THERMOELECTRIC PROPERTIES OF $Pb_{1-x}Sn_xTe/PbTe$ QUANTUM WELL STRUCTURES

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1. Introduction

The search of material with improved thermoelectric properties continues to be important and urgent problem. The first investigation of thermoelectric opportunities of low dimensional structures began about decade ago in papers [1, 2]. Based on the simple model of quantum well (QW) and constant relaxation time approximation the authors had demonstrated theoretically [1, 2] and experimentally [3, 4] the possibility of considerable rise of thermoelectric figure of merit (*ZT*) as the consequence of the effect of density of state increase in such structures. Different approaches to this problem and different QW systems have been considered [5-11]. The general conclusion was that the *ZT* enhancement in quantum wells is not as drastic as predicted by original simple model. At the same time an alternative way of achieving higher *ZT* via the decrease of phonon thermal conductivity in low dimensional structures has been proposed [12]. More recently, attention turned to the structures of even lower dimensionality such as quantum dot arrays [13, 14].

However, up to now *n*-type $PbTe/Pb_{1-x}Eu_xTe$ QWs are most studied. The structures based on *p*-type materials are less investigated. The first experimental investigation [15] of *p*-type $PbTe/Pb_{1-x}Eu_xTe$ QWs (with x=0.073) at 300 K had shown an unusually high value of +240 μV/K of the Seebeck coefficient at very high hole concentration of $2\times10^{20}\,cm^{-3}$. A value of the power factor as high as 160 μW/cmK^2 was measured, five times greater than the best bulk value. For the quantum well material a value of $ZT > 1.5$ has been calculated. Theoretical investigation of *p*- $PbTe/Pb_{1-x}Eu_xTe$ QW was performed in [16].

The aim of this paper is the theoretical estimation of thermoelectric opportunities of *p*-type $Pb_{1-x}Sn_xTe/PbTe$ QW structures. Obtained results are also compared with corresponding in *n* and *p*-types $PbTe/Pb_{1-x}Eu_xTe$ QW structures.

2. Model and method of calculation

The transport properties of bulk $Pb_{1-x}Sn_xTe$ are determined by the three groups of carriers situated i - in four valleys in L points of the Brillouin zone of the conduction band, ii - in the same valleys in the valence band and iii - in the twelve valleys in Σ points. The fundamental gap (the energy gap between L_6^+ and L_6^- terms) in this material decreases when x increases due to closing L_6^+ term to L_6^-. The energy of Σ valleys weakly depends on x . One can expect that in the structure $Pb_{1-x}Sn_xTe/PbTe$ the quantum well formed in the solution $Pb_{1-x}Sn_xTe$ for carriers in L valleys only. The QW in Σ valleys should not form. We also accept that all difference between barrier and well gaps results in valance band offset. At x=0.2 it gives not deep QW with barrier height U=107meV. In order to describe the hole

states in the given valley, we have used, as in [10], the Hamiltonian, which takes into account in the simplest approximation the nonparabolicity of the carrier dispersion law. Bastard boundary conditions at interfaces for hole wave functions give the equation for determining full carrier energy *E*.

We have considered (111) orientation of quantum well. The dimensional quantization in such structures partially lifts the degeneracy of L valleys. Two series of energy levels appear in QW. They correspond to one longitudinal and three times degenerated oblique subband sets. The energies of levels E_α were calculated as a function of QW width *d*. At *T*=300K and x=0.2 the material parameters used in simulations are: $m_{\|}^{W} = 0.303m_0$, $m_{\perp}^{W} = 0.0265m_0$, $m_{\|}^{B} = 0.431m_0$, $m_{\perp}^{B} = 0.0364m_0$, $E_g^W = 217meV$, $E_g^B = 324meV$. The results of calculation are shown in Fig. 1. With increasing of well width, E_α decreases and at $d_\alpha^* = \hbar\pi(\alpha-1)/\left[2m_z^W U\left(1+U/E_g^W\right)\right]^{1/2}$ new levels appear in the quantum well. It is interesting to note that the number of levels does not depend on value of barrier effective masses. The energy of size quantization levels E_α also weakly depends on the barrier effective masses $m_{\|,\perp}^{B}$ and this dependence vanishes in two limit cases of deep ($E_\alpha \to 0$) and shallow ($E_\alpha \to U$) levels in the well structure. In Fig. 1 we also show. The dependences of the Fermi energy on the well width are plotted in Fig.1 for three values of hole concentration. It is seen that two dimensional transport along QW may be realized at $d \geq 35$Å and at carrier densities $p \leq 10^{19} cm^{-3}$. In the opposite cases the contribution of the continuous spectra should be taken into account. The nonparabolicity of initial materials leads to nonparabolic hole dispersion law $\varepsilon_{\mathbf{k}\alpha}$ in QW. Numerical investigation has shown that with a good precision $\varepsilon_{\mathbf{k}\alpha}$ can be approximated by Kane-like dispersion law with new increased effective masses. The values of these masses were calculated analytically. With increasing of E_α effective masses increase and, as a result, the population of the states with high energy increase in comparison with the model which does not take into account this effect. We had found that at $d = 35$Å and $p = 10^{19} cm^{-3}$ about 75% holes are placed in oblique subband and 25% are in the longitudinal subband. At x=0.2 the energy gap between L and Σ valleys is large (of order or greater than 125meV) and at considered carrier concentrations p~10^{19}cm^{-3} and temperature *T*=300K the populations of states of continuous spectra in Σ valleys are negligible.

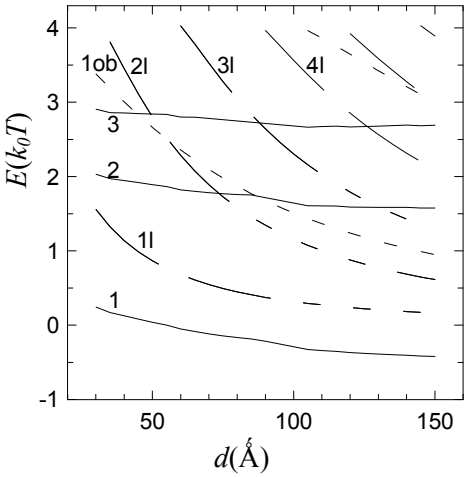

Fig. 1. QW energy level E_1, E_2, … and Fermi energy (curve 1 is for p=10^{18}cm^{-3}; 2 - for p=5x10^{18}cm^{-3}; 3 - for p=10^{19}cm^{-3}) as a function of well width *d*. The curve 1l to 6l denote to levels arising from longitudinal ellipsoid along (111) direction, curves 1ob and 2ob correspond to levels from three oblique ellipsoids.

For the calculation of the kinetic coefficients we have used the approach based on the solution of the system of Boltzmann kinetic equations. The scattering of carriers on bulk acoustical and optical polar phonons, as well as intrasubband and intersubband carrier transitions have been rigorously taken into consideration.

The system of kinetic equations was solved by the iterative method, which gives more exact numerical solution in the case of inelastic carrier scattering on optical phonons, than the

variational method used in [7]. In order to take into account the anisotropy of effective masses, the distribution functions were decomposed into Fourier series and the first non-vanishing for given symmetry terms were used. The tensors of kinetic coefficients were obtained for carrier systems of different valleys, which further were summarized in kinetic coefficients of the entire structure in the corresponding coordinate system. The details of calculations are reported elsewhere [10].

3. Results and discussion

The value of constant of deformation potential E_1 for $Pb_{1-x}Sn_xTe$ given in literature ranges from 19eV to 27eV. So, as a first step, we have calculated bulk carrier mobility by the same method in the same approximations, and the results were compared with experimental data [17]. Best agreement was achieved at $E_1 = 27eV$ [17]. Other parameters of bulk $Pb_{1-x}Sn_xTe$ were taken from [17] too. We have calculated the electrical conductivity σ of $Pb_{1-x}Sn_xTe$/PbTe QW as a function of well width d at different hole densities. Qualitatively, the dependences of σ on d are similar to those for n-PbTe/$Pb_{1-x}Eu_xTe$ QW with same orientation. At great d =150 Å conductivities (and mobility) of $Pb_{1-x}Sn_xTe$/PbTe QW structures are smaller by 15%, but at small d are greater by 15% than corresponding in n- PbTe/$Pb_{1-x}Eu_xTe$ QW. In the considered structures the well and barrier masses are smaller than in n-PbTe/$Pb_{1-x}Eu_xTe$ QW and renormalized masses especially in thin QWs are smaller too.

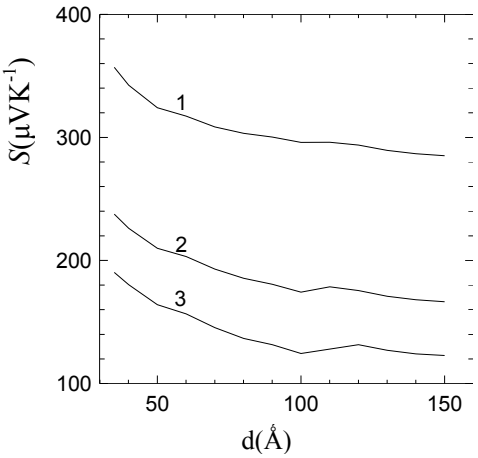

Fig. 2. Calculated Seebeck coefficient S of $Pb_{1-x}Sn_xTe$/PbTe QW as a function of well width d at T=300K, x=0.2 and different hole densities: 1 for p=10^{18}cm^{-3}, 2 for p=5· 10^{18}cm^{-3}, 3 for p=10^{19}cm^{-3}.

The results of calculation of Seebeck coefficient S as a function of well width are shown in Fig. 2. It is seen that the highest values of S are reached at small d (effect of density of states increases in low dimensional structures [1,2]). With increasing of d Seebeck coefficient decreases and at great d weakly depends on well width. The nonmonotonic behavior of S in the vicinity of d=100Å is connected with the appearance of new level of dimensional quantization in oblique valleys. Calculated values of Seebeck coefficient are a little higher (by about 8%) than in n-type PbTe/$Pb_{1-x}Eu_xTe$ QW, but essentially lower than in p- PbTe/$Pb_{1-x}Eu_xTe$ QW structure with the same well width and carrier concentration. Small contribution of twelve Σ valleys to the hole transport in p-type $Pb_{1-x}Sn_xTe$/PbTe QW structure does not permit to achieve so high values of Seebeck coefficient as in p- PbTe/$Pb_{1-x}Eu_xTe$ QW, where the energy gap between subbands arising from L and Σ valleys is considerably lower.

The thermoelectric power factor S^2 σ as a function of well width has been also investigated. Its value increases with decreasing of d and achieves maximum at small d =35 Å. At p=10^{19}cm^{-3} $S^2\sigma$ = 80 μWcm^{-1}K^{-2} that is greater than in n- PbTe/$Pb_{1-x}Eu_xTe$ at the same well width, but smaller than $S^2\sigma$ = 102 μWcm^{-1}K^{-2} at d =20 Å available in later structure. The dependences of thermal conductivity k^e and Lorentz number $L = k^e / \sigma T$ on well width and hole concentration have been studied. Due to lower value of barrier height the additional rise of k^e and L is not so expressed as in PbTe/$Pb_{1-x}Eu_xTe$ QW structures [10].

At d=35 Å L=2.76, k^e=0.152 W/mK for p=10^{18}cm^{-3} and L=2.35, k^e=1.164 W/mK for p=10^{19}cm^{-3}. Using these kinetic coefficients we have calculated thermoelectric figure of merit $ZT = \sigma S^2/(k^{latt} + k^e)$ of the QW layer, where $k^{latt} = 2W/mK$ is the lattice contribution to the thermal conductivity of PbSnTe. The values of ZT are greater than in the bulk and grow with the decrease of well width. As it is seen from Fig. 2 the latter rises mainly from Seebeck coefficient growth at small d - effect of density of states increases. Maximum value of ZT appears at different hole concentration in thin and wide quantum wells. At large d optimum ZT has been achieved, as in the bulk, at $p \sim 4 \div 5 \cdot 10^{18} cm^{-3}$. For small d optimal carrier density is higher. The dependence of ZT on hole concentration for d =35 Å is shown in Fig. 3. Maximum ZT=0.78 at optimum parameters p =8·10^{18}cm^{-3} and d =35Å is higher than ZT =0.55 in n- PbTe/$Pb_{1-x}Eu_xTe$ QW at the same well width and carrier concentration. Lower value of barrier height decreases the effect of valley lifting and provides higher ZT. But this value is smaller than optimal ZT =0.87 at d =20 Å, n=1.5·10^{19}cm^{-3} in n- PbTe/$Pb_{1-x}Eu_xTe$ QW and considerably smaller than optimal ZT =1.7 at d =20 Å, n=5·10^{19}cm^{-3} in p-type PbTe/$Pb_{1-x}Eu_xTe$ QW – the consequence of small contribution of twelve Σ valleys to the hole transport.

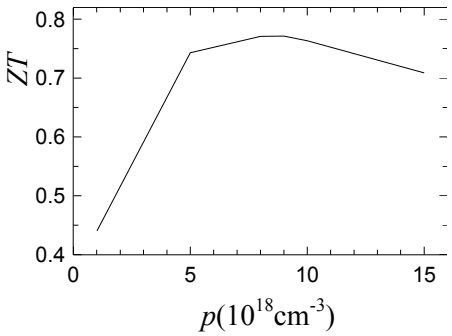

Fig. 3. Thermoelectric figure of merit ZT of $Pb_{1-x}Sn_xTe$/PbTe QW as a function of hole density p at d =35Å, T=300K, x=0.2.

4. Conclusions

We have calculated kinetic coefficients and estimated thermoelectric opportunities of p-type $Pb_{1-x}Sn_xTe$/PbTe QW structures on the base of most realistic model tested on PbTe/$Pb_{1-x}Eu_xTe$ QWs n- and p- types. We have found that lower effective masses and smaller depth of QW provide value of ZT =0.78 higher than in n-PbTe/$Pb_{1-x}Eu_xTe$ QW at the same well width and carrier concentration. However obtained ZT is lower than optimal in n- PbTe/$Pb_{1-x}Eu_xTe$ QW and especially in p-type PbTe/$Pb_{1-x}Eu_xTe$ QW structure, where twelve Σ valleys play essential role in the hole transport.

Acknowledgements

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