PHYSICAL REVIEW B **73**, 161306(R) (2006)

Direct evidence for interfacial superconductivity in two-layer semiconducting heterostructures

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(Received 16 February 2006; published 25 April 2006)

We have discovered superconductivity in the two-layer semiconducting monochalcogenide heterostrutures PbTe/PbS, PbTe/PbSe and PbTe/YbS. By comparing data from two-layer samples with data from single monochalcogenide films we conclude that the superconductivity is connected with the interface between the two semiconductors. Evidence for the low dimensional nature of the superconducting interlayer is presented and a model that explains the appearance of single-interface superconductivity is proposed.

DOI: 10.1103/PhysRevB.73.161306 PACS number(s): 68.35.−p, 68.65.−k, 71.55.Ht, 74.78.Fk

One of the main objectives of modern solid state physics is to produce and characterize composite materials designed on the nanometer length scale. Such composites often reveal unexpected properties, which are not characteristic of the constituent materials. The epitaxial monochalcogenide semiconducting superlattices (SLs), which reveal superconductivity at low temperatures, certainly belong to this category.

The first observations of superconductivity in the semiconducting SLs PbTe/PbS and PbTe/SnTe were reported as early as in the 1980s.[1,2] However, no essential further progress was made until recently, when five new superconducting monochalcogenide multilayered structures were discovered: PbS/PbSe, PbTe/PbSe, PbS/YbS, PbTe/YbS, and PbSe/EuS.[3,4] The transition temperatures $T_c \sim 2.5$–6.4 K for this class of heterostructures are rather high for semiconductors.

For an explanation of superconductivity in these SLs various mechanisms have been proposed. Among them are the formation due to the interdiffusion of ultrathin Pb films at the interfaces or of Pb precipitates, the influence of pseudomorphic conditions at the boundary between the two constituent materials,[5] and the influence of misfit dislocation grids that form at the interface between two isomorphic compounds during epitaxial growth.[2–4,6] The last idea appears to be the most fruitful and guided us towards the discovery of superconductivity in the five additional monochalcogenide SLs mentioned. Experimental results suggest that superconductivity in these SLs most likely is confined to the interfaces between semiconducting layers.[4,6] The theory[4] indicates that superconductivity in epitaxially grown semiconducting SLs is due to the band inversion in narrow gap semiconductors of the PbS type caused by elastic deformation fields created by edge misfit dislocation (EMD) grids; inversion layers near the interface form multiply connected periodic nets.[4]

Different groups have tried to create superconducting *two-layer* monochalcogenide heterostructures, but despite a lot of effort the question of whether superconductivity can be observed in a single-interface structure has not been answered until now. Several authors have even concluded that a three-layer sandwich is the minimal structural block revealing superconductivity.[7,8]

Naively, it seems obvious that if interfaces in multilayered heterostructures can be superconducting, so should the single interface in a two-layer heterostructure (2LH). However, experimental data[7,8] have contradicted this conjecture, which is difficult to explain within the model of dislocation-induced superconductivity. Turning to experiments is therefore the best way to answer the challenging question whether superconductivity is possible in 2LHs and whether it is indeed connected exclusively with the interface. We have made experiments on two-layer sandwiches with considerably thicker layers than in Refs. 7 and 8, where they did not exceed 20 nm. The motivation for working with thick layers is based on our experience that the superconducting transition temperature T_c in SLs depends on the film thickness d;[3,4] in the range 10–100 nmT_c increases rather quickly with thickness, while for $d > 100$ nm its value saturates at approximately 6 K. This approach has indeed led us to the discovery of interfacial superconductivity in two-layer sandwiches with a single interface.

In this paper, we present experimental evidence for the superconductivity of individual interfaces between nonsuperconducting materials (PbTe, PbS, PbSe, and YbS). The observed T_c is rather high, and unlike individual monochalcogenide films the two-layer heterostructures usually reveal metallic conductivity in the normal state. We found that the superconducting properties of PbTe/PbS, PbTe/PbSe, and PbTe/YbS sandwiches differ in many respects from those of SLs with the same composition. The difference is most likely related to the low-dimensional nature of the superconducting interfacial layer in 2LHs. The radical difference between individual films and 2LHs makes it quite clear that it is the presence of an interface that gives rise to superconductivity in the latter case.

We have mainly studied symmetric two-layer sandwiches (i.e., $d_1 = d_2$, where $d_{1,2}$ is the thickness of an individual layer) with layers 40–300 nm thick. The same method was used for preparing 2LHs as previously for the condensation of SLs.[4,6] Samples containing the narrow-gap semiconductors PbTe, PbS, and PbSe were grown by thermal evaporation of the constituent materials from tungsten boats. For the evaporation of YbS an electron gun was used. Several individual films of PbTe, PbS, and PbSe were also made. For substrates we used cleaved KCl single crystal (001) surfaces heated to 520–570 K. This choice guarantees epitaxial growth of the two semiconducting layers of a 2LH and the formation of an EMD grid at the interface between them. The existence of dislocation grids was confirmed by electron microscopy transmission (TEM), electron diffraction, and x-ray diffraction experiments. No particles, due to segregation of Pb or other substances, could be detected (the resolution was about 0.8 nm). Neither did the electron diffraction patterns contain any Pb reflections. X-ray diffraction results showed Pb reflections only in some PbTe/PbS samples and in some PbS single films. We have earlier shown[4] that there is no correlation between the presence of Pb reflections and the appearance of superconductivity.

Resistance measurements were performed with a standard four-probe technique in the temperature range 0.3–300 K using a standard ^{3}He cryostat equipped with a 5 T magnet. Selected temperatures were stable to within 10^3 K and the parallel orientation was identified by finding the minimum resistance. Transition temperatures and critical magnetic fields were defined from the resistive transitions by the criterion $R=0.5R_n$. Sheet resistances of all the 2LHs at 10 K were in the range 10–500 Ω. The critical currents I_c were defined at the level 15 μV.

In most 2LHs we observed a temperature dependence of the resistance R typical for normal-state metals, while for individual monochalcogenide films $dR/dT<0$ untill 0.3 K. In 2LHs the ratio $r=R_{300}/R_n$ was 1.6–8, and all samples became superconducting with $T_c s$ in the range 2.6–5.6 K, i.e., lower than for multilayered compositions of the same materials (5.8–6.5 K). For the thinnest 2LH, with $d=40$ nm, $T_c=0.4$ K, and the transition appeared incomplete at 0.3 K. For this sample dR/dT is negative above T_c. In the case of multilayered structures, a complete superconducting transition is usually observed when $d_{1,2}\geqslant 10$ nm. Comparing data from 2LHs and SLs we conclude that the presence of additional interfaces serves as a stabilizing factor for the structure of layers responsible for superconductivity.

We found the features of the superconducting state in two-layer samples to be strikingly different from what is usually observed in multilayers. While the superconducting transitions in semiconducting SLs are always rather sharp (at most 0.1–0.3 K) they are very broad—always more than 2 K—in all two-layer samples investigated (Fig. 1). Probably, this broadening is due to the low-dimensional nature of the superconducting layers.

As shown in Fig. 2 the anisotropy of the upper critical magnetic field H_{c2} is very large. The coherence length $\xi(0)$, obtained from the derivative of the perpendicular critical field in the vicinity of T_c, is 20–40 nm depending on sample. The data obtained in magnetic fields may also be considered as evidence for the two dimensionality of the superconducting layers. In SLs the behavior of the parallel critical field $H_{c\parallel}$ in the vicinity of T_c is three dimensional $[H_{c\parallel}\sim(T_c-T)]$. It crosses over to two-dimensional (2D) behavior as the temperature is lowered (Fig. 7 in Ref. 4). In the case of a single interface the 2D behavior of the parallel critical field $[H_{c\parallel}\sim(T_c-T)^{1/2}]$ is apparent already at T_c. Moreover, in some of 2LHs unusual features in the form of a rather sharp divergence of $H_{c\parallel}(T)$ at low temperatures are observed (Fig. 2). This may be a manifestation of a 2D-one-dimensional (1D) crossover. Such a crossover should be characteristic, according to theory,[9] for superconducting filamentary ensembles. An anomalous upward curvature is observed in fields perpendicular to the layers, too (inset in Fig. 2), as may be expected for superconducting filaments.[9] These results strongly indicate that the superconducting layer at the interface has a multiconnected form, consisting of two ensembles of superconducting filaments crossing each other at right angles. All these data support the assumption that one deals with dislocation-induced superconductivity in the interfacial layers with a periodic structure of inhomogeneities.

One may estimate the thickness d_{sp} of the superconduct-

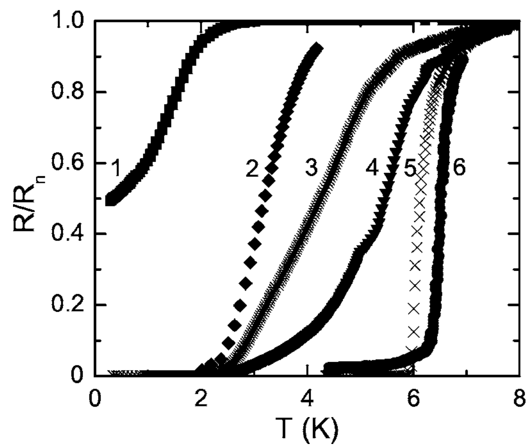

FIG. 1. Normalized resistance R/R_n as a function of temperature T for six PbTe/PbS heterostructures. Data are plotted for five 2LHs of different thickness $d_{1,2}=40$ nm (1), 100 nm (2), 80 nm (3,4) and $d_1=200$ nm, $d_2=40$ nm (6) and one SL, $d_{1,2}=120$ nm (5). Note that the widths of the superconducting transition for the thin 2LHs are much broader than for the SL.

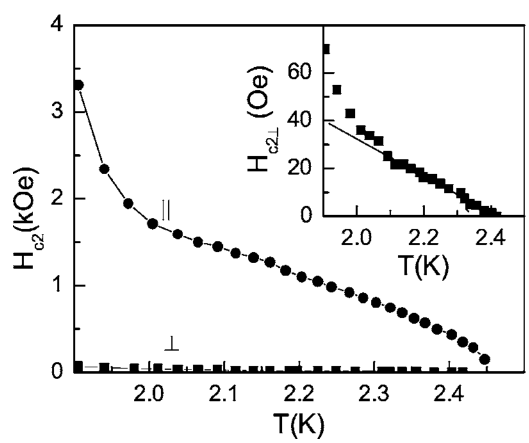

FIG. 2. Upper critical magnetic field H_{c2} for fields parallel (‖) and perpendicular (⊥) to a PbTe/YbS 2LH of thickness $d_{1,2}=100$ nm as a function of temperature T. The T dependence of $H_{c\parallel}$ shows 2D behavior except at low T where a rather sharp divergence may signal a 2D-1D crossover. Inset: $H_{c\perp}$ as a function of T.

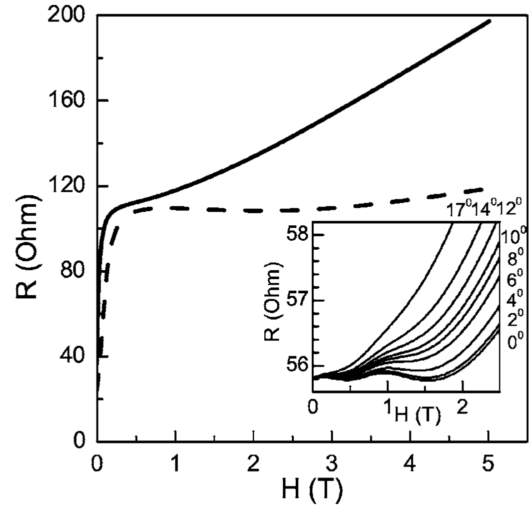

FIG. 3. MR in the normal state of a PbTe/PbS 2LH of thickness $d_{1,2}=200$ nm in parallel (dashed curve) and perpendicular (full curve) fields illustrating the strong and anisotropic MR effect found in 2LHs. The inset shows the oscillatory MR anomaly found for different field directions in a PbTe/PbSe 2LH with $d_{1,2}=100$ nm possibly due to a conducting layer with multiconnected topology.

ing layer in 2LHs from measured critical magnetic-field values by using the Ginzburg formula $d_{sp}^2=6\Phi_0 H_{c\perp}/\pi H_{c\parallel}^2$ valid for homogeneous superconducting films. Such estimates cannot, however, be precise in our case for two reasons: it is not always easy to single out the linear part of the temperature dependence of $H_{c\perp}(T)$, and the superconducting layers are evidently not homogeneous. Nevertheless they do give an effective value $d_{eff}=d_{sp}=20-30$ nm for the thickness of the superconducting layers. For PbTe/PbS superlattices we obtained $d_{sp}=10-30$ nm (recent study and Ref. 6). A comparison between d_{eff} and the coherence length $\xi(0)=20-40$ nm shows that the inequality $d_{sp}\ll\xi(T)$, usually accepted as a criterion for superconducting films to be two dimensional, is fulfilled for 2LHs at practically all temperatures where measurements were made.

Magnetoresistance (MR) measurements in the normal state provide further evidence for the two dimensionality of the superconducting layers in 2LHs. The MR in parallel and perpendicular fields is considerable and quite anisotropic as expected in 2D (Fig. 3). In some 2LHs a MR oscillation-type anomaly appears in relatively weak fields (inset in Fig. 3). The origin of this anomaly may be associated with a multiconnected topology of the conducting layer, but cannot be explained quantitatively without more data. However, it is clear that this phenomenon is hard to explain in terms of precipitated Pb.

Figure 4 shows the critical current I_c for 2LH samples of thickness $d=80-120$ nm. They reveal full superconducting transitions. The critical current per layer for SLs with similar d values are shown for comparison. Clearly, the critical current of two-layer sandwiches and of multilayered samples do not differ markedly if $d\geqslant 100$ nm. For 2LHs with $d=80$ nm the critical currents are significantly smaller than for SLs, as may be expected if the EMD grid structure contains weak links.

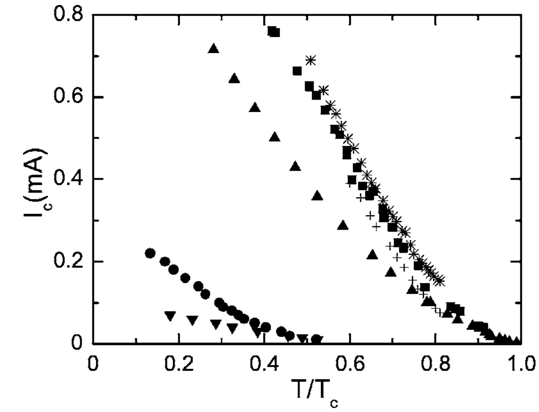

FIG. 4. Critical current as function of T/T_c for PbTe/PbS two-layer sandwiches (square and cross—$d_{1,2}=100$ nm, circle and down triangle—$d_{1,2}=80$ nm) and for PbTe/PbS SL's (star—$d_{1,2}=100$ nm, up triangle—$d_{1,2}=120$ nm). For SLs the critical current is calculated per interface.

Comparing the two types of heterostructures, we find that superconductivity in single-interface structures appears for larger semiconducting layer thicknesses than in the SLs. This observation, as well as the very fact that T_c depends on layer thickness,[3,4] appears to contradict the idea that superconductivity is an entirely local interfacial phenomenon. However, simple physical considerations allow one to explain this seeming contradiction.

For an explanation one has to take into account the sources of the misfit dislocations and the kinetics of the EMD grid formation. Both have a crucial influence on how perfect an EMD grid that will form and, consequently, on the superconducting properties. There are two sources of EMDs. Most important is the free surface—thought to be an unlimited source of dislocations—of the growing second film. However, dislocations formed during the growth of the first layer also participate in the grid formation, creating a "background" for the ordering of the misfit dislocations that arrive from the free surface. This is a particularly significant process for a single-interface layer. The initial mixture of MDs formed by the two mechanisms should slow down the process of perfecting the MD grid until the layer thickness is large. Correspondingly, a full superconducting transition in PbTe/PbS 2LHs appears only when $d\sim 80$ nm.

Also, the higher density of imperfections in the EMD grid in the first interface may be connected with a random and simultaneous nucleation of islands of grids. According to our TEM studies and Ref. 10 this occurs when the top layer thickness is about 5 nm. As they grow, neighboring islands merge with no possibility for the EMDs to line up properly. Hence, an imperfect EMD grid is formed, which may contain Josephson weak links. In SLs the presence of a previous interface and its EMD grid makes it easier for more perfect EMD grids to form on subsequent interfaces. For a sample containing many interfaces, the first imperfect interface becomes unimportant. This is why superconductivity in multilayered systems appear for thicknesses as small as 10 nm.[4]

One notes that the thicker the first layer is, the more perfect a single crystal it is, and the more perfect is the EMD grid that appears at the 2LH interface.[11] To verify this we prepared a 2LH with a 200 nm thick first PbTe layer and a 40 nm PbS top layer. For this sample $T_c=6.5$ K, as shown in Fig. 1, while $T_c=0.4$ K for a sample with $d_{1,2}=40$ nm. This proves that the imperfect first layer of a 2LH, which causes imperfections in the EMD grid, is responsible for the low values of T_c and I_c found in thin two-layer heterostructures.

Elastic deformations created by EMD grids near the interphase boundaries are the main reasons for metallic conduction and superconductivity in layered semiconducting systems.[4] They reduce the band gap E_g and cause band inversion in the narrow-gap semiconductors PbTe, PbSe, and PbS, for which $E_g < 0.3$ eV.[12] Inversion layers[13] appearing as a result of periodically distributed deformations connected with the EMDs should be inhomogeneous.[4] This leads to the conclusion that the surface formed by band inversion points in the narrow-gap film should have a multiconnected periodic shape. From the experimental results reported here it follows that the same concept can equally well be applied to samples with a single interface. However, in 2LHs the superconductivity, being a "local" phenomenon confined to the interfacial area, is more strongly influenced by the surrounding material, mainly the substrate and its effect on the structure of the interface.

In summary, we have discovered superconductivity in two-layer monochalcogenide semiconducting heterostructures (2LHs) with a single interface. To the best of our knowledge, this is the only unambiguous observation of interfacial superconductivity made. A comparison between the properties of 2LHs and individual semiconducting monochalcogenide films provides direct evidence that the superconductivity in two-layer sandwiches is due to an interfacial layer with specific structural properties connected with the presence of EMD grids. It becomes especially obvious that superconductivity is a dislocation-induced phenomenon in the case of a 2LH consisting of narrow-gap (PbTe) and wide-gap (YbS) semiconductors. The only essential difference resulting from the deposition of the top YbS layer, which is insulating, is the appearance of dislocations at the upper boundary of the PbTe layer.

All features of the superconducting state in 2LHs that we observed (transition width, behavior of the critical magnetic fields) and of the magnetoresistance in the normal state testify to the low-dimensional nature of the interfacial superconducting layer. The widely differing values of T_c and I_c in 2LHs and SLs of the same materials are explained by the intrinsic imperfection of the interfacial EMD grid located closest to the substrate. Subsequent interfaces in multilayered heterostructures contain more perfect EMD grids, and this leads to higher values of T_c and I_c for SLs. Improving the bottom epitaxial single crystal monochalcogenide layer in a 2LH has consequences, too. The crystal structure becomes more perfect the thicker the bottom layer is; hence, for a sufficiently thick first layer the superconducting properties improve as for sample 6 in Fig. 1. These observations explain the previous failures to observe superconductivity in too thin two-layer sandwiches.

We thank A. I. Fedorenko for stimulating discussions. Support from the Israel Science Foundation, Grant No. 351/99, (N.Y.F., E.I.B.), the Fundamental Researches State Fund of Ukraine, Grant No. F8/307-2004, (O.I.Y., M.Y.M.), and the Swedish KVA is gratefully acknowledged.

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[13] Inversion layer here refers to a layer of metallized zones close to the surface containing band inversion points.