Peculiarities of the impurity states in the narrow-gap lead telluride-based semiconductors

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Abstract. Starting from mid-70's, a great deal of both experimental and theoretical efforts has been attracted to the unexplained puzzle of impurity states arising in the IV–VI narrow-gap cubic semiconductors doped with some of the group III elements, and to the unusual effects observed in these materials. We review the experimental results obtained in the field: mixed valence phenomena, electrical activity of impurity centers, persistent photoconductivity and related effects. Some of the features of these semiconductors have provided the possibility of construction of the far-infrared photodetector with extremely high characteristics. The theoretical models proposed so far to account for the physical picture of the processes involved are discussed.

1. Introduction

Investigation of impurity states in the group III-doped narrow-gap IV–VI semiconductors based on the lead telluride has a long tradition in the former Soviet Union. It has started in early 70's [1] and has been extensively developed since that time. The unusual effects observed in these materials, such as persistent photoconductivity and photomemory — are quite analogous to the features of III–V and II–VI semiconductors with the DX-centers. The microscopic structure of the DX-centers in III–V is well established now both experimentally and theoretically [2, 3].

The origin of impurity states in the group III-doped IV–VI is still under discussion. There is a considerable difference from the effects due to the "classic" DX-centers in the relatively wide-gap III–V's and II–VI's. First of all, in the IV–VI's the same impurity can be either donor or acceptor depending on the specific composition of the semiconductor. The variable electrical activity of the III group impurities leads to the pinning of chemical potential. Beside that, the impurity centers in the IV–VI reveal the negative-U behavior independently on the impurity level position in the energy spectrum, in contrast to the DX-centers in III–V and

II–VI. Finally, the one-electron local states are hydrogen-like in III–V and II–VI, whereas they are mostly deep in IV–VI. These metastable local states play an important role in a range of strong and unusual non-equilibrium effects.

2. Mixed valence and electrical activity

Indium initially acts as a donor in PbTe providing the increase of a free electron concentration n [1], but then the value of n saturates. The saturation on the $n(N_{In})$ dependence corresponds to the Fermi level pinning. Additional doping with other impurities does not affect the Fermi level position E_F. Besides, E_F is not linked to the actual band edges [4–6].

The position of a pinned Fermi level in the energy spectrum can be changed by variation of the group III dopant. In PbTe(Ga) the Fermi level is pinned within the gap, and in PbTe(Tl) — rather deep in the valence band [4], and the group III element acts already as an acceptor. Moreover, even for the same dopant the position of E_F can be changed by variation of the lead telluride-based alloy composition. In the range of $Pb_{1-x}Sn_xTe$(In) solid solutions the pinned Fermi level shifts to the bottom of the conduction band with increasing x, crosses the gap and enters the valence band, acting therefore as an acceptor [7].

3. Theoretical models of impurity states

Indium is expected to reveal an acceptor behavior in IV–VI since it substitutes metal. However it can obviously act both as a donor and as an acceptor. According to the idea proposed in [8], indium reveals a negative-U behavior, i.e. the neutral with respect to the lattice state In^{2+} is unstable and dissolves to the donor and acceptor states: $2In^{2+} \rightarrow In^{+} + In^{3+}$. Polarization of the impurity environment is a reason for this reaction.

The clear microscopic picture of the processes involved has been proposed in [9-12]. Due to high values of a dielectric constant ($\varepsilon \sim 10^3$) and to small effective masses ($m \sim 10^{-2} m_e$) the Coulomb potential of an impurity is effectively screened, and the short-range potential gives the main contribution to the formation of an impurity energy spectrum. The short-range character on a potential allows to use in the calculations the averaged over the Brillouin zone characteristics of the energy bands, which may be most easily calculated using the tight-bind approximation. The theory is based on the idea of a “pra-phase”, where the IV–VI lattice is considered as a cubic lattice with a superimposed doubling potential due to the chemical difference of the group IV and group VI atoms that form the valence bonds constructed from the atomic p-orbitals. Three filled by half bands originating from the overlapping atomic p-orbitals arise in the “pra-phase”. The

doubling potential provides appearance of the gap in the IV–VI spectrum just at the Fermi energy. The real electronic spectrum may be calculated by taking into account the spin-orbital interaction and the overlapping of the p-orbitals of a non-neighboring atoms.

Understanding of the origin of the actual bands in IV–VI gives a key for the solution of the problem of mixed valence of the group III elements. This element replacing the metal atom can exist in three atomic configurations — one-valent s^2p^1, two-valent s^1p^2 and three-valent s^0p^3 [12]. p-electrons participate in the formation of the actual bands, so therefore the element is acceptor in the first case, neutral impurity in the second one, and donor in the third case. Realization of the particular valence of an impurity atom depends on the Fermi level position E_F. When the total energy of the s^0p^3 and the s^2p^1 configurations becomes equal, the Fermi level is pinned. The total energy of the neutral with respect to the lattice s^1p^2 configuration is higher than E_F, thus the impurity effectively reveals the negative-U behavior. The valence switching corresponds to the transfer of electrons from- and to the deep s-shell, therefore the group III element can reveal electrical activity of both donor and acceptor type.

4. Long-term relaxation processes

Most of attention to the group III-doped IV–VI has been attracted due to the long-term relaxation processes observed in these semiconductors at the low temperatures $T \ll T_c$ under the action of different external factors — infrared illumination [13], magnetic field [14], electric field [15]. The value of T_c is about 25 K in the case of indium doping and about 80 K for the gallium impurity. For the In-doped alloys a strong persistent photoresponse is observed at $T < 25$ K independently on whether the Fermi level is pinned in the allowed band or in the gap. This point makes a substantial difference from the case of the DX-centers in III–V's, where the persistent photoconductivity is observed only when the DX-level lies in the gap [2].

Kinetics of the persistent photoconductivity decay is also unusual. Two parts of the photoconductivity relaxation are observed: the fast part is followed by the slow one [4–6]. The characteristic time τ of the fast process is (1 ms–1 s) whereas for the slow part τ may exceed 10^5 s at the low temperatures. The value of τ for both processes only slightly depends on the temperature when $T \ll T_c$ indicating a non-activation mechanism of relaxation. One more argument in support of this statement is the non-exponential character of both fast and slow relaxation. The rate of the slow relaxation process depends on the history of preceding photoexcitation [5].

5. Local metastable states

The experimental data clearly show that the processes involved cannot be explained if one takes into account only one local state providing the Fermi level pinning. Indeed, observation of two parts of the relaxation curve give a direct indication for the existence of at least two different local states in the energy spectrum of the semiconductor.

In the case of the group III-doped IV–VI's the excited local states are separated by a potential barriers from both ground impurity states and the extended electron states, in contrast to the situation with the DX-centers in III–V's where the excited local states there are shallow. Metastability of the excited local electron states results in an appearance of a range of unusual effects not observed in materials with the "classic" DX-centers.

The giant negative magnetoresistance with an amplitude exceeding 10^6 in some cases has been observed in $Pb_{0.75}Sn_{0.25}Te(In)$ where the Fermi level is pinned in the gap [16]. The explanation proposed in [16] assumes trapping of the injected electrons on the metastable one-electron impurity states $E_1(s^1p^2)$. Application of a magnetic field pushes the E_1 states above the conduction band bottom thus providing electron delocalization.

The idea developed in [12] allows to propose the alternative origin of impurity states responsible for the giant negative magnetoresistance effect. The empty impurity centers (s^0p^3) give rise to a short-range attractive potential that in turn provides splitting of an impurity $(p\text{-like})$ state from the conduction band bottom. Electron localized in this state can have a somewhat different g-factor compared to the conduction band electrons. Therefore application of the magnetic field may push the electrons trapped on this level into the conduction band.

This idea has been further developed in [17] to account for appearance of the long-term non-equilibrium effects at low temperatures. According to this idea, the metastable one-electron impurity states $E_1(s^1p^2)$ lie rather high in the conduction band. The two-electron excitation is forbidden in the first approximation, therefore the transfer of excited electrons from the extended to the ground two-electron local state can proceed only through the one-electron metastable local state. So trapping of excited electrons to the ground state goes in two steps: first one electron must localize on an impurity center, and only after that this center can trap a second electron and transfer to the ground state. The first step implies increase in the center energy, therefore an effective barrier is formed between the ground state and the extended electron state. One can see that no considerable lattice relaxation is needed in this mechanism.

Application of a strong and short $(< 10\mu s)$ microwave pulses to the

$Pb_{1-x}Sn_xTe(In)$ samples results in a complete quenching of the persistent photoresponse [18]. Moreover, if the persistent photoconductivity is quenched by the microwave pulses of a minimal necessary power, the quantum efficiency η of a material increases up to $\sim 10^2$, whereas out of this regime $\eta \sim 1$. Application of the short microwave pulse leads to the localization of electrons to the metastable local state. Some of the metastable centers may form a cluster with strong internal interaction. Excitation of one electron from this cluster leads to the avalanche excitation of other centers providing the increase of a quantum efficiency.

6. New type of the far-infrared photodetectors

Unusual features of the group III-doped lead telluride-based alloys have provided the possibility of construction of the sensitive far-infrared radiometer. The persistent photoresponse in combination with the possibility of fast resetting of an accumulated signal together with the quantum efficiency stimulation provides a giant increment in the signal-to-noise ratio and in a current responsivity of a photodetector. This approach has been realized in [19]. Despite the measurement technique was far from being sensitive (the lowest detectable current only 10^{-7} A) the photon flux of 10^5 ph/s and the power of 10^{-16} W at $\lambda = 18\mu$m have been detected for the operating rate of 3 Hz, the current responsivity was no less than 10^9 A/W. Application of a more advanced measurement technique would definitely improve the NEP value.

Direct comparison of performance of the state of the art Si(Sb) and Ge(Ga) far-infrared photodetectors with a photodetector based on $Pb_{1-x}Sn_xTe(In)$ has been performed in [20, 21]. In these experiments, the same cryogenics and readout electronics has been used for both doped group-IV photodetectors and the $Pb_{1-x}Sn_xTe(In)$ sample. It has been shown that the responsivity of the $Pb_{1-x}Sn_xTe(In)$ photodetector is by 3–7 orders of magnitude higher than for its doped group-IV counterparts, depending on the operating wavelength. Strong persistent photoresponse has been observed in $Pb_{0.75}Sn_{0.25}Te(In)$ at the wavelengths of 90, 116 μm [20] and 176, 241 μm [21]. These wavelengths correspond to the radiation quantum energy, that is considerably lower than the ground impurity state activation energy. It means that the metastable impurity states are responsible for this photoresponse. The cut-off wavelength of this photoresponse is at least higher than 241 μm that is the highest red cut-off wavelength observed so far for the quantum detectors of radiation. It is likely that the operating range of the $Pb_{1-x}Sn_xTe(In)$-based photodetectors covers the whole submillimeter region.

The group III-doped lead telluride-based photodetectors have extremely high radiation hardness $\sim 10^{17}$ cm^{-2} [22]. This value is by 10^4 times higher than for

the other far-infrared photodetectors.

Specifics of impurity states makes very easy the construction of a focal-plane array on $Pb_{1-x}Sn_xTe(In)$. The local infrared illumination leads to the local generation of the nonequilibrium free electrons [23]. So one may construct the focal plane array in which the signal is internally integrated by every effective element. There exists an idea of a simple information readout [19].

Summary

Doping of the lead telluride-based alloys with some of the group III impurities, such as indium or gallium, results in an appearance of the unusual impurity states in these narrow-gap IV–VI semiconductors. In contrary to the DX-centers in III–V's and II–VI's the impurity centers in IV–VI exhibit the negative-U behavior independently on the position of a DX-level in the semiconductor energy spectrum. Another circumstance of a crucial importance is existence of a barrier between excited one-electron local impurity state and both ground two-electron local state and state of an electron in the conduction band. Presence of these barriers results in an appearance of a range of unusual non-equilibrium effects that are absent in the case of "classical" DX-centers, where the one-electron local states are shallow.

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«Металлическая» проводимость, переход металл–диэлектрик и сопуствующие явления в двумерной электронной жидкости

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Две лекции на названную тему являются введением в сравнительно молодую область исследования свойств сильно-коррелированных и разупорядоченных двумерных систем заряженных фермионов. Будут рассмотрены результаты экспериментальных исследований проводимости, магнитосопротивления, спиновой восприимчивости, спиновой намагниченности и эффективной массы, перенормированных межэлектронным взаимодействием и беспорядком.

План лекций

1. Моттовская полуклассическая картина перехода металл–диэлектрик.