

Percolation transition of thermoelectric properties in PbTe thin films

E. I. Rogacheva, I. M. Krivulkin, O. N. Nashchekina, A. Yu. Sipatov, and V. A. Volobuev
Kharkov State Polytechnic University, 21 Frunze Street, Kharkov 61002, Ukraine

M. S. Dresselhaus^{a)}
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 6 October 2000; accepted for publication 30 January 2001)

Extrema were observed in the film thickness d dependence of various thermoelectric parameters (Seebeck coefficient S , electrical conductivity σ , Hall coefficient R_H , charge carrier mobility μ , and power factor P) of epitaxial PbTe/(001) KCl thin films prepared by thermal evaporation in vacuum and protected from oxidation by an EuS layer. We attribute the observed extrema in properties and the high values of μ and P at $d \approx 50$ nm to the percolation transition from an island-like to a continuous film and to the self-organization of the islands, which can occur not only in quantum dot superlattices but also in an individual layer. © 2001 American Institute of Physics.

[DOI: 10.1063/1.1357809]

Lead telluride (PbTe) is considered to have great potential for thermoelectric applications.^{1,2} Recently, interest in PbTe has been stimulated by theoretical predictions³ and subsequent experimental observations^{4–7} of the possibility of significant enhancement in the thermoelectric figure of merit ZT in superlattices (SLs) based on IV–VI compounds. New prospects for applications of IV–VI compounds were opened up by the first observation of semiconductor quantum-dot (QD) SLs.^{8–11} The spontaneous formation of three-dimensional (3D) islands on the epitaxial surface in the strained-layer heteroepitaxial growth of IV–VI compounds has become a new way of preparing self-assembled QDs.^{11–14} A large increase in ZT has been reported¹⁵ in QD SLs based on PbTe.

The spatial distribution of the dots, their size, and their shape determines to a great extent the potential of a particular material for QD device applications. This stimulates interest in studying the island mode of thin film growth and the factors which affect the density, size, and distribution of the islands. In a number of studies^{11–14,16–18} vertical ordering of the dots has been reported in QD SLs. Data on the lateral ordering of QDs are significantly scarcer and the factors controlling this type of ordering are not yet clear. Holy *et al.*,¹³ on the basis of theoretical calculations of the elastic interaction among the dots in QD SLs, related the effectiveness of the lateral ordering for the elastic anisotropy of materials, pointing out that IV–VI compounds have sufficiently high elastic anisotropy to self-order. Tersoff *et al.*¹⁶ found that, with the growth of successive layers, the size and spacing of the QDs become more uniform. It was established that the lateral and vertical correlation of the dots only occurs over a limited range of SL periods.^{11–14} The question arises: Is the lateral ordering of QDs possible in a single layer or can it be observed only in QD SLs?

The goal of the present work is to study the dependences of the thermoelectric properties of PbTe/(001) KCl thin films on the PbTe film thickness d . It is known¹⁹ that epitaxial growth of PbTe on (001) KCl always starts in a three-

dimensional Volmer–Weber growth mode and that the transition from island growth to a continuous film occurs at $d_i \approx 100$ nm. We have found that there is a narrow interval of thickness in the vicinity of $d = 50$ nm where the electrical conductivity σ , charge carrier mobility μ , and power factor $P = S^2\sigma$ (S is the Seebeck coefficient) all have maximum values. Taking into account the high values of μ at $d \approx 50$ nm ($\mu_{77\text{K}} = 30\,000$ cm²/V s), the observed dependences on d can be explained by the self-organization of the islands during the percolation-type transition from an island-like to a continuous film.

Thin films of PbTe ($d = 5–250$ nm) were prepared by the thermal evaporation of PbTe in vacuum ($10^{-5}–10^{-6}$ Pa) and the deposition onto (001) KCl surfaces at temperatures of 520–570 K. The condensation rate and d were monitored with a calibrated quartz resonator. The stoichiometry and its homogeneity were verified by controlling the process parameters and characterizing the samples after preparation. To protect the PbTe films from oxidation, they were covered with an EuS layer, 30 nm thick, which has been shown²⁰ to protect a PbTe film completely from oxidation. Being a wide-gap semiconductor, EuS makes a negligible contribution to the conductivity. The Hall coefficient R_H and σ were measured at 300 K using a conventional dc method and a magnetic field of 0.8 T. Six ohmic contacts were prepared by soldering indium to the film surface. The error in the R_H and σ measurements did not exceed 5%. The Hall mobility was calculated as $\mu = R_H\sigma$ and the charge carrier concentration n was determined as $n = A/(R_He)$, assuming the Hall factor A to be 1. S was measured with regard to copper with an accuracy of $\approx 3\%$. All the films had n -type conductivity, with n in the range of $1.6 \times 10^{17}–4 \times 10^{18}$ cm⁻³.

In Figs. 1 and 2, the d dependences of the thermoelectric properties of PbTe thin films at 300 K are presented. The values of σ , μ , R_H , and S for PbTe “thick” films ($d > 150$ nm) correspond to those of bulk PbTe crystals.^{1,2} In the $\sigma(d)$ and $\mu(d)$ curves, clear maxima are seen at $d \approx 50$ nm, and the maximum $S(d)$ in Fig. 1(b) correlates well with $R_H(d)$, as expected. Assuming the presence of only one type of charge carrier, parabolicity of the conduction band,

^{a)}Electronic mail: millie@mgt.mit.edu

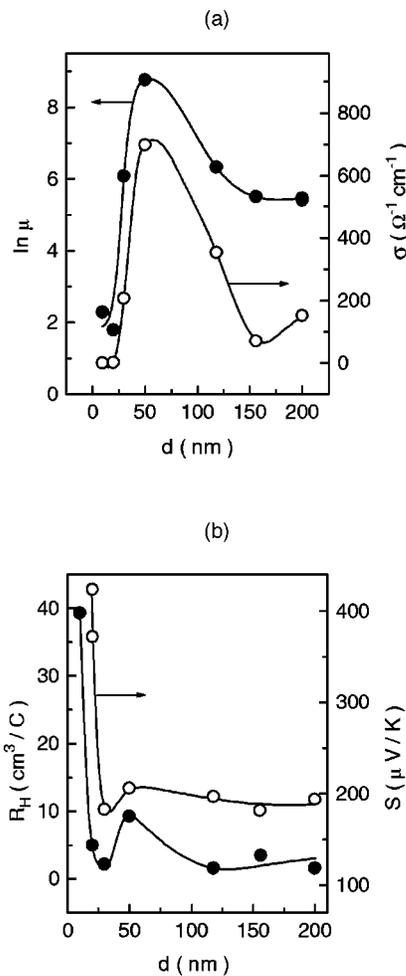


FIG. 1. Room-temperature dependences of the electrical conductivity σ and the charge carrier mobility μ (a) and the Hall coefficient R_H and Seebeck coefficient S (b) on the thickness d of PbTe/KCl(100) thin films covered by a 30 nm EuS layer. The errors in the measurements due to the materials properties are within the size of the points, and the curves drawn are a guide to the eyes.

and the absence of a strong degeneracy, which is quite realistic for our case, we can write

$$S = \frac{k}{e} \left[\left(r + \frac{5}{2} \right) + \ln \frac{2(2\pi m_d^* k_B T)^{3/2}}{n \hbar^3} \right], \quad (1)$$

where r is the exponent in the energy dependence ($\tau \sim \epsilon^r$) of the relaxation time, m_d^* is the density of states effective mass, and $k_B T$ is the thermal energy.²¹ Taking $n = A/(R_H e)$ into account, and assuming that the n -PbTe energy band parameters are unchanged over the entire range of d , one can expect the behavior of the $S(d)$ and $R_H(d)$ curves to be similar, which is actually observed [Fig. 1(b)]. As is seen from Fig. 2, the maximum $P = S^2 \sigma$ ($29.1 \times 10^{-4} \text{ W/mK}^2$) exceeds the highest values observed for bulk crystals and thick films of PbTe,^{1,2} and is comparable to observations in IV–VI-based SLs and QD structures.^{4–7,15}

Several authors who studied $\sigma(d)$ for inhomogeneous films consisting of conducting and nonconducting constituents, observed an abrupt increase in σ , sometimes by several orders of magnitude, within a narrow range of d ,^{22,23} and explained it^{24–26} by percolation theory.²⁷ According to this theory, in a random mixture of conducting (fraction p) and insulating (fraction $1 - p$) materials, an infinite cluster first

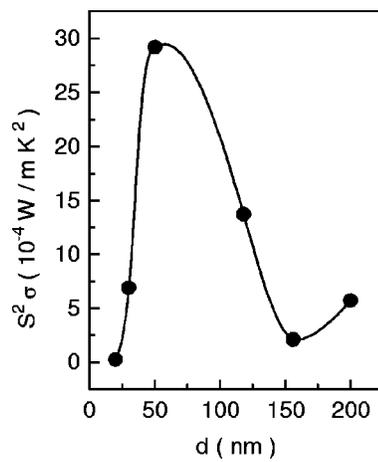


FIG. 2. Room-temperature dependence of the power factor $P = S^2 \sigma$ on the thickness d of PbTe/KCl(100) thin films covered by a 30 nm EuS layer.

forms at a certain critical concentration $p = p_c$ (percolation threshold). At $p = p_c$ the system abruptly exhibits long-range conductivity, where $\sigma = \sigma_0(p - p_c)^t$ obeys a power law, and t is the critical exponent, which equals 1.65 and 1.0 for 3D and two-dimensional (2D) systems, respectively.^{22–27} Sivan and Imry²⁸ predicted a critical behavior for S near p_c and showed that S increases when p approaches p_c from the metallic side. We thus attribute the sharp growth in σ and μ and the decrease in S at $d > 10$ nm to a transition from an island-like to a continuous film.

So, why are such high values of σ and μ observed at $d \approx 50$ nm when we could expect defect formation under island coalescence? We explain the large σ and μ by high structural perfection caused by the self-ordering of islands in the growing thin film. It is known^{29,30} that there are two main mechanisms for epitaxial growth which lead to island formation: the Stranski–Krastanov (SK) and the Volmer–Weber (VW) mechanisms. In SK growth, the initial growth is layer by layer, but thicker layers have a high strain energy, which can be lowered by forming isolated islands. The possibility of dislocation-free SK growth has been demonstrated both theoretically and experimentally,^{29–31} and is usually observed in QD SL fabrication. In the VW growth mechanism, which is realized in our case, 3D island formation occurs without a “wetting layer.” The KCl substrates provide sufficient equilibrium conditions for island nucleation, and even at early stages of condensation, small monocrystalline islands with clear-cut facets grow.³² Island nucleation usually occurs on point defects, which represent local regions of strong bonding between epitaxial particles and the substrate.^{30–33} Due to the lattice mismatch between the condensate and the substrate, and to differences in their thermal expansion coefficients, islands are the centers of elastic distortions spreading over the substrate. The deformation forces are short range and vary as $\sim 1/r^3$ (r is the distance from a defect).³³ In the short-range approximation, one can introduce the radius R_0 of a deformation sphere, outside of which these forces are rather weak. Overlapping of the deformation fields of neighboring islands will create regions with lower strain energies that alternate with highly strained regions. After the formation of percolation channels through the deformation spheres, the processes of elastic interactions can become co-

operative and lead to an ordered and uniform lateral distribution of islands. Electrostatic interactions among islands are also possible, since defects and impurities in KCl are often electrically active. Formation of percolation channels might facilitate ordering, due to an increased diffusion rate.²⁷ The EuS cover layer may itself stimulate self-organization of the PbTe islands and/or stabilize the formation of an ordered structure. Applying a phenomenological approach, one can treat the ordered structure formed at $d \sim 50$ nm [as implied by the maxima in the $S(d)$ and $R_H(d)$] as a dissipative structure, resulting from self-organization processes in a nonequilibrium open system.³⁴

The abrupt decrease in μ starting from $d \approx 50$ nm can be connected with: (1) The introduction of dislocations into islands at some critical coverage. Dislocation-free islands have stress concentrations at the island edges,^{31,33,35,36} and beyond a certain depth and width of the islands, dislocations are introduced at the island edges. (2) The formation of defects on island boundaries during the island coalescence, since these boundaries are favorable sites for defect incorporation.³³ (3) Defect formation in a continuous film, previously shown in PbTe/BaF₂ thin films,³⁷ where the number of screw dislocations increased with increasing d , leading to a drop in μ .

In conclusion, extrema in the thermoelectric parameters were observed at $d \approx 50$ nm in PbTe films protected from oxidation by an EuS cover layer. We attribute the high values of the carrier mobility μ and of the power factor P to island self-organization, which can occur not only in quantum dot superlattices but also in an individual layer, as shown by this work. The major driving force behind this ordering is the interaction between the elastic and electrostatic fields of the island, and the probability of ordering is sensitively determined by both the distance between adjacent islands and the island size. Apparently, self-organization processes can be realized not only for the Stranski–Krastanov but also for the Volmer–Weber growth modes. The effects revealed in this work require detailed microstructure studies and the development of new physical approaches and models.

The authors thank Dr. Gene Dresselhaus for fruitful and stimulating discussions. This work was supported by the U.S. National Research Council Twinning Program, by the U.S. Civilian Research and Development Foundation (Grant No. UE2-2069), and by DARPA Grant No. 66001-00-1-8603.

- ¹G. D. Mahan, *Solid State Phys.* **51**, 81 (1997).
- ²Z. Dashevsky and L. Dudkin, *J. Thermoelectricity* **1**, 93 (1993).
- ³L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B* **47**(19), 12727 (1993).
- ⁴L. D. Hicks, T. C. Harman, X. Sun, and M. S. Dresselhaus, *Phys. Rev. B* **53**, R10493 (1996).
- ⁵T. C. Harman, D. L. Spears, and M. J. Manfra, *J. Electron. Mater.* **25**, 1121 (1996).
- ⁶T. C. Harman, D. L. Spears, and M. P. Walsh, *J. Electron. Mater.* **28**, L1 (1999).
- ⁷A. Yu. Sipatov, V. A. Volobuev, A. G. Fedorov, E. I. Rogacheva, and I. M. Krivulkin, Proceedings of the 18th International Conference on Thermoelectrics, Baltimore, 1999, p. 198.
- ⁸A. Zunger, *MRS Bull.* **23**, 15 (1998).
- ⁹A. P. Alivisatos, *Science* **271**, 933 (1996).
- ¹⁰L. E. Brus, A. L. Efros, and T. Itoh, *J. Lumin.* **70**, R7 (1999).
- ¹¹G. Springholz, V. Holy, M. Pinczolits, and G. Bauer, *Science* **282**, 734 (1998).
- ¹²V. Holy, G. Springholz, M. Pinczolits, and G. Bauer, *Phys. Rev. Lett.* **83**, 356 (1999).
- ¹³V. Holy, J. Stangl, G. Springholz, M. Pinczolits, G. Bauer, I. Kegel, and T. H. Metzger, *Physica B* **283**, 65 (2000).
- ¹⁴M. Pinczolits, G. Springholz, and G. Bauer, *Appl. Phys. Lett.* **73**, 250 (1998).
- ¹⁵T. C. Harman, P. J. Taylor, D. L. Spears, and M. P. Walsh, in Ref. 7, p. 280.
- ¹⁶J. Tersoff, C. Teichert, and M. G. Lagally, *Phys. Rev. Lett.* **76**, 1675 (1996).
- ¹⁷G. S. Solomon, J. A. Trezza, A. F. Marshall, and J. S. Harris, *Phys. Rev. Lett.* **76**, 952 (1996).
- ¹⁸Y. W. Zhang, *Phys. Rev. B* **61**, 10388 (2000).
- ¹⁹L. S. Palatnik and I. I. Papiro, *Epitaxial Films* (Nauka, Moscow, 1971), pp. 178–190 (in Russian).
- ²⁰E. I. Rogacheva, I. M. Krivulkin, O. N. Nashchekina, A. Yu. Sipatov, V. A. Volobuev, and M. S. Dresselhaus, *Appl. Phys. Lett.* **78**, 1661 (2001).
- ²¹Yu. I. Ravich, B. A. Efimova, and I. A. Smirnov, *Semiconducting Lead Chalcogenides* (Plenum, New York, 1970), pp. 156–227.
- ²²J. D. Benjamin, C. J. Adkins, and J. E. Van Cleve, *J. Phys. C* **17**, 559 (1984).
- ²³C. J. Adkins, *J. Phys. C* **20**, 235 (1987).
- ²⁴B. I. Shklovski and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1984), pp. 94–136.
- ²⁵C. Segal, A. Gladkikh, M. Pilosof, H. Behar, M. Witcomb, and R. Rosenbaum, *J. Phys.: Condens. Matter* **10**, 123 (1998).
- ²⁶C.-H. Lin and G. Y. Wu, *Physica B* **279**, 341 (2000).
- ²⁷D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor & Francis, London, 1992), pp. 89–114.
- ²⁸U. Sivan and Y. Imry, *Phys. Rev. B* **33**, 551 (1986).
- ²⁹I. Markov and S. Stoyanov, *Contemp. Phys.* **28**, 267 (1987).
- ³⁰S. A. Chambers, *Adv. Phys.* **40**, 357 (1991).
- ³¹C. Ratsch and A. Zangwill, *Surf. Sci.* **293**, 123 (1993).
- ³²L. S. Palatnik, V. K. Sorokin, and L. P. Zozulya, *Fiz. Tverd. Tela (Leningrad) [Sov. Phys. Solid State]* **11**, 1265 (1969).
- ³³A. N. Orlov, *Introduction to Theory of Defects in Crystals* (Nauka, Moscow, 1983), pp. 75–113.
- ³⁴G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977), pp. 86–129.
- ³⁵D. J. Eaglesham and M. Cerullo, *Phys. Rev. Lett.* **64**, 1943 (1990).
- ³⁶S. Guha, A. Madhukar, and K. C. Rajkumar, *Appl. Phys. Lett.* **57**, 2110 (1990).
- ³⁷G. Springholz, A. Y. Ueta, N. Frank, and G. Bauer, *Appl. Phys. Lett.* **69**, 2822 (1996).