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High-slope photoconductive cells based on screen-printed and sintered cadmium sulfide; the long-term stability properties

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Photoconductive cells based on doped sintered cadmium sulfide were prepared by screen-printing. As a paste binder was used propylene glycol or glycerol sometimes thickened by poly(vinyl alcohol). Chlorides were used as fluxing agent and donor. Acceptors, 2 - 3 mg Cu or a mixture of 0.15 mg Ag, 0.75 mg Cu and 2.9 mg Mn per g of CdS, made it possible to prepare photoconductive cells with the slope (resistance vs. illumination) higher than 1.5. The long-term stability of cell parameters was unfavourably influenced by a higher content of chlorides and by the content of liquid paste components. The latter can be lowered by recrystallization of starting CdS powder. Also the delay time between drying and annealing of the printed layer can affect the long-term stability of resistance and slope of cells.

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1. Introduction

Cadmium sulfide (CdS) has been used as a photosensitive material for a long time. Undoped crystals exhibit a band gap of 2.42 eV at 300 K [1], which corresponds to the absorption edge at 515 nm. The photoelectric sensitivity in the visible region considerably increases by the introduction of donors and acceptors. CdS is the compound of the type $A^{II}B^{VI}$. From this fact follows that metals of Group III (Al, Ga, In), elements of Group VII (halogens) and anion vacancies act as donors. On the other hand, the acceptors are elements of Group V, metals of Group Ib, (Cu, Ag, Au) and cation vacancies. Silver and copper shift the absorption onset to 2.0 and 1.7 eV, respectively [2]. In particular cation vacancies play an important role in the sensitizing process and the properties of CdS may be described by a two-centre recombination model [3]. The halogens act simultaneously as fluxing agents [4]. Adsorbed oxygen causes the formation of a depletion region near the surface [3], which increases resistance of the layer.

Thick film techniques cut the production cost of electronic devices. An effort to use these techniques in the fabrication of solar cells and light sensors is then understandable [5]. Thick films based on CdS powders, which were sintered on adding small amount of a chloride, were successfully prepared [6]. An addition of propylene glycol (PG) as a binder enabled screen-printing of the mixture [7,8]. The screen-printing technique of undoped CdS was studied in the context of window layers for heterojunction solar cells [9-11]. These papers clarified that the prolongation of sintering time decreased the layer conductivity because of cadmium chloride evaporation.

Our work presents simple techniques which enable the manufacture of photoconductive layers exhibiting high slopes (higher than 1.5) in the resistance vs. illumination dependence. Photoconductive cells of this type are able to detect laser flashes of wavelength in the region around 650 nm and power 3 mW. Screen-printing is an appropriate and simple technique for the preparation of large-area position-sensitive detectors.

2. Experimental

2.1. Powder enrichment

CdS as starting material was used in the powder form (pure, Leuchtstoffwerk Bad Liebenstein, Germany). The enriched powder intermediates were prepared by incorporating dopants and/or flux. CdS powder was mixed with deionised water in a porcelain dish to form a mash. Then solutions of $AgNO_3$, $CuCl_2$, $MnCl_2$ or $CdCl_2$ were consecutively introduced by stirring. The mixture was dried at 120 °C. In some cases the dried powder was further placed into a glass crucible with a cap and heated in air in a muffle furnace to 530 °C for 1 h (powder P4) or to 630 °C for 3 h (powder P3). In the latter case the mass sintered and grains had to be released by adding water. Then solid was decanted with water, until the conductivity of the extract decreased below 15 $\mu S\ cm^{-1}$. The flux was incorporated again as mentioned above. The contents of admixtures are given in Table 1.

Deionised water (resistivity higher than 1 MΩcm) was used. Stock solutions of dopants were prepared using chemicals of analytical grade. Cadmium chloride was purified in solution using the exchange reaction with CdS. Since the recrystallized $CdCl_2$ contained various amounts of water, the stock solutions were analysed by atomic absorption spectroscopy to find the exact concentration of Cd^{2+}.

Table 1. Content of admixtures [mg/g CdS] in enriched powders.

Admixture	Powder			
	P1	P2	P3	P4
Ag^+				0.15
Cu^{2+}	2.2	3	2.25	0.75
$MnCl_2$				6.6
$CdCl_2$	94.8	120	161+100[a]	

[a] Flux addition after decantation

2.2. Paste preparation

Two methods of pastes preparation were tested. In the first case the mixing of components was carried out during powder milling in binders. Besides PG, glycerol and poly(vinyl alcohol) (PVA) were tested as binder components. The quality of PG and glycerol complied with the Czech Pharmacopoeia 1997. The second method was used for powder P4 (See Table1). The powder was dry-milled and pastes were prepared by mixing components in a porcelain dish. Paste compositions are given in Table 2. A ball mill Janetzki KM-1 (Poland) with agate ball and dish was used in milling. Granulometric analyses were carried out with a particle size analyzer Cilas 1064 (France). The particle size distributions of starting CdS and powders P3 and P4 are given in Fig. 1.

Table 2. Composition of pastes.

Powder	Components [mg/g of powder]			
	$CdCl_2$	H_2O	PG	PVA
P1			388 - 567	
			559 - 624	1.7 – 5.0
			775[a]	6.2
P2			495	3.5
P3			200	
P4	20	48 - 159	155 - 99	
	50	42 - 152	156 - 62	
	100	81 - 143	155 - 100	

[a] Glycerol was used in place of PG

2.3. Photoconductive cell preparation and measurement of parameters

Pastes were screen-printed through a polyester screen of 77 mesh on substrates of sintered alumina (96%). Substrate surface was planed by grinding (roughness Ra < 1 μm). Printed layers, covering the area 15 x 20 mm, were dried at 120 °C for 1 h and annealed in a diffusion oven at temperatures ranging from 500 to 630 °C. The samples were equipped with vapour deposited tin (5N5) electrodes. The electrode distance was 0.7 mm and the meander length was 233 mm. The annealing of electrodes was carried out at 180 °C for 2 h and at 120 °C for 8 h. After connecting electrodes the samples were coated with a protective acrylic paint. The photoconductive cell is shown in Fig. 2. Applying the same electrode system to the bare substrate we found a resistance of 70 - 90 TΩ at ambient conditions.

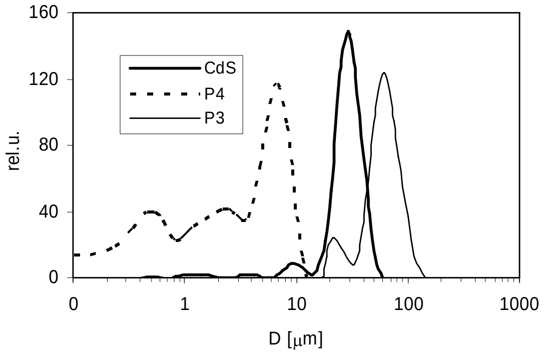

Fig. 1. The particle size distribution of starting CdS powder and powders P3 and P4.

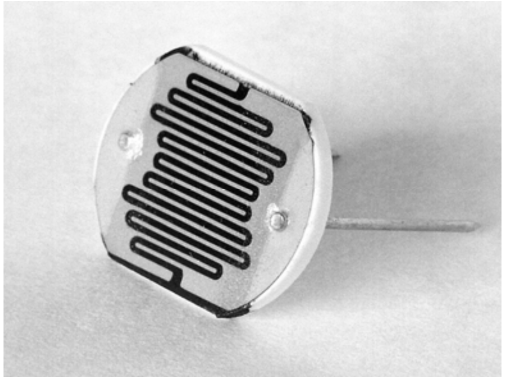

Fig. 2. Photoconductive cell with screen-printed active layer.

The resistances under illumination with 10 and 100 lx (R_{10}, R_{100}) were measured using a photoresistor tester (Tesla, Czech Republic) at a voltage of 1 V. The colour temperature of the light source was 2856 K. The break between the illumination levels was 0.5 s. Dark resistances R_D measured before the illumination and 1 s after switch-off of illumination 100 lx were higher than the tester limit 100 MΩ (in all cases except the data in Table 4).

The slope k was calculated according to the relation

$$k = \log(R_{10}) - \log(R_{100}) \qquad (1)$$

Relative spectral response characteristics were measured using an SPM-2 monochromator (Carl Zeiss Jena, Germany) provided with a flint glass prism. A halogen lamp with filament temperature 2800 K was used as a light source. Photoconductive cells are nonlinear detectors. Therefore the spectral responsivity measurements were performed according to the DIN 44 028 standard. The intensity of sample illumination was adjusted for each wavelength to keep a constant resistance during the measurements. The light intensity was measured using a calibrated silicon photodiode.

The resistance of the sample under illumination varies with the conditions of previous exposition. This is termed the light history effect which is characterised by the parameter L_H. When the sample is kept in the dark for a long time, its resistance under illumination is lower compared with the sample kept at a high illumination level. Our measurements were carried out using the following cycle:

- 3 h of illumination at 1000 lx
- Measurement at 10 lx
- 70 h darkness
- Measurement at 10 lx

The transition from the given illumination level to 10 lx took place continuously during 0.5 s. The time dependence of the resistance R_{10} was observed in both cases; the values obtained after 10 s exposures were used for the calculation of L_H using (2):

$$L_H = R_{10}(\text{after } 1000\,\text{lx}) / R_{10}(\text{after } 0\,\text{lx}) \qquad (2)$$

The time and intensity dependences of photoconductivity were measured under illumination with white light of an iodine lamp using a Keithley 617 electrometer (applied voltage $U = 5$ V).

3. Results and discussion

3.1. Pastes mixed by milling

3.1.1. Powders P1 and P2

Dependences of R_{10} and k on the annealing temperature and time for samples prepared with PG (PVA) and powder P1 are shown in Fig. 3. At the beginning of the sintering process the resistance R_{10} rapidly decreased. After a minimum of resistance was reached, further annealing caused the resistance to increase. The minimum level increased with decreasing temperature of the sintering process. Simultaneously the minimum region broadened. The slope k also decreased in the early sintering stages. However, at longer times the decrease slowed or the k values kept a nearly constant value. The same behaviour was exhibited also by samples based on powder P2 or on glycerol paste. The thickening of pastes with PVA did not inhibit the sedimentation of particles for several days; even 10 h milling did not significantly decrease the particle diameter below 1 μm [12].

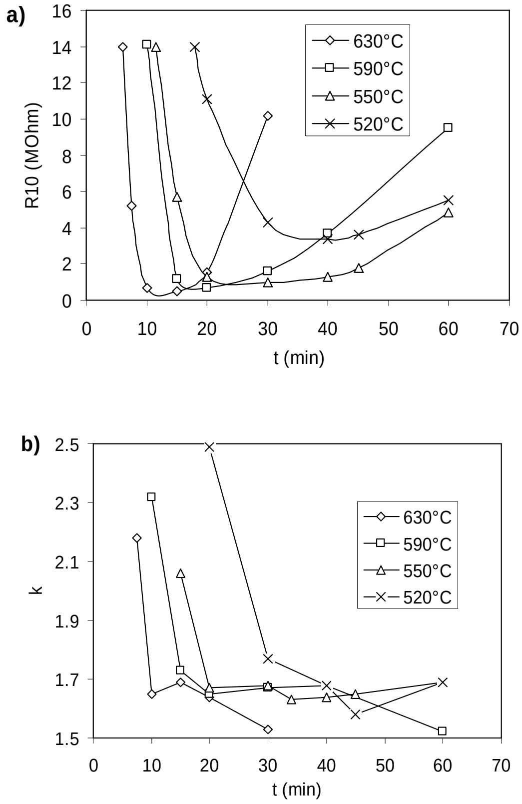

Fig. 3. Dependence of R_{10} (a) and k (b) on temperature and annealing time (powder P1).

The long-term stability of resistance and slope was examined. The values of R_{10} and k were measured after 64-months storage. The magnitude of the changes depended on the annealing time and temperature used in the layer preparation. Typical behaviour is shown in Fig. 4, where an example of samples annealed at 590 °C is used. The values of R_{10} increased in all cases (Fig. 4a). Neglecting the shortest annealing times, where we assume imperfect sintering, we found that the relative change decreases with increasing annealing time, i.e. with increasing starting value of R_{10}. We assume that the resistance growth after storing is due to oxygen diffusion. This opinion is supported by the fact that, after heating samples in the dark at 120 °C, the resistance values decreased again [13]. The prolongation of the sintering time apparently improved the compactness of layers, which subsequently suppressed the oxygen diffusion. As is shown in Fig. 4a, the maximum relative change of R_{10} was 19.3 using the sintering temperature 590 °C. With decreasing annealing temperature, the maximum change also decreased. The annealing temperature 530 °C was preferred in further experiments.

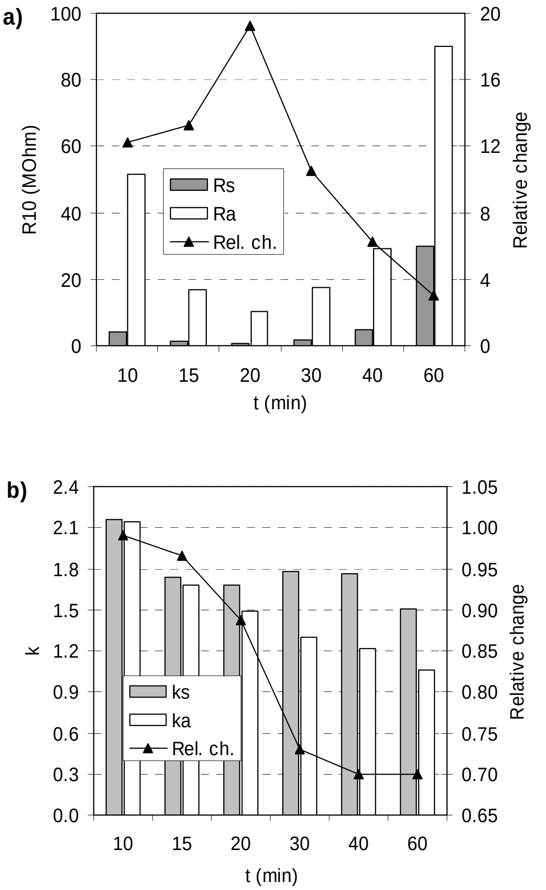

Fig. 4. Changes of R_{10} (a) and k (b) after 64 months of storing (subscripts s and a denote starting values and the values after storing, respectively). Photoconductive layers based on powder P1 were annealed at 590 °C.

We also observed that the cell parameters are influenced by the delay time between drying and annealing of printed layers. We used a paste based on powder P1 and PG. Layers were annealed for 30 min at 530 °C. Varying the delay time in the range 1 – 52 days, we did not find any changes in R_{10} and k. After 64 months of storing, the cells exhibited almost the same values of k, but R_{10} increased. The increase exhibited a maximum at the 17 days delay time.

3.1.2. Powder P3 was recrystallized in flux during preparation, which changed the particle size distribution (see Fig. 1). A well-printable paste was obtained using a smaller amount of PG (see Table 2). Printed layers were annealed for 30 or 60 min at 530 °C. Cell parameters are given in Table 3. Fig. 5 illustrates the changes of R_{10} and k during 78 months of storage on samples annealed for 30 min. The changes are smaller than those of samples made of pastes containing powders P1 or P2. A smaller content of the binder in the paste formed probably layers with smaller pore density, i.e., the penetration of oxygen into the layers is more difficult. Relative spectral responsivity was the same for both annealing times; the relevant curve is shown in Fig. 6.

Table 3. Parameters of a cell based on the paste containing 50 mg of $CdCl_2$ per 1 g of powder P3.

Annealing time [min]	R_{10} [MΩ]	k	L_H
30	1.3	1.89	2.2
60	6.2	1.88	1.5

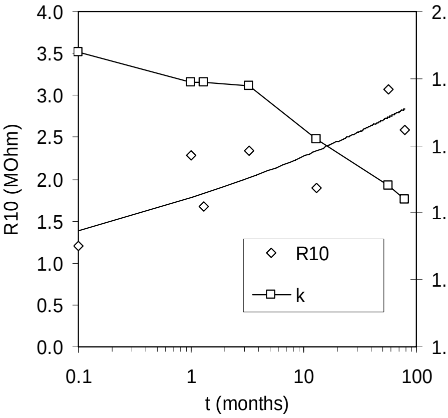

Fig. 50. Changes of of R_{10} and k during 78 months of storing. The layer made of paste with powder P3 was annealed for 30 min at 530 °C.

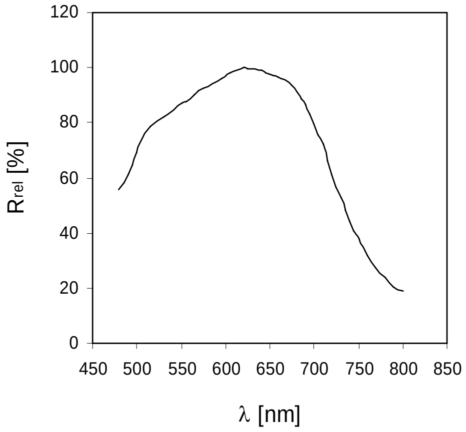

***Fig. 6.** Relative spectral responsivity R_{rel} of a cell based on powder P3.*

3.2. Pastes mixed in porcelain dish

Powder P4 containing a given acceptor amounts (see Table 1) diffused into grains and hence appeared to be suitable for the examination of the influence of paste component concentrations on the layer properties. Printed layers were annealed for 60 min at 530 °C. The pastes mentioned in Table 2 are divided into three groups according to the $CdCl_2$ content. Furthermore, in each group the ratio of water and PG was varied. Two different delay times (1 and 72 days) between drying and annealing of layers were tested. Starting cell parameters and the changes of R_{10} and k after 81 months of storing (R_{10}^{s}, k^{s}) are shown in Table 4. No influence of the water/PG ratio on stability was found. An increase in $CdCl_2$ amount in the paste caused a decrease in both R_{10} and k. The group of samples with long delay times between drying and annealing exhibited higher values of L_H and the long-term stability of R_{10} and k was much better. Samples containing 20 mg of $CdCl_2$ per g of CdS powder combined good stability with a sufficiently high slope.

Table 4. Photoconductive cells based on powder P4. Dependence of cell parameters on the $CdCl_2$ content in the paste and on delay time t between drying and annealing of layers. Changes of R_{10} and k during 81 months of storing (R_{10}^{s}/R_{10}, k^{s}/k).

t [days]	$CdCl_2$ [mg/1g]	R_{10} [MΩ]	k	R_D [MΩ]	L_H	R_{10}^{s}/R_{10}	k^{s}/k
1	20	2.3	1.75	>100	4.2	22.0	0.68
	50	0.5	1.60	>100	4.3	31.3	0.80
	100	0.3	1.49	>100	3.6	20.3	0.85
72	20	3.0	1.69	>100	37	0.95	0.91
	50	0.6	1.61	40	32	0.64	0.89
	100	0.2	1.32	2	16	0.95	0.93

Basic characteristics of the photoconductive cell based on paste containing 50 mg of $CdCl_2$ per g of powder P4 will be described in detail. The relative spectral response of samples annealed for 50 and 100 min are shown in Fig. 7. The dark current-voltage characteristic was ohmic starting from 1 V. Under illumination with white light (100 lx) the resistance decreased by 9 orders of magnitude. The current-voltage characteristic was linear in the whole measured range (up to 30 V).

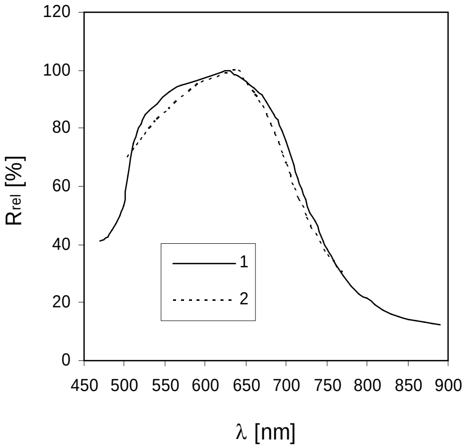

Fig. 7. Relative spectral responsivity R_{rel} of photoconductive cell based on paste containing 50 mg of $CdCl_2$ per g of powder P4. Annealing time of the layer 50 min (curve 1) and 100 min (curve 2).

Photocurrent I_L increased with light intensity Φ (Fig. 8) according to the relation

$$I_L = C\Phi^{\alpha}, \qquad (3)$$

where C is a constant and α = 1.34. The value of α higher than unity agrees well with the two-centre recombination model [3] which can be expected for the used doping procedure.

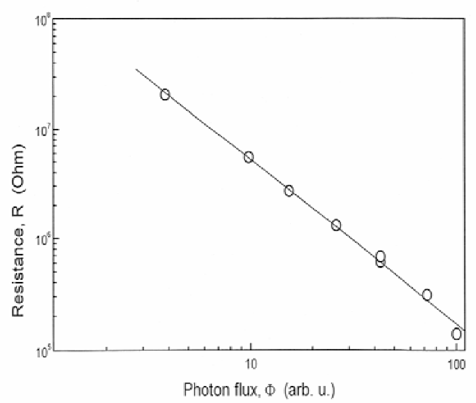

Fig. 8. Resistance vs. photon flux dependence measured on photoconductive cell based on paste containing 50 mg of $CdCl_2$ per g of powder P4.

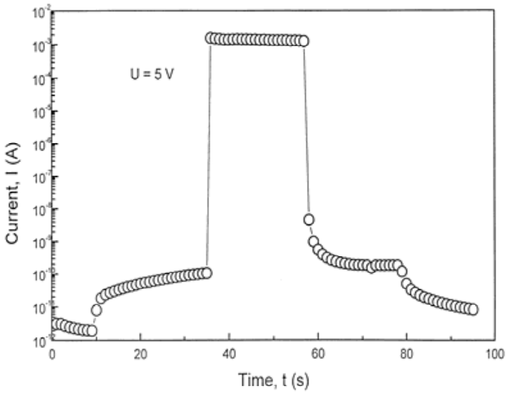

Fig. 9. Kinetics of the photocurrent measured on photoconductive cell based on paste containing 50 mg of $CdCl_2$ per g of powder P4.

The kinetics of the photocurrent is shown in Fig. 9. The behaviour of the photoconductive cell can be described as follows (the regions from the left):

0-10 s:	Voltage (5 V) was applied to the sample. Sample polarization and a slight dark current decrease occurred.
10-40 s:	This region demonstrates a high sensitivity of the photoconductive cell. The current increase of almost two orders of magnitude was caused by the effect of scattered light in the laboratory.
40-60 s:	The sample was illuminated with a white light of an iodine lamp (intensity 100 lx). The relaxation is fast, the resistance change with illumination is about 7 orders of magnitude.
60-80 s:	The current relaxation after switching off the light is fast, within six orders of magnitude. The last part of the relaxation shows the time constant of several seconds which is not a significant effect (it could be lowered by decreasing the applied voltage).
80-100 s:	The sensitivity to scattered light is again observed.

4. Conclusion

Acceptor concentrations of 2 - 3 mg Cu or combination of 0.15 mg Ag, 0.75 mg Cu and 2.9 mg Mn per g of CdS lead to the slope *k* of photoconductive cell (resistance vs. illumination) higher than 1.5. A higher content of chlorides decreases the *k* value and unfavourably influences the long-term stability of cell parameters. The long-term stability is further controlled by the layer porosity and delay time between drying and annealing of the layer. The necessary content of binder may be decreased by suitable recrystallization of the powder. A very good long-term stability of cell parameters was found when the delay time between drying and annealing of layer was 70 days.

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