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Nonstationary photocurrent and pyroelectric response in aged $Sn_2P_2S_6$ films

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Abstract

The photoelectric and pyroelectric properties of $Sn_2P_2S_6$ films were studied by a dynamic method under excitation by periodic rectangular laser beam pulses ($\lambda = 6328$ Å). In this case, an appearance of the nonstationary photoelectric response in the films under visible light irradiation (extrinsic excitation) was observed. It was found that temperature dependence of the unsteady current is connected to features of spontaneous polarization behaviour in $Sn_2P_2S_6$ thin films. A nature of the nonstationary photoelectric response existence due to an electric field of the potential barrier near an interface is discussed.

Keywords: Films; Ferroelectric properties; Electrical properties; $Sn_2P_2S_6$

1. Introduction

In spite of a variety of promising applications of thin ferroelectric films as functional elements of modern microelectronic devices and sensors many aspects of their behaviour under the influence of external factors are known scarcely and need to be studied extensively. In particular, more detailed understanding of the mechanisms of thermally and electrically stimulated changes and ageing effects in ferroelectrics is necessary to improve the stability of ferroelectric functional elements.

Ferroelectric semiconductor tin-thiohypodiphosphate $Sn_2P_2S_6$ films appeared to be very promising for microelectronics applications, e.g. in memory devices.[1] Earlier, we reported on the transient photocurrents arising in $Sn_2P_2S_6$ films under extrinsic and intrinsic light excitation ($h\nu \geq E_g$ and $h\nu < E_g$, $E_g = 2.4$ eV, bandgap energy).[2–4] It was demonstrated that illumination of $Sn_2P_2S_6$ films in the absence of an external electric field is accompanied by a turn-on transient current pulse with relaxation. The same effect is observed for the pyroelectric response. Nature of these transient effects in $Sn_2P_2S_6$ films is still not quite clear and further investigations are necessary.

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At room temperature bulk $Sn_2P_2S_6$ single crystals are proper uniaxial ferroelectrics[5,6] obeying $P2_1/c \Leftrightarrow Pc$ ferroelectric phase transition of second order at the Curie temperature $T_C = 66$ °C. The spontaneous polarization appears roughly along the [1 0 1] direction. The main applications of the $Sn_2P_2S_6$ single crystals are based on their remarkable optical properties, in particular, strong photovoltaic effect. This fact strengthens the interest in the study of stable thin film variants of $Sn_2P_2S_6$ with improved properties.

In the present work, we continue our studies of the effect of ageing on the pyroelectric response and nonstationary short-circuit photocurrent of $Sn_2P_2S_6$ films aged over a period of 10 years.

2. Experimental details

Polycrystalline $Sn_2P_2S_6$ films with a thickness of ≈5 μm were used for photoelectric and pyroelectric measurements. The films were vacuum evaporated on Al substrates of 100 μm thickness and annealed at 200 °C for several hours to avoid possible defects and internal mechanical stresses. Circular aluminium electrodes with diameters of 10 and 3 mm were deposited onto the films through a metal mask to fabricate a MDM structure for photoelectric and pyroelectric investigations. The $Sn_2P_2S_6$

films used in the experiments were prepared 10 years ago and kept in the dark under normal room temperature environment without external perturbations.

The photoelectric and pyroelectric parameters of the samples were determined by the dynamic method using a He–Ne laser ($\lambda = 6328$ Å, $P = 30$ mW). Laser beam intensity was modulated by a mechanical chopper forming irradiation pulses of rectangular shape at a frequency of 24 Hz. The summarized photo- and pyroelectric response was determined with a lock-in amplifier. The reference signal for the determination of the current direction and phase of the summarized response was obtained with the aid of a photodiode.

3. Results and discussion

It was found that the main features of the nonstationary photocurrent behaviour were the same as before the 10-year ageing period. As earlier, the temperature dependence of the nonstationary photoelectric current (NSPC) reveals a wide maximum at ∼40 °C and a wide minimum near 80 °C at heating, and a rounded maximum in the region 80–100 °C at subsequent cooling run (first temperature cycling in the region 20–140 °C, Fig. 1). The inset of Fig. 1 shows a shape of the transient photoelectric response. The temperature dependence of NSPC is plotted for amplitude values of the photoelectric response. It is essential to note a shift of the maximum toward lower temperatures after ageing; before ageing it was observed at 60 °C.[2] Earlier, such a strong displacement of the NSPC maximum was noticed after polarizing of the virgin $Sn_2P_2S_6$ films in a direction opposite to that of natural polarity.

The photoelectric response during cooling is characterized by a smeared peak in the vicinity of 80 °C corresponding to a minimum of NSPC measured during heating. A sharp decrease of the NSPC occurs below 80 °C. Analysis of the NSPC behaviour shows that the photoelectric response of the films is connected to the spontaneous polarization. This follows from the fact that the region of the drastic changes of the NSPC temperature dependence is near the phase transition point of the $Sn_2P_2S_6$ single crystal.

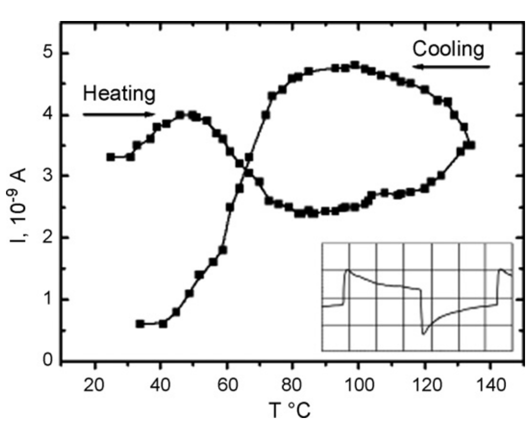

Fig. 1. Temperature dependence of the nonstationary photocurrent in aged samples of the $Sn_2P_2S_6$ films. First thermal cycling. There is a shape of the unsteady photoelectric response in the inset.

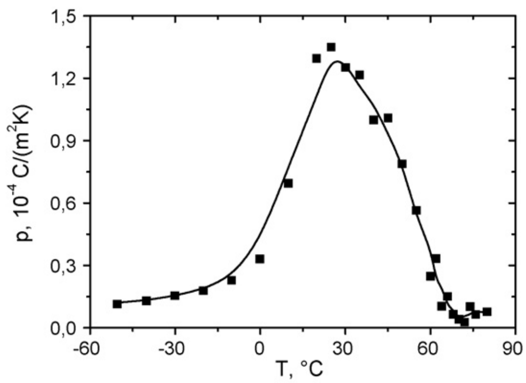

Fig. 2. Temperature dependence of the pyroelectric coefficient of aged $Sn_2P_2S_6$ films determined by the sinusoidal temperature wave method.

It may be concluded that in the course of ageing the films pass on to a state equivalent to that achieved by polarizing the virgin films in the direction opposite to the direction of self-polarization. Therefore, the ageing effect in the semiconductor ferroelectric $Sn_2P_2S_6$ films may be caused by the formation of internal electric fields opposing the direction of natural polarity.

Using the irradiation laser source with a wavelength of 6328 Å results in NSPC noticeably larger than the pyroelectric response at the same conditions. On this account, the pyroelectric measurements were carried out with a sinusoidal temperature wave method. This method is similar to that described by Garn and Sharp.[7] As a result, it was found that the pyroelectric response maximum is shifted to the low-temperature region. In the case under study, it corresponds to $T_m \approx 30$ °C (Fig. 2).

For single crystal samples the pyroelectric current maximum is observed at 66 °C. However, in virgin films the pyroelectric response maximum shifts down to $T_m \approx 55$ °C.[2] So the further shift to $T_m \approx 30$ °C (Fig. 2) is due to the process of ageing. It may be suggested that the strain relaxation which is likely to occur near the substrate/film/top electrode interfaces and between crystalline grains inside the film may lead to a change of mechanical conditions, which is equivalent to the external electric field effect.

We have also studied the thermal cycling effect (repeated heating and cooling in the temperature range 20–150 °C) on the behaviour of the NSPC. It was found that the NSPC maximum at 40 °C and minimum at 80 °C (Fig. 3) are not observed if the second heating is performed immediately after the first thermal cycle. The NSPC maximum shifts to the high temperature region near 100 °C. Thermal hysteresis of the photoelectric response is observed during cooling with the maximum near 90 °C. The location of the latter is in agreement with the results of the first thermal cycling.

It is remarkable that successive thermal cyclings do not change the observed NSPC behaviour of $Sn_2P_2S_6$ films if the cycling is carried out continuously. The previous temperature dependence shown in Fig. 1 recovers within a few days.

Further studies of the specific features of NSPC were made with the samples subjected to high temperature annealing in air at

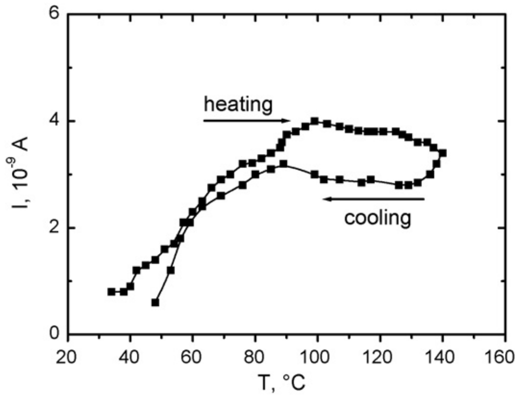

Fig. 3. Temperature dependence of the nonstationary photocurrent in aged samples of the $Sn_2P_2S_6$ films. Second thermal cycling.

350 °C for 2 h. The temperature dependence of the photoelectric response of annealed $Sn_2P_2S_6$ films is shown in Fig. 4 for the processes of heating and cooling. As seen from the presented figure, the NSPC reaches the maximum at 80 °C both in the heating and cooling processes. Thus, in the annealed samples the thermal hysteresis is not observed.

It is known[8] that a transient photoelectrical response is observed in film structures of lead zirconate-titanate (PZT). Its appearance is attributed to the depletion of deep traps and separation of nonequilibrium charge carriers by an electric field of the Shottky barrier. The NSPC observed in $Sn_2P_2S_6$ films may have the similar nature. In this case, the surface energy levels near the top interface may play a role of the traps. An existence of the local surface levels leads to “sticking” of charge carriers to the surface. As a result, there is a space charge near the surface. It induces another space charge of the same magnitude but opposite sign in the surface layer of the film. Therefore, there is an electric field in the interface region inducing bending of the energy bands. A difference of potentials between the surface of the film and its bulk defines the surface electric potential.[9] A surface photoelectromotive force (photo-emf) in the $Sn_2P_2S_6$ films originates from an existence of the energy potential barrier near the surface due to the surface levels. At the light generation of electron-hole pairs near the interface, the photo-stimulated charge carriers are separated by the electric field of the barrier. However, the NSPC depends on a temperature change.

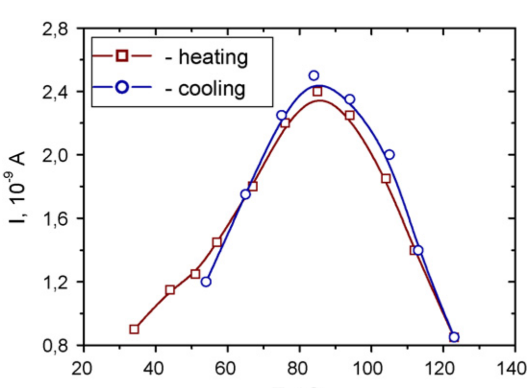

Fig. 4. Temperature dependence of the nonstationary photocurrent in aged samples of the $Sn_2P_2S_6$ films after annealing.

The observed temperature anomalies of the transient photocurrent in the $Sn_2P_2S_6$ films may be attributed to the change of the free nonequilibrium charge carriers lifetime. It is known that in ferroelectrics the carrier lifetime strongly changes in the phase transition region. According to the experimental data, the NSPC varies considerably in the temperature region where the spontaneous polarization of $Sn_2P_2S_6$ material vanishes with heating from the low-temperature phase and appears with cooling from the high temperature one.

4. Conclusion

In the work, we have examined the nonstationary photoelectric current in ferroelectric semiconductor $Sn_2P_2S_6$ films in the temperature range from 20 to 150 °C. It is shown that in the aged samples the maximum of the NSPC and that of the pyroelectric response obtained by the sinusoidal temperature wave method are significantly (by 20–30 °C) shifted downward with respect to the phase transition point of a single crystal $Sn_2P_2S_6$. However, both heating up to a temperature well above the Curie point T_C and annealing at 350 °C result in a NSPC maximum in the temperature range ∼15 °C above the phase transition point. Furthermore, the high temperature annealing removes the thermal hysteresis of the NSPC. The downward shift of the NSPC maximum is connected to the formation of an internal electric field during ageing, in a direction opposite to that of the natural polarity of the samples. Apparently the heating above T_C during thermal cycling and annealing destroy this field. There remains an electric field connected to the natural polarity which produces the upward shift of the NSPC maximum. The appearance and disappearance of the internal electric fields have an effect on the free nonequilibrium charge carrier lifetime thereby modifying the NSPC temperature behaviour.

Acknowledgements

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