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DIFFUSION LENGTH DETERMINATION IN THIN FILM CdS/$CuInSe_2$ SOLAR CELLS BY THE EBIC METHOD

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Summary

Minority carrier diffusion lengths in thin film p-$CuInSe_2$ and n-CdS were determined from the decay of the short-circuit current generated by the electron beam of a scanning electron microscope (SEM) for different accelerating voltages. The bulk diffusion lengths were determined taking into account the surface recombination velocity at the scanned surface: they were 0.6 μm in $CuInSe_2$ and 1.17 μm in CdS.

1. Introduction

CdS/$CuInSe_2$ is a promising device for photovoltaic conversion. Air Mass 1 (AM1) 10% conversion efficiency has been obtained [1] in such thin film heterojunctions. The minority carrier diffusion length, L_m, in p-$CuInS_2$ was determined for a single crystal [2]. In this paper we report an L_m measurement for a thin film by the electron beam induced current (EBIC) method. This method has been applied to several semiconductors by many authors [2, 4]; it consists in the generation of electron–hole pairs in highly localized regions of the thin film cell: the decay of the generated short-circuit current *vs.* the distance from the junction plane is a function of the diffusion length. Theoretical analysis of the EBIC signal [4] shows that the relationship between the bulk diffusion length L_b and the measured diffusion length L_m is a function of the surface recombination velocity and the depth of the electron–hole pairs generation. Thus the use of these depths permitted us to determine the bulk diffusion length and the surface recombination velocity.

2. Experimental method

Thin CdS/$CuInSe_2$ films were prepared as follows: A 1.5 μm film of $CuInSe_2$ is grown by rf-sputtering on a gold-plated alumina substrate, as des-

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cribed in ref. 3, then a 4 - 5 μm CdS film is grown on the ternary compound film by vacuum evaporation. An indium grid is evaporated on the surface of the CdS as an ohmic contact. This heterojunction gives a photovoltaic conversion efficiency of about 3%.

The alumina of the device was previously sawn in the centre (without being cut through) with the object of making the cleavage of the sample easier after the growth of the film. The sample was then broken perpendicular to the junction, contacts were made to the gold and the indium, and the $I-V$ characteristic checked. The sample was then inserted in the chamber of a scanning electron microscope (SEM) in such a way that the cleaved edge was normal to the scanning beam. The energy dispersive analysis of the X-ray (EDAX) mode was used to locate the metallurgical junction.

An electron beam of diameter about 0.02 μm was slowly scanned over the surface along a line normal to the junction from one side of the junction to the other. The EBIC signal, amplified through a current amplifier, was monitored and recorded on an x–y plotter. Figure 1 is a schematic diagram of the apparatus.

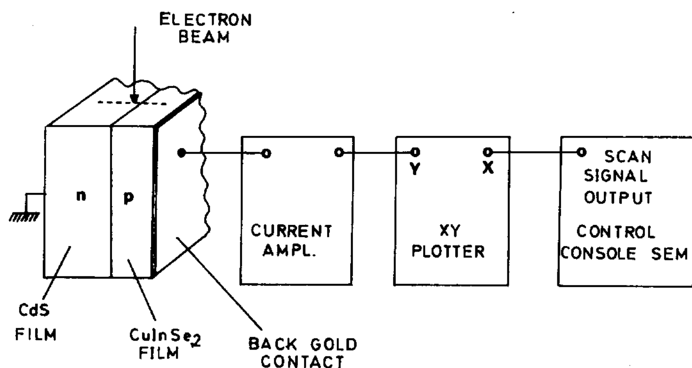

Fig. 1. Schematic diagram of the EBIC measurements.

The cleaved edge was not homogeneous; the scanned regions were selected as a function of their smoothness. The EBIC signal was quite reproducible over the smooth regions. The scanning was repeated for three accelerating voltages, namely, 10, 20 and 30 kV at a magnification of 14 000 times.

The sample's responses to the 30 kV and 20 kV electron beams were sufficiently high to give an accurate plot, but the 10 kV response was also taken into account as shown in Fig. 2. On completion of the measurements the as-cleaved surface was polished with increasingly fine alumina powder, the final size was 0.05 μm. The alumina-polished surface was etched in a light bromine–alcohol solution. The sample, whose surface was flat and smooth, was inserted in the chamber of the SEM. The EBIC signal was obtained for all the scanned regions. The plot of $\log(I)$ *vs.* the distance is shown in Fig. 3 for the three acceleration voltages.

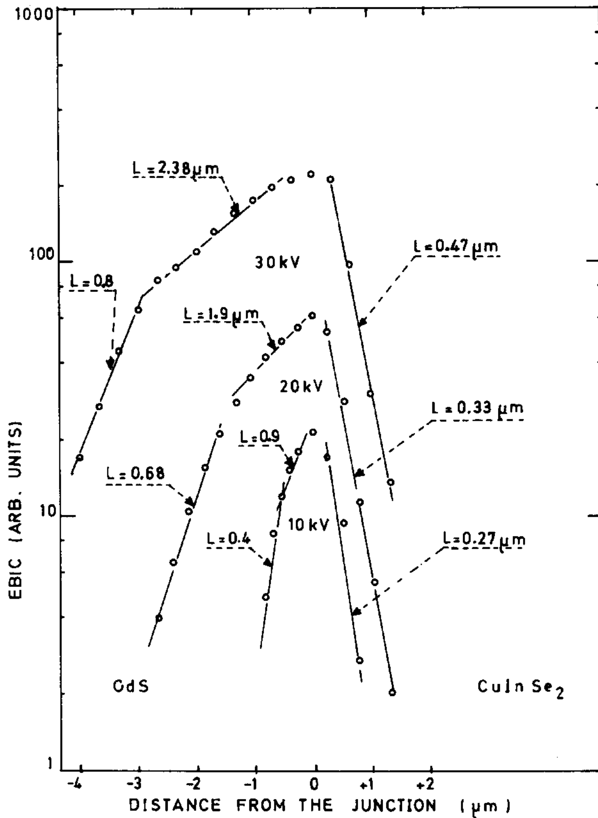

Fig. 2. Semilog plot of EBIC *vs.* distance from the junction n-CdS/p-$CuInSe_2$ for accelerating voltages 10, 20 and 30 kV. As-cleaved surface.

3. Data analysis

We assume that the equations of the plots of Figs. 2 and 3 can be written as:

$$I(x) = I_0 \exp - (x/L_m) \qquad (1)$$

where x is the distance from the electron spot to the junction and L_m is a diffusion length. L_m is related to the bulk diffusion length by the relationship [4]:

$$L_m^2 = L_b^2 \left[1 - \left(\frac{S^*}{S^* + 1} \exp - z/L_b\right)\right] \qquad (2)$$

where S^* is a reduced surface recombination velocity related to the actual surface recombination velocity, S, by the relationship:

$$S^* = S(\tau/L_b) \qquad (3)$$

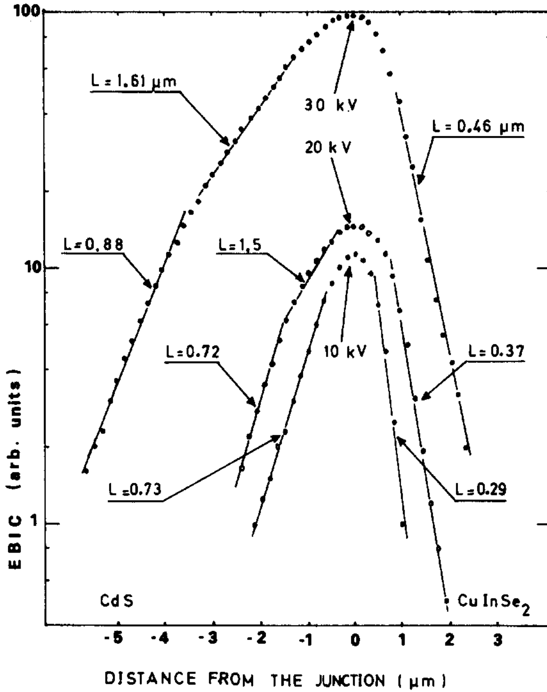

Fig. 3. Semilog plot of EBIC *vs.* distance from the junction n-CdS/p-$CuInSe_2$ for 10, 20 and 30 kV accelerating voltages. Polished and etched surface.

τ and L_b are, respectively, the lifetime and the diffusion length of the minority carriers; z is the penetration depth of the electron beam into the sample.

The value of z was taken as being proportional to the interaction range of the electron beam with the material and equals one-half the 1/e generation volume length [4], which leads to the relationship $z = 0.085\ R$. The values of R are [2] 5.6 μm, 2.9 μm and 0.9 μm, repectively, for 30 kV, 20 kV and 10 kV.

To determine L_m in Figs. 2 and 3 we used the least-square method. For each plot, L_m was determined for 3 regions, one region in $CuInSe_2$ and two regions in CdS. We assume that the highest value of L_m in CdS (*i.e.*, near the maximum response) is due to the electric fields of the space charge region. Using eqn. (2) we calculated the diffusion length in the bulk, L_b, and the reduced recombination velocity S^*. Tables 1 and 2 summarize the values obtained for the as-cleaved and polished sample.

The existence of two slopes on the CdS side, as in Figs. 2 and 3, was noticed in ref. 4 for Cu_2S/CdS thin films; the very large diffusion length resulting from this slope may be explained by the enhancement of the bulk diffusion length due to the space charge electric field. Such enhancement was measured and computed in other materials such as CdHgTe [5] in the presence of an electric field due to the graded band gap.

TABLE 1

Measured L_m and calculated L_b and S^* from EBIC measurements
As cleaved surface

	Accelerating voltage (kV)			Calculated L_b (μm)
	30	20	10	
Measured L_m (μm)	(calculated S^*)			
First slope CdS	0.8 (4.1)	0.68 (4.5)	0.4 (25)	1.17
Second slope CdS	2.38 (5.7)	1.9 (8.9)	0.9 (76.6)	5.00
Third slope $CuInSe_2$	0.47 (11.9)	0.33 —	0.27 (11.8)	0.62

TABLE 2

Measured L_m and calculated L_b and S^* from EBIC measurements
Polished and etched surface

	Accelerating voltage (kV)			Calculated L_b (μm)
	30	20	10	
Measured L_m (μm)	(calculated S^*)			
First slope CdS	0.88 (1.9)	0.72 (3.3)	0.73 (1.9)	1.17
Second slope CdS	1.61 (5.1)	1.5 (4.4)	—	3.0
Third slope $CuInSe_2$	0.46 (11.1)	0.37 (15.7)	0.29 (7)	0.6

The reduced recombination velocity can be taken as the mean of the values of Tables 1 and 2. $S^* = 11$ for the as-cleaved surface and $S^* = 6$ for the polished surface. By using eqn. (3) and Einstein's relation one can obtain the surface recombination velocity, S, from:

$$S = S^* \mu_n kT/qL_n$$

For $CuInSe_2$ we took $\mu_n = 250$ cm^2/V s and $L_n = 0.62$ μm, which give $S = 1.1 \times 10^6$ cm/s for the as-cleaved sample; for the polished sample $S^* = 6$ and then $S = 6.3 \times 10^5$ cm/s.

The rear contact (Au–$CuInSe_2$) recombination velocity S' was not taken into account in our analysis; it may be infinity. The calculations of ref. 4 show that if the measured diffusion length is about one-half the thickness of the film the actual diffusion length is about 1.2 times the measured value when $S' = \infty$. We may assume then that the value of $L_n = 0.62$ μm is

the lowest limit of the bulk diffusion length and the actual value may be nearer to 0.7 μm.

4. Conclusion

The minority carrier diffusion length has been measured by the EBIC method on as-cleaved and polished surfaces of thin film CdS/$CuInSe_2$. The highest measured value of L_m in $CuInSe_2$ was 0.47 μm.

Analysis, taking into account the surface recombination velocity and the depth of electron–hole pairs generation showed that the bulk diffusion length is around 0.6 μm. The analysis did not take into account the surface recombination velocity at the gold–$CuInSe_2$ contact.

The value of the bulk diffusion length in CdS, namely 1.17 μm, is very high compared with that of ref. 4. We think that the high resistivity, at least in the inner part of the CdS, causes this high value and essentially is the cause of the space charge region (SCR) occurring in the CdS.

High resistivity $CuInSe_2$ film associated with low resistivity CdS films may give better conversion efficiency by shifting the SCR in the $CuInSe_2$ film, and then the diffusion length would be enhanced by the electric field due to the space charge region.

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