Mott spectroscopy of localized states in amorphous gallium antimonide

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The localization radius, $a \sim 20$ Å, and density of state at the Fermi energy, $g(E_F) \sim 1.5 \times 10^{19}$ $\mathrm{cm}^{-3}/\mathrm{eV}$, in bulk amorphous gallium antimonide a-GaSb synthesized under high pressure have been determined using Mott spectroscopy of localized states based on simultaneous measurements of conductivity vs temperature and magnetoresistance vs field in the hopping conductivity regime. Structural relaxation of a-GaSb due to stepwise isothermal annealing at $T_{an} \leqslant 120$ °C leads first to a simultaneous increase in the localization radius and density of states and, second, a shift of the mobility edge closer to the top of the valence band. In the origianl a-GaSb samples, the correlation length of the amorphous network and the localization radius are almost equal, $a \sim L_c \sim 20$ Å, and annealing leads to a considerable increase in the localization radius relative to the correlation length, $a \sim 4L_c$ at $T_{an} = 120$ °C. We propose a model relating changes in parameters of localized states to the increase in the number of structural defects, and to changes in the shape of the random potential due to relaxation of locally strained regions in the sample volume. © *1996 American Institute of Physics.* [S1063-7761(96)02507-3]

1. Amorphous semiconductors synthesized by quenching under pressure[1] occupy a special place among noncrystalline materials. Unlike conventional amorphous semiconductors, which are obtained by various deposition techniques,[2] the amorphous state of these materials is generated when a high-pressure metastable phase relaxes to normal conditions. Extensive research over the past decade[1,3–5] has demonstrated that this group of amorphous materials has highly unusual properties, such as amorphization-induced superconductivity.[4]

At the same time, some fundamental parameters characterizing electronic properties of the amorphous state, such as the electron localization radius a or the density of states at the Fermi level $g(E_F)$, have yet to be determined for this class of materials.

This paper addresses the experimental determination of these parameters, and the influence on them of structural relaxation of the amorphous network produced by isothermal annealing in the stability region of the amorphous phase.

2. For our research, we selected bulk samples of gallium antimonide (a-GaSb), whose synthesis technique and physical characteristics have been investigated in great detail.[4,5] In the case of a-GaSb,[5] two classes of materials can be manufactured, depending on the conditions of high-pressure synthesis. Samples obtained by the first technique contain a small admixture of the crystalline phase and, in addition, regions with non-stoichiometric composition with a typical dimension of about 200 Å, the local excess of gallium being responsible for the superconductivity of such samples.[4]

In the second case, the fractions of both crystalline and nonstoichiometric inclusions are negligible, and the sample is an essentially homogeneous amorphous network of a-GaSb. The low-temperature conductivity of such samples obeys Mott's law for variable-range hopping.[5]

We selected samples of the second kind for our research. A detailed description of synthesis conditions and characterization of the amorphous state appears elsewhere.[5]

Given Mott hopping conductivity, one can easily implement a spectroscopy of localized states near the Fermi level. In this case, the resistivity is

$$\rho(T) = \rho_0 \exp[(T_0/T)^{1/4}], \tag{1}$$

$$T_0 = 17.6/g(E_F)a^3 k_B, \tag{2}$$

and the positive contribution to the magnetoresistance due to wave function shrinkage in the magnetic field is

$$\ln \frac{\rho(H)}{\rho(0)} = t_1 a^4 H^2 (T_0/T)^{3/4}/c^2\hbar^2, \tag{3}$$

where $t_1 = 5/2016$.[6,7] Thus the parameter T_0 can be derived from the resistivity as a function of temperature [Eq. (1)], and the localization radius a can then be derived from Eq. (3). The density of states $g(E_F)$ is then given by Eq. (2).

But such an application of Mott spectroscopy to amorphous materials involves a number of problems. First, conventional amorphous films usually have high resistivity, so accurate measurements of conductivity and magnetoresistance at helium temperatures, where hopping conductivity shows up, are difficult. Second, in addition to the positive contribution to the magnetoresistance [Eq. (3)], there is a negative contribution due to quantum interference, which can be dominant under certain conditions.[8] Therefore the spectroscopy of localized states based on Mott's law has been applied to amorphous materials in only a few cases.[9]

From a theoretical standpoint, the problem is also far from simple, as it requires that electronic correlations be

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properly taken into consideration. In the case of Mott's law described by Eq. (1), it is sufficient to consider short-range Hubbard correlations.[7] In the presence of correlations, Eqs. (1)–(3) must be modified, yielding only a renormalized density of states and localization radius. It can be shown[9] that if Eq. (3) is taken to define the empirical localization radius a_H, the renormalized density of states $\tilde{g}(E_F)$ calculated using Eqs. (1) and (2) differs from the real density of states by a factor of order $(1+\delta)B^{1/4}(\delta,\xi)$, where $B(\delta,\xi)$ is Zvyagin's function[7] that takes into account corrections to the percolation criterion due to correlations. The parameter δ is a function of the Hubbard correlation energy U:

$$\delta = g(E_F - U)/g(E_F),$$

and ξ is the ratio of the localization radius to the localization radius in the upper Hubbard band[7,9]:

$$\xi = a/a_D \sim 1/4.$$

In experimentally studied materials, the condition $\delta \ll 1$ usually holds, and the principal reason for renormalization is the modification of the bond percolation criterion.[9] For example, at $\delta \sim 10^{-3}$ and $\xi \sim 1/4$, the correction factor for $g(E_F)$ is of order $B^{1/4} \sim 1/7$. The correction factor for a is of the same order[9]:

$$a \sim B^{1/4} a\,.$$

3. The experimental data on hopping conductivity in a-GaSb are plotted in Figs. 1 and 2. The initial rising parts of the $\rho(T)$ curves in Fig. 1 correspond to the activation energy $E_{ac} \sim 0.2$ eV, which is in agreement with previously reported data.[5] In the temperature range $T \leqslant 100$ K the curves in coordinates $\ln \rho = f(T^{-1/4})$ have extensive linear parts (Fig. 1). At liquid helium temperatures, in the hopping conductivity regime, the magnetoresistance contains both negative and positive contributions, and since the latter are significant, the asymptotic behavior $\ln[\rho(H)/\rho(0)] \propto H^2$ can easily be identified (Fig. 2).

Interestingly enough, the magnetoresistance in the activation temperature range $T > 100$ K is negative at a magnetic field of up to $H \sim 150$ kOe (insert in Fig. 2), which indicates that the positive contribution to the magnetoresistance is directly related to magnetic field-induced shrinkage of the wave function in the regime of variable-range hopping conductivity.

Since the sign of the thermal emf in the samples studied corresponds to p-type conductivity at all temperatures, we believe, based on the standard model of the density of states in amorphous materials,[2] that hopping transport in a-GaSb takes place in a band of intrinsic acceptor defects that is separated from the mobility edge in the valence band by a gap of about 0.2 eV. In this case, conductivity due to activation at the mobility edge is characterized by negative magnetoresistance (Fig. 2).

We now consider the effect of stepwise isothermal annealing on the parameters of hopping conductivity. The technique of isothermal annealing is described in detail elsewhere.[4] The annealing time at each temperature T_{an} was about 60 min. Note that the samples were annealed at temperatures $T_{an} \leqslant 120$ °C, at which the a-GaSb amorphous

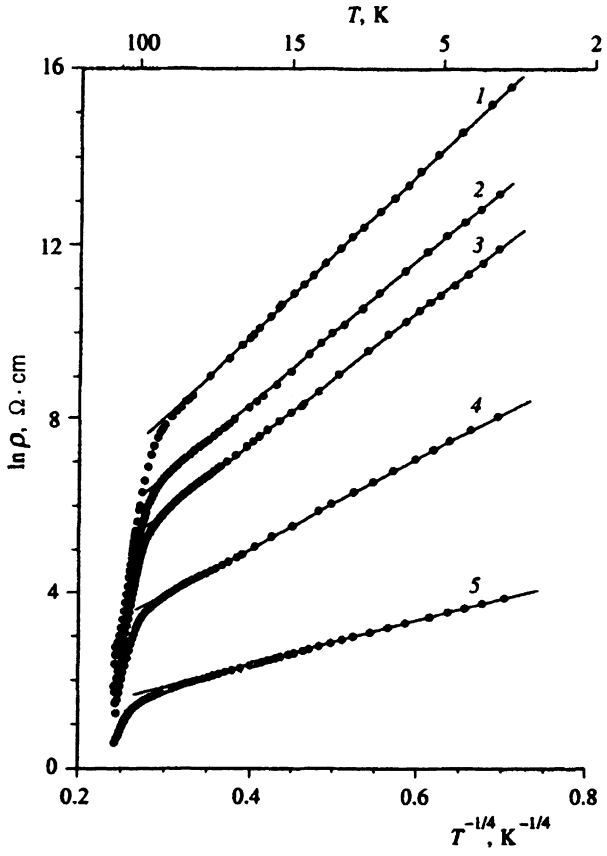

FIG. 1. Hopping conductivity in a-GaSb at different annealing stages. Numbered curves correspond to different annealing temperatures: (*1*) original sample; (*2*) 90 °C; (*3*) 110 °C; (*4*) 120 °C; (*5*) 130 °C.

phase does not transform to the crystalline one, and all changes in parameters of electronic states are due exclusively to relaxation processes in the amorphous network of a-GaSb. Furthermore, x-ray diffraction was used at all annealing stages to verify that there were no crystalline inclusions.

Figures 1 and 2 demonstrate that annealing changes both the linear parts of the curves $\ln \rho = f(T^{-1/4})$ and the asymptotic behavior $\ln[\rho(H)/\rho(0)] \propto H^2$. In the temperature range $T > 100$ K changes in the activation energy were also detected. We have derived the parameters a_H and $\tilde{g}(E_F)$ from the data of Figs. 1 and 2 using Mott spectroscopy techniques described in the previous section. These quantities and the activation energy E_{ac} are plotted as functions of the annealing temperature in Fig. 3.

It is noteworthy that both the localization radius a_H and density of states $\tilde{g}(E_F)$ increase simultaneously during annealing, which results in a considerable decrease in the parameter T_0 in Mott's law (Fig. 1). Note that the condition $a \approx$ const is usually assumed *a priori* when the region of stability of the amorphous phase in amorphous semiconductors is considered.

4. The increase in the density of states observed in this work (Fig. 3) is also quite unusual because it would be natural to expect that the concentration of intrinsic defects forming the band of localized states should be reduced, rather

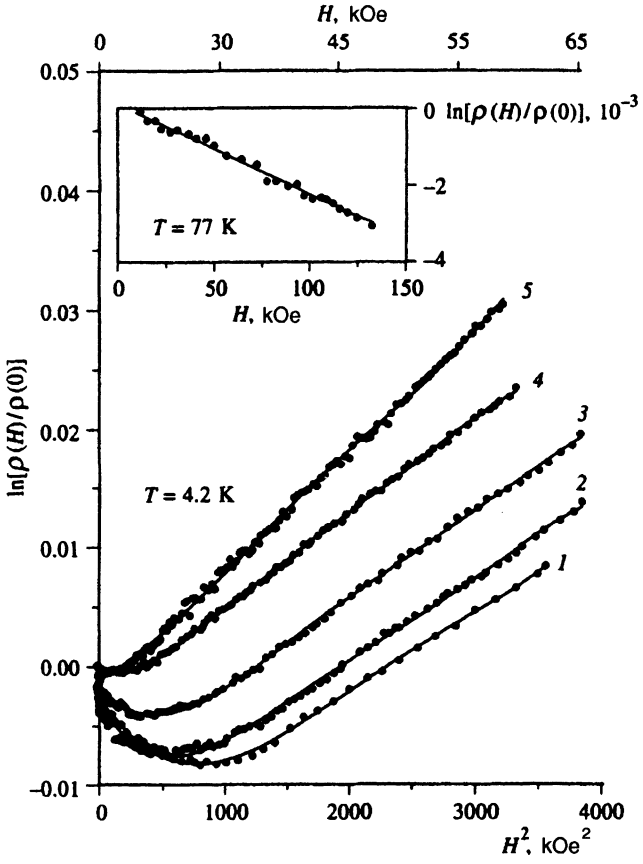

FIG. 2. Effect of annealing on magnetoresistance of a-GaSb in the regime of Mott hopping conductivity ($T=4.2$ K). Numbered curves correspond to the same temperatures as in Fig. 1. The insert shows the magnetoresistance curves at $T=77$ K (activation region at the mobility edge).

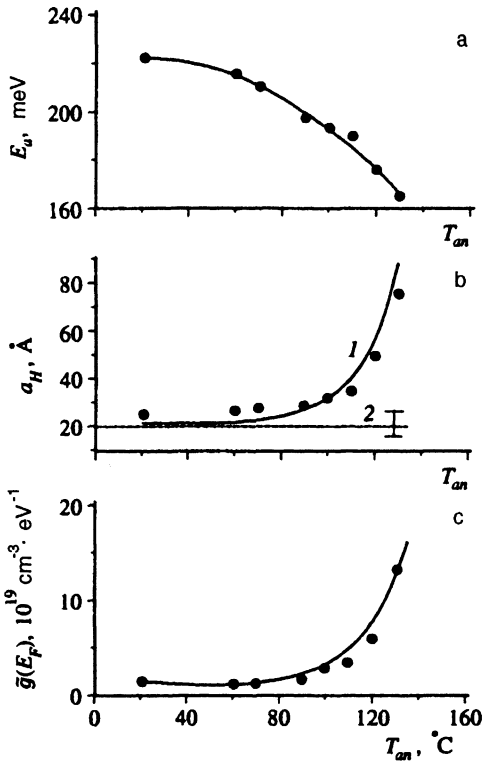

FIG. 3. Variations in parameters of electronic states in a-GaSb due to annealing: (a) activation energy; (b) (*1*) localization radius and (*2*) correlation length of the amorphous network; c) density of states.

than increased, by annealing. Since calculations with Eqs. (1)–(3) yield not a real, but renormalized density of states and localization radius, while the character of correlations can also change by annealing, the influence of correlation effects must, above all be evaluated.

It follows from the discussion above that

$$\tilde{g}(E_F)/a_H \sim (1+\delta)g(E_F)/a$$

and this ratio should not strongly depend on the bonding criterion given by the function $B(\delta,\xi)$. We suggest that the observed increase in a_H and $\tilde{g}(E_F)$ does not reflect a variation in the actual localization radius a and density of states $g(E_F)$, but that the similarity between a_H and $\tilde{g}(E_F)$ as functions of annealing temperature (Fig. 3) is due to the common correction factor $B^{1/4}(\delta,\xi)$.

It follows from the data given in Fig. 3 that the ratio $\tilde{g}(E_F)/a_H$ does not remain constant during annealing, but drops by a factor of about four at $T_{an}=120$°C as compared to the initial state of the sample ($T_{an}=20$ °C). Therefore the interpretation of the increase in a_H and $\tilde{g}(E_F)$ in terms of correlations demands a considerable change in the parameter $\delta=g(E_F-U)/g(E_F)$. By estimating the bandwidth Δ of localized states using the temperature of transition from activation to hopping conductivity (Fig. 1), one can easily obtain $\Delta\sim 10$–20 meV. On the other hand, since $a_D \gg a$, the parameters E_{ac} and U are usually comparable, and Fig. 3 indicates that $E_{ac}\sim U \gg \Delta$ over the full range of annealing temperatures studied here. Under these conditions, it seems unlikely that δ will vary appreciably.

Therefore the contribution of the Hubbard correlations to the functions $a_H(T_{an})$ and $\tilde{g}(E_F)=f(T_{an})$ is probably not decisive. We suggest that the data of Fig. 3 do indeed reflect real changes in the density of states and localization radius: $\tilde{g}(E_F)\approx g(E_F)$ and $a_H \approx a$.

Thus the relaxation of a-GaSb due to annealing leads to an increase in the density of states of intrinsic defects. This behavior can be explained by assuming that the local strains generated in the process of high-pressure synthesis persist in the amorphous network of a-GaSb. Relaxation of these strains under annealing can lead to an increase in the concentration of structural irregularities,[10] and, hence, to a higher density of states $g(E_F)$. This process can also generate charge carriers and change the filling of the localized-states band. If the Fermi level moves from the tail of the density of states closer to the peak, the localization radius will also increase. Note that the gap between the Fermi level and the mobility edge in the valence band (i.e., the activation energy E_{ac}) will decrease. Given that, according to Fig. 3, the change in the energy gap $E_c-E_F \approx E_{ac}$ is greater than 60 meV, and the estimated width of the band is 10–20 meV it is natural to suppose that structural relaxation in a-GaSb leads to a shift in the mobility edge closer to the top of the valence band. The proposed shape of the density of states and its variation due to annealing are sketched in Fig. 4.

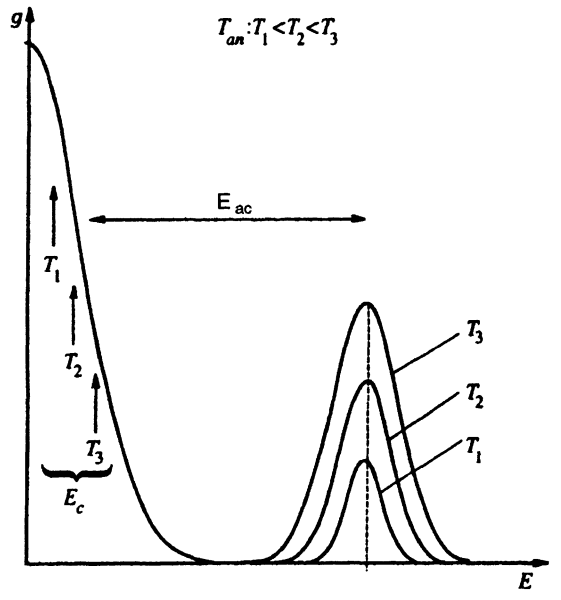

FIG. 4. Proposed shape of the density of states after annealing at different temperatures.

It is also interesting to compare changes in the localization radius to those in the amorphous network correlation length L_c. This parameter was derived from x-ray diffraction measurements.[4,5] We found that the parameter L_c is 20 ± 4 Å, and is independent of T_{an} within the experimental uncertainty (dashed line in Fig. 3). In the initial state L_c and a are essentially equal, and after annealing the localization radius is significantly different from the correlation length L_c, which determines the scale of fluctuations of the random potential $\varphi(\mathbf{r})$ in which charge carriers move. This indicates that the size of "hills" and "valleys" of the random potential are not so important as the characteristics of the barrier separating regions of size $\sim L_c^3$. If the potential $\varphi(\mathbf{r})$ becomes smoother after relaxation (the gradient of $\varphi(\mathbf{r})$ decreases), the barrier becomes more transparent, and as a result, the region accessible to an electron and the localization radius become larger. Similar effects in localization due to quantum interference were detected previously in doped semiconductors.[11] Note that the importance of quantum interference in formation of electron states in a-GaSb derives directly from the negative magnetoresistance in the regime of Mott variable-range hopping conductivity, which was observed in our experiments (Fig. 2), and the decrease in the amplitude of negative magnetoresistance due to annealing also finds a natural interpretation in a model with variable barrier transparency.[11] Higher transparency leads to lower intensity of the back-scattered wave, and as a result the amplitude of the negative magnetoresistance drops.

5. Summarizing the results of our research, we see that Mott spectroscopy of localized states can be applied to amorphous semiconductors synthesized under high pressure, and Hubbard correlations probably do not lead to appreciable renormalization of the measured parameters, such as the localization radius and density of states at the Fermi level.

Our investigation of structural relaxation in a-GaSb indicates that this process leads to an increase in both a and $g(E_F)$, which can be ascribed to an increase in the concentration of intrinsic defects upon relaxation of regions with local strains. At the same time, the mobility edge in the valence band shifts towards its top, as a result, of which the activation energy decreases. We have found that in the initial state of a-GaSb samples, prior to structural relaxation, the correlation length of the amorphous network is essentially equal to the localization radius: $a\sim L\sim 20$ Å, and after annealing the localization radius is notably larger than the correlation length.

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