than a factor of two for the same dislocation and by not more than three times for different 60-degree dislocations.

RESULTS OF EXPERIMENTS

Figure 1 shows the CVC of a junction between a tungsten microprobe and a 60-degree dislocation (curve 1). The figure shows also the CVC of the contact of the microprobe with a dislocation-free surface (curve 2) and the CVC of two ohmic contacts (curve 3). We see that the forward current of the junction with the disloca-

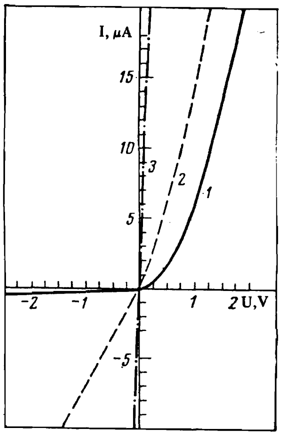

FIG. 1. General view of current-voltage characteristics: curve 1—microprobe located at point of emergence of 60-degree dislocation; curve 2—microprobe located on dislocation-free surface; curve 3—for two gold ohmic contacts.

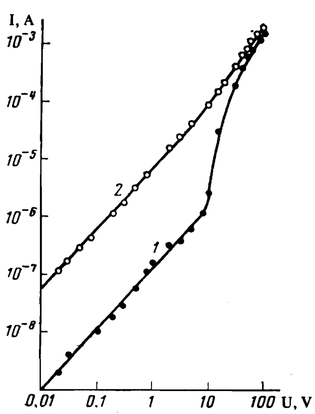

FIG. 2

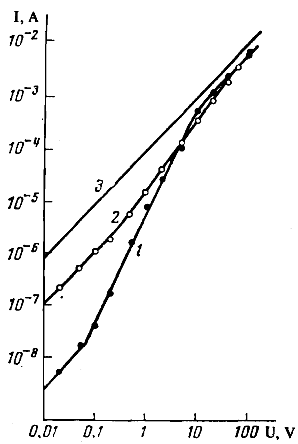

FIG. 3

FIG. 2. Reverse branch of current voltage characteristic: curve 1—junction at the point of emergence of the dislocation; curve 2—contact with dislocation-free surface.

FIG. 3. Forward branch of current-voltage characteristic: curve 1—junction at point of emergence of dislocation; curve 2—contact with dislocation-free surface; curve 3—two gold ohmic contacts.

tion greatly exceed the reverse currents, so that one can speak of reactifying action of a 60-degree dislocation.

1. Reverse branch of current-voltage characteristic. Figure 2 shows the dependence of the current on the voltage when the negative terminal of a battery is connected to the metallic probe placed either in the dislocation etch pit (curve 1) or on the dislocation-free surface of the crystal (curve 2). It is easily seen that in the voltage interval $U \sim 0.01-10$ V the currents in both case increase practically linearly with increasing voltage, $I \propto U^n$ with $n = 1 \pm 0.2$. The values of the currents in the case of the junction with the dislocation are lower by almost two orders of magnitude than the currents flowing through the junction with the dislocation-free surface. At voltages higher than 8 V the dependence of the current on the voltage becomes nonlinear. In the range $U \sim 10-100$ V it can be described for the microjunction on the dislocation-free surface by the expression $I = BU^{1.5}$. The character of the increase of the reverse current of the dislocation diode in this interval of voltages is more complicated. First I increases very rapidly ($\propto U^4$), and the growth rate slows down gradually and above 30 V the current gradually approaches the values for the junction on the dislocation-free surface. It can be assumed that breakdown of the diode takes place at voltages above 10 V, since the rectification practically vanishes. It should be noted that a certain time after the removal of the high voltage the CVC of the junction with the dislocation is fully restored, i.e., no significant irreversible changes in the crystal structure are caused by the breakdown.

2. Forward branch of the current-voltage characteristic. Figure 3 shows plots of the forward currents against the voltages for a dislocation diode (curve 1), for the junction of the microprobe with a dislocation free surface (curve 2), and for the two ohmic contacts (curve 3). For the dislocation-free surface, the character of the variation of the forward current with increasing voltage is analogous to that described for the reverse currents: At a low value of the voltage we have $I \propto U^{1.5}$; and high voltages $I \propto U^{1.5}$. The region of the nonlinear dependence of I on U in the case of forward bias begins to manifest itself at lower voltages (~0.1 V) than in the case of reverse bias. On the forward branch of the dislocation diode, at low voltages (up to 0.1 V), a linear dependence of I on U is also observed, and the values of the dislocation-diode currents are lower by 1.5–2 orders than the currents flowing through the junction with the dislocation-free surface. The forward current of the junction with the dislocation (starting with $U \sim 0.1$ V) increases nonlinearly with increasing voltage ($I \propto U^2$), and at $U \sim 10$ V it becomes comparable in magnitude with the currents typical of the contact with the dislocation-free surface.

It follows from the foregoing that at room temperature the diode effect on the dislocations appears in the voltage interval 0.1–10 V. All the subsequent measurements were restricted to this range.

3. Dependence of the current-voltage characteristic on the temperature. In the interval 20–200°C, the forward currents of the contact on the dislocation-free surface are independent of the temperature T within the limits of error. A statistical reduction of a large number of measurements of the reverse currents reveals a small tendency to increase (by up to 80%) when T is varied in the entire range.

The reverse current of the dislocation diode varies in the interval from −30 to 100°C like $I = I_0 \exp(-\Delta E/kT)$, where $\Delta E = 0.4 \pm 0.1$ eV (see Fig. 4). At $T \sim 120°$ the current I_{rev} reaches the same values as the reverse current of the contact with the dislocation-free surface, and with further rise of temperature it remains practically unchanged. The initial linear section of the forward branch ($U \leq 0.1$ V) of the CVC depends on the temperature in accord with the same law as the reverse current. At voltages above 1 V, the forward current is independent of temperature within the limits of errors.

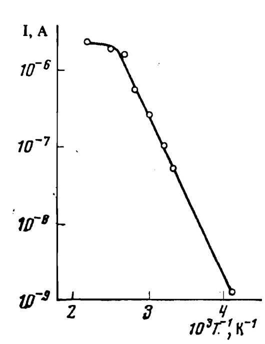

FIG. 4. Temperature dependence of the current of the junction with the dislocation at a reverse bias of 1 V.

4. Determination of the dimensions of the region in which the diode effect is formed under the influence of the dislocation. A detailed comparison of the shapes of the etch pits and of the microprobe has shown that microprobes with tip radii larger than $1\ \mu$ do not extend to the bottom of the sharply-pointed etch pit, and the contact is with its lateral surface at a certain distance from the dislocation line. This distance can be varied by using microprobes with different tip radii or by performing the measurements with small ($\sim 3-10\ \mu$) etch pits, using thick microprobes (with tip radius $\sim 10\ \mu$). The thinnest needles made possible a contact with the pit surface at a distance $r \approx 0.5\ \mu$ from the dislocation. Measurements have shown that when r is increased to $2.5\ \mu$ there is always rectification in the junction, and the reverse current is practically independent of r. At $r \gtrsim 5\ \mu$, the reverse currents reached the values of the currents for the dislocation-free surface, and the rectification ceased. In the interval $2.5-5\ \mu$, the reverse current increased with increasing r, but the character of this dependence could not be determined.

5. Dependence of the diode properties on the microprobe characteristics. To obtain additional information on the mechanism whereby the diode effect is formed under the influence of the dislocation, we studied the effect of the characteristics of the microprobe material and of the load on the microprobe on the CVC. Experiments on the influence of the microbe material on the diode action of the dislocation were carried using microprobes made of Mo and of an alloy W + 20% Re, for which the work functions (4.3 and 4.7 eV, respectively[6]) differ from the work function 4.5 eV of tungsten. The CVC for the same dislocations, obtained with microprobes made of different materials, were practically the same.

A load applied to the microprobe, in the range from 0.3 to 1.5 g, had practically no effect on the forward and reverse currents within the observed scatter of the experimental values. Further increase of the load yielded results that were not reproducible, since thin tips ($\sim 1\ \mu$) crumpled, and thicker ones at higher loads produced microcracks and brittle chips of the adjacent material. To extend the range of pressures, further work is needed to obtain loading conditions such as to decrease the probability of stress concentrations exceeding the ultimate strength of the silicon in the critical volumes.

6. Dependence of the CVC on the degree of doping of the sample. The experiments on the dependence of the CVC characteristic of the junction with the dislocation on the degree of doping of the sample were performed on n-Si samples with resistivities $\rho = 1$, 10, 150, and 1500 Ω-cm, doped with phosphorus during the course of growth by the Czochralski method. The samples were deformed by pressing-in an indentor into the $\{111\}$ surface at 800°C. The deformation was effected in 10 seconds, after which the sample was removed from the oven. It was shown earlier[7] that sections of prismatic half-loops placed in the rosette rays intersecting the external $\{111\}$ surface have a 60-degree orientation.

The measurements were performed on such single dislocations. The forward and reverse currents of the junction with the dislocations, in samples with $\rho = 150$ Ω-cm deformed by pressing-in an indentor and by the method of four-point flexure did not differ from one another. Since the samples were kept for different times at high temperature during the deformation process, it follows that the impurity atmosphere produced around the dislocation either has no effect on its rectifying properties, or, more probably, the formation of the impurity atmosphere is completed in the main within a very short time interval.

The reverse currents of the junction with the dislocation and the forward currents at voltages $U < 0.1$ V increase with increasing φ like $I \sim \rho^{-0.8 \pm 0.25}$. The forward currents at voltages $U > 1$ V are practically independent of ρ. The forward and reverse currents of the contact with the dislocation-free surface are independent of the degree of doping of the sample within the limits of the measurement error.

DISCUSSION OF RESULTS

The presented data indicate that at the employed silicon processing methods and for small metallic microprobe tip dimensions, the contact with the dislocation-free surface acquires an asymmetrical CVC characteristic, but not with diode properties in the generally accepted case. The barrier that causes the asymmetry of the characteristics is formed under the influence of the surface states. If the decisive role in its formation were played by the difference between the work functions of the metal and the semiconductor, then the junction with W + Re would have rectifying properties, since its work function is larger than that with n-Si.

Under the influence of the 60-degree dislocation emerging to the silicon surface, the microjunction of the silicon with the metal acquires clearly pronounced diode features. The rectification at room temperature becomes noticeable at $U > 0.1$ V, and for samples with $\rho = 150\ \Omega$-cm it reaches maximum values on the order of 10^3 at voltages ~ 10 V. Using our results, let us analyze the possible mechanisms of the observed phenomenon.

In the simplest model, the rectification effect at a metal-semiconductor junction can be attributed to the appearance, on the surface of the semiconductor, of a barrier equal to the difference of the work functions of the metal and of the semiconductor. To produce the barrier layer in an n-type semiconductor it is necessary that the work function of the metal exceed the semiconductor work function. The reverse current, in this model, depends exponentially on the difference of the work functions. In the experiments, however, no dependence of the reverse current on the microprobe material was observed, although at the realized change of the work function the reverse current should have changed by several orders of magnitude.

On the other hand, since the asymmetry of the CVC of the contact with the dislocation-free surface is governed by the surface states, it can be assumed that the dislocation gives up electrons to the surface states, increasing thereby their charge, and hence also the barrier bending of the bands on the surface near the dislocation. But this contradicts the acceptor action of the dislocations and, although the interaction of the dislocation with the surface levels does apparently take place, there is little likelihood that this mechanism can lead to an increase of the negative charge of the surface states and play the decisive role in the observed rectification effect.

The stresses attained at the contact of the microprobe with the surface are quite high. In principle they can cause a phase transition in the silicon. Then the rectification could occur on the boundary between the diamond and the hypothetical new phase of the silicon. But the absence of the diode effect on the dislocation-free surface under the same conditions, and on screw dislocations, indicates that the discussed influence cannot lead to the diode effect on a 60-degree dislocation. This can raise at once the question whether the stress field of only the 60-degree dislocation is capable of helping the formation of the new phase in the field of the contact stresses. An analysis of the character of its deformation field rejects this possibility: the signs of the dilatation and of the shifts in the different sections near the dislocation are opposite. This means that even if any type of internal dislocation stresses does lead to a phase transition, it does not cover the entire region surrounding the dislocation and the junction. Therefore the remaining part of the crystal will shunt the hypothetical p-n junctions on the phase boundary and no resultant diode effect will be registered. Any contribution of the deformation potential connected with the external contact stresses, just as the role of the deformation potential due to the dislocation stresses, is refuted by analogous deductions. This is also evidenced by the results of the investigation of the influence of the load applied to the microprobe on the characteristics of the dislocation diode.

It remains thus to consider the last possible explanation of the observed phenomena, wherein it is assumed that the diode effect is formed not on the interface between the metal and the silicon, but in the interior[8] under the influence of the electrostatic potential connected with the electrons captured by the broken bonds in the core of the 60-degree dislocation. This model not only explains the features of the aging of the CVC of the dislocation diode, and their independence of the work function of the metal and of the load on the junction, but can also result in agreement between some of the presently obtained experimental data and the results of studies of dislocation-induced changes in the spectrum of the electronic states of Si. When the dislocation captures electrons on the broken bonds, it becomes negatively charged. This bends the bands near the dislocation and produces a space charge around the dislocation. If the distance r from the dislocation to the point of contact is less than the radius of the space-charge region, then such a system can exhibit diode properties at a height of the potential barrier (at a distance r from the dislocation) larger than kT.

The reverse current of such a dislocation diode is $I \sim \exp[-e\varphi(r)/kT]$. Then it follows from the experimental dependence of the reverse current on T that the height of the potential barrier that causes the nonlinearity of the CVC is equal to 0.4 ± 0.1 eV. In our model, this quantity determines the height of the potential barrier at the distance r from the dislocation.

Measurements of the dependence of the reverse current on the distance r between the point of contact and the dislocation show that, within the limits of errors, the current does not depend on r as the latter ranges from 0.5 to 2.5 μ. Consequently, when r changes in this range the electrostatic potential changes by not more than kT. Assume that the potential changes little also when $r < 0.5\ \mu$, i.e., we assume the potential at the dislocation to be equal to 0.4 eV. For numerical estimates we use Read's theory.[9] Strictly speaking, Read's theory does not hold at room temperatures, since all the donors are ionized and it is necessary to allow for the screening of the dislocation charge by the free carriers. In our case, however, the electrostatic potential $e\varphi \gg kT$, the free-carrier density near the dislocation is low, and the screening is produced essentially by the ionized donors. The use of Read's theory for the estimates is therefore fully justified. In Read's theory the height of the potential barrier at the dislocation is

$$|e\varphi_0| = fE_0[3\ln f/f_c - 1.232], \quad (1)$$

where $E_0 = e^2/\epsilon c$, $f = c[\pi(N_d - N_a]^{1/2}$, ϵ is the dielectric constant, c is the distance between the broken bonds, $N_d - N_a$ is the effective donor concentration, and f is the dislocation filling factor. Putting $|e\varphi_0| = 0.4$ eV, we obtain from (1) for n-Si with $\rho = 150\ \Omega$-cm the value $f = 0.11 \pm 0.02$.

Read's theory makes it also possible to estimate the position of the dislocation level. Using the minimal-energy approximation, which is valid for $fE_0 \gg kT$, we obtain the lower bound $E_X = E_V + 0.34 \pm 0.1$ eV, and in the case of the "Fermi statistics" approximation ($fE_0 \ll kT$) we obtain the upper bound $E_D = E_V + 0.39 \pm 0.1$. In our case $fE_0 \approx kT$. It can therefore be assumed that E_D lies in the interval $E_V + 0.24$ to 0.49 eV. The obtained values of f and E_D agree with the values determined from measurements on n-Si with large dislocation density[10], which yielded for n-Si with $\rho = 150\ \Omega$-cm the value $f = 0.1$, and where two levels connected with the dislocations, $E_V + 0.27$ eV and $E_V + 0.44$ eV, were observed. The width of the space charge is approximately equal to radius $R = [(N_d - N_a)c\pi/f]^{-1/2}$ of the Read cylinder. Using the obtained value $f = 0.1$ for the sample with $\rho = 150\ \Omega$-cm, we get $R = 1.3\ \mu$. It follows from our experiments that the width of the space-charge region exceeds 10 μ, so that at distances $r \sim 3\ \mu$ the potential still remains practically unchanged. Thus, the experimental value of the width of the space-charge region is larger by one order of magnitude than that obtained by calculation. A broad space-charge region (25 μ) near the dislocation was observed also by Matare.[11] This increase was attributed by the authors to the influence of the strong electric field applied perpendicular to the dislocation, which does not exist in our experiments.

The broadening of the space-charge region can be explained by assuming that the effective concentration of the ionized donors around the dislocation decreases. In our opinion, the most probable cause of this decrease is that the impurity atmosphere around the dislocation contains an excess acceptor concentration. The role of these acceptors can be played by complexes consisting of point defects produced in the course of the deformation, as well as electrically-inactive impurities (such as oxygen or carbon). It is possible that the concentration of such complexes near the dislocation exceeds the concentration of the phosphorus in the initial sample, and the anomalous course of the potential near the dislocation is determined by the charge of these complexes and by their distribution. A similar effect can result from the presence, near the surface, of a carrier-depleted layer connected with the surface states. Our experiments do not make it possible to distinguish between these two possibilities. It appears that both are realized, and this makes a detailed description of the potential around the dislocation near the surface more complicated.

It must be noted that the decrease of the effective donor concentration alters R relatively strongly, but has little effect on the results of the calculations of f and E_D within the framework of Read's theory. Thus, when the effective donor density is changed by three orders of magnitude, R increases from 1.3 to 50 μ and f changes from 0.11 to 0.08. Hence, if a decrease in the effective donor density does indeed occur near the dislocation, then Read's theory can be used to estimate f and E_D. The broadening of the space-charge region explains also the quadratic dependence of the forward current on the voltage, since conditions for the onset of space-charge-limited current can be produced if this region is broad enough, and this determines the forward current of the junction with the dislocation.

We did not take into account the possible distortion of the electrostatic potential around the dislocation by the surface (the finite character of the dislocation line). As noted above, data on the position of the dislocation level and on the filling coefficient, obtained from measurements on an individual dislocation, are in satisfactory agreement with the results of measurements on samples with large ($\sim 10^9$ cm^{-2}) dislocation density, where the influence of the surface can be neglected. This can be regarded as evidence in favor of the insignificant role of the distortion of the electrostatic potential of the dislocation by the surface in the determination of the position of the dislocation level, and a small distortion of the electrostatic potential correlates with the theoretical estimate.[8]

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