

Quantum size effects in PbSe quantum wells

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In PbSe epitaxial thin films grown by thermal evaporation on KCl(001) substrates and covered with an EuS protective layer, oscillatory dependences of the galvanomagnetic and thermoelectric properties (electrical conductivity σ , the Hall coefficient R_H , charge carrier mobility μ , and the Seebeck coefficient S) on the PbSe layer thickness d ($3 < d < 200$ nm) were observed at room temperature. Oscillations of the transport properties are associated with quantum size effects due to electron confinement in the PbSe quantum wells. © 2002 American Institute of Physics.

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Among the various systems under current investigation, low-dimensional structures have attained considerable theoretical and experimental attention.^{1,2}

It is well known^{1,2} that an electron subsystem changes its properties qualitatively when the size of that system in at least one direction becomes comparable to both the mean free path and to the de Broglie wavelength of the carriers. In this case, the electron movement in that direction becomes quantized and causes changes in the energy spectrum and properties. Theoretical predictions³ for an oscillatory behavior of the thickness dependences of the transport and thermodynamic properties due to the quantization of the energy spectrum in thin films and subsequent experimental evidence⁴ in Bi semimetallic layers stimulated an interest in looking for quantum size effects (QSEs) in thin films. By now, a great number of works have been devoted to studying oscillations of the transport properties as a result of the QSE in thin films, but the objects of the majority of studies have been semimetal and metallic films (see, for example Refs. 4–11). There are far fewer studies of the oscillatory behavior of the transport coefficients in semiconducting thin films. However, the probability of observing QSEs in semiconducting films is higher than in metallic layers since the Fermi energy ϵ_F in semiconductors can be rather low, whereas the Fermi wavelength λ_F is larger.

The present study is on PbSe, a semiconductor from the group IV–VI compounds, which are widely used for optoelectronic and thermoelectric applications. Interest in these compounds has been stimulated by the observation of a high thermoelectric figure of merit ZT in IV–VI superlattices (SLs),^{12–14} which was previously predicted theoretically.^{15–17} Still higher values of ZT were obtained in quantum dot SLs with PbSe as one of the constituents.¹⁸ The interpretation of the properties of SLs requires detailed information about

their constituents. QSEs observed in a single quantum well (QW) should be separated from QSEs associated with the periodicity of the sequence of wells and barrier layers in SLs.

Available works on the QSE in IV–VI thin films are devoted mainly to the quantization of space-charge layers at the PbTe surface.^{19–22} In PbTe/EuS bilayers we observed²³ pronounced extrema in the dependences of the transport properties on the PbTe layer thickness at $d \sim 50$ nm.

The goal of the present work is to study the room temperature dependences of the electrical conductivity σ , the Hall coefficient R_H , charge carrier mobility μ , the Seebeck coefficient S on the PbSe layer thickness d in (100)KCl/PbSe/EuS structures. EuS, a wide gap semiconductor, plays a dual role, both as a barrier layer and as a coating, protecting the underlying PbSe from oxidation. Our studies revealed an oscillatory dependence of the transport properties on d . We attribute these oscillations to the manifestation of QSEs in the PbSe QW.

The PbSe/EuS bilayers were prepared by thermal evaporation of PbSe, electron-beam evaporation of EuS in vacuum $\sim 10^{-6}$ Pa, and deposition onto (001)KCl surfaces at (570 ± 10) K, d was varied in the 3–200 nm range, at a fixed EuS layer thickness of ~ 30 nm. The structure of the samples was studied by transmission electron microscopy (TEM). R_H and σ were measured, using a conventional *dc* method. The charge carrier concentration n was determined assuming the Hall factor to be 1. The error in the measurement of R_H , σ , and S did not exceed 5%.

TEM studies showed that PbSe films grow epitaxially on (001)KCl according to the vapor-crystal growth mechanism.²⁴ The film growth started with the formation of islands. At $d \sim (4–10)$ nm, the films had a semicontinuous channel structure, and at $d > 10$ nm, the films were practically continuous. EuS also grew epitaxially on the PbSe surface in a (001) orientation.

In Figs. 1 and 2, the dependences of σ and μ (Figs. 1(a)

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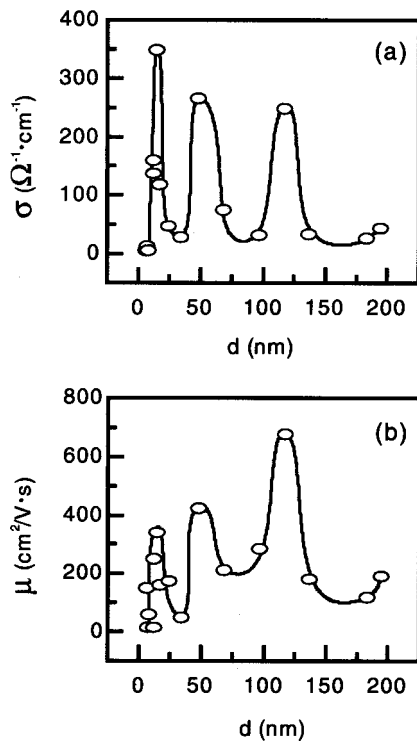


FIG. 1. Room temperature dependencies of the electrical conductivity σ (a) and the charge carrier mobility μ (b) on the PbSe layer thickness d in (100) KCl/PbSe/EuS bilayer structures. Curves are plotted through the experimental data points.

and 1(b)), n , and S (Figs. 2(a) and 2(b)) on d are presented.

A measurable electrical conductivity first appears at $d \sim 5$ nm and sharply increases with increasing d , reaching its maximum near $d \sim 14$ nm. At this d value, maxima in n , σ ,

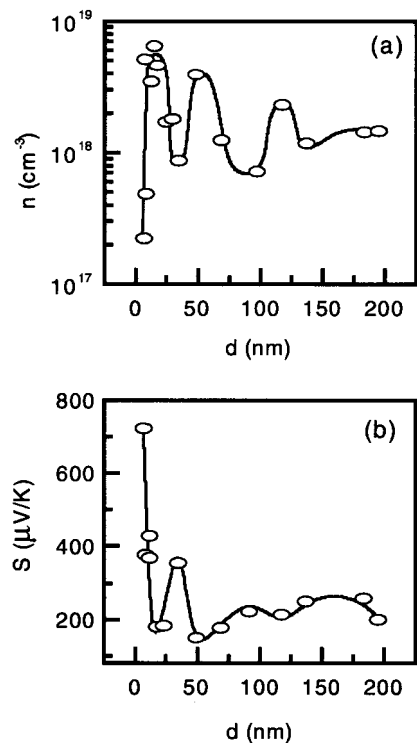


FIG. 2. Room temperature dependencies of the carrier density (a) and the Seebeck coefficient S (b) on the PbSe layer thickness d in (100) KCl/PbSe/EuS bilayer structures. Curves are plotted through the experimental data points.

and μ are seen, corresponding to minima in S . A further increase in d leads to an oscillatory behavior for each parameter.

In the $\sigma(d)$, $\mu(d)$, and $n(d)$ curves, three distinct maxima and three minima are observed. In the $S(d)$ curve, the maxima and minima are less distinct. The distance Δd between the first two maxima in the $\sigma(d)$, $n(d)$, and $\mu(d)$ curves and the first two minima in the $S(d)$ curves is (35 ± 3) nm, whereas the distance between the second and the third maxima and the corresponding minima is doubled (70 ± 5) nm. The observed differences in the two oscillation periods Δd may be due to the lack of experimental data points for $d = (50-100)$ nm. It should be noted, however, that although σ , n , and S were measured independently in all the d -dependent studies, distinct oscillations with approximately the same periods were observed for all the variables.

The simplest explanation of the oscillatory character of these d dependences is the manifestation of QSEs. The PbSe thin film sandwiched between two insulators—KCl and EuS, provides a QW within which carriers are effectively confined. This leads to a quantization of the transverse component of the quasi-momentum and the formation of subbands. As d increases, the number of populated subbands N changes in a jumplike fashion: every time that d increases by $\lambda_F/2$, a further subband drops below ϵ_F , and becomes conducting. This interrelation between d and N leads to an oscillatory behavior of the physical properties.¹⁻⁴

Making a number of simplifying assumptions, specifically, assuming isotropic and parabolic carriers, a specular character for the carrier scattering, both barriers to be identical and to have infinite barrier heights, and the absence of impurities and other defects, one can then make an approximate estimate of Δd and N , using the formulas¹⁻⁴

$$\Delta d = \frac{h}{\sqrt{8m^*\epsilon_F}}, \quad (1)$$

$$N = \frac{2d}{\lambda_F} = \frac{2d}{h} \sqrt{2m^*\epsilon_F}. \quad (2)$$

Of course, such a model can be used only for rough estimates, not taking into account that the energy bands in the lead salts are anisotropic, with ellipsoidal constant energy surfaces having two effective mass components (longitudinal and transverse), and a nonparabolic dependence of the charge carrier energy on quasi-momentum at sufficiently high energies.²⁵ Moreover, the model of an infinitely deep QW does not take into consideration either the specific band structure nor the nonidentity of the barriers at the interfaces. Certainly the film contains both volume and surface defects, such as Se vacancies or Pb interstitials acting as the suppliers of conduction electrons to undoped PbSe.²⁵

Knowing the effective masses of the charge carriers in n -PbSe ($m_t^* = 0.04m_0$, $m_l^* = 0.07m_0$ ²⁵) and having estimated the ϵ_F corresponding to the mean electron concentration observed in the films studied in this work ($n \approx 1.5 \times 10^{18} \text{ cm}^{-3}$),²⁶ one can roughly estimate the oscillation period using Eq. (1), obtaining $\Delta d = 27$ nm, which is in reasonable agreement with the experimentally measured oscillation

period $\Delta d = (35 \pm 3)$ nm. An approximate estimate of N based on Eq. (2) yields $N=2$ for $d=50$ nm, and $N=4$ for $d=100$ nm.

According to theoretical calculations²⁷ for a perfect film, within a single subband, an increase in d leads to a decrease in the density of states ($g(E) \sim 1/d$), to yield a linear increase in the relaxation time τ and in the charge carrier mobility μ ($\tau \sim d, \mu \sim d$). If we attribute the increase in μ and σ to populating a subband, it is shown that a simultaneous increase in n is observed.

The first theoretical study of the QSEs in thin films^{27,28} and a later study²⁹ were related to films with perfect surfaces. However, a number of authors have pointed out the significant role played by the surface roughness scattering in QWs.^{9,30–38} It was shown that scattering-induced level broadening suppresses QSE oscillations, and can lead to deviations from the $\lambda_F/2$ period, and even to a metal-insulator transition with decreasing d . Taking into consideration the high sensitivity of the QSE to the surface quality, one can conclude that the clearly observed oscillations in PbSe films provide evidence for a high structural perfection of the studied films. Combined with the specular character of the carrier scattering, which is typical of the PbSe surface,³⁹ favorable conditions for observing the QSE are created. It can be also concluded from the experimental results that under certain conditions (a sufficiently high charge carrier density and a sufficiently low m^*) the observation of a QSE is quite possible even for epitaxial films growing in the island fashion.^{40–42}

The fact that the QSE is already manifested at room temperature may imply, on the one hand, a rather high degree of structural perfection in the films, and, on the other hand, possible effects due to other factors. One can suggest that electron processes accompanying size quantization may affect the lattice subsystem by stabilizing the structure at critical d values satisfying the quantization conditions. The recent studies of the mechanism of metallic film growth on an insulator^{43,44} support this proposition.

In conclusion, oscillatory dependences of the transport properties of (100)KCl/PbSe/EuS epitaxial structures on the PbSe layer thickness were obtained at room temperature. The observed oscillations are attributed to the quantization of the electron energy into discrete subbands as a result of the two-dimensional confinement in the growth direction.

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