

## Exciton-Mediated Photovoltaic Effect in $\text{Cu}_2\text{O}/\text{Cu}$

E. Tselepis and E. Fortin

*Ottawa-Carleton Physics Institute, University of Ottawa, Ottawa, Ontario, Canada K1N6N5*

and

André Mysyrowicz

*Groupe de Physique des Solides de l'Ecole Normale Supérieure, Centre National de la Recherche Scientifique,  
75251 Paris Cedex 05, France*

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Low-temperature photovoltaic spectra in  $\text{Cu}_2\text{O}/\text{Cu}$  are attributed to the diffusion of  $n=1$  excitons and their subsequent dissociation at the metal-semiconductor interface.

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When illuminated, many metal-semiconductor contacts exhibit an external voltage (photovoltaic effect). The photovoltaic effect has been extensively studied and has found wide-ranged applications as a current generator, for instance in solar cells.<sup>1</sup> It is usually discussed in terms of free carriers photoinjected in the semiconductor. The charged electrons and holes diffuse to the depletion region of the semiconductor from where carriers of appropriate polarity are swept across the interface by the built-in contact potential difference, giving rise to an external current.

In this Letter we examine the photovoltaic effect in  $\text{Cu}_2\text{O}/\text{Cu}$  at low temperatures. This system is one of the early materials showing electric rectifying properties and the first in which this effect has been explained<sup>2</sup> by the presence of a Schottky barrier between the metal and the semiconductor. From our experimental results, we are led to the conclusion that, in this material, excitons play an essential role at low temperature in the conversion of light into electric energy. An exciton-mediated photovoltaic effect is expected to show properties different from the usual ones. Because of charge neutrality, the motion of excitons is less sensitive to the presence of electric fields than that of free carriers, which are subject to a field-induced drift. On the other hand, excitons may display extremely high diffusion coefficients up to  $10^3 \text{ cm}^2 \text{ s}^{-1}$  at low temperatures.<sup>3,4</sup> The photovoltaic effect may provide a simple method for the study of energy transport via exciton migration. This method can prove especially valuable if the lowest lying excitonic states are optically inactive, preventing the use of techniques on luminescence detection. Interest in the photovoltaic effect is further compounded here by the fact that excitons in  $\text{Cu}_2\text{O}$  display a highly quantum degeneracy of the Bose type,<sup>5,6</sup> raising the possibility of a lossless transport of energy current via exciton superfluidity.

Two types of samples with widely different qualities have been examined. In a first series of experiments,  $\text{Cu}_2\text{O}$  layers of different thicknesses have been grown by

thermal oxidation on high-purity copper.<sup>7</sup> Such samples are of relatively poor quality, as witnessed by the short exciton lifetimes at low temperatures.<sup>8</sup> A semitransparent gold electrode was deposited on the  $\text{Cu}_2\text{O}$  face, to act as an Ohmic contact. A weak light source (tungsten lamp and monochromator) irradiated the sample, through the gold electrode (back-cell configuration). Photovoltaic spectra were recorded by the measurement of the photocurrent across a  $10^8\text{-}\Omega$  external resistor as a function of light wavelength for different sample thicknesses. The sample resistance was always higher than  $10^9$ . All signals have been normalized to a constant input light intensity. Typical photovoltaic spectra are shown in Fig. 1(a).

As is clearly apparent, a current is detected even if electron-hole pairs are photogenerated in the semiconductor directly in the form of excitons. The spectral region of Fig. 1(a) corresponds in fact to the region of the yellow excitonic series, below the semiconductor band gap. Excitons created inside the  $n=1$  phonon-assisted absorption band or in higher terms of the yellow series quickly thermalize to the bottom of the  $n=1$  band<sup>10</sup> and convert into long-lived paraexcitons.<sup>8</sup> Given the large binding energy ( $E_x \approx 0.15 \text{ eV}$ ) and low sample temperature, a thermal dissociation of  $n=1$  paraexcitons into free carriers is highly unlikely. The problem is to explain how paraexcitons can lead to the observed photocurrent. Any model should also account for the behavior observed at the position of the  $n=2$  term, where a positive or negative structure appears in the photovoltaic spectra, depending on the sample temperature and thickness.

It is possible to understand the main features of the photovoltaic spectra of Fig. 1(a) by the assumption that the external current results from a field-induced dissociation of excitons in a narrow region at the metal-semiconductor interface. Since the Schottky junction is between a  $p$ -type semiconductor and the metal, electrons transit to the metal after dissociation and holes are repelled to the semiconductor. Such an exciton-mediated

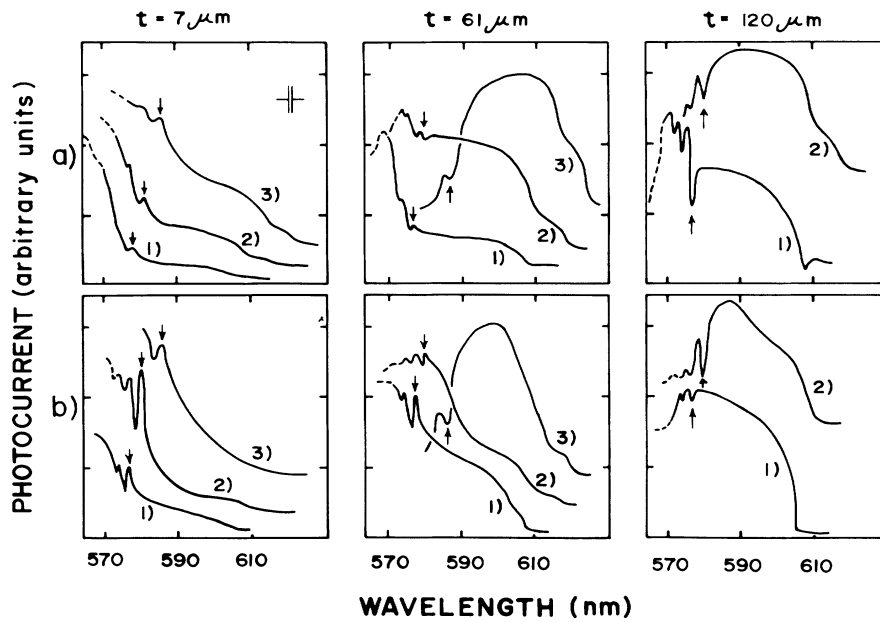


FIG. 1. (a) Photocurrent spectra of  $\text{Cu}_2\text{O}$  recorded in the back-cell geometry for three different  $\text{Cu}_2\text{O}$  thicknesses,  $t = 7, 61,$  and  $120 \mu\text{m}$ . Curves 1, 2, and 3 correspond to temperatures  $T = 6, 77,$  and  $170 \text{ K}$ , respectively. The arrows indicate the positions of the  $n = 2$  exciton absorption line. The dashed parts of the lines correspond to the ionization continuum above the band gap. (b) Photo-voltaic spectra calculated with use of Eq. (1) (see text) and exciton absorption spectra from Ref. 9. The following values of the diffusion length  $L$  have been adopted for best fits: (1)  $L = 45 \mu\text{m}$ , (2)  $L = 45 \mu\text{m}$ , (3)  $L = 14 \mu\text{m}$ . The various curves in (a) and (b) are not to relative scale.

photocurrent will comprise two contributions, a direct one from excitons photoproduced in the dissociation layer at the interface, and the other stemming from a diffusion of excitons created in the semiconductor volume. When we solve the continuity equation, and assume negligible recombination at the illuminated surface and total dissociation in the interface region, the magnitude of the photocurrent can be expressed as<sup>11</sup>

$$J = aq\phi \left[ \exp(aw) - 1 \right] \exp(-at) + \frac{\alpha L}{\alpha^2 L^2 - 1} \left[ (\alpha L - 1) \exp[-\alpha(t-w)] + \frac{\exp[-(t-w)(\alpha - 1/L)] - \alpha L}{\cosh[(t-w)/L]} \right]. \quad (1)$$

Here  $\alpha(\lambda)$  is the absorption coefficient at wavelength  $\lambda$ ,  $L = (D\tau)^{1/2}$  is the exciton diffusion length, with  $\tau$  the exciton recombination time and  $D$  its diffusion coefficient,  $t$  is the total semiconductor thickness,  $w$  is the width of the dissociation region,  $q$  is the electron charge,  $\phi$  is the incident light flux with reflection losses at the input surface taken into account, and  $a$  is an overall efficiency factor. Reflection at the semiconductor-metal interface has not been included. (Its effect is to increase the direct contribution by a factor  $\approx 2$ .)

To estimate  $w$ , we note that for field ionization to occur, the magnitude of the built-in electric field should be of the order

$$F \approx E_x / a_x e \approx 10^5 - 10^6 \text{ V/cm}, \quad (2)$$

where  $E_x \approx 0.15 \text{ eV}$  is the exciton binding energy and  $a_x \approx 10 \text{ \AA}$  its radius. With knowledge of the barrier voltage  $V \approx 0.8 \text{ V}$ ,<sup>12</sup>  $w$  becomes of the order  $\approx 10 - 100 \text{ nm}$ . The presence of an ultrathin dipole layer from accumulated charges at the interface is expected in the presence

of semiconductor surface states, as first proposed by Bardeen.<sup>13,14</sup> Figure 1(b) shows spectra computed from Eq. (1) with  $\alpha(\lambda)$  from the literature<sup>9</sup> and  $w < 1 \mu\text{m}$ . The exciton diffusion length  $L$  is taken as an adjustable parameter.

As can be seen, the general features are well reproduced by the simple model, including the reversal in the structures observed at the  $n = 2$  or higher terms of the yellow series.<sup>15</sup> The physical origin of this reversal can be understood as follows: A decrease of the photocurrent will occur upon an increase of the absorption coefficient  $\alpha$  if the diffusion length  $L$  and  $\alpha^{-1}$  are smaller than the sample thickness. This translates the fact that an increasing fraction of paraexcitons which are formed closer to the front surface recombine before reaching the dissociation region, and therefore do not contribute to the signal. These conditions are met for the sharp absorption lines of the higher terms of the yellow series, either in the case of thicker samples or if the underlying back-

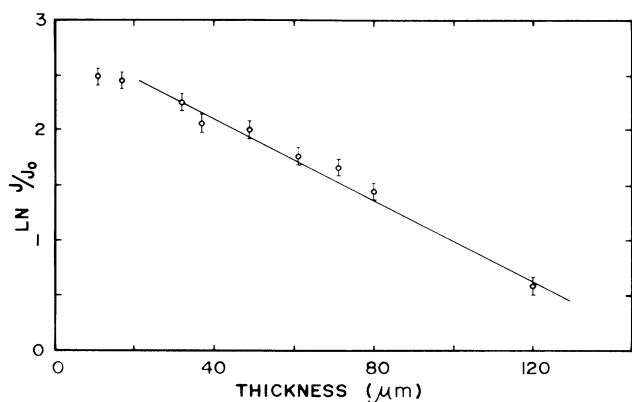


FIG. 2. Photocurrent of  $\text{Cu}_2\text{O}/\text{Cu}$  measured at  $T=80$  K as a function of sample thickness. The incident light wavelength is  $\lambda=580$  nm. The slope (straight line) yields a diffusion length  $L=50$   $\mu\text{m}$ , longer than  $\alpha^{-1}(\lambda=580$  nm)  $\approx 14$   $\mu\text{m}$ .

ground absorption from the  $n=1$  phonon-assisted continuum has sufficiently increased, because of temperature.

We also note that for small sample thickness ( $t=7$   $\mu\text{m}$ ) the calculated photovoltaic spectra tend to reproduce the excitonic absorption spectra. The experimental data differ, however, in the sense that the  $n=2,3,\dots$  excitons appear markedly reduced. This can be understood in view of the fact that excitons are now mostly created in the depletion region close to the interface where an electric field is also present.<sup>1</sup> It is well known that the presence of a field leads to a broadening and reduction of exciton oscillator strength, especially for higher excitonic terms.<sup>16,17</sup> No attempt has been made to include this effect in our theoretical fits.

One can also extract  $L$  without relying on a detailed knowledge of the excitonic absorption spectra, simply by plotting the measured photocurrent as a function of sample thickness at a constant temperature and illumination condition. Indeed, it is seen that expression (1) reduces to  $T_{\text{tot}} \propto e^{-t/L}$  in the limit  $\alpha^{-1} < L, t$ . Such a plot is shown in Fig. 2 for  $T=80$  K. The value of  $L$  deduced from the slope is consistent with the diffusion length obtained from spectral fits on the same samples.

Further to confirm our interpretation, we have also studied photovoltaic spectra in a high-purity, natural-growth single crystal for which values of exciton lifetimes and diffusion coefficients are available.<sup>4,8</sup> A thin ( $\approx 100$   $\text{\AA}$ ) copper layer was deposited on one of the (110) surfaces, and a semitransparent Ohmic gold contact on the opposite face of the 2-mm-thick crystal. The sample resistance was higher than  $10^{12}$   $\Omega$ . Representative spectra at  $T=72$  and  $T=2$  K are shown in Fig. 3.<sup>18</sup>

Consider first the spectrum at  $T=72$  K. Although its shape is different from the corresponding case of Fig. 1, it reflects the same physical situation, if one takes into account the much larger sample thickness  $t=2$  mm. Only those  $n=1$  excitons created deep into the bulk by

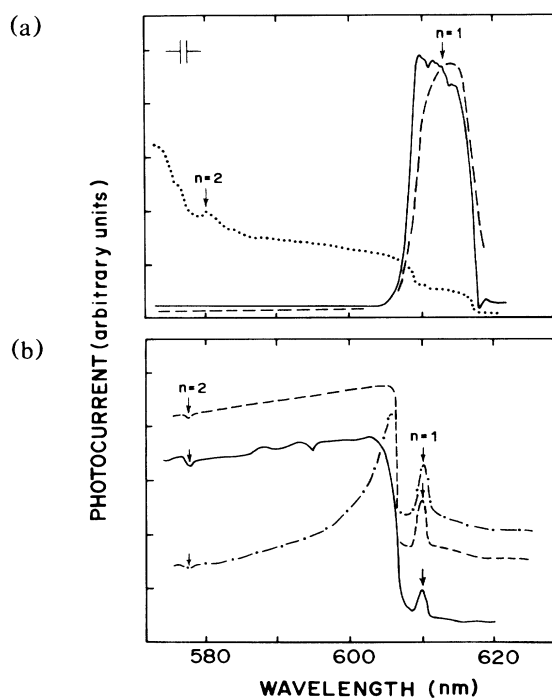


FIG. 3. Photocurrent spectra recorded on a 2-mm-thick, natural-growth  $\text{Cu}_2\text{O}$  single crystal at (a)  $T=72$  K and (b)  $T=2$  K. Solid line: experimental results obtained in the back-cell geometry. Dotted line: experimental result at 72 K in the front-cell geometry. Dashed lines: computer-generated curves with  $L=50$   $\mu\text{m}$  ( $T=72$  K),  $L=1000$   $\mu\text{m}$  ( $T=2$  K). Also shown for comparison is a computed curve (dash-dotted line) with  $L=500$   $\mu\text{m}$  ( $T=2$  K).

light with wavelength at the edge of the  $n=1$  exciton phonon-assisted absorption continuum contribute to the signal, giving rise to a photocurrent in a limited spectral range. By contrast, the photovoltaic spectrum obtained in the front-cell geometry displays the behavior of a very thin sample, as expected [see Fig. 3(a)]. The value of  $L=50$   $\mu\text{m}$  introduced to fit the spectrum is in good agreement with the value calculated with use of the relation  $L=(\tau D)^{1/2}$  where  $\tau=1.7$   $\mu\text{s}$  is the exciton lifetime<sup>8</sup> and  $D=20$   $\text{cm}^2 \text{s}^{-1}$  the diffusion coefficient extrapolated from measurements at lower temperatures.<sup>4</sup>

The photovoltaic spectra recorded below  $T=50$  K differ markedly from those of Fig. 1, even after appropriate scaling for the sample thickness  $t$ . They can be fitted by the introduction of exciton diffusion lengths which increase exponentially with decreasing temperature and which reach values comparable to the sample thickness at  $T=2$  K. An exponential increase of  $D$  for paraexcitons at lower temperatures has been reported in a similar sample,<sup>3,4</sup> and explained in terms of exciton diffusion limited by phonon scattering.<sup>4</sup> At sufficiently low temperatures, the exciton thermal velocity becomes comparable to or even smaller than the sound velocity, thereby

effectively decoupling excitons from the lattice. Such a behavior, however, is only expected to occur in sufficiently pure crystals, for which scattering by defects is negligible. This is apparently not the case in our synthetic crystals.

In conclusion, we have reported an investigation of the photovoltaic effect in  $\text{Cu}_2\text{O}/\text{Cu}$  at low temperatures in samples of different thicknesses and quality. The results have been interpreted with the assumption of exciton migration and field-induced dissociation at the semiconductor-metal interface. We believe that this type of measurement may provide a simple method for detecting exciton diffusion lengths.

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<sup>18</sup>The magnitude of the photocurrent was larger in this high-purity crystal than in the synthetic ones. This fact alone excludes the possibility of another origin for the photocurrent, in which excitons would be dissociated by defects scattered in the bulk (the reverse trend would be expected in that case).