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Metallic and non-metallic longitudinal conductance of grain boundaries in bicrystalline and polycrystalline germanium doped with mercury and antimony

A K Fedotov[1], **A V Mazanik**[1], **T Figielski**[2], **A Makosa**[2] **and Yu M Ilyashuk**[1]

[1] Belarusian State University, F Skaryna av. 4, 220050 Minsk, Belarus
[2] Institute of Physics of PAS, Al. Lotnikow 32/46, 02-668 Warsaw, Poland

E-mail: fedotov@bsu.by

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Abstract

The influence of temperature and magnetic and electric fields on the grain boundary (GB) longitudinal conductance σ at low temperatures in mercury-doped polycrystals and bicrystals of germanium was studied. It was shown that the $\sigma(T)$, $\sigma(E)$ and $\sigma(H)$ dependences for GBs in bicrystals are determined by metallic and hopping mechanisms, whereas we could not find a hopping channel in bicrystalline samples. The behaviour of the $\sigma(H)$ dependences for low magnetic fields (super-linear) and the linearity of the current–voltage characteristics at $T < 100$ K indicate merely the presence of a metallic mechanism in bicrystalline samples. All of the results obtained indicate that during the zone-melting process, the segregation of impurities at grain boundaries develops differently in bicrystalline and polycrystalline ingots.

1. Introduction

The semiconductor–semiconductor interface (SSI) is a rather interesting quasi-2D object where effects characteristic of disordered systems near the metal–insulator transition (MIT) can occur. A grain boundary (GB) in a semiconductor bicrystal or polycrystal provides an excellent example of a SSI where two similar semiconductors are in contact. There are many papers (see [1–6]) reporting convincing arguments in favour of an 'extrinsic' rather than 'intrinsic' nature of general GB electrical activity. Moreover, this is strongly supported by a particular behaviour of carrier transport along GBs in polycrystals or bicrystals resulting in variable activation energy of the weak temperature dependence of the conductance along GBs at low temperatures. The occurrence of curvature in low-temperature Arrhenius plots of the longitudinal conductance for non-barrier GBs in polycrystals of gold-, iron- and mercury-doped p-type Ge [7–10] is probably strong evidence of a fundamental role of impurity segregation in the boundary carrier transport.

As shown previously [9, 10], a general GB in a mercury-doped germanium bicrystal or polycrystal behaves like a highly conductive thin layer that appears at low temperatures when the bulk conductance is 'frozen out'. Taking into account that no potential barrier appears (no dangling bonds!) at the boundaries in p-type germanium, the above-mentioned behaviour was attributed to an 'extrinsic' property: segregation of doping impurities around GBs.

This work is an extension of the experiments of [9, 10], highlighting a role of impurity segregation specific to low-temperature carrier transport along general GBs in polycrystalline and bicrystalline mercury-doped germanium. It is devoted to the simultaneous analysis of both temperature and field (magnetic and electric) dependences of the GB longitudinal conductance (when the vector of an electric field lies within the GB plane), carried out in order to obtain additional information about the mechanisms of carrier transport along such grain boundaries.

2. Experimental details

Polycrystalline and bicrystalline ingots of germanium doped by mercury and antimony have been prepared by zone-melting techniques [9, 10]. The number of GBs in an ingot (multiple or single) was dependent on the speed of the melting-zone expansion. In ingots grown at speeds of melting-zone movement greater than 5–10 mm min^{-1} (their polycrystalline form being determined by multiple GBs), the grains can be varied in size between 0.1 and 5–10 mm. Ingots grown at speeds of melting-zone expansion <5 mm min^{-1} were bicrystalline and, as a rule, had a single GB extended along the ingot at a small angle to its axis.

In this study, mercury as the main dopant was introduced into ingots from vapour. The content of mercury atoms in the grain bulk amounted to $N_{Hg} \approx (9–10) \times 10^{15}$ cm^{-3}. Antimony as a compensating impurity was introduced by 'spreading' of a small amount on moving the melting zone from one side of the ingot to another. The antimony content in the bulk was about $(1–9) \times 10^{15}$ cm^{-3}. The method of doping used allowed us to produce ingots with a gradually change of the compensation coefficient (the ratio $K = N_{Sb}/2N_{Hg}$) along the ingot. So, cutting a bicrystalline ingot into a system of parallel plates (normally to the growth ingot axis) has enabled us to produce a whole set of samples with the same GB and mercury content but different contents of the compensating impurity (antimony).

Mercury was chosen as the main dopant for two fundamental reasons:

(a) the absence of an intergrain barrier in polycrystalline germanium of p-type conductance and

(b) the presence of two deep acceptor-like levels in the germanium gap, which are above the valence band edge by 90 and 230 meV [9, 10].

The latter results in 'freezing out' of the carrier concentration in the grain bulk (due to carrier trapping by deep impurities) and hence high conductance along general GBs already at the temperature of liquid nitrogen being exhibited. Therefore, doping of germanium with mercury provided an excellent opportunity to study just the effect of impurity segregation on the carrier transport along general GBs at low temperatures, without any influence of the barrier band bending due to the presence of dangling bonds. Varying the K-ratio enables one to study its influence on GB conductance, which is very important for detecting the carrier transport by the hopping mechanism.

The electric measurements and the sample preparation procedures were similar to those used in [9–11].

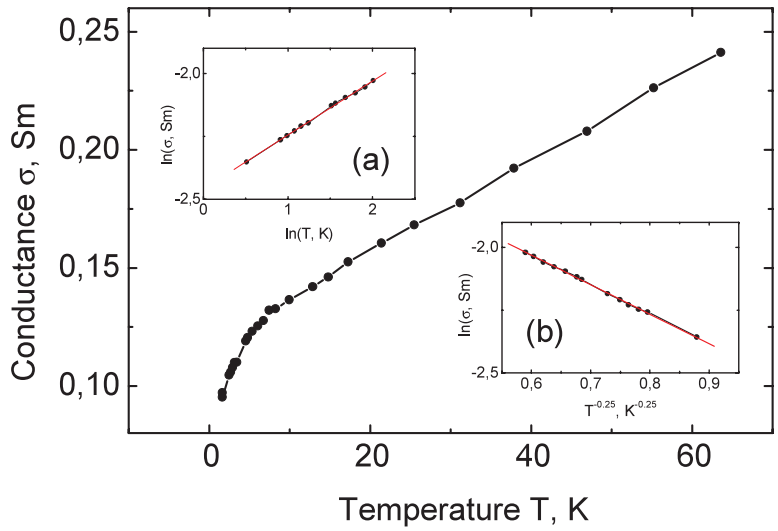

Figure 1. The temperature dependence of the GB longitudinal conductance for a bicrystalline sample with $K = 0.4$ in the temperature range 1.2–70 K. Low-temperature parts of this dependence for the temperature range 1.2–15 K are presented in insets (a) and (b) on different scales.

3. Results and discussion

Our study of carrier transport along single GBs in mercury-doped germanium bicrystals shows that, as for polycrystalline samples with multiple GBs (see [9, 10]), the mechanisms of longitudinal conductance are also determined by the character of occupancy of two mercury acceptor levels (90 and 230 meV above the top of valence band) controlled by the K-ratio. For the mercury and antimony contents used $0 \leqslant N_{\mathrm{Sb}} \leqslant 2N_{\mathrm{Hg}}$ ($K < 1$) in the grain bulk, the conductance of samples was already 'frozen out' upon cooling down to 100 K, so in the bicrystals studied, GB longitudinal conductance at temperatures lower than that of liquid nitrogen can be considered as the superposition of two different contributions. An example of such behaviour for a single-GB sample with $K = 0.4$ is shown in figure 1. As can be seen, $\sigma(T) \sim T$ for the temperature range 10–77 K, whereas for $T <$ 10–15 K this dependence can be represented either by $\sigma(T) \approx \sigma_0 \exp[-(T_0/T)^{0.25}]$ (inset (b) in figure 1) or $\sigma(T) \sim T^{0.5}$ (inset (a) in figure 1). In our earlier works [9, 10], the exponential behaviour of $\sigma(T)$ in polycrystalline samples was attributed to hopping conductance. But as is seen from the slope of the Arrhenius plot in inset (b) in figure 1, the value of T_0 in the exponential contribution (in the shape of Mott's law [12]) is about 2 K, which is too low for a hopping mechanism over the temperature range studied. Recall that, for the sample with multiple GBs, low-temperature ($T <$ 10–15 K) $\sigma(T)$ dependences exhibited metallic ($\sigma_m(T) \approx \sigma(0) + \alpha T^{0.5}$) and non-metallic ($\sigma_{nm}(T) \approx \sigma_0 \exp[-(T_0/T)^{0.25}]$) contributions simultaneously [9, 10]. In accordance with [9, 10], $\sigma(0)$ and root-like terms were ascribed to a minimal metallic conductance and 3D quantum corrections to the metallic conductance of GBs, respectively [12]. Unfortunately, for bicrystalline samples we cannot simultaneously fit the low-temperature part of $\sigma(T)$ by a superposition of the root-like and exponential-like contributions.

Additional evidence of the presence of a metallic channel along single GBs in bicrystalline samples was found when studying the transverse magnetoconductance of GBs at magnetic fields H up to 16 T. As seen from figure 2, the behaviours of the curves $\Delta\sigma(H)/\sigma(0) = [\sigma(H) - \sigma(0)]/\sigma(0)$ measured at the temperatures 1.2 and 4.2 K are very similar to the

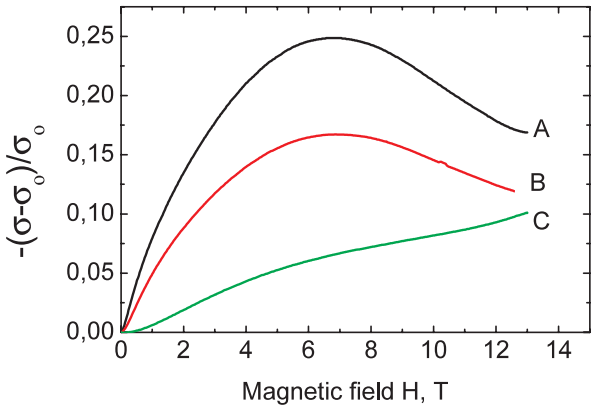

Figure 2. Relative GB conductance $\Delta\sigma(H)/\sigma(0) = [\sigma(H) - \sigma(0)]/\sigma(0)$ versus magnetic field for a bicrystalline sample with $K = 0.4$ measured at 1.5 (A), 4.2 (B) and 25 K (C).

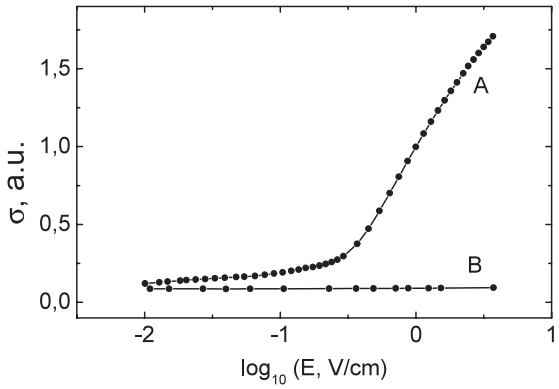

Figure 3. The electric field dependence of the GB conductance for a bicrystalline sample with $K = 0.4$ measured at 77 K before (A) and after (B) exposure to a 100 V cm^{-1} electric field.

behaviour at the onset of Shubnikov–de Haas oscillations due to the magnetic quantization of carrier levels [13]. Taking into account the 'freezing out' of carriers in the conductance band of the bulk and the lack of a hopping contribution, such behaviour can be attributed to a metallic channel only. The substantial transformation of the $\Delta\sigma(H)$ curve at the temperature 25 K is naturally ascribed to violation of the condition for quantization in a magnetic field $h\omega_c/kT \gg 1$ (ω_c is the Larmor precession frequency) for this temperature. Note that for 25 K the value of $h\omega_c/kT \approx 0.5$, whereas for 4.2 and 1.2 K it equals 3.2 and 8.9 respectively.

Recall that for the samples with multiple GBs the magnetoconductance in the metallic channel is fundamentally different in nature, exhibiting the dependence $\Delta\sigma(H) \approx \beta H^{0.5}$, where β is a constant [9, 10]. The temperature independence of β and its negative sign allow us to attribute magnetoconductance in GBs in the region of classically low magnetic fields to the known mechanisms of weak localization described by a theory of 3D quantum corrections to the Boltzmann conductance [12]. Therefore, as for the temperature dependences of the low-temperature GB longitudinal conductance in mercury-doped germanium, the above-described behaviour of the magnetoconductance in multiple-GB polycrystals is also substantially different from the behaviour of single GBs in bicrystals.

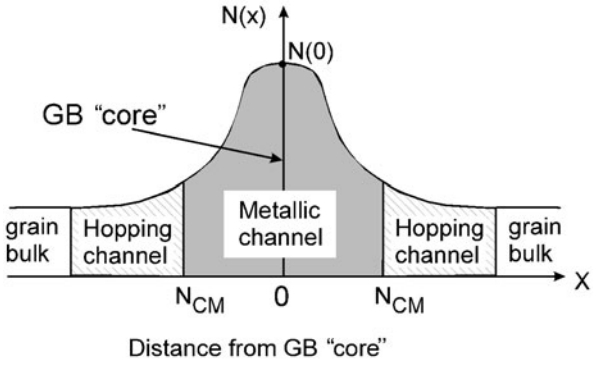

Figure 4. A schematic diagram of the distribution of impurities around the GB 'core', giving a qualitative representation of the formation of conductive channels along GBs.

To obtain additional information concerning the mechanisms of carrier transport along GBs in polycrystalline and bicrystalline samples, their I–V characteristics for electric fields $E \leqslant$ 1–2 V cm^{-1} in the temperature range 1.2–77 K were investigated. Our study has shown that the low-field I–V curves were linear for bicrystalline samples and highly non-linear for polycrystalline ones. An example of the $\sigma(E)$ behaviour of a polycrystalline sample with $K = 0.4$ is presented as curve 1 in figure 3. The analysis of the dependences of GB longitudinal conductance on electric field have shown that they can be fitted by the relation

$$\sigma(E) = \sigma_m + \sigma_{nm}(E) = \sigma_m + \sigma_0 \exp(AE^n), \tag{1}$$

where σ_m, σ_0 and A are constants for the samples studied, depending only on the K-ratio and the temperature. The index n is determined by the K-ratio but not by the temperature. In the above context, σ_m and σ_{nm} for the samples with multiple GBs can be treated as metallic and non-metallic contributions respectively. The relationship between these two contributions at 77 K varies with the K-ratio in the bulk. For most of the samples, the values of $\sigma_m/\sigma(E)$ were $<\sigma_{nm}/\sigma(E)$, being between 5 and 50%. The index n changed from 0.15 to 0.95.

The change of the non-metallic (exponential) contribution to the I–V characteristics of multiple GBs with change of the K-ratio in the bulk could be evidence of a hopping mechanism being operative. However, the lack of constancy of index n could be evidence of a percolative conductance mechanism that is inherent to semiconductors with highly inhomogeneous distributions of impurities being operative [5, 12]. So to draw find the correct solution to this problem, it is essential to carry out experiments with the same samples but more homogeneous distribution of impurities. Accordingly [11], we can change the distribution of dopants around GBs by passing a high current along them at low temperatures.

The low-temperature measurements for polycrystalline samples have shown that the application of longitudinal electric fields of more than 100 V cm^{-1} caused irreversible changes in the GB conductance (figure 3). After such a 'treatment' of the samples with multiple GBs, a significant fall in the full GB conductance was observed, and the fraction of the metallic contribution σ_m in relationship (1) increased by up to 100%, resulting in linearity of the I–V curves for $E <$ 2 V cm^{-1} (see curve B in figure 3).

As follows from the $\sigma(T)$, $\sigma(E)$ and $\sigma(H)$ dependences of the GB longitudinal conductance, the presence of exponential and non-exponential contributions to the low-temperature carrier transport along multiple GBs in a polycrystalline sample enables us to propose a phenomenological model to explain this behaviour. As shown in [14, 15], segregation of impurities at GBs should result in enrichment of the GB 'core' with dopants and non-

monotonic decay of their content down to its value in the bulk (figure 4). If the concentration of a dopant (in our case, mercury) at the GB 'core', $N(0)$, exceeds the Mott concentration, N_{CM}, then this region of boundary should exhibit metallic conductance (region 1 in figure 4). The presence of a compensating impurity (in our case, antimony) can lead to 'breakdown' of the metallic conductance in the region around the GB where $N(x) < N_{CM}$ and the emergence of a hopping channel (peripheral regions 2 in figure 4). As we have shown in [15], due to the additional influence of elastic forces (owing to the positive sign of these forces associated with the difference between the effective radii of germanium and antimony atoms), antimony is 'pushed out' of the GB 'core', causing compensation of just the peripheral part of the mercury distribution. For these reasons alone, the central part of the impurity distribution in figure 4 is on the metallic side of the metal–insulator transition (MIT), providing a metallic mechanism of conductance. At the same time, the peripheral part of the mercury distribution is on the insulator side of the MIT, making possible hopping and/or percolative mechanisms.

In discussing the distribution of dopants around the GB in figure 4, it is necessary to take into account one more circumstance. Since the process of GB nucleation during expansion of the melted zone in the ingot is random, the type of the GBs differs substantially in different parts of ingot. Therefore, segregation processes at different GBs, i.e. the character of the distribution $N(x)$ (its 'width' and 'height'), will be profoundly different for different regions of the highly conductive GB layer.

The model presented in figure 4 can also explain the irreversible changes in the GB conductance (figure 3) caused by the application of electric fields $E > 100$ V cm^{-1}. Taking into account similar results exhibited for silicon bicrystals in [11], such irreversible changes in $\sigma(E)$ could be associated with the redistribution of dopants at and around GBs. This redistribution of dopant atoms in an inhomogeneous highly conductive GB layer is due to migration of mercury and antimony under the influence of ohmic overheating, the exposure to an electric field and the action of elastic forces. The character of this migration at a given value of the electric field depends on local gradients of dopant atoms at GBs, i.e. on peculiarities of the initial $N(x)$ distributions for every sample.

For all the above-mentioned reasons, this redistribution of dopants can result in both ordering of impurities and smoothing out of their concentration along a highly conductive GB layer. As a result, the distribution of dopants around GBs becomes more homogeneous and the highly conductive layer itself narrows due to the gathering of impurities by the GB 'core' [15]. These processes alone could be responsible for the decrease of the exponential conduction contribution (at least, its percolative part) and the above-mentioned irreversible fall of the common $\sigma(E)$ in figure 3. It is also not impossible that redistribution of mercury and antimony around the GB 'core' could change the ratio between the widths of regions 1 and 2 in figure 4 and therefore the relation of their contributions to the longitudinal GB conductance.

Now we try to correlate the results obtained on the influence of temperature and magnetic and electric fields on the GB longitudinal conductance in mercury-doped polycrystals and bicrystals of germanium. Firstly, we should note a particular behaviour of the carrier transport along GBs in polycrystals and bicrystals associated with a weak temperature dependence of the GB conductance at low temperatures. According to [9, 10], this behaviour is strong evidence of an essential role of the impurity segregation by GBs in the boundary carrier transport. Secondly, we should draw attention to a significant difference in behaviour between the $\sigma(T)$, $\sigma(E)$ and $\sigma(H)$ dependences for GBs in bicrystals, on one hand, and polycrystals, on the other. In particular, one distinctive property is the impossibility of finding a hopping channel in bicrystalline samples unlike the case for polycrystalline ones. A second feature consists principally of the difference in the behaviour of the $\sigma(H)$ dependences for low magnetic fields (<10 T): sub-linear (root-like) for polycrystals [9, 10] and super-linear for bicrystals

(figure 2). Therefore, the character of the conductance as a function of the magnetic field and the linearity of the I–V curves at temperatures lower than 10–15 K indicate merely the presence of a metallic channel for GB conductance in bicrystalline samples. On the other hand, for temperatures $T > 15$ K we can see some new mechanism of carrier transport with a linear temperature dependence of the conductance (figure 1).

The preceding results indicate that, during the zone-melting process, segregation of impurities at grain boundaries proceeds differently in bicrystalline and polycrystalline ingots. Moreover, the properties of a highly conductive GB layer in bicrystals are rather similar to those in polycrystalline samples influenced by high electric fields. In both cases, linear I–V characteristics and the predominance of the metallic (non-exponential) contribution in the conductance are observed. In accordance with the above arguments, this attests to a more homogeneous distribution of dopants (with identical 'widths' of $N(x)$ profiles) in the vicinity of the single GB in a bicrystal along all of its length. This is quite natural, because a single GB is planar and its crystallographic type does not change along its full length.

4. Conclusions

A study of the effect of temperature and magnetic and electric fields on the GB longitudinal conductance σ at low temperatures in mercury-doped polycrystals and bicrystals of germanium shows that the $\sigma(T)$, $\sigma(E)$ and $\sigma(H)$ dependences for GBs in polycrystals are determined by metallic and hopping mechanisms, and the hopping channel was not found in bicrystalline samples. The behaviour of the $\sigma(H)$ dependences for low magnetic fields (super-linear) and the linearity of the current–voltage characteristics at $T < 100$ K merely indicate the presence of the metallic channel in bicrystalline samples. All the above indicates that during the zone-melting process, the segregation of impurities at grain boundaries proceeds differently in bicrystalline and polycrystalline ingots. In other words, the characteristics of impurity distributions around and over the GB plane depends strongly on the number of GBs or, strictly speaking, on the pre-history of the ingot (specifically, on the speed of the melted-zone expansion during the crystal growth).

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