EXCITON DIFFUSION IN THIN Cu$_2$O FILMS*

E. FORTIN AND E. TSÉLÉPIS

Ottawa-Carleton Physics Institute, University of Ottawa, Ottawa K1N 6N5 (Canada)

A novel method is described to measure the diffusion length L of 1s exciton in Cu$_2$O films grown thermally on copper sheets. The method consists of measuring the photovoltaic response of the Cu$_2$O/Cu backwall junction as a function of the Cu$_2$O film thickness. Measurements performed at temperatures of 2–170 K for film thicknesses of 7–170 μm give values of up to 50 μm for L, apparently limited by the quality of the film rather than by phonon-related dissociation processes.

1. INTRODUCTION

One of the most interesting questions in exciton physics is the problem of diffusion measurements of the neutral particles. Because of the lack of electrical charge, exciton diffusion cannot be detected by the usual methods applied to *e.g.* electron holes. Purely optical methods of diffusion measurement, based on time and spatially-resolved photoluminescence, have been used in some cases[1]. Exciton diffusion measurements are interesting because they are used to study a chargeless— and sometimes lossless—transport of energy within a semiconductor or in organic solids.

We introduce here an original and relatively simple method of measuring exciton diffusion lengths in Cu$_2$O, a material in which excitonic spectra have been well studied for several decades[2]. The method involves measuring the photovoltaic current of thin Cu$_2$O films of varying thicknesses, grown on copper plates in a controlled-atmosphere furnace. The normalized low-temperature photosignal in the excitonic region of the spectrum, when measured in a Cu$_2$O/Cu backcell configuration as a function of the Cu$_2$O layer thickness, may yield directly the diffusion length L of the excitons.

In this paper, we give an outline of the experimental aspects of the method and a short theoretical description of the physical processes involved. Typical results for synthetic layers in the 7–170 μm thick range are then presented and discussed.

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2. EXPERIMENTAL DETAILS

The Cu_2O layers were grown thermally on high-purity copper sheets by thermal oxidation in a controlled-atmosphere furnace. The general conditions needed to obtain good Cu_2/Cu junctions have been described elsewhere[3]. Figure 1 shows the resulting Cu_2O layer thickness as a function of oxidation time in an atmosphere of pure O_2 at a pressure of 55 Torr and a temperature of 980 °C. The Cu_2O/Cu cells discussed here were grown under those conditions and yielded excellent photovoltaic spectra. For exciton migration studies, the Cu_2O layers were coated with a thin (7 nm) semi-transparent Au ohmic contact, mounted in a variable temperature optical cryostat and illuminated from the Au side in a "backcell" configuration, as seen in Fig. 2. Illumination in the yellow exciton region of the spectrum creates an exponential profile of excitons extending from the Au side of the $Au/Cu_2O/Cu$ cell to the back junction. The excitons created outside the interfacial region w will diffuse as bound electron-hole pairs towards that region without creating any photocurrent. The Cu_2O/Cu interface, with a barrier height of about 0.8 V (see ref. 4) and a width of a few tens of nanometres[5], results in electric fields of the order of 10^5–10^6 V cm^{-1}, capable of dissociating the excitons which "make it" to the interface before recombining, resulting in a photovoltaic current. A measure of that photovoltaic current as a function of the Cu_2O layer thickness t is thus directly related to the diffusion length of those excitons. Highly monochromatic chopped radiation from a 1 m monochromator was used to illuminate Cu_2O cells ranging in thicknesses from 7 μm to 170 μm. Photovoltaic spectra at temperatures from 170 K down to below 2 K were taken by standard synchronous detection techniques.
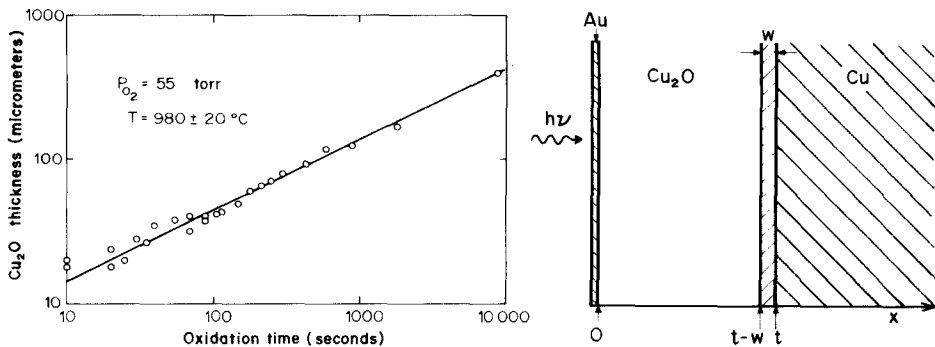

Fig. 1. Cu_2O film thickness *vs.* oxidation time in pure O_2 atmosphere at $P = 55$ Torr, $T = 980$ °C.

Fig. 2. Sample configuration for the measurement of exciton diffusion (Au, 7 nm ohmic gold film; t, Cu_2O film thickness; w, interfacial region; Cu, copper substrate).

3. RESULTS

A typical photocurrent spectrum of a 37 μm thick Cu_2O film, taken at $T = 80$ K, is shown in Fig. 3. The $n = 2, 3$ and 4 yellow exciton structures are clearly visible.

Assuming dissociation of all the excitons at the Cu_2O/Cu interface and negligible front surface recombination, the magnitude of the "exciton" photocurrent

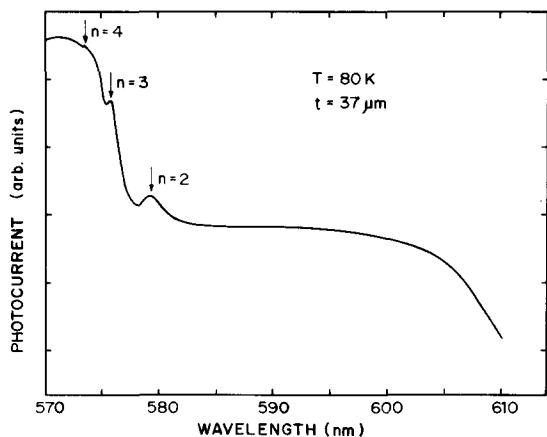Fig. 3. Photovoltaic spectrum at $T = 80$ K of a 37 μm thick Cu_2O film.

can be deduced from the continuity equation[6] as

$$J = \theta q \phi \left\{ \exp(\alpha w - 1) \exp(-\alpha t) + \frac{\alpha L}{\alpha^2 L^2 - 1} \left[(\alpha L - 1) \exp\{-\alpha(t - w)\} \right. \right.$$

$$\left. \left. + \frac{\exp\{-(t - w)(\alpha - 1/L)\} - \alpha L}{\cosh\{(t - w)/L\}} \right] \right\} \tag{1}$$

where θ is an overall efficiency factor, q is the electronic charge, ϕ is the incident light flux, w is the width of the interfacial region, $\alpha(\lambda)$ is the optical absorption coefficient and L is the exciton diffusion length.

The first term of eqn. (1), corresponding to the photocurrent produced directly within w, can be neglected because the interfacial region is very thin (about 10–50 nm) compared with the oxide film thickness.

Three cases can then be distinguished under the assumptions $t \geqslant L$, $1/\alpha$ and $L, t \gg w$.

Case 1. If $L \approx 1/\alpha$, the diffusion length can be obtained by using L as an adjustable parameter in eqn. (1) to fit the experimental thickness dependence of the photocurrent.

Case 2. If $L \gg 1/\alpha$, then eqn. (1) reduces to

$$J = 2\theta q \phi \exp(-t/L)$$

$$= J_0 \exp(-t/L) \tag{2}$$

where, $J_0 = 2\theta q \phi$, a constant. A plot of the normalized photocurrent *vs.* sample thickness gives L directly.

Case 3. If $L \ll 1/\alpha$, then eqn. (1) reduces to

$$J = 2\theta q \phi \exp(-\alpha t)$$

$$= J_0 \exp(-\alpha t) \tag{3}$$

A plot of the normalized photocurrent *vs.* sample thickness yields the absorption coefficient α.

To test the validity of limiting cases 2 and 3, the two curves shown in Fig. 4 were
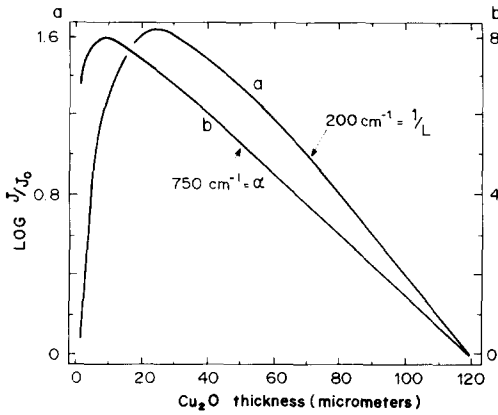
Fig. 4. Computer generated graphs of photocurrent vs. Cu$_2$O film thickness using eqn. (1).

generated by using eqn. (1). The first term was neglected as explained above, and w was set equal to zero because it is very small compared with t, L and $1/\alpha$. Figure 4, curve a, corresponds to $\alpha = 750\,\text{cm}^{-1}$ ($1/\alpha \approx 14\,\mu\text{m}$) and $L = 50\,\mu\text{m}$ (case 2). The slope obtained for $t \geqslant L$ is equal to the inverse of the diffusion length (eqn. 2). The absorption coefficient and the diffusion length in Fig. 4, curve b, were taken to be $750\,\text{cm}^{-1}$ and $5\,\mu\text{m}$ respectively (case 3). Here the slope for $t > 1/\alpha$ is equal to the absorption coefficient as is evident from eqn. (3).

In Fig. 5, each data point corresponds to a photocurrent value at $T = 80\,\text{K}$ and $\lambda = 580\,\text{nm}$ ($n = 2$ yellow exciton), normalized with respect to the response at $\lambda = 620\,\text{nm}$ for each sample thickness. The photocurrent is normalized with respect to a spectral region where the photosignal gives a measure of the junction quality. As this is Case 2, the inverse of the slope is equal to L.
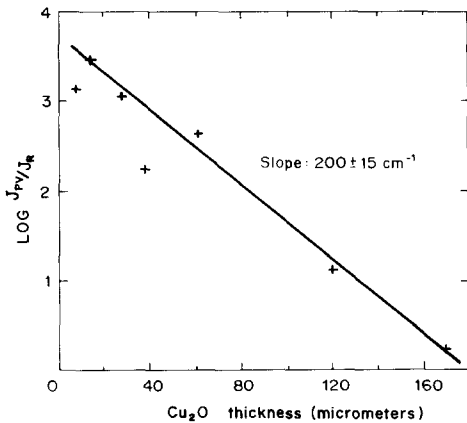

Fig. 5. Typical thickness dependence of the excitonic photocurrent in the limit $L \gg 1/\alpha$.

Table I gives the diffusion length values in Cu$_2$O films obtained at three temperatures, using the above techniques. The diffusion length saturates for $T \leqslant 80\,\text{K}$ in these synthetic films, apparently limited by defects rather than phonon-related processes. Similar measurements made on a 2 mm thick natural-growth

TABLE I

DIFFUSION LENGTH OF EXCITONS IN SYNTHETIC Cu_2O FILMS AT VARIOUS TEMPERATURES *(Case 1, L ≈ 1/α;*
Case 2, L ≫ 1/α)

Case	Temperature (K)	Diffusion length (μm)
1	6	50 ± 5
2	80	50 ± 5
1	170	16 ± 4

Cu_2O single crystal yielded L values of over one order of magnitude higher at $T \leqslant 5 \, K$ [7].

4. CONCLUSION

The $n = 2$ yellow, exciton state has a lifetime of 10^{-12} to 10^{-11} s transforming into a 1 s yellow exciton with a lifetime of the order of 10^{-9} s [8]. We thus conclude that the diffusion length measured here is that of the 1s exciton.

The simple method described here to measure exciton migration can be also applied to other semiconductor films forming a rectifying junction with the substrate they are grown on.

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