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Structural phase transition and manifestation of eddy currents in IR reflection spectra of PbSnTe semiconductor films

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Abstract. **Infrared reflection spectra of thin (~60 nm) $Pb_{1-x}Sn_xTe$ (x = 0.25, 0.53, 0.59) films grown by molecular beam epitaxy on GaAs/CdTe hybrid substrates have been measured at frequencies from 20 to 5500 cm^{-1} and temperatures from 5 to 300 K. The spectra have been used to determine temperature-dependent transverse phonon and plasmon frequencies in the films, which has made it possible to identify a structural phase transition at $T_C \approx 50$ K. The plasma frequency of the films has been shown to increase with decreasing band gap on cooling from 300 to 77 K. The increase in plasma frequency is mainly attributable to the increase in carrier concentration and a transition of the carriers from vortex states on the film surface to the valence band.**

Keywords: *reflection spectra, dispersion analysis, transverse phonons, phase transition, plasma frequency, eddy currents.*

1. Introduction

IV–VI compounds and related alloys are narrow band gap semiconductors crystallising in various structures, depending on composition, pressure and temperature. The lead–tin–tellurium ternary compound, whose band gap depends on Sn content, is of great practical importance. This compound is used in the fabrication of photoresistors, photodiodes and lasers operating in the IR at wavelengths from 3 to 40 μm. Recent years have seen the advent of $Pb_{1-x}Sn_xSe$ ($x \sim 0.14$) based terahertz lasers emitting at 50 μm.

PbSnTe and SnTe solid solutions are known to undergo a ferroelectric phase transition on cooling, from a high-temperature, cubic phase to a low-temperature, rhombohedral one. Lead telluride crystallises in a cubic structure, which persists down to the lowest temperatures. Tin telluride crystals have a cubic structure, but transform into a rhombohedral phase at temperatures from 15 to 100 K (depending on composition). SnTe crystals with a hole concentration of 10^{20} cm^{-3} undergo the phase transition at 100 K [1, 2]. With increasing p-type carrier concentration, the phase transition temperature decreases [2]. There is experimental evidence [3, 4] that the phase transition temperature is influenced by not only Sn concentration in the alloys but also carrier concentration.

As the solid solution is cooled, the Pb and Te sublattices shift relative to each other, which leads to a decrease in ('softening' of) the transverse phonon frequency [5]. In PbSnTe materials, there is a strong coupling between interband electron excitations and transverse lattice vibrations, resulting in transverse optical (TO) phonon frequency renormalisation. It follows from the theory of electron–phonon interaction [1, 6–8] that free carriers influence the transverse phonon frequency (ν_{TO}) through the electron–phonon interaction parameter, i.e. the logarithm of the $E_g + 2E_F$ sum, where E_g is the band gap and E_F is the Fermi energy [6, 7]. According to experimental data [7], the ν_{TO} frequency rises with increasing $E_g + 2E_F$. The band gap of $Pb_{1-x}Sn_xTe$ solid solutions depends on their composition and temperature and is given by [9, 10]

$$E_g(x, T) = 0.19 - 0.543x + 4.5\times10^{-4}\frac{T^2}{T+50}\ [\text{eV}]. \qquad (1)$$

However, formula (1) is only applicable to the alloys with $x \leqslant 0.42$ [11]. At higher Sn concentrations, relation (1) is incorrect and, below 80 K, band inversion occurs in the range $x = 0.5–0.6$ [12].

Recently, angle-resolved photoelectron spectroscopy [12] was used to study surface states with a Dirac spectrum in thin $Pb_{1-x}Sn_xTe$ ($x = 0.7$) films, which can be classified as topological insulators (TIs) below 80 K. According to Chenhui Yan et al. [12], the probability to detect such states increases with Sn concentration. According to (1), at $x = 0.25$ the band gap remains positive down to the lowest temperatures, and $Pb_{0.75}Sn_{0.25}Te$ does not exhibit topological properties. Note that the band structure of the alloys with $x = 0.5–0.6$ is poorly studied, but according to Chenhui Yan et al. [12] there is band inversion below 80 K, and E_g increases in magnitude but is negative. Thus, the x = 0.53 and 0.59 materials can only be classified as topological insulators below 80 K.

There is particular interest in eddy currents on the surface of narrow band gap semiconductors. Theory of this effect was developed by Vinogradov [13]. It has been shown theoretically that, in planar homogeneous structures of two-band semiconductors, spin-polarised vortex states with a linear dispersion law are possible at any sign of E_g. They are localised at the surface and have a total angular momentum of 1/2.

There is currently great interest in TIs, whose key feature is that their spectrum contains spin-polarised linear-momentum current states. Under certain conditions, such states

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appear on the semiconductor–vacuum interface and have the form of vortex states. If the surface is homogeneous, vortices emerge at any of its points. In what follows, this theory is used to account for the unusual phenomenon observed by us and related to an increase in plasma frequency with decreasing band gap on cooling.

Note that the electronic and phonon properties in the bulk of films with $x > 0.2$ have been little studied, and no IR reflection spectra of such thin films have been measured previously. The only report dealing with the IR reflectivity of In-doped $Pb_{1-x}Sn_xTe$ with $x = 0.2$ is that by Belogorokhov et al. [4], who determined the frequency of a transverse mode from the loss function.

In connection with this, the objectives of this work were to study temperature dependences of the soft transverse phonon mode, determine the temperature of the structural phase transition in $Pb_{1-x}Sn_xTe$ films with $x > 0.2$ by IR reflectivity measurements and investigate the temperature dependence of their plasma frequency in relation to the decrease in the band gap of $Pb_{1-x}Sn_xTe$ films of different compositions on cooling.

2. Samples and measurement techniques

Thin $Pb_{1-x}Sn_xTe$ films were grown by molecular beam epitaxy in vacuum (10^{-10} Torr) on (001) GaAs substrates, using pure Pb, Sn and Te sources. Prior to epitaxial film growth, a CdTe buffer layer was produced on the substrate. The films and buffer layer were similar in lattice parameter: a_{PbTe} = 6.461 Å and a_{CdTe} = 6.481 Å. The Sn content of the films was 25%, 53% and 59%, as determined by X-ray diffraction, and the thickness of the films was 50–60 nm.

Reflection spectra of the $Pb_{1-x}Sn_xTe$ films were measured at near-normal incidence in the frequency range 20–5500 cm^{-1} and temperature range 5–300 K on a Bruker IFS 125HR Fourier transform IR spectrometer (resolution of 2–4 cm^{-1}). In the far-IR reflection measurements, a liquid-helium-cooled silicon bolometer (Infrared Laboratories) was used as a detector. The measured spectra were normalised to the reflection spectrum of a gold mirror. In the mid-IR (400–5500 cm^{-1}), we used a DLaTGS uncooled pyroelectric detector. A sample was placed in a CryoVac KONTI Spectro A helium cryostat, which allowed an insert with a cold finger having two identical apertures, for a reference mirror and sample, to be automatically translated in vacuum. Reflection measurements were made sequentially for the sample and mirror at the same temperature.

3. Results and discussion

We measured reflection spectra of three $Pb_{1-x}Sn_xTe$ films, with x = 0.25, 0.53 and 0.59. The energy spectrum of the x = 0.25 sample remains uninverted down to the lowest temperatures (the wave functions of p-type carriers in the conduction and valence bands have L_6^- and L_6^+ symmetries, respectively). The band gap of this material is 0.17 eV at 300 K and decreases with decreasing temperature. As mentioned above, according to Ferreira et al. [11] the structures with x = 0.5–0.6 can be classified as TIs below 80 K, because at these temperatures band inversion occurs and E_g rises.

Figure 1 shows the reflection spectra of the samples with x = 0.25 and 0.53 at different temperatures. There are three bands corresponding to transverse phonons in the GaAs substrate (268 cm^{-1}), CdTe buffer layer (140 cm^{-1}) and film (35 cm^{-1}). The TO phonon frequencies are indicated for T = 300 K. In our ν_{TO} measurements, uncertainty was ~20%. In addition, three weak features are seen in the range 350–600 cm^{-1}, which we assign to vibrational modes of tin oxide [14]. As seen in Fig. 1, the TO phonon frequencies in CdTe and GaAs increase with decreasing temperature.

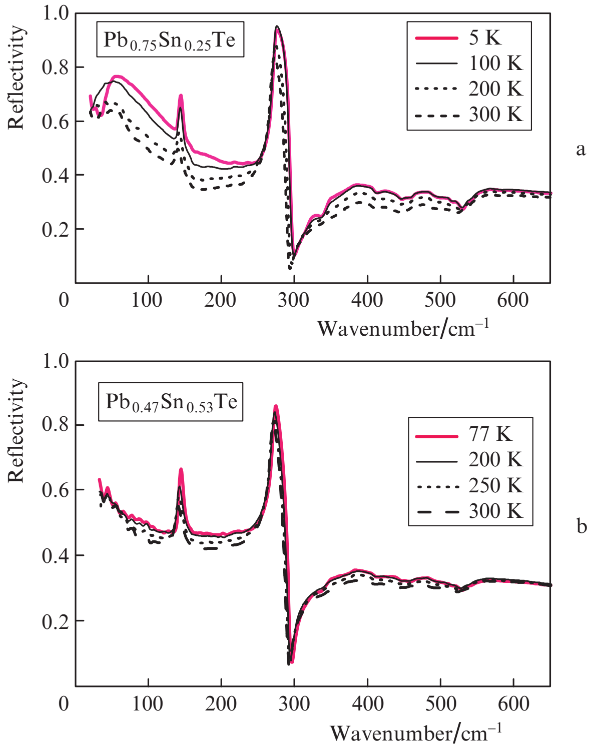

Figure 1. Reflection spectra of the (a) $Pb_{0.75}Sn_{0.25}Te$ and (b) $Pb_{0.47}Sn_{0.53}Te$ films at different temperatures.

Using dispersion analysis of the reflection spectra and SCOUT software [15, 16], we obtained parameters of optical phonons and plasmons. Table 1 indicates the thickness d of the films, their high-frequency dielectric permittivity ε_∞, the frequencies of transverse and longitudinal optical (LO) phonons (ν_{TO} and ν_{LO}), plasma frequency ν_{pl}, concentration n of p-type carriers and their relaxation time $\tau = 1/(2\pi c\nu_\tau)$ at 300 K (where ν_τ is the carrier collision frequency).

Figure 2 shows temperature dependences of the square of the TO phonon frequency (ν_{TO}^2) for the $Pb_{1-x}Sn_xTe$ films with x = 0.25 and 0.53. It is seen from Fig. 2a that, at temperatures from 77 to 300 K, ν_{TO} varies little, from 37 to 35.3 cm^{-1}. Below 77 K, the TO phonon frequency rises sharply, which we believe is due to the structural phase transition of the material to the rhombohedral phase. The temperature of the phase transition lies in the range 50–77 K. According to theoretical studies [6, 7], the temperature dependence of ν_{TO}^2 is determined by interaction between interband excitations and transverse vibrational modes. The parameter that determines this interaction is the $E_g + 2E_F$ sum. The E_g of the x = 0.25 film decreases with decreasing temperature, whereas its E_F rises because, as shown below, the carrier effective mass decreases. Thus, the decrease in E_g is compensated for by the increase in E_F and, as a result, $E_g + 2E_F$ varies little in the range 77–300 K. The inset in Fig. 2a shows the temperature dependence of $1/\varepsilon_s$, where ε_s is static dielectric permittivity.

Table 1. 300-K parameters of the $Pb_{1-x}Sn_xTe$ films.

Film	d/nm	ε_∞	ν_{TO}/cm^{-1}	ν_{LO}/cm^{-1}	ν_{pl}/cm^{-1}	n/10^{17} cm^{-3}	τ/10^{-14} s
$Pb_{0.75}Sn_{0.25}Te$	65	38	35.7	107	213	7.9	0.5
$Pb_{0.47}Sn_{0.53}Te$	85	37.5	41	140	206	7.6	2.6
$Pb_{0.41}Sn_{0.59}Te$	57	38	49	–	775.6	85	1.7

From these data, the Curie temperature was determined to be $T_C \approx 49$ K, in satisfactory agreement with the phase transition temperature of this film. In the $x = 0.53$ film, the TO phonon frequency decreases with decreasing temperature (Fig. 1). In the range 77–200 K, ν_{TO}^2 is a linear function of temperature (Fig. 2b), extrapolation of which yields a phase transition temperature $T_C \approx 50$ K.

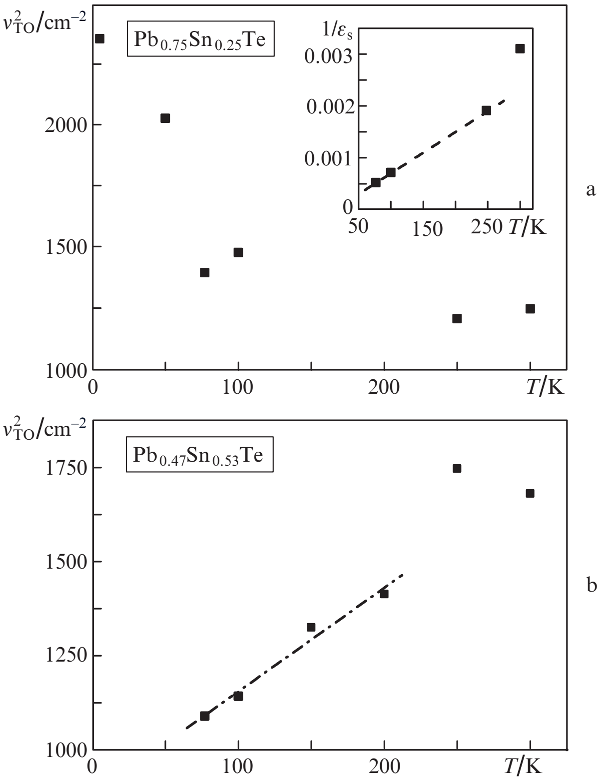

Figure 2. Temperature dependences of ν_{TO}^2 for the (a) $Pb_{0.75}Sn_{0.25}Te$ and (b) $Pb_{0.47}Sn_{0.53}Te$ films. Inset: temperature dependence of $1/\varepsilon_s$, where ε_s is static dielectric permittivity. Uncertainty in our ν_{TO} measurements was ~20%.

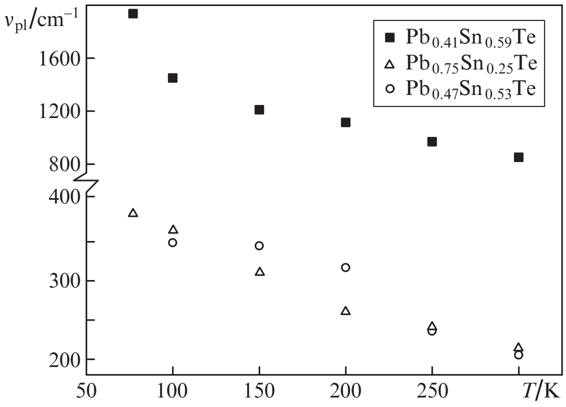

Figure 3. Plasma frequency ν_{pl} as a function of temperature for the $Pb_{1-x}Sn_xTe$ films with $x = 0.25$, 0.53 and 0.59.

The plasma frequency $\nu_{pl} = \nu_p/\sqrt{\varepsilon_\infty}$ (where $\nu_p = [ne^2/(\pi m_c^*)]^{1/2}$ is the plasma frequency of free carriers and m_c^* is the carrier effective mass) was found to increase with decreasing temperature in all the films (Fig. 3), the ratio of ν_{pl}^2 at 77 K to that at 300 K being 2.6 ± 0.1.

An unexpected finding that needs explanation is the strong temperature dependence of the plasma frequency: ν_{pl}^2 rises by almost three times as the temperature is lowered from 300 to 77 K. It can be determined by the temperature dependences of ε_s, m_c^* and n. Consider these possibilities. Static dielectric permittivity is a strong function of temperature through the transverse optical phonon frequency ν_{TO}. However, plasmons are observed at frequencies considerably higher than ν_{TO}, where permittivity is temperature-independent and approaches high-frequency permittivity ε_∞. In semiconductors with a Dirac electronic spectrum, the effective mass can be described in the isotropic approximation by the following formula: $m_c^* = (\Delta^2 + v^2 p_F^2)^{1/2}/v^2$, where $\Delta = E_g/2$ is the gap parameter; $v \approx 10^8$ cm s^{-1} is the speed of electrons; and $p_F = \hbar(3\pi^2 n)^{1/3}$ is the Fermi momentum. The mass m_c^* depends on temperature through the parameter Δ, which has the strongest effect on m_c^* at the band bottom, where $p_F \to 0$. In this case, the ratio $r = m_c^*(T_2)/m_c^*(T_1)$ (at $T_1 = 70$ K, $\Delta(T_1) = 0.5 \times 90$ meV, $T_2 = 300$ K and $\Delta(T_2) = 0.5 \times 170$ meV) is ~1.9. At $p_F \neq 0$ and $n \approx 0.3 \times 10^{18}$ cm^{-3}, the ratio is $r \approx 1.12$. At $n \approx 10^{18}$ cm^{-3}, we have $r \approx 1.06$. The above considerations and estimates lead us to conclude that the first two possibilities are incapable of accounting for the observed dependence, so we turn to the third one: $n(T)$ dependence. For this possibility to be a reality, the semiconductor should have a system to which free carriers with a sufficient number of states and excitations other than plasmons would be able to pass. Suitable properties are offered by a system of vortices [13] that emerge on the interface between two media strongly differing in spin–orbit coupling parameters (two semiconductors or a semiconductor and vacuum, like in our case). They have a linear dispersion law, like surface states, but in contrast to them they require no gap parameter inversion. A vortex can emerge at any point of a homogeneous plane. Its wave function falls off exponentially in going from its centre in all azimuthal directions parallel to the plane and propagates as a plane wave into the semiconductor. Let us count the number of states in a system of vortices. The number of vortices per unit area is $1/\pi R^2$, where $1/R = \Delta/\hbar v$ and R is the vortex radius. The number of states, n_v, distributed over the band in the semiconductor across the interface (z-direction) can be calculated in a standard manner, like in the case of free electrons. Taking into account the linear dispersion law, $\varepsilon(k_z) = vk_z$, we obtain $n_v = \Delta^2 \varepsilon_F/(2\pi^2\hbar^3 v^3)$. All vortices are thought to have the same spin direction. With allowance for two spin directions, the number of states of free carriers is then $n_f = (\varepsilon_F^2 - \Delta^2)^{3/2}/(3\pi^2\hbar^3 v^3)$. The energy in the formulas for n_v and n_f is measured from midgap. The number of carriers in the band becomes equal to that in the vortex states at $\Delta/\varepsilon_F \approx 0.59$. As this parameter decreases, the number of carriers in the band becomes larger than that in the vortex states. In all the films studied here, this parameter is ~0.5 at 300 K and decreases with decreasing band gap. Thus, a transition of carriers from vortex states to an allowed band of the film is possible.

Figure 4 illustrates the effect of temperature on the loss functions $\mathrm{Im}(-1/\varepsilon)$ of the films with $x = 0.25$ and 0.53. The peaks of the loss functions correspond to the frequencies of plasmon–LO phonon hybrid modes (positive branches). It is seen that, with decreasing temperature, the loss functions shift to higher frequencies because of the increase in plasma frequency. From loss functions, one can determine LO phonon frequencies. We obtained 107 cm^{-1} in the $x = 0.25$ film and 140 cm^{-1} in the $x = 0.53$ film at 300 K (Table 1). Knowing ν_{TO}, ν_{LO} and ε_∞ in the temperature range 77–300 K and using the Lyddane–Sachs–Teller relation, we evaluated $1/\varepsilon_s$ as a function of temperature for the $Pb_{0.75}Sn_{0.25}Te$ film (Fig. 2, inset). The Curie temperature of this material is 49 K, in agreement with the temperature of the structural phase transition in this film.

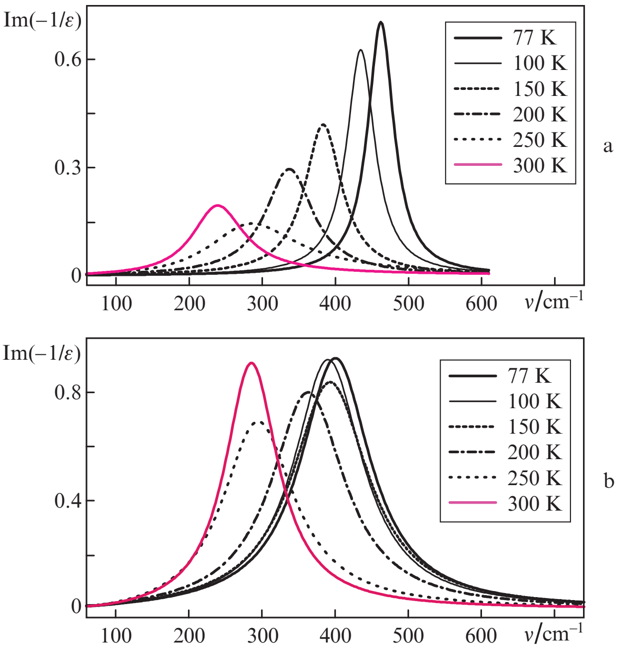

Figure 4. Loss functions $\mathrm{Im}[-1/\varepsilon(\nu)]$ of the (a) $Pb_{0.75}Sn_{0.25}Te$ and (b) $Pb_{0.47}Sn_{0.53}Te$ films at different temperatures.

4. Conclusions

Measurements of IR reflection spectra have been used for the first time to find temperature-dependent parameters of phonons and plasmons in $Pb_{1-x}Sn_xTe$ ($x > 0.2$) films, which has made it possible to identify a structural phase transition at $T_C \approx 50$ K. In all the films, the plasma frequency increases with decreasing band gap on cooling. This result is due in part to the decrease in carrier effective mass, but the main mechanism is the increase in carrier concentration due to the formation of eddy currents on the film surface and a transition of the carriers from vortex states to the valence band.

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