Relaxation phenomena in a naturally disordered Pb₃O₄ semiconductor

M P Sevryugina, N S Pshchelko and Ya S Kadi
National University of Mineral Resources «The University of Mines», Vasilevsky Island, 21st line, 2, St. Petersburg 199106, Russia
E-mail: marysevrugina@yandex.ru

Abstract. Charge transfer in Pb₃O₄ structures has been investigated. Electric current dependences on time at temperatures of 300−370 K and at the dc electric field strength in the range of 2·10⁵−9·10⁵ V/m were measured. Flowing of relaxation polarizing current is shown to result in charge accumulation in the sample surface area. Experimental regularities coordinate with provisions of the relay mechanism of transfer of a charge with the participation of deep local levels. Values of the charge transfer parameters were determined.

1. Introduction
Among the components of the lead oxide series, Pb₃O₄ is distinguished by the stability of its phase composition in thin layers, photoelectric sensitivity in the visible spectral range, and pyroelectric and ferroelectric properties [1, 2]. Its high resistivity combined with a high density of deep localized states enables the use of the oxide Pb₃O₄ in electret structures. The defect and impurity states in high resistance Pb₃O₄ are responsible for the energy spectrum with a complex distribution of the energy levels of localized electron states in the band gap, which determines the charge state of the structure. Polarization and charging processes determine the operation of most semiconductor devices, controlling the conditions of creation of the potential profile on the surface of photosensitive layers, as well as its variation under optical excitation. To establish the charge transport mechanisms and the nature of the local centers in high-resistivity photoconductors, experimental study and theoretical analysis of the mechanisms of polarization in electric fields of different intensities appeared to be effective.

Charge relaxation in semiconductor bulk can be assumed as one of the factors that determine the stability of characteristics of electronic elements. Relaxation phenomena in a high-resistivity structure are associated with the manifestation of any form of disorder since the possibility of revelation of relaxing elements in an ideally ordered system is reduced to a minimum. The investigation of temporal dependence of the currents of isothermal relaxation makes it possible to acquire information on the population kinetics of capture centers arranged nonuniformly over the semiconductor thickness as well as on the capture processes in near-electrode regions [3]. In the following, the results of the study of the polarization relaxation in photoconductive Pb₃O₄ layers are presented.

2. Experimental
Kinetic dependences of polarization currents were measured for the Pb₃O₄ layers with the binder—cyanoethyl ester of polyvinyl alcohol—deposited on a glass substrate with the ITO conducting film based on tin-doped indium oxides. A layer of current-conducting paste (aquadag) with the area of 1
cm² and 50 μm thick was deposited on the surface of the material under study as the upper electrode. Currents of isothermal polarization were detected using a Keithley 6517A electrometric amplifier. The electric field strength was varied in the range of $E = 2 \cdot 10^5 - 9 \cdot 10^5$ V/m. The sample was heated using an electric furnace mounted into a holder. The furnace was dc-supplied from a stabilized current source. The heating rate in the limits of 3–5 K/min could be fixed in the range of $T = 300–370$ K.

### 3. Results and discussion

Figure 1 shows the results of the study of the kinetics of isothermal polarization currents in Pb$_3$O$_4$ layers measured for different electric fields. The shape of the polarization relaxation curves for Pb$_3$O$_4$ indicates that there are two phases of the process (fast and slow) corresponding to time intervals $\Delta t_1 = 1–30$ s and $\Delta t_2 = 30–200$ s. At the initial stage after switching the voltage on, rapid current decay is observed in polycrystalline Pb$_3$O$_4$ layers, obeying the empirical Curie–von Schweidler relation $I \propto t^{-n}$ ($n = 0.8$). A slow polarization kinetics component corresponds to the exponential dependence. As the voltage increases, the temporal range of the initial portion of the kinetics of the polarization current decreases, while the decay rate of function $I(t)$ increases.

![Figure 1. Kinetics of the polarization current measured for Pb$_3$O$_4$ layers at electric fields $E$: 1 – 2 · 10$^5$, 2 – 4 · 10$^5$, 3 – 6 · 10$^5$, 4 – 8 · 10$^5$ V/m. $T = 300$ K.](image-url)

The data on the kinetics of the isothermal relaxation currents was interpreted within a model according to which the transfer of an electric charge injected into a crystal occurs through the relay-race mechanism [4, 5]. The charge transfer from the contact into the sample occurs through the mechanism of hopping conduction over the trap centers, which are located in the band gap and have deep trapping levels of free charge carriers. This process is also accompanied by the formation of an energy barrier at the boundary with the anode, which hinders the transfer of electrons (injected from the cathode) to the anode. The energy barrier at the boundary with the anode arises from the energy difference between the electron affinity for the local center and the work function of the anode metal. Thus, the electric current is limited by both the space charge in the bulk of the semiconductor and the energy barrier at the boundary with the anode, which leads to a redistribution of the voltage across the crystal and decrease of electric current passing through the crystal.

Long-time relaxation processes established for the structures under study on the basis of polycrystalline Pb$_3$O$_4$ layers can also be accompanied by the formation of depletion regions at the
grain–intergrain layer boundary. A nonuniform potential profile of the boundary regions in the polycrystalline structure studied is the same as that created by a quasi-continuous energy spectrum of the traps.

The current relaxation decay observed for the structure is accompanied by the accumulation of charge whose value can be determined from the area lying under the curve of the time dependence of the current. In figure 2, the values of this charge are plotted as functions of the applied electric field. We can notice that in low electric fields, the accumulated charge increases to a first approximation by the quadratic law, while with the further increase, the polarization varies according to linear dependence.

As follows from the theory developed in [5], the electric current passing through the system and the accumulated charge are related by the expression

\[ Q = C_e U - \sqrt{\frac{C_e L^3 I}{\mu_{\text{eff}} d_e}}. \] (1)

It can be seen from expression (1) that, at each instant of time, the accumulated charge is proportional to the square root of the current flowing through the system. Relationship (1) holds for the voltages and times corresponding to the descending branches of the relaxation characteristics. It is worth noting that the lower the voltage and the shorter the time, the better the fit of relationship (1) to the experimental data.

Figure 3 shows the experimental dependences of the charge accumulated in the Pb$_2$O$_4$ within different time intervals on the electric current measured at the same times. These dependences were obtained at the applied electric field \( E = 8.0 \cdot 10^5 \) V/m (curve 1) and \( 9.0 \cdot 10^5 \) V/m (curve 2) in the range of the descending branches of the relaxation characteristics. In this case, the currents \( I \) are the experimental values after subtracting the background current \( I_b \), which corresponds to the leakage current. The background current \( I_b \) was chosen equal to the minimum value in the descending branch of the relaxation characteristic at a specified voltage and a longer time. The dependences constructed in the \( \sqrt{I} - Q \) coordinates exhibit linear behavior in accordance with the relationship (1).
Figure 3. Charge accumulated in the Pb₃O₄ layers for fixed time intervals of the effect of voltage as a function of the current corresponding to the ends of these intervals for the electric fields \( E \): 1 – 8.0 \( \times \) 10⁵, 2 – 9.0 \( \times \) 10⁵ V/m. \( T = 300 \) K.

The curves of current decay for Pb₃O₄ layers at different temperatures are shown in figure 4. It was noted that at high temperatures, the power dependence \( I(t) \) goes into exponential. The main contribution to conductivity is probably caused by thermal activation of charge carriers from deep capture levels. In accordance with the relay mechanism, their electron drift mobility \( \mu \) depends exponentially on temperature [4].

Figure 4. Kinetics of the polarization current measured for Pb₃O₄ layers at temperature \( T \): 1 – 320, 2 – 340, 3 – 360, 4 – 370 K. \( E = 5 \times 10^{5} \) V/m.
The exponential decay of current can be determined by the following expression [6]:

$$I(t) = \frac{q\mu \mathcal{E} S}{\tau_d} \exp \left( -\frac{t}{\tau_d} \right)$$

with

$$\tau_d = \frac{1}{N_c \sigma_i} \exp \left( -\frac{E_t}{kT} \right),$$

where $n_i$ is the initial density of trapped electrons, $S$ – the area that the current is flowing through, $\mathcal{E}$ – intensity of applied electric field, $\sigma_i$ – the conduction of trapped electrons, $N_c$ – the concentration of electrons in the conduction band, $E_t$ – the energy of trapped electrons, $k$ – Boltzmann constant.

According to (2) and (3) the current decays exponentially in time with a time constant equal to $\tau_d$. Thus, if the measurements are repeated at slightly different temperature, $\tau_d$ can be obtained as a function of temperature by plotting $\ln(I)$ versus $t$. Therefore, on the basis of (3), $E_t$ can be deduced from the slope and the intercept, respectively, of the straight line representing $\ln \tau_d$ against $1/kT$.

In figure 5 the plot of $\ln \tau_d$ versus $1/kT$ for Pb$_3$O$_4$ is reported. Temperature dependence of $N_c \sigma_i$ has been neglected in comparison to the exponential term of the temperature. The slopes of the dependence $\ln \tau_d (10^3/T)$ were determined to be $E_{t1} = 0.13$ eV and $E_{t2} = 0.38$ eV.

![Figure 5](image-url)  

**Figure 5.** Semi-logarithmic plot of $\ln \tau_d (1/T)$ for Pb$_3$O$_4$ layers, $E = 5 \cdot 10^5$ V/m.

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4. Conclusions
Thus, the behavior of main characteristics of the relaxation process occurring in Pb₃O₄ layers are in agreement with the theory of the relay mechanism of charge transport under the conditions of nonuniform distribution of local centers in metal–(high-resistivity semiconductor)–metal structures. The study of current relaxation related to the accumulation and redistribution of space charge extends our understanding of photoconductivity mechanisms and charge transport in IV–VI compounds with variable ionic–covalent bonding and a tendency towards the formation of naturally disordered structure.

References
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