Low-temperature charge transport in photosensitive nanocrystalline PbTe(In) films

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Abstract. We have investigated conductivity of the PbTe(In) nanocrystalline films in dc and ac modes at temperatures 4.2-300 K in the frequency interval 20 Hz – 1 MHz in darkness and under illumination. Conductivity of the as-grown films is determined by charge transport along the inversion channels at the grain surface and activation (or tunneling) through the grain barriers. Persistent photoconductivity appears in the films due to spatial separation of non-equilibrium charge carriers at temperatures lower 150 K. As grown films have been annealed in oxygen at 300°C and 350°C. Oxidation at 300°C leads to resistivity increase, grain barrier height growth and higher photoresponse. Annealing at 350°C results in resistivity reduction and photoresponse decrease. The main contribution to charge transport at low temperature in this case is related to the hopping conductivity along the inversion channels.

1. Introduction

Lead telluride is a narrow gap semiconductor with the energy gap $E_g = 190$ meV at $T = 0$ K. PbTe and its solid solutions are extensively used in different fields of opto- and microelectronics. Unique properties of the lead telluride are related to the effect of Fermi level pinning induced by doping with indium [1]. For the In-doped lead telluride, the Fermi level is pinned at 70 meV above the conduction band edge resulting in high mobility ($\mu > 10^5$ cm²/V s at $T = 4.2$ K) and stable concentration of free charge carriers ($6\times10^{18}$ cm⁻³ at low temperatures) independently on fluctuations of the doping level in a sample. For nanocrystalline PbTe(In) films, the Fermi level pinning effect provides high homogeneity of electrical properties of individual grains.

For nanocrystalline materials, conductivity may be determined not only by the charge transport via the bulk of grains but also by conductivity through the grain surface as well as via barriers formed on nanocrystallite boundaries. Nanocrystalline PbTe(In) films deposited to cooled glass substrates are characterized by high photosensitivity due to energy barriers at grain boundaries. Measurements of impedance spectra performed previously have demonstrated that conductivity of these films is determined by two mechanisms: charge transport along the inversion channels at the grain surface and activation process at grain boundaries.

One of possible ways allowing to modify the nanocrystalline structure properties is oxidation. That is a complex process which leads to appearance of oxide phases and additional acceptor states at the grain surface due to chemisorption of oxygen diffusing along the grain boundaries. We have investigated effect of oxidation on conductivity of the nanocrystalline PbTe(In) films.
2. Samples and experimental technique

PbTe(In) films were prepared by physical vapor deposition using an electron gun. The glass substrate was cooled down to –120 °C. The source for the fabrication of nanostructured films was a PbTe single crystal doped with 0.5 at % In. The growth rate was 0.2 nm/s. The thickness of the films was 1 µm. The nanocrystallite size was estimated from atomic force microscopy (AFM) images. According to the scanning electron microscopy (SEM) results, PbTe(In) films possess a columnar structure [2]. The mean column diameter is about 70 nm. Though the bulk of grains should reveal the n-type conductivity due to indium doping, the sign of the Seebeck and Hall coefficients of the films corresponds to the p-type conductivity. It indicates that carriers transport in the films is related to the hole transport along inversion channels on the surface of grains [2]. Gold contacts on a chromium sublayer were prepared by thermal evaporation technique. The distance between the contacts was 0.1-0.2 mm and the width of the films was 4 mm. The current-voltage characteristics of the films were linear in the entire temperature range of 4.2-300 K. Part of the as-grown films was oxidized in two regimes: at \( T_{\text{ann}} = 300 \) °C during 400 min and at \( T_{\text{ann}} = 350 \) °C during 180 min.

All measurements were performed in a special cell that screens completely a sample from the background radiation. Temperature dependence of the film resistance in the dc mode was measured in darkness and under illumination in the temperature interval 4.2-300 K using the two-probe technique. A miniature incandescent lamp located inside the cell was used as the illumination source. Frequency dependence of the impedance components were studied using the QuadTech 1920 Precision RLC meter in the frequency range from 20 Hz up to 1 MHz in the temperature interval 4.2-300 K. The impedance modulus and phase were measured and recalculated into the real \( Z' \) and imaginary \( Z'' \) parts of the impedance \( Z^* = Z' - jZ'' \) and conductivity \( \sigma' \), \( \sigma'' \).

3. Experimental results and discussion

The temperature dependence of resistivity \( \rho \) of the as-grown and oxidized films measured in the dc mode in darkness (solid symbols) and under illumination (open symbols) is shown in the figure 1. At high temperatures, the activation behavior of the resistivity is observed. The activation energies \( E_A \) calculated using the equation \( \rho \sim \exp(E_A/kT) \) are 70, 80 and 30 meV for non-oxidized (as-grown) film and films oxidized at 300 and 350 °C, respectively. At \( T < 150 \) K, a noticeable photoresponse appears. High temperature of the photoresponse appearance is due to the band modulation induced by formation of barriers at grain boundaries. Increase of the annealing temperature leads to non-monotonous variation of the activation energy and the photoresponse amplitude. The low-temperature oxidation resulted in an increase in the activation energy and the photoresponse amplitude. At higher oxidation temperature, the activation energy and the photoresponse amplitude decrease sharply.

Figure 1. Temperature dependence of resistivity \( \rho \) for PbTe(In) films measured in the dc mode taken in darkness (solid symbols) and under illumination (open symbols).
Figure 2 represents the Nyquist plots, or impedance hodographs (a dependence of $Z''$ on $Z'$ with the frequency as a variable parameter) of all investigated samples (a – as-grown, b - $T_{\text{ann}}$= 300, c - $T_{\text{ann}}$= 350 °C) at $T = 4.2$ K. Analysis of frequency dependence of the impedance components was performed in terms of equivalent circuit approximation. The Nyquist plot $Z''(Z')$ of the as-grown PbTe(In) film is composed of two well-distinguished semicircles. In this case, the equivalent circuit is composed of two parallel RC circuits connected in series. These two RC-circuits correspond to two different mechanisms of the charge transport. For the high frequency circuit, the parameters $R$ and $C$ may be determined using the equations

$$Z' = R / [1+(2\pi f RC)^2],$$
$$Z'' = 2\pi f R^2 C / [1+(2\pi f RC)^2]$$

(1).

Similar equations may be used to calculate parameters of the low frequency circuit, but in this case, a shift of the corresponding semicircle along the Z' axis should be taken into account.

![Figure 2](image)

The calculated curves corresponding to the parameters given in the insets of figures 2 a, b, c are shown as lines. For comparison of the data taken for different films, the parameters are represented by the specific quantities. $C_0 = \varepsilon_0 S/d$ is a geometry capacitance of the sample, where $\varepsilon_0$ is a dielectric constant of vacuum, $S$ - a capacitor plate area, $d$ - a distance between capacitor plates. Analysis of the impedance spectra at temperature variation and under illumination allowed to conclude that the high frequency branch of the hodograph is determined by the grain barriers and the low frequency branch corresponds to the transport along the inversion channels [3].

Only one semicircle is well-distinguished in the impedance-spectra of the oxidized films. Comparison of the capacitance values corresponding to each semicircle with the values obtained for the as-grown film shows that for the film annealed at 300 °C, grain barriers give dominating
contribution to the charge transport. In contrary, the charge transport is almost completely defined by the inversion channels in the film oxidized at 350 °C.

It should be mentioned that the oxide phase formation as well as additional acceptor states of chemisorbed oxygen may only increase the barrier height. Reduction of the film resistivity under oxidation may be attributed to tunnel transparency of highest barriers, so they do not affect the charge transport effectively. The activation behavior of resistivity at high temperatures may be due to the contribution of comparatively low barriers at grain boundaries. The nanocrystalline films are nonhomogeneous systems for which a dispersion of the barrier heights at grain boundaries is quite probable.

For highly oxidized films, an opportunity to receive additional information on the mechanism of charge transport along the inversion channels appears. The frequency dependence of the real part of conductivity under illumination at $T = 4.2$ K for the film oxidized at 350 °C is presented in figure 3. The real part of conductivity increases with frequency in the high-frequency region as $\sigma' \sim f^{0.7}$. This type of the conductivity frequency dependence is typical for a hopping conductivity [4].

![Figure 3](image)

Figure 3. Frequency dependence of the real part of conductivity measured under illumination at $T = 4.2$ K for the film oxidized at 350 °C.

Maximal value of the photoresponse was observed for the film oxidized at 300 °C. In the same film the highest activation energy was found. Reduction of the activation energy and the barrier heights results in photosresponse decrease. Thus the film annealed at 350 °C appears to be of lowest photosensitivity.

References
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