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Photoelectric State with Long-Term Relaxation in CdTe:(Ag, Cu, Cd) and Sb₂Se₃:Se Photovoltaic Films

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Abstract

The results of an experimental study of long-term relaxation of the photoelectret state of polycrystalline CdTe:(Ag, Cu, Cd) and Sb₂Se₃:Se films with an anomalous photovoltaic property are presented. In such films, the residual photovoltage is caused by the separation of photocarriers by the built-in electrostatic field of the near-surface region of space charges and their asymmetric capture by deep levels of impurities or complexes, including impurity atoms and intrinsic defects, both in the bulk and on the surface of crystal grains. It has been shown that in activated films, a two-step exponential temporary relaxation of the initial photovoltage of the order of $V_{APV} \approx (500 - 600)$ V is detected, and only 10% of it experiences long-term relaxation (t ≈ 100 - 120 min).

Keywords

Thin Polycrystalline Films, Doping, Deep Centers, Anomalous Photovoltage, Photoelectret State, Long-Term Relaxation

1. Introduction

Recently, in opto- and photoelectronics, considerable attention has been paid to the development of cheap light emitters, photodetectors, ionizing radiation detectors and efficient solar cells with improved optical and photoelectric properties based on solid solutions and heterostructures of cadmium chalcogenides [1] [2] [3] [4]. At the same time, cadmium telluride, which has deep centers with significantly different electron and hole capture cross sections, remains a very attractive object with unique physicochemical properties [5] [6] [7] [8]. In this re-

gard, the study of long-term relaxation of anomalous photovoltage (*APV*) during dark depolarization of photoelectrets depending on the polarization conditions is of interest when analyzing the mechanisms of formation and destruction of the photoelectret state (*PES*) without an external field in semiconductor polycrystalline films of *CdTe:M* [9] [10] [11] [12]. Previously, in [11], the results of studying the time kinetics of photopolarization of film photoelectrets "without an external field" were presented, and photopolarization curves and polarization isopaacs were analyzed. In this work, we will consider the relaxation processes for *APV* and *PES* in *CdTe:*(*Ag*, *Cu*, *Cd*) and *Sb₂Se₃:Se* films depending on the method of photopolarization and dark depolarization at different temperatures. It is shown that in the studied polycrystalline films, a two-stage time relaxation of the maximum stationary value of *APV* of the order of $V_{APV} \approx (500 - 600)$ *V* is detected with characteristic times $\tau_{init} \approx (2 - 3)$ *min* and $\tau^* \approx (20 - 45)$ *min*, and almost 90% - 95% of V_{APV} disappears within ~(10 - 20) *min*, and the rest, as photoelectret voltage (*PEV*), experiences long-term relaxation (~100 - 120 *min*), which confirms the formation of *PEV* in activated films.

2. Technological Method

The studied films from CdTe and Sb₂Se₃ in size 5×20 mm² and a thickness of 1.0 - 1.2 μm were produced by thermal evaporation in vacuum 10^{-3} - 10^{-4} mm. Hg alloying with appropriate impurities directly during the deposition of semiconductor material at an angle of 40˚ - 50˚ to a glass substrate, heated to 250˚C - 300˚C.

In this case, the impurity materials *Ag*, *Cu*, *Cd*, and *Se* evaporated from a separate crucible at a rate of 1.8×10^{-6}, 1.3×10^{-6}, 2.9×10^{-6} and 3.5×10^{-6} *g/cm² s* for 4, 10, 6, 8 *s*, respectively. The evaporation of impurities was carried out for films of cadmium telluride and Sb₂Se₃ no later than 35 *minutes* and 22 *minutes* from the initial moment of semiconductor deposition. After deposition of the impurity, the growth of films continued for another 30 - 50 *minutes*.

Samples of *CdTe* photoelectret films with *Ag*, *Cu* and *Cd* impurities were obtained at a substrate temperature in the range from 150˚C to 350˚C. Table 1

Table 1. Maximum values of V_{APV} and V_{PEV} CdTe films depending on the substrate temperature.

Films	t_{ϑ}, ˚C	150	180	210	230	250	275	300	325	350
CdTe:Ag	V_{APV}, V	215	265	320	460	525	550	580	320	210
	V_{PEV}, V	15	28	43	52	62	69	78	36	14
CdTe:Cu	V_{APV}, V	195	220	240	275	310	380	455	270	195
	V_{PEV}, V	10	17	22	28	35	39	45	14	8
CdTe:Cd	V_{APV}, V	205	268	315	457	514	532	556	280	200
	V_{PEV}, V	12	17	21	31	44	51	62	21	11
CdTe	V_{APV}, V	200	260	305	450	510	525	550	300	205

shows the maximum values of V_{APV} and V_{PEV} generated by photoelectret films *CdTe:Ag*, *CdTe:Cu* and *CdTe:Cd*, as well as V_{APV} by pure *CdTe* film, depending on the substrate temperature t_s under stationary illumination with a mercury lamp with an intensity of 500 *lux*. Measurements of V_{APV} and V_{PEV} were carried out with an electrostatic voltmeter with sufficient internal resistance at room temperature in atmospheric air. It can be seen that such values of V_{APV} and V_{PEV} gradually increase with increasing t_s to 300˚C, and then drop sharply.

The main distinctive technological parameters of obtaining films of triselenite antimony (Sb_2Se_3:Se), which have optimal photoelectric properties, are the following (see Table 2): temperature of selenium evaporation was $t_e = 165$ ˚C, degree of vacuum was ~5×10^{-5} *mm Hg*, the average deposition time of Sb_2Se_3 was ~50 *min*, the thickness of both activated and initial films was ~1.5 *μm*, the deposition angle was ~45˚, the time interval for deposition of impurity material from the beginning of deposition of the semiconductor material was 20 *min*, the optimal deposition rate of the Sb_2Se_3 film was $v \le 0.5$ *nm/s*.

3. Experimental Results and Their Discussion

Photopolarization [11] and dark depolarization curves of anomalous (*APV*) and photoelectret (*PEV*) voltages were recorded in the dark and in idle mode at room temperature. Figure 1(a) shows the time dependence on a semi-logarithmic scale for doped *CdTe:Ag* (1, 2, 3) and control *CdTe* (4) films. Curves 1 and 2 correspond to the relaxation of V_{APV} in *CdTe:Ag* films in air and in a vacuum of 10^{-2} *mm Hg*, and Curve 3 represents the relaxation of the photovoltage of the same film in air after incomplete photopolarization (polarization time: 2 - 3 *s*). Straight line 4 characterizes the progress of V_{APV} relaxation of the control sample obtained under identical conditions with activated films. From relaxation of Curves 1 – 4, it is clear that the long-term decay time of the *APV* of the doped *CdTe:Ag* film ($t \approx 120$ *min* at $V_{APV} = 1$ *V*, and $V_{APV}(t = 0) \approx 600$ *V*) is significantly longer than the decay time of the undoped cadmium telluride film ($t \approx 20$ *min* at $V_{APV} = 1$ *V*, and $V_{APV}(t = 0) \approx 500$ *V*). So, from the initial sections of Curves 1 - 3, collinear to straight line 4, we determine that $\tau_M \approx 3$ *min*. If we take into account the resistance of the films under study $R \approx 10^{12}$ Ohm, we will obtain for their electrical capacity the value $C \approx 200$ *pF* ($\tau_M = R \cdot C$). Secondly, for a *CdTe:Ag* film, the stationary value of $V_{APV} \approx 600$ *V*, regardless of the depolarization method (Curves 1, 2), first relaxes with a characteristic time $\tau_{init} \approx 3$ *min* to a value of

Table 2. Maximum values of V_{APV} and V_{PEV} Sb_2Se_3 films depending on the substrate temperature.

Films	t_s, ˚C	150	175	200	225	250	275	300	325
Sb_2Se_3:Se	V_{APV}, V	95	200	335	448	512	455	352	213
	V_{PEV}, V	5	12	27	41	58	43	22	8
Sb_2Se_3	V_{APV}, V	92	210	330	445	505	450	345	205

$V_{APV} \approx 55$ *V*, with almost 90% of V_{APV} disappearing for ~10 *min*. Next, long-term relaxation is detected, and the decay time to the values of $V_{APV} = 1$ *V* for the same *CdTe.Ag* film in air and in vacuum differed by tens of minutes (120 *min* of Curve 1 and 90 *min* of Curve 2 in **Figure 1(a)**). This is explained by the fact that the value of V_{APV} of films exposed to air or in an atmosphere of other gases is affected by ions and electrons adsorbed on the surface of the sample.

To separate the "pure" *PEV* from the *APV*, the contacts of the photopolarized sample were short-circuited for 2 - 3 *s*. When the film was again connected to the electrometer, then after ~10 *s* a stationary $V_{PEV} \approx 100$ - 150 *V* was established.

Figure 1(b) shows the depolarization curves of "pure" *PEV* for two samples of activated *CdTe.Ag* films obtained under the same technological conditions.

From the depolarization curves V_{PEV}, it is clear that each of them has two characteristic straight sections, just like the curves $V_{APV}(t)$ in **Figure 1(a)**, for which the depolarization of the photovoltage is described by an exponential dependence:

$$V_{PEV} = V_{PEV}^{ST} \exp\left(-\frac{t}{\tau^*}\right) \tag{1}$$

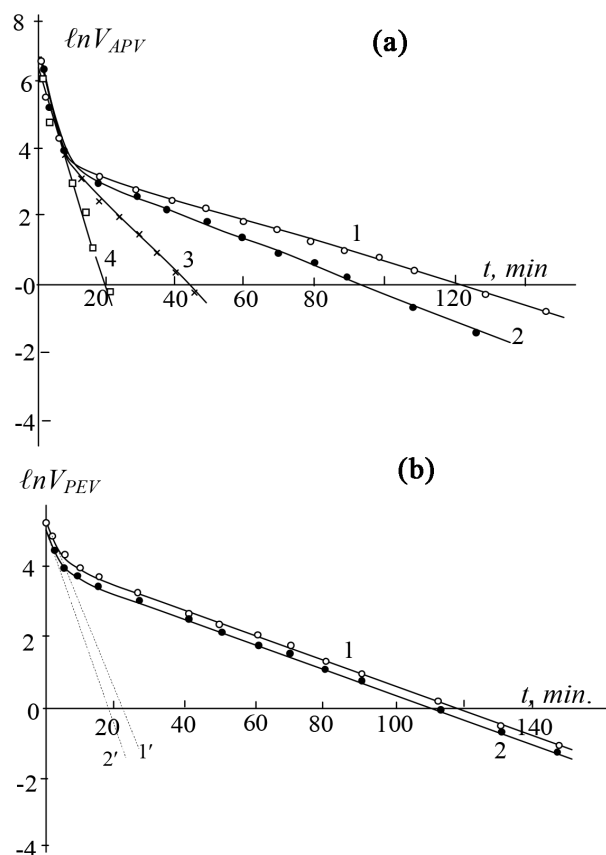here, V_{PEV}^{ST} is the initial value of the stationary *PEV* (in **Figure 1(b)** $V_{PEV}^{ST} =$

Figure 1. Time relaxation curves of V_{APV} for films of *CdTe.Ag* (1, 2, 3), *CdTe* (4) (*a*) and depolarization curves of "pure" V_{APV} for two *CdTe.Ag* samples obtained simultaneously (b). *T* = 293 *K*.

$V_{PEV}(t = 0) \approx 150$ *V* for the initial section, and for the second section $V_{PEV}^{ST} \approx 50$ *V*), τ^* is the characteristic lifetime of minority charge carriers at deep impurity levels, the value of which is different for sections of curves with different slopes.

The initial sections (for clarity, dashed straight lines 1′, 2′ are drawn) of the relaxation curves correspond to a relatively rapid decline in V_{PEV} (where $\tau = \tau^* \approx$ 2 *min*) and are associated with the presence of not very deep levels of adhesion in the films, leading to the formation of weak *PES*. Naturally, the second region with long-term relaxation V_{PEV} ($\tau = \tau^* \approx 35$ *min*) is due to deeper levels of minority carrier capture centers and the manifestation of significant *PES* in the *CdTe:Ag* film.

Figure 2 shows the V_{PEV} relaxation curves for *CdTe* (Curve 1), *CdTe:Cu* (Curve 2), Sb_2Se_3:*Se* (Curve 3) films after complete photopolarization. As can be seen from the figure, for Curves 1 - 3 the maximum *PEV* values are $V_{PEV}^{ST} \approx 70$, 60 and 50 *V*, and the decay times at $V_{PEV} = 1$, *V* are 150, 85 and 60 *min*, respectively. The region of the relatively rapid decline in V_{PEV} in all studied samples has a qualitatively identical character and practically does not depend on the exposure $Z = L \cdot t$. The second section of the curves, corresponding to the long-term decline in V_{PEV}, significantly depends on exposure (compare the curves in **Figure 1(b)** and **Figure 2**).

The values of τ_{init} and τ^* were determined from the slope angles of the dark depolarization curves V_{PEV} as:

$$\tau = t \left/ \ell n \frac{V_{PEV}^{ST}}{V_{PEV}(t)} \right. . \tag{2}$$

Figure 3 shows the dependences of the characteristic relaxation times τ_{init} and τ^* calculated by (2) on the photopolarization time in the case of excitation of the films under study with natural light of intensity $L = 8 \times 10^{-2}$ *W/cm²* at room temperature.

As can be seen from the figure, the maximum value of τ^* for the *CdTe:Cd, CdTe:Ag, CdTe:Cu* and Sb_2Se_3:*Se* films (Curves 1-4) reached values of 40 - 45, 30 - 35, 25 - 30 and ~24 *min*, while the value of $\tau_{init}(1' - 4')$ was only 2 - 4 *minutes* at $t > 10$ *s* and did not depend on the photopolarization time. It further turned out
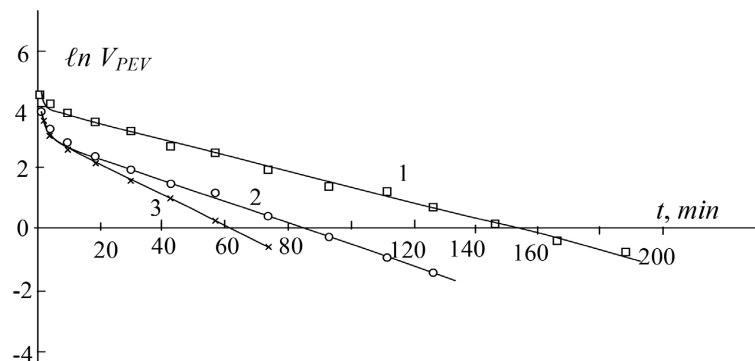

Figure 2. V_{PEV} depolarization curves for photovoltaic films *CdTe:Cd* (Curve 1), *CdTe:Cu* (Curve 2) and Sb_2Se_3:*Se* (Curve 3) at T = 293 K.
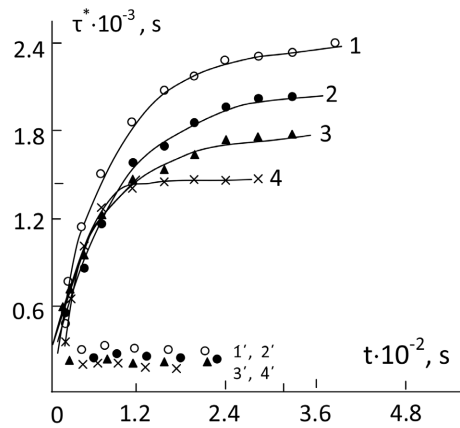
Figure 3. Dependences of $\tau_{init}(1' - 4)$) and τ^* (1 - 4) on photopolarization time for films $CdTe{:}Cd$ (1, 1'), $CdTe{:}Ag$ (2, 2'), $Sb_2Se_3{:}Se$ (3, 3'), $CdTe{:}Cu$ (4, 4').

that with decreasing temperature, the value of τ^* increased sharply and was measured in hours, and the value of τ_{init} weakly depends on temperature. These results once again show a significant difference in the depth of the energy levels of the attachment centers responsible for the rapid (τ_{init}) and long-term (τ^*) relaxation of the *PES* in the films under consideration. The experimental value τ allows using the expression [9]:

$$\tau = \lambda\tau' = \frac{M}{N_\upsilon}\exp\frac{\Delta\varepsilon_M}{kT}\cdot\tau' \tag{3}$$

determine the activation energy of deep levels of adhesion $\Delta\varepsilon_M$, responsible for a particular relaxation of the *PES* film. Here, τ' is the effective lifetime of the minority carrier at the local level, M is the concentration of deep centers, N_v is the effective density of states in the valence band. From the second linear section of the dependence $V_{PEV}(t)$ in **Figure 1(b)**, we find the characteristic relaxation time $\tau = \tau^* = 35$ *min*.

If we assume that this main section of the *PEV* relaxation curve is associated with the capture of holes at a deep impurity level, then taking for this level $M = 5 \times 10^{17}$ cm^{-3}, $\tau' = 10^{-7}$ s and $kT = 0.025$ eV, we obtain the following value of its depth occurrence:

$$\varepsilon_{M2} = \varepsilon_v + 0.025\,\text{эB}\times(40 - 15\times2.3 + 7.69) = \varepsilon_v + 0.33\,\text{эB}, \tag{4}$$

which coincides well with the position of the main impurity level of Ag in $CdTe$ [14]. This value of the activation energy is also confirmed by the results of studies of the temperature dependence $\tau^*(T)$ (**Figure 4**), in which a level of 0.3 $\pm$ 0.02 eV appears in the temperature range of 300 - 400 ˚K, and in the temperature range of 200 - 250 ˚K, described by the dependence $ln\tau^*{\sim}T^{-1/4}$ (it is assumed that τ^* is determined by electrical conductivity as in a disordered semiconductor of the Mott's law type, which is observed in highly compensated $CdTe$)—one small level $\varepsilon_{M1} = \varepsilon_v + (0.05 - 0.11) \pm 0.02$ eV [12].

The energy levels $M1$ and $M2$ discovered here by the method of temporary relaxation of *PES* are also observed in the temperature dependences of $R_{fl}(T)$,

$V_{PEV}(T)$, and a level with an activation energy of 0.32 eV was previously observed in the optical spectra of the stationary photoelectret voltage $V_{PEV}(\lambda)$ and short-circuit current $I_{s.c.}(\lambda)$ of *CdTe:Ag* films [12] From this we can make the statement that the *PES* of activated *CdTe:Ag* films without an external polarizing field is due to deep impurity levels of *Ag* or its complexes, which is also the case for other studied films *CdTe:Cd, CdTe:Cu* and *Sb₂Se₃:Se.*

The experimental relaxation curves of V_{PEV} allowed us to estimate the effective values of the electrical capacitance of the activated films. The film capacitance (C_{fl}) was determined from the formula $\tau^* = R_{fl}(C_{cc} + C_{fl})$, where C_{cc}-circuit capacitance (in our measurements $C_{cc} \approx 3$ pF).

Table 3 shows the values of the electrical capacitance of the *APV* films of *CdTe* and *Sb₂Se₃*, determined by us for control and activated samples, where a
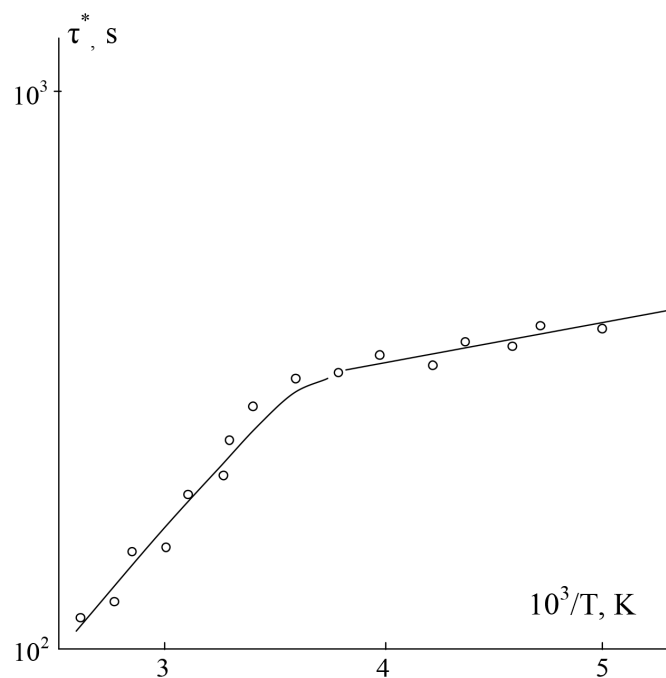

Figure 4. Temperature dependence for *CdTe:Ag* films.

Table 3. Comparison of the electrical capacity of films *CdTe* and *Sb₂Te₃*.

Electrical capacity of films according to the results of well-known works [9] [13], C_{fl}, pF		Electrical capacity of control and activated films, C_{fl}, pF			
		Tests		Activated	
CdTe 9]	3.7	*CdTe*	4.1	*CdTe:Ag*	320
CdTe 9]	2.8	*CdTe*	3.5	*CdTe:Cd*	315
CdTe 9]	3.6	*CdTe*	4.1	*CdTe:Cu*	270
Sb₂Te₃ 13]	1.0	*Sb₂Se₃*	3.2	*Sb₂Se₃:Se*	310

Note that increasing the electrical capacity and power of *APV* films, as a system of series-connected microphotocells that directly generates high photovoltage, is one of the pressing problems of photoelectronics.

comparison is made with the results of [9] [13].

The table shows that at room temperature, activated films of *CdTe:Cd, CdTe:Cu* and *Sb₂Se₃:Se* have significantly larger (almost two orders of magnitude) capacitances compared to undoped films of cadmium telluride and antimony triselenide. Naturally, such an increase in the capacity of *APV*-activated films is associated with the possibility of charge accumulation at deep adhesion levels [10].

4. Conclusion

In thin photovoltaic films of *CdTe:Cd, CdTe:Cu* and *Sb₂Se₃:Se*, a two-stage exponential time relaxation of the initial photovoltage $V_{APV} \approx$ (500 - 600) *V* was discovered, and ~10% of it experiences long-term relaxation (t~60 - 150 *min*) due to the formation of *PES*, due to the fact that deep centers with significantly different electron and hole capture cross sections predominate in photocarrier recombination processes. Analysis of the obtained experimental results allows us to conclude that the probable centers responsible for the *PES* are impurity complexes consisting of a *Cd* vacancy and a metal ion (*Ag, Cu*) in the *Cd*:($V^{2-}M^+$) position. Some parameters of such centers have been determined.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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