Novel Superconducting Semiconducting Superlattices: Dislocation-Induced Superconductivity?

N. Ya. Fogel, A. S. Pokhila, and Yu. V. Bomze
Institute for Low Temperature Physics and Engineering, 47 Lenin Avenue, Kharkov 310164, Ukraine

A. Yu. Sipatov and A. I. Fedorenko
Kharkov Polytechnic University, Kharkov 310002, Ukraine

R. I. Shekhter
Department of Applied Physics, Chalmers University of Technology, S-412 96, Goteborg, Sweden
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Novel superconducting superlattices with transition temperature in the range 2.5–6.4 K consisting only of semiconducting materials are discovered. Among them there are multilayers, including a wide-gap semiconductor as one of the components. It is shown that superconductivity is connected with the interfaces between two semiconductors containing regular grids of the misfit dislocations. The possibility of the dislocation-induced superconductivity is discussed.

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The first attempts to fabricate artificial superlattices (SL), consisting of alternating thin layers of a superconductor and some insulating material, were inspired by the expectation to obtain high transition temperature T_c due to the excitonic mechanism of superconductivity [1]. The great body of the experimental data showed that the T_c of the artificial multilayers as a rule does not exceed the transition temperature of the superconducting films constituting SL [2]. As a single exception the semiconducting superlattices PbTe/PbS and PbTe/SnTe revealing T_c up to 6 K [3–5] may be considered. Appearance of superconductivity in these SLs looks rather fascinating because it is inherent only to the multilayered compositions, while the materials constituting SLs are not superconductors (with the only exception being SnTe having a T_c value of 0.22 K [6]). Single thin films of Pb and Sn chalcogenides ($d \leq 150$ nm) do not reveal superconductivity either [4,7]. The suggestions explaining the origin of superconductivity in semiconducting SLs are rather controversial [3–5], and not one of them can be considered as satisfactory. One of the assumptions is rather trivial and it relates the superconductivity in a PbTe/SnTe system with the Pb precipitates [3]. This explanation cannot be excluded for those particular SLs because of the specific way of sample preparation (extra Pb was condensed simultaneously with semiconductors). In [5], superconductivity of a PbTe/PbS system is explained as a strain-induced effect arising due to the band inversion in PbTe and to the appearance of interfacial electronic states. Finally, in Refs. [4,9] the regular grids of the misfit dislocations on the interfaces of the epitaxial PbTe/PbS SLs is regarded as a phenomenon related to the superconductivity. The validity of this idea was confirmed in our further experiments. The full superconducting transition occurs only on SLs with continuous dislocation grids, i.e., on the samples with large thicknesses d_1, d_2 of the layers. On the thin layer SLs ($d_1, d_2 \leq 8$ nm), where only the islands of disconnected dislocation grids are observed (see Ref. [4]), only the partial superconducting transitions take place. An additional indication pointing out the essential role of the dislocations follows from the data [9]. It was shown that the layers responsible for superconductivity are located on interfaces between two semiconductors.

Based on the assumption discussed, we tried to find other superconducting compositions consisting of the monochalcogenides of Pb, Sn, and rare earth metals with NaCl structure. Such a choice is associated with the fact that all of these compounds are isomorphic, and interfacial misfit dislocations should appear during the epitaxial growth of the alternating layers of these materials. The idea has turned out to be fruitful, and here we report on the discovery of four new superconducting "members" in a class of semiconducting SLs. Among them are even the SLs which include wide-gap semiconductors.

Samples were grown on two types of substrates. Mostly the samples were grown epitaxially on a cleaved (001) face of KCl single crystals by the method described in Ref. [9] for SLs PbTe/PbS. Preparation of other SLs does not differ in any essential detail from one used in the case of PbTe/PbS. To exclude possible sources of uncertainties, such as the superconductivity in PbTe doped by Pb [8], we used only stoichiometric compounds for evaporation, and single films of PbTe, PbS, and PbSe were also prepared. All single films ($d \leq 300$ nm) appeared nonsuperconducting. Some of the SLs were condensed on the (0001) face of mica. All SLs contained ten bilayers. Three-layer sandwiches were prepared as well. The necessity to study sandwiches was dictated by the fact that, for the heterostructures studied the problem of structural stability is very serious. Their degradation is mainly caused by elastic stresses arising around the interfaces [10]. The value of the stresses depends on the misfit $f = 2(a_1 - a_2)/(a_1 + a_2)$ between crystal lattice parameters a_1 and a_2 in two compounds. At the initial stage of the epitaxial growth

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the stresses are rather large. However, when the thickness of the growing layer exceeds critical magnitude d_c the partial stress relaxation takes place due to the formation of misfit dislocations or, in a less favorable case, due to the mechanical destruction of the sample [10]. The stresses diminish essentially with the appearance of the misfit dislocations, but the complete relaxation of the stress cannot be attained [11]. The less the misfit f, the higher the level of the stress retained until large d [11]. For samples with a small amount of layers the risk of the destructive scenario becomes less. This is why for some compositions only sandwiches were successfully tested for superconductivity.

The list of the systems studied is presented in Table I. In Table I the experimental values of the dislocation grid periods D_g obtained by the transmission electron microscopy method are shown as well. In another column the calculated D_g values are presented obtained by the formula $D_g = |\vec{b}_e|/f$ [12]. Here $\vec{b}_e$ is a projection of the edge component of misfit dislocation Burgers vector on the interface. It appears that the experimental data on D_g are in good agreement with the expected values. The dislocations have not been observed in sandwiches PbS/EuS with the small misfit $f = 0.6\%$ and calculated $D_g = 74$ nm. All low temperature measurements have been carried out by a resistive method with four-probe geometry. The T_c values were determined at a middle point of the resistive transition. We will refer to the samples that do not reveal superconductivity at $T \geq 1.5$ K as nonsuperconducting samples. For PbTe/PbS SLs the resistance ratio $r = R_{300\,\mathrm{K}}/R_n$ varies in a range 1.5–10.7, while, for new superconducting SLs, $r = 2.1$–4.5. Any correlation between the T_c and r is absent. The x-ray diffractometry data obtained in the $\theta - 2\theta$ scanning mode show that only the lines of (h00) type are present for all compounds in SLs and for KCl. The data of other special scan modes, allowing one to get the reflections from the crystal planes with different (hkl) values, testify that all crystallographic directions in substrate and in SL components coincide.

Before reporting on the T_c of the novel superconducting SLs we will describe some properties of the PbTe/PbS system which may be of importance for the further presentation of our results. Figure 1 shows the T_c dependence on the thickness d_{PbS} for the samples PbTe/PbS. In this figure the data for symmetric SLs with $d_{\mathrm{PbS}} = d_{\mathrm{PbTe}}$, asymmetric ones with $d_{\mathrm{PbS}} \neq d_{\mathrm{PbTe}}$, and sandwiches are shown. For asymmetric samples $d_{\mathrm{PbTe}} = 12$ nm. There is a sharp T_c increase in the d_{PbS} range 7.5–20 nm. At $d_{\mathrm{PbS}} >$ 40 nm the T_c shows a tendency to saturation. Figure 1 shows that the T_c's for different types of samples practically coincide. It is an important observation because, due to the various stabilities of different compound combinations, we will need to compare the T_c of the samples with various layer amount. The T_c's of asymmetric SLs and sandwiches with the constant value of $d_{\mathrm{PbS}} = 12$ nm and variable d_{PbTe} are practically independent on d_{PbTe}. For the explanation of the T_c behavior the additional data on another combination of semiconductors are necessary, and it will be presented elsewhere.

Taking into account the results for the PbTe/PbS system we investigated the properties of SLs and sandwiches of different compositions with equal thicknesses of two semiconducting films ($d_1 = d_2 = 100 \pm 10$ nm). The resistance dependences on temperature for some samples prepared on KCl are shown in Fig. 2. The typical $R(T)$ dependence for the extended range of temperatures is shown in the inset of Fig. 3. The T_c values of the layered systems under consideration are presented in Table I.

Four new compositions with T_c in the range 2.5–6.4 K have been discovered. Among them there is one new heterostructure consisting of two narrow-gap semiconductors (PbS, PbSe) such as in the previously known superconducting semiconducting SLs. Some SLs including one narrow-gap and one wide-gap semiconductor (YbS, EuS), also reveal superconductivity. It is the first observation of superconductivity in such a layered semiconducting system.

Table I also reveals other noteworthy features: (i) The samples consisting of only two semiconductors with wide gaps are not superconducting in spite of the presence of dislocation grids. (ii) For superconducting compositions

TABLE I. Parameters of the semiconducting SLs.

System	Misfit f (%)	D_g nm (calc)	D_g nm (exp)	T_c K
PbTe/PbS	8.3	5.2	5.2	6.03
PbTe/SnTe	2.0	23.0	23–25	2.97
PbS/PbSe	3.16	13.5	13.5–14	4.59
PbTe/YbS	13.0	3.3	3.3	5.93
PbS/YbS	4.8	8.5	8.5–8.8	6.39
PbSe/EuS	2.5	17.0	18.0	2.48
YbS/EuS	5.3	7.7	7.7–7.8	No
YbS/YbSe	3.83	10.6	11–12	superc.

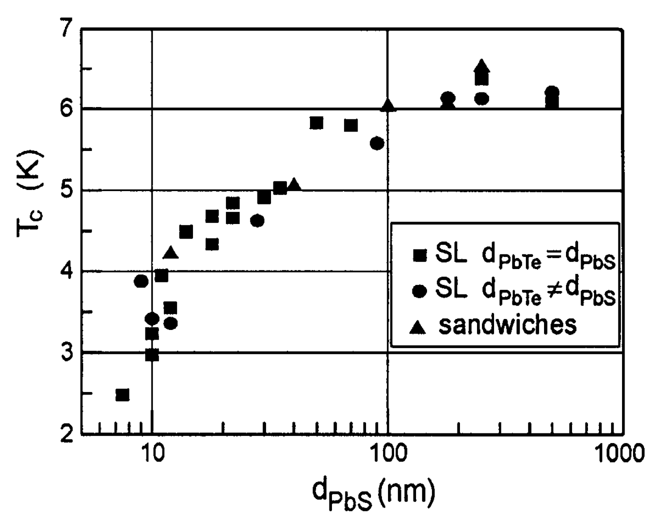

FIG. 1. Transition temperature as a function of d_{PbS} for PbTe/PbS layered samples.

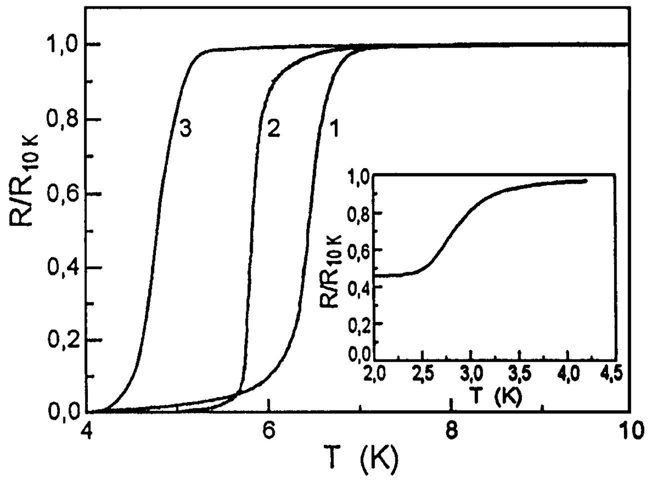

FIG. 2. Resistive transitions for semiconducting SLs and sandwiches. 1—PbS/YbS; 2—PbTe/YbS; 3—PbS/PbSe. Inset: resistive transition for PbTe/PbS SL with $d_1 = d_2 = 7$ nm.

there is a correlation between T_c values and the period of the misfit dislocation grid (it is also shown in Fig. 3). In the D_g range, 3.3–8.6 nm, there is practically no dependence of T_c on the interdislocation distance. At $D_g > 10$ nm the reduction of T_c is observed with D_g increasing. These data may be considered as evidence that Tc depends on the density of the dislocations at the interface.

From our point of view, for the understanding of the origin of superconductivity in the investigated layered structures, one of the crucial points is to determine all possible correlations between dislocations and superconducting properties. The best way to clarify this point is to compare the heterostructures with and without dislocations. Unfortunately, we were not successful with low temperature measurements on the PbS/EuS system [13], where dislocations are absent. These samples are very unstable, and the cracks destroying continuity of the samples appear just after their preparation. Such instability is characteristic for compound combinations with small f values [10]. However, the measurements on the samples where dislocation grids have island-type structure also give important information. Two types of PbTe/PbS samples with such dislocation structure have been studied: thin layer SLs and SLs prepared on mica. In the first case, when the ratio of the layer thickness to a critical one is not very large, only islands of the dislocation grid appear; they become continuous at d, noticeably larger than d_c. In the case of SLs prepared on mica, there is no good epitaxy, and the samples consist of blocks with two different orientations (with the axes [001] and [111] normal to the layer planes). In this case island-type dislocation grids cover only a small part of the interfaces over the crystallites with [001] texture. In both cases only partial superconducting transitions occur (see, for example, inset of Fig. 2), while, if the grid is continuous, one observes a full superconducting transition (with the sensitivity allowed by experimental setup: on different samples with $R_n = 4$–200 ohm we can detect the values of $R/R_n = 2 \times 10^{-4}$–5×10^{-6}). These facts most probably imply that superconducting phase may form a disconnected island system.

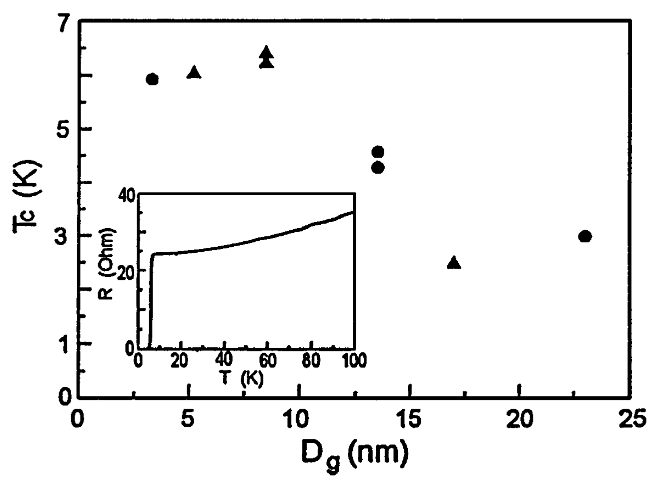

FIG. 3. T_c as a function of the dislocation grid period. Inset: resistance as a function of temperature for PbS/PbSe SL.

There is another experimental fact attracting attention to the dislocations as to a phenomenon related to superconductivity. In an earlier study of PbTe/PbS symmetric SLs it was shown that superconducting layers in this system are confined to the interfaces between two semiconductors [9]. This conclusion follows from the measurements of the critical magnetic fields. On these SLs typical for multilayers dimensional crossover is observed in a field parallel to the layers. From crossover field $H_{cr} = \phi_0/\pi\gamma D^2$ [$\gamma = (dH_{c\parallel}/dT)/(dH_{c\perp}/dT)|_{T_c}$ is an anisotropy parameter], one may calculate the wavelength D [14] which is usually defined as $D = d_1 + d_2$. We have found that the superstructure period determined from H_{cr} on symmetric SLs is 2 times less than that obtained from x-ray diffractometry. It means that the repeating distance between the centers of the superconducting layers is equal to the individual semiconductor film thickness, but not to the bilayer thickness $d_1 + d_2$, as it is for all conventional SLs. This means that the layers responsible for superconductivity are located on all interfaces. The latter contain dense grids of misfit dislocations.

All of the data presented lead to the suggestion that the origin of superconductivity in the semiconducting SLs may be associated with the dislocations. We believe that for the explanation of the superconductivity origin in semiconducting heterostructures two circumstances should be taken into account. Dislocation in a semiconductor is able to capture the charge carriers; their motion along the dislocation is infinite, while the motion in the plane orthogonal to the dislocation line is finite [15]. As was shown in Ref. [15], the dislocation energy band arises, and the width of this band may be comparable with that of conducting or valence bands; the overlapping of the dislocation band with bands of semiconductors is possible. Actually, the "dislocation doping," similar to that from impurities, occurs [16]. In this case the carrier concentration and their distribution in the semiconductor is determined by dislocations. If dislocations are parallel to each other, the conductivity along dislocation lines is essentially higher than in any other direction. In our case, it is the interfaces that should be the regions of high conductivity. From Table I it follows that the presence of dislocations is not the only condition necessary for the appearance of superconductivity. A narrow-gap semiconductor should be present as a source of electrons for the dislocation band. For such compositions a typical for metals dependence $R(T)$ is observed (Fig. 3).

On the other hand, in the intrinsically superconducting materials the dislocation strain fields may lead to the formation of localized superconducting domains, surrounding the dislocations, at a temperature higher than the "bulk" transition temperature T_{c0} [17,18]. At large dislocation density the superconducting domains may be coupled due to a proximity effect, giving rise to global enhancement of T_c [18]. In Ref. [17] the T_c enhancement $\triangle T = T_c - T_{c0}$ is obtained for a single dislocation line in a conventional superconductor. If the dislocation density N is small the effect from all superconducting domains is summed. In a case of large N all the set of dislocations may be considered as a "superdislocation" with the Burgers vector $N\vec{b}$. The approach used in [17] does not permit one to obtain the numerical results for this situation. However, the authors state that the dislocation-induced superconductivity as one of the possibilities may be considered. We suggest that is a case for the investigated semiconducting SLs. In our compositions the high density of dislocations exists in the interfacial areas. We have varied the dislocation density and the continuity of the dislocation system, changing the semiconductor and substrate materials and the thickness of the layers. As Fig. 1, the inset of Fig. 2, and especially Fig. 3 show, in all of the cases the average dislocation density reduction leads to the deterioration of superconductivity. Experimental observations allow us to suggest that superconducting layers are confined to the interfaces [9], and superconductivity appearance is due to the specific interface state conditioned by the dislocations.

It should be mentioned that in some SLs, according to x-ray diffractometry data, the precipitation of Pb was observed. However, there is no correlation between the presence of free Pb and the appearance of superconductivity. In particular, free Pb has never been observed in the PbTe/YbS system. In the combination PbTe/PbS, in some cases the weak lines of Pb appear after several months of aging, but superconductivity is observed in fresh samples without precipitates. Thus, the origin of superconductivity cannot be attributed to the Pb segregation. The systematic dependences of the T_c on the layer thickness (Fig. 1) and on the dislocation grid period (Fig. 3) also rule out the trivial explanation of the superconductivity appearance due to the Pb precipitates. The features mentioned are in an obvious controversy with irregular behavior expected in a case when noncontrolled Pb precipitation occurs. Also, the idea about the essential role of the band inversion [5] may hardly be relevant. Necessary for inversion the large strain fields can arise only in the case of pseudomorphic interface conditions [5], but due to the presence of misfit dislocations such strains cannot be reached.

In summary, we have first discovered superconductivity in four semiconducting layered systems: PbS/PbSe, PbS/YbS, PbTe/YbS, and PbSe/EuS. This resulted from the purposeful search of superconducting semiconducting SLs which was based on the idea that the appearance of superconductivity should be associated with the dense dislocation grids saturating the interfaces in the epitaxial layered structures. The new superconducting systems, along with the previously known ones, form a new class of SLs differing in many respects from all conventional multilayers. It is suggested that the dislocation-induced change in electronic and elastic properties in the interfaces may be responsible for the appearance of superconductivity. The correlations between interfacial dislocation structure and the superconducting properties are discussed. The results obtained enable one to predict the probability to find superconductivity in other semiconducting heterostructures. For example, superconductivity may be expected in such SLs as PbTe/EuS, PbTe/EuSe, etc.

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