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PROCESS FOR FABRICATING REPRODUCIBLE PHOTOCONDUCTORS

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This invention relates to a process step in the fabrication of either single or multielement sintered layer cadmium selenide photoconductors resulting in devices of greatly enhanced reproducibility of current-voltage characteristics and, in general, exhibiting greater light sensitivity than would be obtained in an identical process in which this process step was not included. This process step may be employed in either post treatment of electroded photoconductors or as a final step simultaneous with the affixing of thermal setting electrodes.

Several serious problems are present in the fabrication of single or multielement CdSe sintered layer photoconductor arrays by known processing techniques. Photoconductor elements generally exhibit nonlinear current-voltage characteristics (nonohmic) which become more pronounced when elements having greater sensitivity are prepared. In addition, nonreproducibility in photoreponse characteristics due to these nonlinear characteristics may exhibit a spread as great as ten-to-one or more. In multielement photoconductor arrays, this spread in photoresponse characteristics necessitates discarding a great number of entire multielement arrays and, consequently, results in extremely poor process fabrication yields. In single element fabrication, a single bad photoconductor may be discarded without resulting in the loss of other photoconductor elements as in the case of multielement arrays. Thus, the problem of low yield in single element fabrication is not as great. However, even in this case, if single element photoconductors are required that possess a small photoreponse spread (close tolerances), the process yields are still much lower than is desirable and may in fact be economically unsuitable. The use of single or multielement photoconductor arrays having non-uniform characteristics in computer or other circuits has required incorporation of accessory components and circuits to compensate for the relatively poor reproducibility of the photosensitive elements, thus increasing the cost of the total circuitry. Concomitantly, such use results in the photoconductor elements operating below the capabilities of the superior single elements in given circuits, i.e., the effective performance of all of the photoconductors in the circuit will be limited by the performance of the least efficient photoconductor. Since photoconductor circuits are, at best, slow-speed circuits operating at speed levels commensurate with the most efficient photoconductor present in the circuit, it is highly desirable to be able to operate at speed levels commensurate with the most efficient photoconductor present in the circuit. Consequently, the availability of reproducible multielement arrays or reproducible ganged single element photoconductors is highly desirable so that circuit complexity can be minimized, the need for expensive compensating components can be eliminated or greatly reduced and component matching can be minimized. In addition, the higher acceptance rates of the photosensitive elements all result in reducing the overall cost of the circuits.

The advantage of the process described and disclosed herein is that it may be incorporated directly into conventional fabrication processes for sintered layer photoconductor elements or may be utilized even after a given fabrication process has been completed. Thus, where

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photoconductor sintered layer elements are fabricated by an underlay electrode technique in which electrodes are affixed to substrates, followed by a time-temperature sintering cycle in which the photoconductors are sintered directly upon the electrodes or in a process in which the electrodes are affixed subsequent to sintering cycles, comparable end results may be obtained.

An object of the invention is a process step in the fabrication of single or multielement sintered layer photoconductors which results in those elements exhibiting reproducible current-voltage characteristics.

Another object of the invention is a process step in the fabrication of single or multielement sintered layer photoconductors having reproducible current-voltage characteristics and, in general, exhibiting greater light sensitivity.

A further object of the invention is a process for treating either underlay or overlay electroded photoconductors in pure H₂ for specified lengths of time at a temperature between 150°-190° C. and a flow rate of .5-1.5 cu. ft. per hour for 12-18 hours.

Still another object of the invention is a process for treating either underlay or overlay electroded photoconductors in oxygen-nitrogen mixtures for specified lengths of time at a temperature between 150°-190° C. and a flow rate of 0.5-1.5 cu. ft. per hour for 12-18 hours.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention.

The process of the invention involves the treatment of either underlay or overlay electroded photoconductors in either pure H₂ or O₂-N₂ mixtures for specified lengths of time at a temperature between 150°-190° C. or application of said treatments directly during the electrode affixing process when an overlay electrode technique is employed.

Using a given fabrication process for preparing sintered layer photoconductors, the final characteristics obtained by use of different atmosphere treatments while of comparable reproducibility are different, depending upon the atmosphere employed. In general, the use of a reducing atmosphere when continued for sufficient time so that photoconductor characteristics become stabilized, 12-18 hours, yields slightly lower resistance values than obtained using O₂-N₂ mixtures. The use of inert gas atmospheres such as He or N results in characteristics similar to those obtained by the use of reducing conditions as supplied by H₂ or forming gas. In general, however, the time required using inert gases is considerably greater than the time required using reducing or oxidizing gases and is not as reliable. Essentially, the same end result is obtained when a specified sintering process is used, independent of whether the gas temperature treatments are incorporated during the complete fabrication process or subsequent to it.

The preferred process is effected simultaneously with the affixing of electrodes by an overlay technique such as described in U.S. patent application Ser. No. 206,930, filed July 2, 1962, entitled, "Stabilization of Photoconductor Materials at Low Temperatures," by G. Cheroff et al., now U.S. Patent No. 3,175,091 issued Mar. 23, 1965. The process, however, works satisfactorily if the electrodes are not affixed simultaneously but rather in a step following the time temperature sintering cycle described in U.S. patent application Ser. No. 172,699, filed Feb. 12, 1962, entitled, "Method for Controlling Flux Pressure During a Sintering Process," by G. Cheroff et al., now U.S. Patent No. 3,145,120 issued Feb. 19, 1964.

Single or multielement CdSe sintered layer photoconductors separately or in stacked arrays are placed in a system through which a continuous flow of gases at from 0.5-1.5 cu. ft. per hour may be effected at temperatures

from 120°–200° C. for periods of from 12–18 hours. The preferred temperature is 165°±2° C. for 16 hours at a flow of 1.0 cu. ft. per hour. The gases which can be used are pure H₂ or mixtures of O₂–N₂ (e.g., those O₂–N₂ mixtures containing 0.5–7% O₂ by volume—the preferred O₂–N₂ mixture being 1% O₂–99% N₂). Other gases such as pure He or pure N₂ yield results somewhat similar to those obtained in reducing atmospheres, but require much longer time periods of treatment. Specifically, treatments in reducing gas environments result in photoconductors exhibiting the greatest sensitivity and the most superior resistance distribution spread. The use of O₂–N₂ mixtures results in photoconductors having somewhat faster switching times. While the spread in resistance characteristics of O₂–N₂ treated photoconductors is not quite as good as that obtained using reducing conditions, it is still superior by approximately an order of magnitude to those obtained by conventional fabrication techniques. In addition to the superlative reproducibility of each of the individual processes described herein, the resulting photoconductors in general exhibit very unusual stability to a variety of adverse conditions known to seriously affect photoconductor properties.

The following examples specifically illustrate the process disclosed herein:

EXAMPLE 1

(A) 2928 CdSe sintered layer photoconductor elements doped with Cu are prepared by the following time-temperature sintering cycle as described in the process that follows:

17 gm. of CdSe powder doped with Cu at a doping level of 175 p.p.m. are ground together with 3 gms. of CdCl₂ flux in a mortar. Glycerine is added drop by drop to this mixture while stirring until a slurry of suitable viscosity for silk screening is obtained. Using conventional silk screening techniques, this slurry is then silk screened on 1 x 3 inch alumina substrates in the form of 16 rectangular patterns and the substrate is then air dried at 100° C. These screened substrates are placed face down on a quartz container having a volume of 1½ cubic inches such that the entire area of the substrate upon which material to be sintered is located faces into the interior of the container. The container and substrate are drawn into a furnace having a peak temperature of 522° C. over a length three times the substrate length in which a .2% O₂–99.8% N₂ atmosphere is maintained. The sintering is effected for 20 minutes. The sintered layers are cooled, washed with water to remove remaining flux.

Silver paste electrodes are then affixed via a silk screen technique described as follows:

Silver particles (200–400 mesh in size) are admixed with a binder and a volatile vehicle. Thus, the composition would be as follows: 53–54% by weight of silver, 1–2% by weight of epoxy resin (reaction product of epichlorohydrin and bisphenol A, e.g., Epon 828) plus a curing agent (triethylene tetramine), and the remainder the volatile vehicle (butyl Cellosolve, i.e., ethylene glycol monobutyl ether). Prior to use, the slurry is brought to a Brookfield viscometer reading of 80% using a Brookfield TA spindle at 50 r.p.m. (the Brookfield viscometer is that manufactured by the Brookfield Engineering Laboratories). This may require evaporation of some of the initial solvent or addition of new solvent depending on the silver particle size employed. This slurry is screened as an electrode pattern on the sintered photoconductor layer and the substrate at room temperature. The assembly is air dried at room temperature. Now the assembly is ready for application of the process of the invention.

(B) 2880 of the 2928 CdSe sintered layer photoconductor elements prepared by the process described in 1A above are treated at 165° for 16 hours in pure H₂ flowing at a rate of one cu. ft. per hour. The sintered layer photoconductors are measured and exhibit the following characteristics as set forth in Table I.

Table I

	Light resistance in ohms:	Number of photoconductor elements having the specific resistance
5	500 -----	51
	600 -----	2794
	700 -----	35

The sintered layer photoconductors exhibited response times when light was turned off to reach a resistance of 400K ohms of 55 milliseconds±36% and mobilities of 120±33%.

(C) The remaining 48 of the 2928 CdSe sintered layer photoconductor elements prepared by the process described in 1A above are heated in an ambient air atmosphere at 165° C. for two hours. The photoconductor elements are measured and exhibit the light resistance characteristics shown in Table II.

Table II

	Light resistance in ohms:	Number of photoconductor elements having the specific resistance
20	1000 -----	14
	2000 -----	14
25	3000 -----	6
	4000 -----	5
	5000 -----	4
	6000 -----	2
30	7000 -----	1
	8000 -----	2

(D) The 48 photoconductor elements which had their electrodes treated according to the process of 1C are now heated at 190° C. in pure H₂ flowing at a rate of one cu. ft. per hour for four hours. Table III shows the light resistance of these photoconductor elements after the H₂ treatment.

Table III

	Light resistance in ohms:	Number of photoconductor elements having the specific resistance
40	1000 -----	48
	2000 -----	0
	3000 -----	0
45	4000 -----	0
	5000 -----	0
	6000 -----	0
	7000 -----	0
50	8000 -----	0

EXAMPLE 2

(A) 5792 CdSe sintered layer photoconductor elements were prepared by the process described in 1A.

(B) 2896 of the 5792 CdSe sintered layer photoconductor elements prepared by the process described in 2A were treated in a 1% O₂–99% N₂ (by volume) mixture at 165° C. for 16 hours at a flow rate of one cu. ft. per hour. The sintered layer photoconductor elements were measured and gave the results set forth in Table IV.

Table IV

	Light resistance in ohms:	Number of photoconductor elements having the specific resistance
65	700 -----	34
	800 -----	2797
	900 -----	43
	1000 -----	15
70	1100 -----	7

(C) The remaining 2896 CdSe sintered layer photoconductor elements prepared in 2A were treated in ambient air atmosphere for two hours at 165° C. The sintered layer photoconductor elements are measured and exhibit the following characteristics set forth in Table V.

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Table V

Light resistance in ohms:	Number of photoconductor elements having the specific resistance	
1000	497	5
2000	672	
3000	621	
4000	422	
5000	293	
6000	177	10
7000	56	
800	32	
900	30	
10,000	51	
11,000	20	15
12,000	14	
13,000	11	

(D) The 2896 CdSe sintered layer photoconductor elements treated in 2C were further treated in an ambient air temperature for 14 hours at 165° C. These sintered layer photoconductor elements were measured and the results are set forth in Table VI.

Table VI

Light resistance in ohms:	Number of photoconductor elements having the specific resistance	
1000	0	25
2000	365	
3000	380	30
4000	381	
5000	207	
6000	192	
7000	173	
8000	105	35
9000	90	
10,000	106	
11,000	114	
12,000	111	40
13,000	115	
14,000	102	
15,000	114	
16,000	144	
17,000	105	
18,000	92	45

Example 3

(A) 48 CdSe sintered layer photoconductor elements were prepared by the process described in 1A and then treated as described in 1C (i.e., in an ambient air atmosphere). These photoconductor elements were measured and exhibited the light resistance characteristics set forth in Table VII.

Table VII

Light resistance in ohms:	Number of photoconductor elements having the specific resistance	
1000	12	
2000	16	
3000	20	60

(B) These 48 CdSe sintered layer photoconductor elements prepared as described in 3A were treated in 1% O₂-99% N₂ (by volume) mixture at 187° C. for four hours at a flow rate of one cu. ft. per hour. These sintered layer photoconductor elements were measured and gave the results set forth in Table VIII.

Table VIII

Light resistance in ohms:	Number of photoconductor elements having the specific resistance	
1000	48	70
2000	0	
3000	0	75

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EXAMPLE 4

(A) 48 CdSe sintered layer photoconductor elements were prepared by the process described in 1A and then treated as described in 1C (i.e., in an ambient air atmosphere). These photoconductor elements were measured and exhibited the light resistance characteristics set forth in Table IX.

Table IX

Light resistance in ohms:	Number of photoconductor elements having the specific resistance	
1000	28	
2000	16	
3000	2	
4000	2	

(B) These 48 CdSe sintered layer photoconductor elements prepared as described in 4A were treated in 5% O₂-05% N₂ mixture (by volume) at 190° C. for four hours at a flow rate of one cu. ft. per hour. The sintered layer photoconductor elements were measured and gave the results set forth in Table X.

Table X

Light resistance in ohms:	Number of photoconductor elements having the specific resistance	
1000	45	
2000	3	
3000	0	
4000	0	

EXAMPLE 5

(A) 3690 CdSe sintered layer photoconductor elements were prepared by the process described in 1A.

(B) 2890 of these 3690 CdSe sintered layer photoconductor elements prepared by the process described in 5A were treated in pure H₂ at 185° C. for 12 hours at a flow rate of one cu. ft. per hour. The sintered layer photoconductor elements were measured and the results are set forth in Table XI.

Table XI

Light resistance in ohms:	Number of photoconductor elements having the specific resistance	
500	12	
600	2862	
700	6	

(C) The remaining 800 of the 3690 CdSe sintered layer photoconductor elements prepared in 2A were treated in an ambient air atmosphere for two hours at 165° C. The sintered layer photoconductor elements are measured and exhibited the following characteristics set forth in Table XII.

Table XII

Light resistance in ohms:	Number of photoconductor elements having the specific resistance	
1000	204	
2000	234	
3000	126	
4000	41	
5000	32	
6000	11	
7000	16	
8000	75	
9000	28	
10,000	33	

Thus, the photoconductor elements resulting from the process of the invention may be used in computer logic circuits or any other application in which CdSe photoelectric sensing devices have previously been employed, such as photographic exposure meters.

The process of the invention describes a means of processing fabricated sintered layer photoconductor elements for greatly eliminating nonlinear current-voltage characteristics which are the prime cause of nonreproducible photoresponse phenomena, thereby greatly increasing close tolerance yields of both multielement arrays and single element photoconductors. It also yields photoconductors having enhanced stability characteristics. The process involves treatment of photoconductors during or subsequent to an electrode affixing process in either pure H_2 or oxygen-nitrogen mixtures at specified temperatures and flow rates for specified lengths of time.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A process for fabricating reproducible CdSe photoconductor elements having enhanced reproducible current-voltage characteristics and enhanced light sensitivity which comprises subjecting photoconductor elements having silver paste electrodes attached to a temperature of 150°–190° C. in a hydrogen atmosphere at a flow rate of 0.5 to 1.5 cu. ft./hr. for 12–18 hours and then cooling.

2. The process of claim 1 wherein the pure hydrogen atmosphere is replaced with an oxygen-nitrogen gas mixture containing 0.5 to 7% oxygen by volume.

3. The process of claim 2 wherein said oxygen-nitrogen mixture contains 1% oxygen–99% nitrogen by volume.

4. A process for fabricating reproducible CdSe photoconductor elements having enhanced reproducible current-voltage characteristics and enhanced light sensitivity which comprises subjecting photoconductor elements having silver paste electrodes attached to a temperature of 165° C. in an ambient air atmosphere for 2 hours and thereafter subjecting said photoconductor elements to a temperature of 165° C. in a hydrogen atmosphere at a

flow rate of 0.5 to 1.5 cu. ft./hr. for 4 hours and then cooling.

5. The process of claim 4 wherein the hydrogen atmosphere is replaced by an oxygen-nitrogen gas mixture containing 0.5% to 7.0% oxygen by volume.

6. The process of claim 5 wherein the oxygen-nitrogen gas mixture is 1% O_2 –99% N_2 by volume.

7. The process of fabricating reproducible CdSe photoconductor elements having enhanced reproduced current-voltage characteristics and enhanced light sensitivity which comprises the steps of:

- (1) providing an alumina substrate;
- (2) silk screening a cadmium selenide-cadmium chloride flux powdered mixture onto said substrate;
- (3) sintering the thus coated substrate at a temperature of 522° C. in a .2% O_2 –99.8% N_2 by volume atmosphere for 20 minutes;
- (4) cooling and washing with water to remove the remaining cadmium chloride flux;
- (5) silk screening silver paste electrodes in an electrode pattern on said sintered photoconductor layer and substrate at room temperature and air drying at room temperature;
- (7) heating the thus formed assembly to 150°–190° C. in a hydrogen atmosphere at a flow rate of 0.5 to 1.05 cu. ft. per hr. for 12–18 hours and cooling.

8. The process of claim 7 wherein the hydrogen is replaced by an oxygen-nitrogen atmosphere containing .5%–7% by volume of oxygen.

9. The process of claim 8 wherein said oxygen-nitrogen atmosphere is 1% oxygen–99% nitrogen by volume.

10. The process of claim 7 wherein the assembly is heated to 165° C. in a hydrogen atmosphere at a flow rate of 1 cu. ft. per hour for 16 hours.

No references cited.

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