Dislocation states in germanium

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An investigation was made of the influence of high-temperature annealing, impurity composition, and method of plastic deformation on the nature of the photoconductivity spectra of n-type germanium containing dislocations. An analysis of the newly obtained and already published results on the photoconductivity, and also on the photoluminescence and electrical properties of plastically deformed germanium led to the conclusion that all these properties could be explained by the presence of the same dislocation states forming one-dimensional bands. The optical properties are then governed by direct transitions of electrons between the conduction band and the dislocation bands.

INTRODUCTION

The influence of dislocations on the electron spectrum of covalent semiconductors is mainly due to the fact that the dislocation cores consist of rows of atoms with broken bonds. These atoms can capture electrons from the conduction band or, vice versa, can give up unpaired electrons to other centers. Our views on the energy spectrum of electrons localized in dislocation cores have changed several times in the course of their evolution. Initially the spectrum has been regarded as due to one level[1] or a half-filled band,[2] and then has been represented[3] by two narrow bands (donor $\mathscr{E}_1$ and acceptor $\mathscr{E}_2$) separated by a gap. Further development of the model of the energy spectrum of dislocation states has involved an allowance for the structure of the dislocations themselves in real crystals, namely for the possibility of alternation of regular parts of dislocation lines with local defects such as jogs, split regions, impurity atoms, etc. An energy scheme of dislocation states proposed in Refs. 4 and 5 is based on this model and postulates the existence not only of the bands $\mathscr{E}_1$ and $\mathscr{E}_2$, but also of donor ε_1 and acceptor ε_2 states of local defects on a dislocation line, located below the band $\mathscr{E}_1$, as well as a narrow band band $\mathscr{E}_1'$ of dislocation holes split off from the band $\mathscr{E}_1$.

However, an analysis of the photoconductivity and photoluminescence spectra[6–8] shows that, for example, in the case of germanium the spectrum of the acceptor dislocation states located below $\mathscr{E}_1$ is more complex and includes several density-of-states peaks in the energy interval $E_v + 0.14$–0.25 eV. In an earlier paper[7] we argued that the presence of these states cannot be reduced to the presence of dislocations of different types. If the latter were true, then the form of the photoconductivity and photoluminescence spectra could be regarded as a manifestation of the theoretically predicted[9,10] complex structure of the spectrum of electrons from broken bonds.

Further progress in understanding this topic was made in the present study by investigating the photoconductivity spectra of plastically deformed n-type germanium samples with as ordered a structure of 60° dislocations as possible; these samples were annealed in a wide range of temperatures and were characterized by quite different dopant concentrations. The results obtained and a comparison with those of other measurements did indeed show that the states manifested in the photoconductivity (PC) and photoluminescence (PL) spectra were most likely associated with the regular parts of dislocations of just one type. This made it possible to explain the experimental results on plastically deformed germanium using the band model of the spectrum of dislocation states with several extrema of the dispersion curve $E(k)$.

It should be pointed out that an attempt had been made earlier[11] to explain the photoconductivity spectra of deformed samples using the $E(k)$ dependence. However, the scheme of dislocation states in germanium proposed in Ref. 11 has not been confirmed by subsequent experiments.

METHOD

We used n-type germanium samples with donor concentrations in the range $N_d = 2\times10^{12}$–2×10^{14} cm^{-3}. An ordered structure of 60° dislocations was created by plastic bending of the samples about the [110] axis at 420 °C by a method described in Ref. 6. Some of the samples were deformed by compression.[12] All the deformed samples were coated with gold and annealed in vacuum at a definite temperature in the range 680–880 °C for 20 min and this was followed by slow cooling at a rate less than 3 °C/min. The anisotropy of the dislocation structure, deduced from the ratio of the number of etch pits on different faces of the bent samples, amounted to 3–5 after annealing at these temperatures, and the dislocation density N_D ranged from 2×10^5 to 2×10^7 cm^{-2}. All the samples retained n-type conduction after deformation and annealing.

The photoconductivity was measured by a method described in Ref. 6. The photoconductivity spectra were recorded at temperatures 25–250 K in the spectral range $h\nu = 0.4$–0.7 eV.

EXPERIMENTAL RESULTS

1. We found that the nature of the photoconductivity spectrum of samples of plastically deformed n-type germanium (i.e., the energy positions on the $\Sigma(h\nu)$ curve of such singularities as a threshold E_1 and steps $E_2 - E_4$ (Fig. 1), and the relative amplitudes of these singularities) was independent of the donor concentration in the original crystals when this concentration was within the range 2×10^{12}–2×10^{14} cm^{-3} (curves 1–3 in Fig. 1). An increase in the measurement temperature from 25 to 250 K shifts the whole spectrum toward lower energies (curves 3 and 5 in Fig. 1), in

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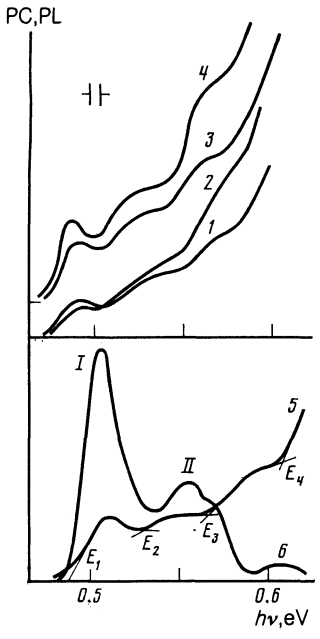

FIG. 1. Photoconductivity (PC, curves 1–5) and photoluminescence (PL, curve 6) spectra of deformed germanium samples with different types of doping: 1) $N_d = 1.2\times10^{14}$ cm^{-3}, $N_D = 6\times10^{6}$ cm^{-2}; 2) $N_d = 3\times10^{12}$ cm^{-3}, $N_D = 2\times10^{5}$ cm^{-2}; 3)–6) $N_d = 3\times10^{13}$ cm^{-3}, $N_D = 2\times10^{6}$ cm^{-3}. Measurement temperature 160 K (1–4) and 30 K (5, 6). Annealing after deformation at temperatures 880 °C (4) and 680 °C (1–3, 5, 6).

accordance with the reduction in the band gap of germanium; this accords with Ref. 6. Similar dependences on the impurity composition and on the measurement temperature were reported earlier for the photoluminescence spectra.[7] The dependence $\Sigma(h\nu)$ differed little for germanium samples deformed by bending and compression, although the dislocation structure of these samples could be very different: compression provided greater opportunities for the appearance of dislocations of different types and of different defects on dislocation lines.

2. Investigations of the photoconductivity spectra of plastically deformed n-type germanium, annealed at various temperatures in the range 680–880 °C, showed that variation of the annealing temperature had no significant influence on the photoconductivity and its spectrum (curves 3 and 4 in Fig. 1).

3. The photoconductivity spectra were determined also for deformed samples for the same values of N_d and N_D as those for the samples used in Ref. 7 to determine the photoluminescence spectra. A comparison of the photoconductivity and photoluminescence spectra recorded at the same temperature in the range 25–60 K (curves 5 and 6 in Fig. 1) showed that the threshold E_1 and the step E_2 in the photoconductivity spectrum coincided with the long-wavelength edge of a peak I (to within 2 meV) and with a peak II (to within 5 meV), respectively, in the photoluminescence spectrum, whereas the value of E_3 coincided with the energy at which an additional shoulder of lower intensity appeared in the short-wavelength wing of the peak II in the photoluminescence spectrum. The step E_4 in the photoconductivity spectrum corresponded to a weak rise observed at the same energy in the photoluminescence spectra of many samples.[7] Therefore, to within the limits given above, the positions of the singularities in the photoconductivity and photoluminescence spectra coincided.

4. We also determined the amplitudes and forms of the dependences $\Sigma(h\nu)$ when a current was flowing along ($\Sigma_\parallel$) and across ($\Sigma_\perp$) the preferential direction of dislocations in n-type germanium samples with $N_d = 2.4\times10^{13}$ cm^{-3} and $N_D = 3\times10^{6}$ cm^{-2} (samples No. 1) and $N_D = 4\times10^{6}$ cm^{-2} (sample No. 2). The dark conductivities $\sigma_\parallel$ and $\sigma_\perp$ were determined earlier for these samples.[13] According to Ref. 13, cooling increased the anisotropy of the dark conductivity and at 50 K the anisotropy became $\sigma_\parallel/\sigma_\perp \approx 10^3$ for sample No. 1 and ≈ 20 for sample No. 2. In the case of these samples we found a considerable difference also between the values of $\Sigma_\parallel$ and $\Sigma_\perp$, although the spectra $\Sigma_\parallel(h\nu)$ and $\Sigma_\perp(h\nu)$ were completely identical. For example, at some particular illumination intensity with a photon energy of $h\nu = 0.50$ eV the conductivity along the dislocations in samples Nos. 1 and 2 increased by just 3%, whereas across the dislocations it increased by factors of 1.2 and 2.5, i.e., we found that $\Sigma_\parallel/\sigma_\parallel = 0.03$ for both samples whereas $\Sigma_\perp/\sigma_\perp \approx 0.2$ for sample No. 1 and ≈ 1.5 for sample No. 2. A large difference between the values of $\Sigma_\parallel$ and $\Sigma_\perp$ was observed throughout the investigated spectral range and for any illumination intensity, Therefore, the influence of the illumination intensity was manifested mainly by a considerable reduction in the anisotropy of the conductivity of the samples compared with the dark conductivity.

DISCUSSION OF RESULTS

It follows from Fig. 1 and from the published measurements of the photoconductivity and photoluminescence[6,7] that all the features of the photoconductivity and photoluminescence spectra of plastically deformed germanium occur in the same energy interval $h\nu = 0.45$–0.60 eV and that the positions of steps in the photoconductivity spectra practically coincide with the positions of the corresponding singularities in the photoluminescence spectra (there are no Stokes losses). It follows from the results of Refs. 6 and 8 and from the present data that the photoconductivity and photoluminescence spectra are due to the same electron transitions between the conduction band and dislocation states lying in the lower half of the band gap of germanium. The positions of these states are in good agreement with the levels deduced in Ref. 14 from deep-level transient spectra of plastically deformed p-type germanium.

The results of the present study show that these dislocation states are highly immune to changes in the annealing temperature, impurity composition, and dislocation structure. In fact, the photoconductivity and the form of the $\Sigma(h\nu)$ curve are independent of the temperature of annealing of deformed samples in the range from 680 to 880 °C (Fig. 1). Using the photoluminescence data of Ref. 7, we find that the range of stability of the dislocation centers now extends further to lower temperatures right down to 420 °C. The nature of the photoconductivity spectra is retained (Fig. 1) in deformed samples differing in respect of the concentration of the electrically active impurities ($N_d = 2\times10^{12}$–2×10^{14} cm^{-3}) and also in respect of the composition of electrically inactive impurities (samples obtained from different sources).

The nature of the optical spectra is not affected greatly

either by an increase in the measurement temperature from 8 to 250 K (see Fig. 1 and the data of Refs. 6 and 7) if we allow for the energy shift of the spectra. Therefore, the ratios of the various components of the photoconductivity spectra remain fairly stable, typical of any deformed n-type sample even when the deformation method is varied. Such ratios are also independent of temperature in the case of the photoconductivity and photoluminescence spectra.

All these results allow us to attribute the complex nature of the photoconductivity and photoluminescence spectra to optical transitions between the conduction band and dislocation states of just one type. These states are most probably the electrically active extended regions of dislocations of one type. The presence of these regions has already been invoked in explaining the low-temperature hf and microwave conductivity of germanium with dislocations.[15–17] A relationship between the singularities in the photoconductivity and photoluminescence spectra of plastically deformed samples and the presence of various isolated centers (including macrodefects and dislocation line defects) is unlikely in view of the just-mentioned stability of these spectra when the impurity composition, dislocation structure, and annealing temperature are varied within a wide range (known point defects and complexes in germanium dissociate at temperatures $T \lesssim 700$ °C—see Refs. 18–21) and also in view of the absence of such singularities in the case of control samples.[6]

In an analysis of the regular parts of dislocations of the same type regarded, as the most probable reason for the appearance of the photoconductivity and photoluminescence spectra, we have to consider the nature of these dislocations. The deformation geometry and the number of etch pits on different faces of bent samples[6,22] indicate that these sample contain mainly 60° dislocations directed along the bending axis. A comparison of the anisotropy of the dislocation structure with the measured anisotropies of the Hall effect, dc electrical conductivity,[6,13] and microwave conductivity[22] of samples deformed in the same way shows that it is the 60° dislocations in germanium that have the highest concentration of electrically active centers. A good agreement between the energy positions of the levels deduced from the photoconductivity, photoluminescence, and deep level transient spectra, and from electrical measurements[8,23] demonstrates that all these physical properties are governed by the same states which predominate in the investigated samples. It is natural to assume that these states are associated with the 60° dislocations. When electrons are captured by these states, nonconducting space charge regions (Read cylinders) form around these dislocations. When the anisotropy of the dislocation structure is strong, the dark conductivity along dislocations is due to almost obstacle-free motion of free carriers along Read cylinders, whereas at right-angles such motion is limited because of the need to overcome barriers between nonconducting cylinders which are nearly in contact (this is true when the fraction of the volume of the sample occupied by such cylinders is significant).[24] Then, the excitation of electrons from these states by light of $h\nu > E_1$ energy should reduce the radius of the Read cylinders and weaken the conductivity anisotropy when the measurements are made of $\Sigma_\parallel$ and $\Sigma_\perp$, but the spectra should not be affected, exactly as found in our experiments. All this allows us to discuss extended regions of just the 60° dislocations.

Electron microscopic investigations have revealed that the 60° dislocations in germanium[25] are split over most of their lengths into partial 30° and 90° dislocations.

The splitting of the 60° dislocations is independent of the deformation temperature if the latter is varied from 420 to 800 °C (Refs. 25 and 26). Both types of partial dislocations are present in nonreconstructed and reconstructed (with closed dangling bonds) states. However, according to Ref. 27, reconstruction of the 30° dislocations is more likely.

In a situation of this kind an analysis of all the experimental results obtained for plastically deformed germanium leads to the hypothesis that the states manifested in the photoconductivity and photoluminescence spectra are most probably due to broken (dangling) bonds of the 90° partial dislocations.

In view of the overlap of the wave functions of closely spaced (at distances of $a = 4$ Å in germanium) dangling bonds and because of the translational symmetry along the directions of dislocations, the dislocation states form a one-dimensional energy band with a dispersion $E(k)$ and a quasimomentum k ranging from $-\pi/a$ to π/a. The calculations reported in Refs. 9, 10, and 28 demonstrate that the dependence $E(k)$ for germanium has minima at the points $k = 0$ and $\pm\pi/a$ and maxima at certain intermediate values of $k = \pm k_0$. It is important to note that the presence of minima (or more exactly of extrema) at the points $k = 0$ and $\pm\pi/a$ is independent of the actual nature of the function $E(k)$, but is determined by its symmetry.

It was demonstrated in Ref. 9 that, in principle, it is possible to explain the experimental results on electronic properties of plastically deformed silicon and germanium on the basis of the band model of dislocation states with several extrema of the dispersion curve of $E(k)$. Using this model, we shall now try to explain the singularities in the photoconductivity and photoluminescence spectra as due to direct transitions of electrons between the same (in the photoconductivity and photoluminescence cases) states in the conduction band and in the dislocation band, namely between the minima of the conduction band and the dislocation states which are filled with electrons in n-type germanium. The justification for this hypothesis is the coincidence of the singularities in the photoconductivity and photoluminescence spectra at all measurement temperatures and for different doping (see Fig. 1 and Ref. 7), i.e., when the degree of occupancy of the dislocation states changes considerably. In the case of indirect transitions an increase in the number of electrons captured by a dislocation would have increased the occupancy limit of these dislocation states and, consequently, would have shifted the photoconductivity and photoluminescence edges toward longer wavelengths.

Direct transitions in the photoconductivity and photoluminescence processes imply conservation of the projection of the quasimomentum of the conduction states and of the dislocation band along the direction of the dislocations. We shall assume specifically that the dislocations are directed along the [110] axis. The minima located on the boundary of the Brillouin zone along the $[1\bar{1}1]$ and $[1\bar{1}\bar{1}]$ directions project on a point $k = 0$, whereas the minima along [111] and $[11\bar{1}]$ project on points $k = \pm\pi/a$, i.e., these projections coincide with the minima of the dislocation energy band. It follows hence, that the transitions between the minima of the conduction band and the minima of the dislocation

band are direct for the same values of k. When electrons are captured by dislocations the minima of the dislocation band are the first to fill. In view of the one-dimensional nature of the dislocation band, there are sharp maxima of the density of states at its extrema and, therefore, the same minima are manifested as levels in electrical measurements and in deep-level transient spectra.

In accordance with the above scheme there should be only two photoconductivity steps and two peaks in the photoluminescence and deep-level transient spectra, i.e., the number of these singularities should be half that found experimentally. Therefore, following our model, we have to assume the existence of two closely spaced acceptor-type dislocation bands. In fact, in the case of an unreconstructed partial 90° dislocation, which is the type of dislocation of main interest to us, the theoretical calculations of Refs. 10 and 28 predict the existence of crossing dislocation bands, because the core of such a dislocation contains two rows of oppositely directed bonds.

According to Refs. 9, 10, and 28, the energy of the minima of the dislocation band is greater for $k = 0$ than for $k = \pm \pi/a$, which is related—like the whole $E(k)$ dependence—to the actual form of the dispersion of the conduction and valence bands of germanium. Therefore, we shall assume that the energies E_1 and E_2 correspond to direct transitions characterized by $k = 0$, whereas the energies E_3 and E_4 correspond to direct transitions with $k = \pm \pi/a$ (Fig. 2). Since the theoretical calculations give only the qualitative nature of the $E(k)$ dependence, we cannot exclude the possibility that the correspondence between the energies E_1–E_4 and these transitions can be different. The independence of the form of the photoconductivity and photoluminescence spectra of the degree of occupancy of dislocations demonstrates that the energy at the minima of the dislocation band and possibly the whole $E(k)$ spectrum are practically independent of the number of electrons captured by dislocations.

It should be pointed out that all the theoretical calculations of $E(k)$ ignore the existence of a gap in the spectrum of the dislocation states, although it has been found experimentally.[4] The presence of dislocation bands of different types (donor $\mathscr{E}_1$ and acceptor $\mathscr{E}_2$) should modify the numerical results reported in Refs. 9, 10, and 28. On the other hand, as shown in Ref. 29, even in the presence of a Coulomb gap in the dislocation energy spectrum, the qualitative conclusions reached in these numerical studies remain in force: all the energy bands have a complex dispersion curve with minima at $k = 0$ and $\pm \pi/a$. Since we are concerned only with the acceptor dislocation states, the results plotted in Fig. 2 are mainly concerned with the $\mathscr{E}_2$ states; the donor states $\mathscr{E}_1$ located near the valence band are shown only schematically. According to the estimates reported in Ref. 9, the width of the density-of-states peaks with their centers at the minima of the dislocation bands is ~ 0.01 eV, which is not in conflict with the experimental results. Then, an estimate of the width of the dislocation band $\Delta\mathscr{E}_2$ obtained using the experimental values of the occupancy factor[6] gives $\Delta\mathscr{E}_2 \lesssim 1$ eV.

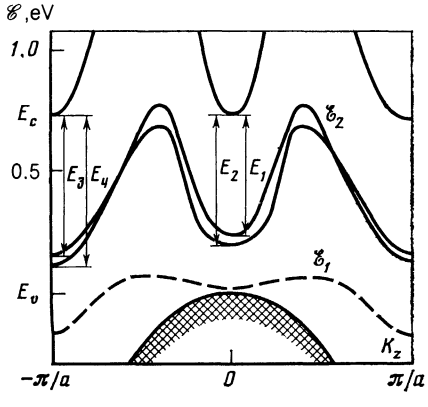

FIG. 2. Direct optical transitions between the conduction band and the acceptor dislocation bands of germanium. The valence band is shaded.

We shall conclude by stressing that all the available experimental data on the photoconductivity, photoluminescence, and deep level transient spectra together with electrical measurements on plastically deformed germanium can be explained in a self-consistent manner employing a model in which all these properties are attributed to the same dislocation states. The acceptor dislocation states are regarded as two closely spaced displaced dislocation bands with a complex structure, so that the optical properties are due to direct transitions of electrons between the minima of the dislocation bands and the minima of the conduction band.

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