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High Reliability Photoconducting System CdS : Cr_2O_3 Using Ceramic Technology

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Abstract

The preparation of photoconducting chalcogenide layers using a ceramic technology combined with a vapor deposition technology is presented. These photoconducting, polycrystalline layers A_2B_6 (CdS, CdTe) have a high reliability (more then 10 000 hours mean time between failures). The Cr_2O_3 used in this technology was obtained by quenching of α—Cr_2O_3 from 1100 K in a reactive atmosphere. The initial α—Cr_2O_3 which contained only few oxygen vacancies turned into a nonstoichiometric Cr_2O_{3-x} ($x \approx 0{\cdot}5$). The final product consists of a ceramic pellet from porous sintered Cr_2O_3 with a CdS photoconducting layer. This pellet includes the impurities gettered from CdS as chromites. The photoconductivity, TSC and photoluminescence spectra are presented. By analysing the experimental spectra, the influence of the nonstoichiometric α—Cr_2O_3 is discussed. © 1997 Elsevier Science Limited.

1 Introduction

The chalcogenide materials (compounds of oxygen, sulfur, tellurium and selenium) have been extensively investigated for a long time mainly due to their photoelectric properties. A typical representative of the A_2B_6 chalcogenide compounds is cadmium sulfide. A variety of techniques to prepare photoconducting cadmium sulfide devices have been reported, such as: powder firing, sintered layers and sintered pellets, vapor-deposited layers and evaporated layers. By introduction of certain donor and acceptor impurities or by diverse thermal treatments, the material photosensitivity has been increased. However, a certain long-time degradation of photoconducting cadmium sulfide has been reported. The presence of mobile donor concentration is considered as the main reason for these degradation processess.[2] These disadvantages have been partially overcome.[3–5] The method reported in this paper presents some advantages in comparison with other methods. It allows the preparation of, starting from chalcogenide materials, thin, ultrapure photoconducting layers with low mobile donor concentration. Acting as photoresistors, these layers show an increased sensitivity for the low-level illumination (up to 20 lx) as well as a high reliability (more than 10 000 hours mean time between failures).

2 Materials and methods

2.1 Material preparation

As raw materials we used high purity CdS (Merck code 2020) and Cr_2O_3 (Merck code 2483) with a BET surface area of $\approx 36\,m^2\,g^{-1}$ for CdS and $4\,m^2\,g^{-1}$ for Cr_2O_3. The nonstoichiometric Cr_2O_{3-x} ($x \approx 0{\cdot}5$) was obtained by thermal treatment starting from the above mentioned chromium oxide and has been characterized by Electron Paramagnetic Resonance (EPR), Differential Thermal Analyses (DTA) and Thermo Electric Power (TEP) measurements.[6,7] The ratio of CdS to Cr_2O_{3-x} was 9·5 : 0·5. For a better homogenization, the mixture of these compounds has been milled for 1 h in an agate mortar. The resulting powder was pressed in a double action die ($3\,10^4$ kPa). Finally, we obtained pellets with a diameter of 11 mm and a thickness of 1·5 mm (the only binder used consisted of the water vapors present in air). At higher pressure we observe the presence of laminations. The water was removed either by keeping the pellets for 24 h in an desiccator containing silicagel, or by heating them in a graphite crucible. The pellets obtained were gathered in columns of 10 and then introduced into a graphite crucible with two stoppers. The crucible was fixed onto a vertical rod which executed a vertical alternating movement combined with a rotation (10 rpm) within a vertical oven with a temperature gradient greater than 70 K cm^{-1}. The crucible movement between two positions allows the transport of chalcogenide material by sublimation and condensation. The method presented uses the well-known property of chalcogenide materials to sublimate, followed by dissociation and then followed by condensing onto a cool wall in accordance with the equation:[8]

$$MeX_{solid} \Longleftrightarrow Me + 1/2X_{2gas} \qquad (1)$$

where *Me* represents a metal; *X* represents the chalcogen element.

During the sublimation, an additional purification of the material takes place by two possible processes: (i) a reaction between CdS and nonstoichiometric Cr_2O_{3-x} and (ii) a separation of less volatile impurities which remain inside the pellet.[9] In this way an optically pure CdS polycrystalline layer with a thickness of between 20 and 50 μm (individual microcrystalline diameter not greater than 20 μm) can be obtained. These layers are sustained by a Cr_2O_3 sintered pellet having a Cd_2CrO_4 core.[9] Depending on the composition of the initial mixture of CdS and Cr_2O_{3-x} the final pellets exhibit an average contraction of 5–10%. In order to provide electrode contacts, we have sprayed liquid tin through a mechanical mask by means of a CO_2 stream.

The activation of the photoconduction has been investigated as a function of the layer thickness by heating the samples in air for 10 to 60 min at a temperature between 300 and 400°C.[10–14] The thermal treatment was performed on an isothermal table in total darkness.

2.2 Experimental measurements

To characterize the prepared material, we have measured the spectral distribution of the Photoconduction Current (PCC), the temperature dependency of the Thermostimulated Current (TSC) and the spectral distribution of the Photoluminiscence Current (PLC).[5,15]

The samples were placed and investigated under high vacuum conditions (10^{-5} torr) by using a quartz windows cryostat. The TSC as well as PCC room temperature spectra were determined by using a SPM 2 Zeiss type monochromator provided with a quartz prism and an entrance slit of 0·35 mm. The light source consisted of a tungsten filament incandescent bulb (6 V, 30 W). The intensity of both currents was measured using a Keithley 642 electrometer connected to an $x-y$ Hewlett-Packard 7004 plotter. The samples were polarized in an electric field of 5 V cm^{-1}. All the measured intensities were normalized both to the incident light intensity and maximum intensity of the photocurrent.

The TSC were measured at liquid nitrogen temperature in total darkness. Prior to being measured, the sample was illuminated for 20 min with a monochromatic light ($\lambda = 0{\cdot}55\ \mu$m) corresponding to the 77 K PCC maximum. After illumination, the samples were polarized as described below and gradually heated at a rate of 0·1 K s^{-1}.

The PLC were measured at room temperature, in a wavelength range 450–1200 nm, using a double grattice monochromator (100 and 1200 lines mm^{-1} respectively) and an Ar laser as a light source.

3 Results and discussions

In the low temperature range (T $\leq$ 125 K) we observed the presence of two TSC maxims (105 and 123 K) (see Fig. 1). As the experimental TSC spectra represents Arrhenius curves we calculated two numerical values of the activation energy from the rising slope of the two maxims, i.e. 0·12 and 0·18 eV. After heating the sample to 345 K for 10 min we noticed a decrease by two orders of magnitude of the TSC maximum simultaneously with a significant diminishing of the PCC. Thus, the experimentally determined activation energy could be ascribed to two energetic levels within the gap. As a possible explanation of both the TSC and PCC decreasing we suppose a 'thermal healing' of defects produced during the activation treatment.

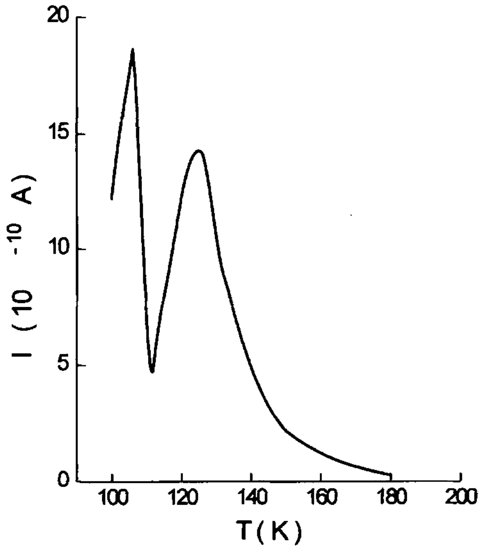

Fig. 1. The temperature dependency of thermostimulated current of CdS.

The presence in the high energy range of a 'shoulder' of the PCC spectral distribution (see Fig. 2) could be explained by the presence of an extrinsic photoconduction together with an intrinsic one.[15]

The experimentally recorded PLC spectrum (see Fig. 3) presents three distinct emission maxims corresponding to $\lambda_1 = 505$ nm (E1), $\lambda_3 = 830$ nm (E3) and $\lambda_4 = 1010$ nm (E4) while the fourth (E2), in the range of 570–650 nm, is less visible in comparison with E3 and especially E4.

The peculiarities of this spectrum can be explained by taking into account the previous results on CdS crystals obtained by crystal growth in vapor phase with various impurifications.[16] Due to the fact that the PCC spectrum is similar for both moncrystalline[1] and polycrystalline samples and the monocrystalline as well as the polycrystalline layers containing large crystallites have been grown using the same method, i.e. vapor phase condensation[16–18], we can assign the observed PLC maxims to the same centers.

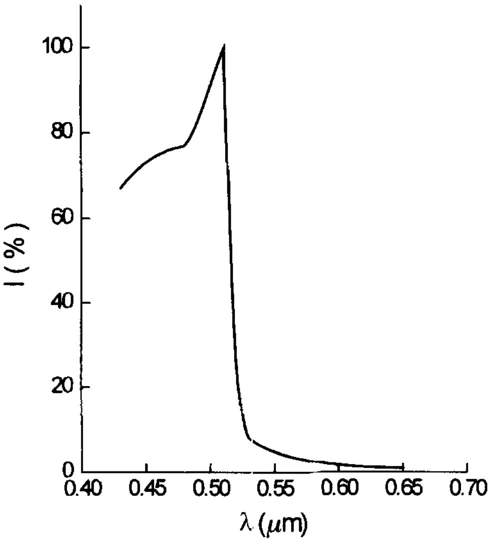

Fig. 2. The spectral distribution of the photoconduction current of CdS at room temperature.

The E1 can be attributed to radiative interband recombination, electrons to holes transitions, as well as to transitions of free electrons to bound holes on acceptor levels. The possible nature of acceptors levels can be regarded as interstitial sulfur defect (S_i'').[16–18] This assumption is based upon the effect of the impurities incorporated onto the E1 observed on CdS monocrystals.[16]

The E2 maximum is assigned to the *O* centers associated to ($V'_{Cd}\, Cd_i^{\cdot}$). The presence of these centers has also been observed in CdS monocrystals containing Cu as well as Ag impurities associated with the Cd_i as reported.[16] The fact that E2 is less distinguishable is in good agreement with our assumption concerning the lack of interstitial Cd. This can also be correlated with the presence of a reaction between nonstoichiometric Cr_2O_{3-x} and interstitial Cd atoms as explained.[9] As a result of this reaction, the concentration of mobile donors, i.e. interstitial Cd, decreases.

The last two bands, E3 and E4, partially superimposed, are probably associated with *K* and *r* centers, whose physical nature consists of ($V'_{Cd} V_S^{\cdot}$) and (V'_{Cd}) respectively.

The E3 band, considered to be the most exposed to the influence of various impurities, has been assigned[16] to both ($V'_{Cd}\, V_S^{\cdot}$) and ($Cu'_{Cd} V_S^{\cdot}$) centers, the last one being excluded in our case.

The E4 band has been associated with (V'_{Cd}) due to a weak influence of the donor impurities as well as to a strong influence of the acceptor impurities on its position in the spectrum.[16] The simplest model of this center consists of a one charge acceptor (V'_{Cd}) or (C'_{Cd}), i.e. (V'_{Cd}) in our case.

The fact that the E4 is more intense than the E3 band enabled us to conclude that the above

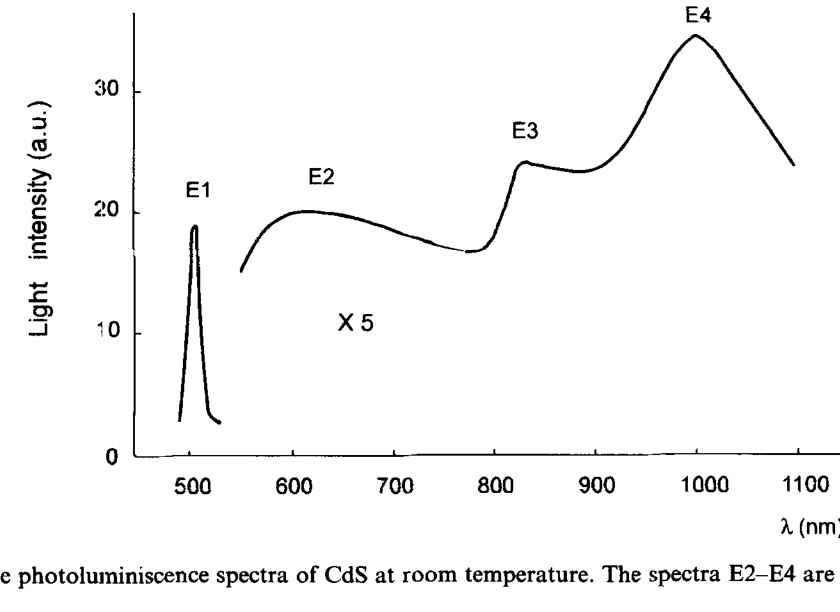

Fig. 3. The photoluminiscence spectra of CdS at room temperature. The spectra E2–E4 are magnified × 5.

described treatment carries a decrease of the number of both *O* and *K* complex centers. The predominance of E1 and E4 bands shows the presence of radiative interband transition, as well as band to acceptor level transitions (*r*) confirming our hypothesis of the extrinsic photoconduction together with an intrinsic photoconduction.

4 Concluding remarks

By using a combined method we were able to prepare thin, polycrystalline photoconducting layers in the presence of nonstoichiometric Cr_2O_{3-x}. The latter considerably influences the layer parameters by reducing the concentration of *O* as well as the *K* centers and ultimately the concentration of the interstitial Cd atoms. In this way, we believe an increased reliability of such devices can be achieved.

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