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ELECTRIC PROPERTIES OF SOME XEROGRAPHIC LAYERS OF AMORPHOUS SELENIUM DOPED WITH ARSENIC. PART I*

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Electrophotographic and fatigue properties of some xerographic layers made of amorphous selenium doped with arsenic (0—10.5 at. % As) and deposited on aluminium substrates at temperatures varying from 10 to 80°C are investigated and discussed.

Introduction

Selenium-arsenic alloys exhibit vitreous properties over a wide range of As concentrations (from 0 to *ca.* 60 at. %) and temperatures [1], [2], [4]. Previous studies [3] on the conductivity — temperature dependence for bulk alloys suggest that arsenic admixtures up to 5 at. % practically do not change the electric properties of selenium. Further addition of arsenic (from 4.8 to 44.5 at. %) enhances the conductivity, but simultaneously it stabilizes the durability of the alloys and improves the reproducibility of their physical properties [3].

The Se-As xerographic layers exhibit increased photoconductivity (as compared with pure Se layers) in the long-wavelength range of the visible spectrum [4], [5], in spite of the fact that doping selenium with As (in contrast with Te) does not appreciably affect the location and slope of the absorption edge of selenium [6]. Fotland [4] suggested that the As atoms (over some concentration range) may terminate the selenium chains, what probably causes the annihilation of deep electronic traps and diminishes the fatigue effects of the electrophotographic layers. However, Laugwitz [5] noticed that increasing concentration of As considerably enhances the residual potentials of the negatively-charged layers.

The aim of the present paper is mainly to elucidate the effect of doping of selenium with arsenic on the fatigue properties of xerographic layers.

Preparation of the samples and the method of measurements

"Black powder" selenium (redistilled 3 times) [7] and spectrally pure arsenic ("Matthey Arsenic", containing 10^{-5} wt. % of Fe, Si, Mg, Al and Ca) were used to prepare their alloys. The finely powdered elements were introduced into "Termisil" glass ampoules, which were

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subsequently evacuated (10^{-4} torr) and sealed; then the ampoules were uninterruptedly rocked in a furnace at 600°C for 5 hrs. After being slowly cooled down to 320°, the alloys were quenched in glacial water.

The Se-As alloys (containing 0–10.5 at. % As) were evaporated onto aluminium substrates maintained at various temperatures (10–80°C); a common vacuum depositing system was applied [7].

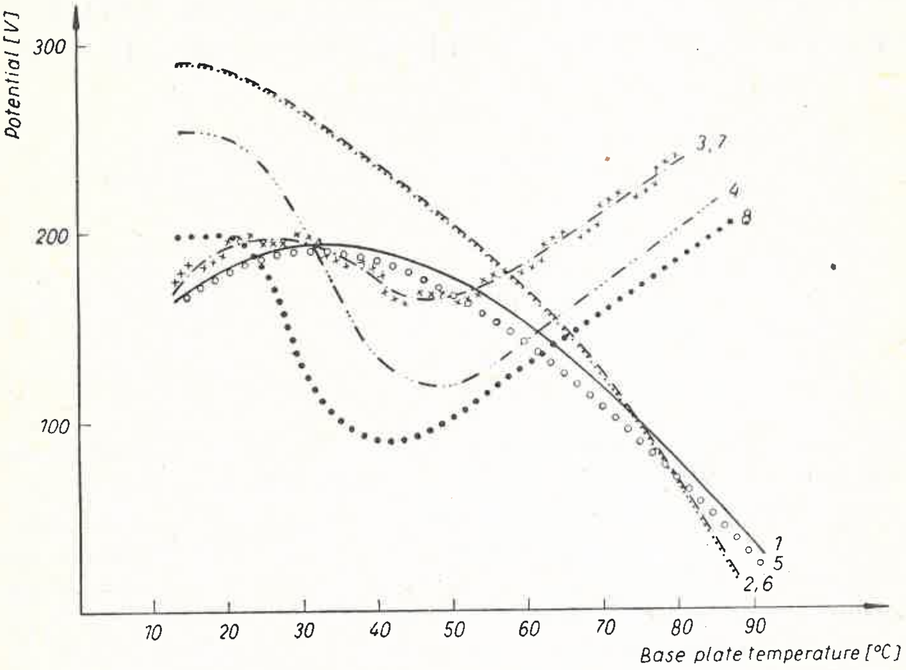

Fig. 1. U_0 as a function of the base plate temperature maintained during the selenium layer forming process: *1, 2, 5, 6* — negative polarity; *3, 4, 7, 8* — positive polarity; *1, 3, 5, 7* — concentration As 0.52 at. %; *2, 4, 6, 8* — concentr. As 3 at. %; *1, 2, 3, 4* — unfatigued layers; *5, 6, 7, 8* — fatigued layers

The selenium saturated vapour pressure for the tantalum boat temperature (235°C) is 9.29×10^{-3} torr [9]. Using the Raoult equation applied earlier by Dushman [8] for "diluted alloys", the saturated vapour pressures for the alloys were calculated: depending on the As content they varied from 8.8×10^{-3} to 9.3×10^{-3} torr. Spectral analyses of the corresponding layers removed from the glass substrates confirmed that the investigated Se–As system is stable also in the gas phase (*cf.* [3], [5]).

TABLE I

Confrontation of the As concentration in the starting bulk alloys and in the deposited layers

As, wt. % in the alloys	0.10	0.51	1.00	1.51	1.51	1.97	3.00	6.00	10.00
As, wt. % in the layers	0.08	0.52	1.00	1.60	1.58	2.10	3.00	6.20	10.00

The layers thus obtained were 10 μm thick and exhibited fairly uniform local saturation potentials, *e. g.*, 210 ∓ 25 V, over their entire surfaces [10].

The method of measurement of the electrophotographic properties, the definitions and notation used in this paper, as well as other experimental details, are explained elsewhere [7].

Results of measurements

The general character of initial potential U_0 as a function of substrate temperature maintained during the course of layer forming is fairly close to that characteristic of pure selenium layers [7]: great differences are found in the curves corresponding to negative and positive polarities (Fig. 1).

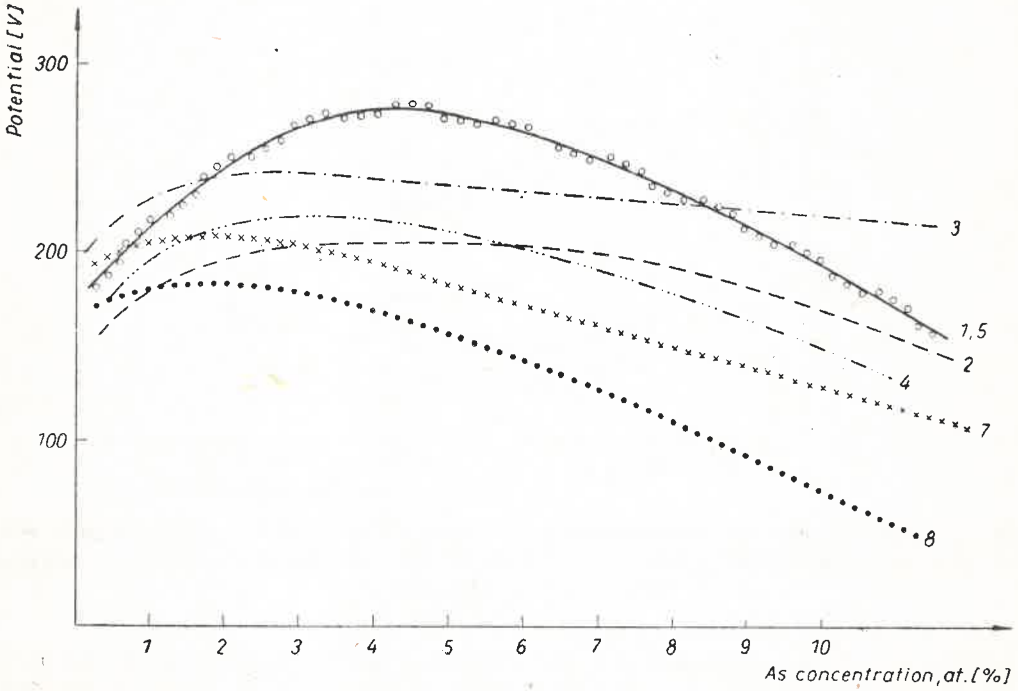

Fig. 2. U_0 as a function of arsenic concentration in selenium layers, $d = 10$ μm, $i = 0.5$ μA cm^{-2}. *1, 2, 5* — negative polarity; *3, 4, 7, 8* — positive polarity; *1, 3, 5, 7* — base plate temp. 27°C; *2, 4, 8* — base plate temp. 70°C; *1, 2, 3, 4* — unfatigued layers; *5, 7, 8* — fatigued layers

The negatively-charged layers show a shift of the potential U_0 maximum towards the lower substrate temperatures when the As concentration is growing (Fig. 1, curves *1* and *2*): 60°C, 35°C and 20°C for 0, 0.52 and 3.05 at. % As, respectively. The potential U_0 increases as the As concentration rises from 0 to 4 at. %, but its further growth results in a drop in U_0 (Fig. 2, curves *1* and *2*).

For positive polarity the experimental dependence of U_0 on base plate temperature is more complicated. The plates exhibit the lowest potentials U_0 when they are deposited at 40–60°C (Fig. 1, curves *3* and *4*). For the layers deposited below *ca.* 40°C there is a quicker increase in U_0 for the greater As concentrations. The As concentrations exceeding 3 at. % lower the positive initial potential considerably, particularly for the plates deposited on strongly heated aluminium substrates (Fig. 2. curves *3* and *4*).

The investigated layers show, similarly to those made of pure selenium [7], pronounced changes in the dark dacay rates depending both on applied polarity and substrate temperature. The time of dark dacay $t_{0.5d}$ for positive polarity depends only slightly on As concentration in all cases studied (Figs 3 and 4, curves *3* and *4*). Thus, the admixture of As slightly enhances the dark conductivity of the layers deposited both at room temperature (which was noted by Laugwitz [5]) and at the higher temperatures usually applied in the process of preparing xerographic plates. A comparison of curves *3* and *4* shown on Fig. 3 with those corresponding to pure Se shows that the As admixture has a distinct stabilizing effect, favourable for plate production.

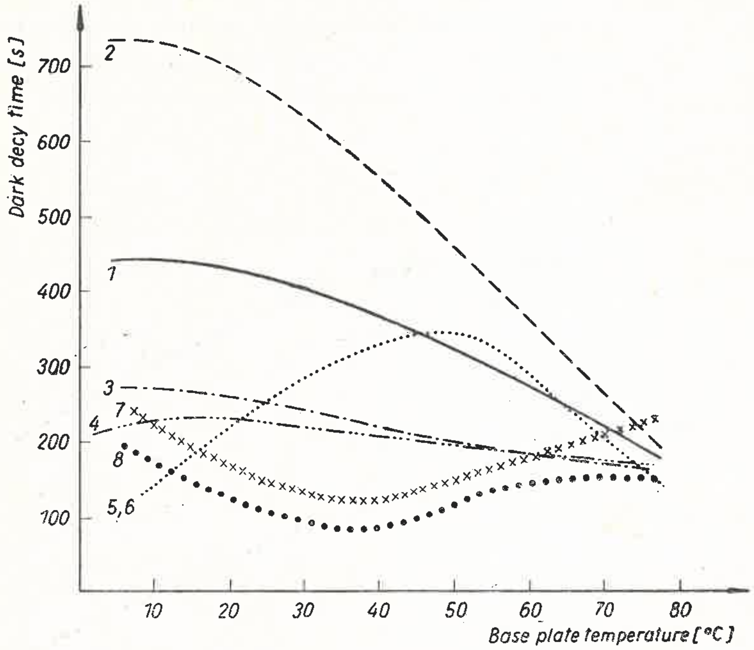

Fig. 3. $t_{0.5d}$ as a function of base plate temperature, $d = 10$ μm, $i = 0.5$ μA cm^{-2}. *1, 2, 5, 6* — negative polarity; *3, 4, 7, 8* — positive polarity; *1, 3, 5, 7* — 0.52 at. % As; *2, 4, 6, 8* — 3 at. % As; *1, 2, 3, 4* — unfatigued layers; *5, 6, 7, 8* — fatigued layers

The dark decay rate is lower for negative than for positive polarity, particularly for the layers prepared at 10–30°C, but both of them are greater than those for layers made of pure Se. The decay rate rises considerably as the base plate temperature is increased (Fig. 3, curves *1* and *2*). An increase of the As content, particularly above 5 at. %, only slightly affects the layer conductivity.

The selenium layers studied previously [7] did not show any residual potential U_r, irrespective of the polarity applied or whether they had been previously severely fatigued.

The As admixture results in the appearance of U_r (which is more pronounced for positive polarity); U_r grows as the As concentration is increased ($U_r = 30$ V for 10 at. % As) (Fig. 6, curves *1*, *2*, *3* and *4*). The highest values of U_r are found for the layers deposited onto plates maintained below 40°C (Fig. 5, curves *1*, *2*, *3* and *4*).

The general potential — sensitivity dependence for the investigated layers is fairly close to that found for pure Se layers (Fig. 7). Hence, the sensitivity drops as the plate potential increases. For the pure Se plates this drop is particularly abrupt for the potentials lower than 80 V (Fig. 7, curve *5*). It may be assumed that doping with As results in a decrease of the sensitivity at lower potentials and in its slight improvement at potentials exceeding 100 V (Fig. 7, curves *1*, *3* and *5*), the potentials usually applied in copying xerographic devices. The layers containing 5–7 at. % As clearly exhibit an increase in conductivity (Table II, column *3*).

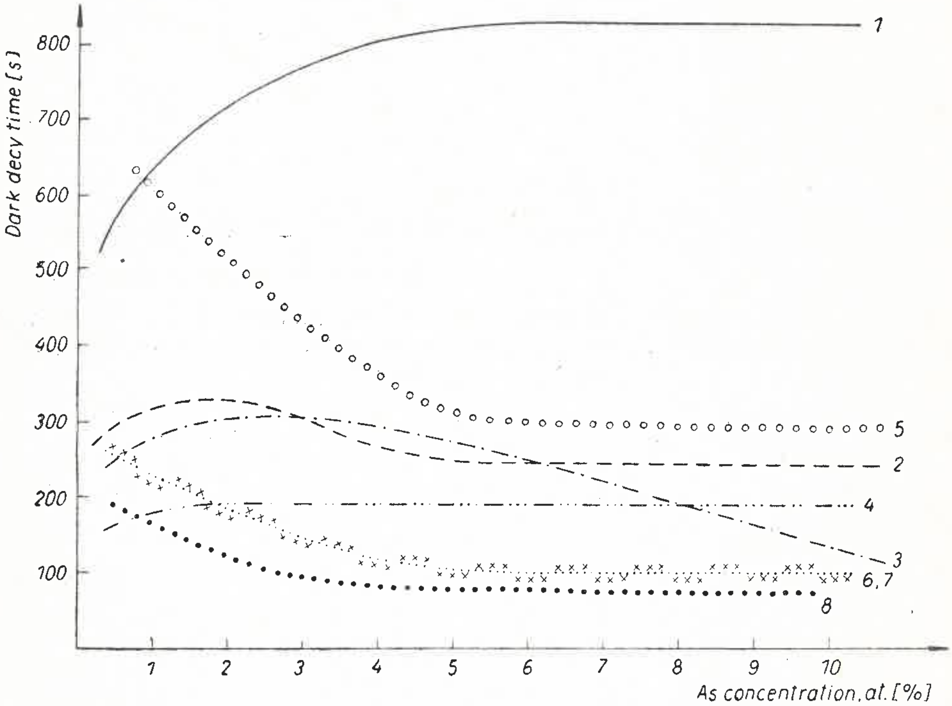

Fig. 4. $t_{0.5d}$ as a function of arsenic concentration in selenium layers, $d = 10$ μm, $i = 0.5$ μA cm^{-2}. *1, 2, 5, 6* — negative polarity; *3, 4, 7, 8* — positive polarity; *1, 3, 5, 7* — base plate temp. 27°C; *2, 4, 6, 8* — base plate temp. 70°C; *1, 2, 3, 4* — unfatigued layers; *5, 6, 7, 8* — fatigued layers

Fatigue effects of the layers

The fatigue due to strong pre-illumination by white light (2000 lx, 2 min) increases the potential U_r, diminishes the time $t_{0.5d}$ and the contrast K'', and only slighthtly affects the sensitivity $S_{0.5}$ (in like manner as for pure Se). The magnitude of changes of these parameters depends on the direction of the applied electric field within the layers. The changes in dark

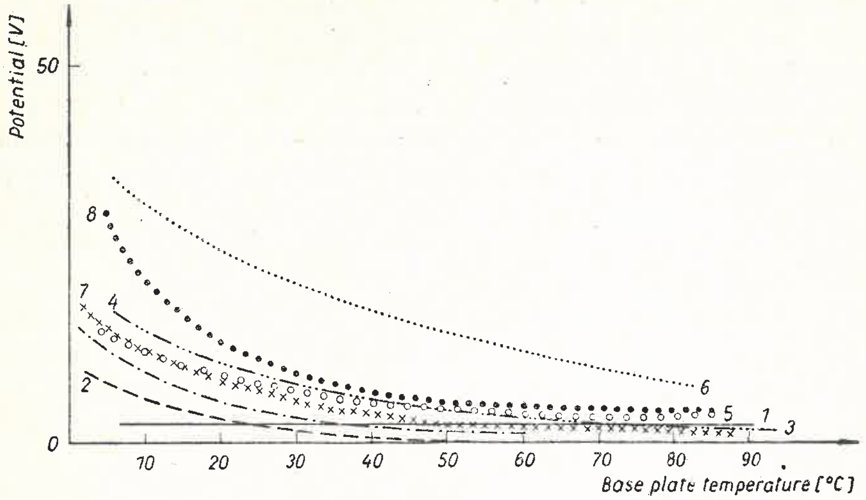

Fig. 5. U_r as a function of base plate temperature, $d = 10$ μm, $i = 0.5$ μA cm^{-2}. *1, 2, 5, 6* — negative polarity; *3, 4, 7, 8* — positive polarity; *1, 3, 5, 7* — 0.52 at. % As; *2, 4, 6, 8* — 3 at. % As; *1, 2, 3, 6* — unfatigued layers; *5, 6, 7, 8* — fatigued layers

Fig. 6. U_r as a function of arsenic concentration in selenium layers, $d = 10$ μm, $i = 0.5$ μA cm^{-2}. *1, 2, 5, 6* — negative polarity; *3, 4, 7, 8* — positive polarity; *1, 3, 5, 7* — base plate temp. 27°C; *2, 4, 6, 8* — base plate temp. 70°C; *1, 2, 3, 4* — unfatigued layers; *5, 6, 7, 8* — fatigued layers

decay time $\Delta t_{0.5d}$ being independent of the polarization direction and substrate temperature, become larger as the As concentration increases. For 5 at. % As content, $\Delta t_{0.5d}$ attains 70% of the $t_{0.5d}$ value reached by the unfatigued layers. Further increase of the As concentration bears a negligible effect (Figs 3 and 4, curves *5–8*). Only a slight (*ca.* 25%) lowering of the initial potential ΔU_0 is observed when the layers are charged positively, no matter what the substrate temperatures and As concentrations are (Figs 1 and 2, curves *5–8*). The

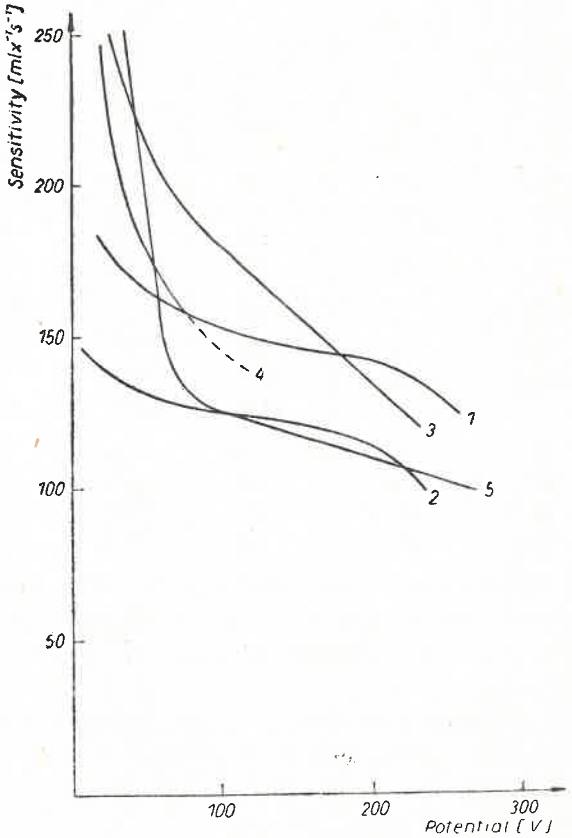

Fig. 7. $S_{0.5}$ as a function of potential (negative charging), $d = 10\ \mu m$, $I = 0.5\ lx$. *1* — 10 at. % As 27°C; *2* — 10 at. % As 70°C; *3* — 3 at % As 12°C; *4* — 3 at. % As 80°C; *5* — pure selenium 27°C

fatigue manifests itself mainly as an increase in U_r. For positive corona charging ΔU_r grows a little as the substrate temperature is lowered below 50°C, independently of the As concentration; $\Delta U_r < 200\%$ of the value attained by the unfatigued plates (Figs 5 and 6, curves *7* and *8*). On the contrary, for the negative polarity ΔU_r grows very strongly with the growth of the As concentration and attains a value reaching 3500% U_r for the unfatigued plates produced at low temperatures (Figs 5 and 6, curves *5* and *6*). The increasing As concentration is followed by a drop in the sensitivity $S_{0.5}$ of the negatively-charged fatigued layers (Table II, column 5). It may be assumed that the negatively-charged 10 at. % As layers may

TABLE II

$S_{0.5}$ as a function of arsenic concentration in selenium layers, $d = 10$ µm, $I = 1.9$ lx, $i = 0.5$ µA cm^{-2}; columns 3, 4 — unfatigued layers, columns 5, 6 — fatigued layers

1	2	3	4	5	6	7
As at. [%]	Base plate temp. [°C]	$S_{0.5}$ [mlx$^{-1}S^{-1}$]	U_0 [V]	$S_{0.5}$	U_0	$\frac{\Delta K''}{K''}$ [%]
0.5	27	95	−190	105	−190	12
3	27	130	−270	90	−270	25
6	27	150	−260	45	−260	45
10	27	115	−190	50	−190	68
0.5	70	110	−160	100	−150	14
3	70	160	−200	90	−150	36
6	70	170	−200	65	−100	56
10	70	130	−170	40	−120	79
0.5	27	80	+210	85	+200	16
3	27	130	+240	145	+200	22
6	27	165	+230	205	+170	34
10	27	100	+220	100	+130	53
0.5	70	80	+170	90	+170	9
3	70	130	+220	140	+180	32
6	70	130	+200	140	+140	46
10	70	100	+150	105	+70	62

change the character of their sensitivity-potential characteristics under the influence of fatigue. An apparent rise in sensitivity for the positive-sensitized layers (Table II, column 5) is very likely due to the decrease of potential U_0 under the influence of fatigue and to the unaffected dependence $S_{0.5} = f(U)$.

As a result of the aforementioned changes of the parameters caused by fatigue there appears a decrease in the electrostatic contrast K'' (Table II, column 7). This effect is markedly enchanced by the increase in As concentration and substrate temperature during layer formation and is independent of applied polarity.

Conclusions

Doping of selenium layers with arsenic results in the appearance of large $U_r(-)$ and $\Delta U_r(-)$ potentials of the layers deposited at lower temperatures; these potentials are greater than in pure Se. This indicates the formation of deep admixture traps for electrons and their subsequent filling during the fatigue process. $U_r(-)$ is practically absent on the layers deposited at high temperatures, which is probably due to elimination of the action of the As admixture centres in the layers produced above 50°C. In these layers the influence of the centres characteristic of selenium polymer structures is predominant. Further evidence is obtained for high-temperature Se and Se–As layers which exhibit fairly close values of $t_{0.5d}(-)$.

Doping of Se with As does not eliminate deep trap levels present in selenium, but rather increases their concentration and enhances the fatigue effects (in contradition with Fotland's assumptions [4]). However, it should be remembered that some surface trap levels may become formed by oxidation of the surface As atoms [12].

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