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SPECTRAL DEPENDENCE OF PHOTOCURRENT FOR Cu_2S - CdS SOLAR CELLS

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Résumé. — On montre que la variation spectrale du photocourant de photopiles au Cu_2S - CdS dépend de l'intensité de l'éclairement reçu par la photopile et de son état de polarisation électrique en influençant la contribution du CdS . Cette contribution, pour des longueurs d'onde voisines de $0,51\ \mu\text{m}$ peut surpasser celle du Cu_2S grâce à la multiplication des phototrous créés dans la région de charge d'espace du CdS et puissamment injectés dans le Cu_2S .

Abstract. — It is shown that the spectral response of Cu_2S - CdS photocells depends on the illumination level and electrical bias, which influence the CdS contribution. This contribution, for wavelengths about $0.51\ \mu\text{m}$ may exceed that of the Cu_2S , by means of a multiplication of the photoholes generated in the CdS space charge layer and strongly injected into the Cu_2S part of the heterojunction.

1. Introduction. — The Cu_2S - CdS solar cells, illuminated through the Cu_2S , must present a spectral response resulting from the photogenerated electrons in the p type Cu_2S and from the photogenerated holes in the n type CdS , as it is shown by figure 1a.

The energy gaps for Cu_2S and CdS are respectively 1.2 and 2.4 eV, so the spectral response of the short circuit current has to peak for wavelengths about 0.51 and $0.7\ \mu\text{m}$ [1, 3] (Fig. 1b).

However, the Cu_2S optical absorption coefficient in the visible part of the solar spectrum is very strong ($\alpha > 10^4\ \text{cm}^{-1}$) and the corresponding radiations are practically absorbed in the $0.3\ \mu\text{m}$ thick Cu_2S layer. As the hole diffusion lengths are small in the CdS layers [4], only the photoholes generated in the CdS space charge region can contribute to the photocurrent. Consequently, Palz *et al.* [5] have concluded that the photocurrent results from the injection of photoelectrons from the Cu_2S into the CdS . However, Gaswell *et al.* [6] have shown that the CdS contribution cannot be neglected and depends upon the cell preparation conditions. Recently, Rothwarf [7] has indicated that the spectral photosensitivity is related to the ionization of deep levels in the CdS space charge region.

The aim of this letter is to show that the spectral response of Cu_2S - CdS cells depends essentially on the light illumination and electrical bias.

FIG. 1. — a) Schematic photovoltaic mechanism in a p-n heterojunction of Cu_2S - CdS . b) Schematic spectral response of the above heterojunction.

2. Experimental. — The photocells were prepared by S.A.T. (Paris) [5]. A 40 μm thick CdS layer was evaporated onto a zinc covered kapton substrate. After etching in a normal HCl solution for 10 s, the CdS layer was dipped in a saturated CuCl solution at 90 °C and pH4 for 6 s. This dipping produces a 0.3 μm thick Cu_2S layer. The photocell preparation was achieved by the soldering of a gold plated copper grid and mylar encapsulation.

Three cells were cut to obtain six samples of 0.5 cm^2 .

The samples are introduced into a pumped thermostat vessel where they can be illuminated and electrically biased. A grating monochromator (5 $\mu\text{W} \cdot \text{cm}^{-2}$) and interference filters (1 $\text{mW} \cdot \text{cm}^{-2}$) are used for the cell illumination. The monochromatic light levels may be adjusted with neutral filters and measured with standard U.D.T. photodetectors.

3. Results. — The spectral response of the short-circuit photocurrent for different light levels E_λ , are plotted in figure 2. The relative contribution of the peak at $\lambda \simeq 0.51 \mu\text{m}$ decreases as the power increases.

FIG. 2. — Modification of the spectral variation of the short circuit photocurrent for two illumination levels : a) 1 $\text{mW} \cdot \text{cm}^{-2}$; b) 5 $\mu\text{W} \cdot \text{cm}^{-2}$.

In contrast, a reverse bias U_r enhances the photo-sensitivity for $\lambda \simeq 0.51 \mu\text{m}$ as it is shown by the figure 3 (the cells operate as photodiodes with an external load of 20 Ω).

The photocurrent for $\lambda \simeq 0.51 \mu\text{m}$ increases sublinearly with E_λ , when the devices are short circuited or reverse biased, as seen in figure 4, while at $\lambda \simeq 0.73 \mu\text{m}$, the photocurrent increases linearly with E_λ .

FIG. 3. — Spectral variation of the photocurrent at 5 $\mu\text{W} \cdot \text{cm}^{-2}$ illumination level for different reverse biases (external load 20 Ω).

FIG. 4. — Photocurrent versus illumination level : (1) $\lambda \simeq 0.51 \mu\text{m}$, zero bias; (2) $\lambda = 0.51 \mu\text{m}$, $U_r = -1 \text{ V}$; (3) $\lambda = 0.7 \mu\text{m}$, zero bias; (4) $\lambda = 0.7 \mu\text{m}$, $U_r = -1 \text{ V}$.

The current voltage curves of figure 5 give a further distinction : the characteristics are conventional for $\lambda \simeq 0.73 \mu\text{m}$ while for $\lambda \simeq 0.51 \mu\text{m}$, a soft break-

FIG. 5. — Current voltage characteristics : (1) : in dark ; (2) : $\lambda = 0.73\text{ }\mu\text{m}$ and $E_{\lambda} = 1\text{ mW.cm}^{-2}$; (3) : $\lambda = 0.51\text{ }\mu\text{m}$ and $E_{\lambda} = 1\text{ mW.cm}^{-2}$.

down appears at a few tenths of a volt and the corresponding photocurrent J_p increases with $|U_r|$ as $J_p \sim |U_r|^n$ with $n \simeq 4$ for $|U_r| > 0.5\text{ V}$. The short circuited cells follow a 0.2 ms light pulse whereas in reverse bias a decay tail in the 10 ms range occurs. The influence of a forward bias U_f on the spectral response is shown in the figure 6. When U_f increases the peak at 0.51 μm tends to disappear.

FIG. 6. — Spectral variation of the photocurrent at $E_{\lambda} \simeq 1\text{ mW.cm}^{-2}$ for $U_f = 0, +0.1, +0.25\text{ V}$.

4. Discussion. — The preceding results indicate that the photosensitivity amplitude for $\lambda \simeq 0.51\text{ }\mu\text{m}$ is dependent on the illumination level and the heterojunction electrical bias. For $\lambda \simeq 0.51\text{ }\mu\text{m}$, the observed photocurrents are essentially generated in the CdS space charge region, in spite of the strong optical absorption of the 0.3 μm Cu₂S layer (about 80 % of the incident photons are absorbed). Indeed, it is well known that the CdS photoconduction peaks at $\lambda \simeq 0.51\text{ }\mu\text{m}$, and that the band profile of the Cu₂S-CdS heterojunction is similar to that of figure 1a with practically, a space charge region entirely in the CdS because of the strong Cu₂S degeneracy [7-12]. So, only the CdS contribution to the photocurrent must be influenced by an electrical bias. Assuming that, for $\lambda \simeq 0.51\text{ }\mu\text{m}$ only 20 % of the incident photons may reach the CdS, a quantum efficiency and a collecting factor of about unity are necessary in order to obtain a photocurrent of 400 nA.cm⁻² for $E_{\lambda} = 5\text{ }\mu\text{W.cm}^{-2}$, as in figure 2. In this case, the strong increase of the photocurrent with $|U_r|$ cannot result from a collecting factor increase. Several interpretations may be cited in order to explain these results (such as combinations of photo-voltaic and photoconductive effects), but actually we believe that the holes photogenerated in the CdS are strongly injected in the Cu₂S by the junction field, producing ionization and multiplication of carriers (this agrees particularly with the observed $J_p \sim |U_r|^4$ variation). So the cells operate like avalanching photodiodes for $\lambda \simeq 0.51\text{ }\mu\text{m}$ for reverse bias, and also for zero bias. This behaviour was also observed by Jordan [13] with Cu₂S-CdS cells made by dipping chemically sprayed CdS layers into a CuCl solution. The necessary fields for such a multiplication may result from the field and electronic density distribution in the space charge layer conceived by Boer [11], who makes the point that an illuminated junction is effectively reverse biased up to a solar illumination of about 50 mW.cm⁻². Consequently, the multiplication of photoholes decreases when the junction is forward biased or when the illumination increases, so the photocurrent at $\lambda \simeq 0.51\text{ }\mu\text{m}$ decreases.

5. Conclusions. — The spectral dependence of the Cu₂S-CdS solar cell photocurrent results essentially from the contribution of the photoelectrons generated in the Cu₂S. However, the CdS contribution (for $\lambda \simeq 0.51\text{ }\mu\text{m}$) is amplified (probably by photohole multiplication) and exceeds that of Cu₂S at $\lambda \simeq 0.51\text{ }\mu\text{m}$, provided the illumination intensity is low or the cell is reverse biased.

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