

Chlorine doping of Cu₂O

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ABSTRACT

Cu₂O is a semiconductor suitable for photovoltaic applications. However, the highest efficiency obtained for a solar cell based on Cu₂O is, to date, one order of magnitude lower than its theoretical limit. This could be due to the difficulties in the doping processes. In this paper we investigate the effects of chlorine doping on Cu₂O. The doped material has a conductivity about one order of magnitude greater than the undoped material. The measurements of the carrier concentration as a function of temperature suggest that chlorine acts both as a donor, substituting the oxygen, and as an acceptor, sitting in an interstitial position. Moreover the p-type persistent photo-conductivity (PPC), shown by undoped samples after illumination, is very weak in the doped samples and it has a much longer decay time. Finally the effect of chlorine doping on the minority carrier lifetime is investigated by measurements of external quantum efficiency on Schottky junctions and the possible role of excitons is also discussed.

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1. Introduction

Cuprous oxide (Cu₂O) is a naturally p-type semiconductor with an optical gap of 1.95 eV at room temperature.

Thanks to the value of its energy gap and to the low production cost, cuprous oxide could be used in the top cell of a multi-junction solar cell or as the host material for an intermediate band solar cell. Until now no reliable doping process of bulk Cu₂O has been developed and the best solar cells [1], with an efficiency of about 2%, were made using undoped substrates.

Both experiments [2] and *ab initio* calculations [3,4] suggest that the p-type conductivity at high temperature is due to the presence of copper vacancies. Even though the *ab initio* calculations do not predict a donor with a small formation energy, the experiments at low temperature [5,6] ($T < 450$ K) show that Cu₂O is a compensated material with a compensation ratio N_A/N_D which varies from values just slightly larger than 1 to values of the order of 10 [5,7]. The nature of the compensating donor is still controversial. The simplest model identifies the donor centers with the oxygen vacancies [8]; however a more refined model [9] proposes the defect complex ($V_{Cu}-V_O$) as the compensating donor.

Cu₂O shows p-type persistent photo-conductivity (PPC) [10,11]: after some minutes of illumination with white light the material shifts to a high conductivity state which is stable in the dark at room temperature and which can be annealed out in tens of minutes at 400 K. This metastable state of Cu₂O has also

been observed in junction devices based on this material which show a dependence of their characteristics (capacitance, series resistance, V_{oc} and J_{sc}) on the history of the sample [6,9]. Different explanations of this phenomenon have been proposed in the past. Some of them were based on electron trapping in deep donors [10–12]. Other authors proposed an alternative mechanism based on formation and dissociation of defect complexes [9,13].

Several attempts to dope Cu₂O have been performed. The oxidation of copper in the presence of chlorine, obtained from the thermal decomposition of MgCl₂, was one of the most successful methods to reduce the resistivity of cuprous oxide [14,15]. However a decrease of the solar cell quantum efficiency at long wavelength is observed in devices prepared from the more conductive substrates, suggesting a reduction of the minority carrier lifetime with increasing chlorine content.

In this paper we investigate the effect of chlorine doping on Cu₂O, using two doping techniques: the classical method with the MgCl₂ and an alternative one based on the evaporation of a layer of CuCl over copper sheets before oxidation. We perform several experiments on both doped and undoped substrates and devices suggesting the possible amphoteric behavior of the chlorine which can act both as an acceptor and as a donor.

2. Sample preparation

Cu₂O substrates were prepared by oxidizing copper sheets of 5 cm × 3 cm. The sheets were cut from a larger foil of purity

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99.999% of thickness 100 µm and then etched in nitric acid 4 M for about 10 s and rinsed in distilled water. Before etching, two little holes were made on one side of the copper sheets to hang them in the furnace by a platinum cage.

The oxidation process was carried out in a tube furnace with a tunable N₂/O₂ gas mixture. The temperature was raised at a rate of 10 °C/min up to 930 °C in nitrogen flux. Then a 90 min long oxidation in a partial oxygen pressure of 2.7 Torr was done. The oxidation was followed by two annealings: the first one at 1150 °C for 60 min and the second one at 800 °C for 600 min, both under a 0.27 Torr oxygen partial pressure. The first annealing is needed to increase the grain dimensions up to 1 mm² while the second one is to get a partial equilibration of the sample to a lower defect density to increase the mobility. Finally, after switching to the nitrogen flux only, the sample was cooled down to room temperature or quenched from 450 °C to room temperature by dipping it into deionized water.

Chlorine doping of Cu₂O was performed in two ways. In the first one, already reported in the literature [14], chlorine is obtained by the thermal decomposition of dried MgCl₂ put in a chamber along the gas mixture flow. During the oxidation step at 930 °C the chamber temperature was raised up to 230 °C and the Cl₂ vapor was carried into the furnace by the gas flux.

The second way to dope the cuprous oxide is based on CuCl. Before oxidation, the copper sheets were covered on both sides by an evaporated layer of CuCl, followed by another 200 nm thick copper layer needed to avoid the evaporation of CuCl during the oxidation. This latter technique is simpler and more reproducible than the former one but it gives the same experimental results.

All the doped substrates were not quenched in order to isolate the effect of doping.

The analysis of these substrates was made on two types of devices, photo-conductors and solar cells based on Cu/Cu₂O Schottky junctions. These devices all have an active area of 0.5 cm² and a back contact made by 120 nm of evaporated gold. The photo-conductors were fabricated by evaporating a 7 nm thick semitransparent front gold contact covered by an anti-reflection layer of ZnS (32 nm) and by a gold grid. The solar cells were fabricated in the same way but substituting the gold of the front contact with a 7 nm thick semitransparent copper layer, evaporated keeping the substrates at 80 °C.

3. Experiments

Resistivity measurements at room temperature, performed using the Van der Pauw configuration, show a decrease of the doped samples resistivity of about one order of magnitude with respect to the best undoped ones. For example the doped substrate S98 has a resistivity of 200 Ω cm under ambient light illumination whereas the undoped S94 has a resistivity of 2000 Ω cm under the same conditions. Hall effect measurements show the same p-type character and the same mobility, about 90 cm²/(Vs), for both doped and undoped substrates. Therefore the increase in conductivity must be attributed to a greater concentration of holes.

3.1. Carrier concentration vs. temperature

As we have already mentioned in the Introduction, Cu₂O shows the (PPC) persistent photo-conductivity effect (PPC). Under illumination the conductivity increases as is expected in a normal semiconductor. However, after the light is switched off, the samples remain in a highly conductive state and reach the dark value only after a long time depending on temperature. It is therefore interesting to study Cu₂O samples in two different

conditions: *equilibrated* and *preilluminated* states. The former was reached by annealing the sample at 400 K for some hours in the dark until the conductivity reached its minimum, while the latter was obtained by illuminating the sample with white light (about 5×10^{17} photons cm⁻² s⁻¹ with 350 nm < λ < 750 nm) for about 15 min.

Conductivity measurements as a function of temperature were made on doped and undoped samples in order to have an estimate of the acceptor and donor concentration (N_A and N_D). To avoid surface contribution to sample conductivity, the measurements were performed using the photo-conductor structures described above.

The concentration of holes was calculated using the relation $p = \sigma/(\mu_p e)$, where σ is the conductivity, μ_p is the hole mobility and e is the module of the electron charge. The mobility as a function of temperature was taken from the literature [16] and rescaled to fit the room temperature value in our samples. The comparison of the hole concentration p as a function of temperature T of three typical doped and undoped samples is reported in Fig. 1, for both equilibrated and preilluminated conditions.

It is possible to note two distinct effects of chlorine doping. The first is the increment of hole density in the chlorine doped sample equilibrated in the dark, which is larger by about one order of magnitude with respect to the intrinsic samples in the same condition. The second effect is that the introduction of chlorine strongly reduces PPC: the curve of preilluminated samples is almost superimposed to the one obtained in equilibrated condition, while for undoped cases it is translated upward of about a factor of 7 with respect to the dark curve.

For a p-type semiconductor with a concentration of N_A acceptors compensated by N_{D+} ionized donors per unit volume, experimental data can be fitted with the following expression [5]:

$$p(T) = -\frac{1}{2} \left(\frac{N_v}{e^{E_A/kT}} + N_{D+} \right) + \frac{1}{2} \sqrt{\left(\frac{N_v}{e^{E_A/kT}} + N_{D+} \right)^2 + \frac{4N_v N_A}{e^{E_A/kT}}} \quad (1)$$

where $N_v = 2.13 \times 10^{15} T^{3/2} \text{ cm}^{-3}$ is the valence band effective density of states, E_A is the acceptor energy level, k is the Boltzmann constant and the degeneracy of the acceptor is assumed to be 1. This expression holds if the concentration of ionized donors N_{D+} remains constant during the measurement and if the acceptors are described by a single electronic level.

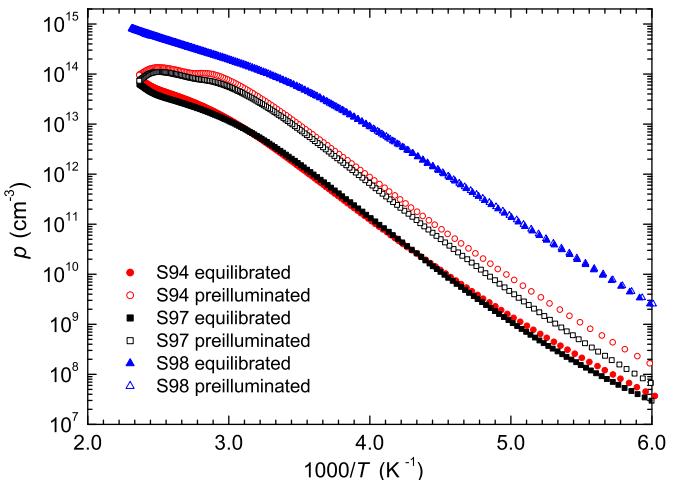


Fig. 1. Hole carrier concentration as a function of temperature for three substrates S94, undoped and quenched, S97, undoped and non-quenched and S98, doped and non-quenched. Each measurement is performed in two initial conditions of the sample, *equilibrated* in the dark or *preilluminated* for several minutes with white light.

Table 1

Acceptor concentration N_A , ionized donor concentration N_{D^+} and acceptor energy level E_A obtained from the fit of $p(T)$ using Eq. (1) on the equilibrated samples. The value of free carrier concentration p at room temperature and the compensation ratio N_A/N_{D^+} are also reported.

Sample	Quenched	Doping	$p(300\text{ K}) (\text{cm}^{-3})$	$N_A (\text{cm}^{-3})$	$N_{D^+} (\text{cm}^{-3})$	$E_A (\text{eV})$	N_A/N_{D^+}
S94	Yes	No	3.0×10^{12}	1.93×10^{14}	1.03×10^{14}	0.385	1.87
S97	No	No	3.3×10^{12}	0.71×10^{14}	0.23×10^{14}	0.402	3.06
S98	No	MgCl ₂	8.6×10^{13}	8.74×10^{14}	1.29×10^{14}	0.330	6.72

However, since a variation of the activation energy of $p(T)$ among different samples has been often observed, this latter assumption was criticized by some authors who proposed that the acceptors are distributed in a band [11].

If this hypothesis is true, a different low temperature activation energy of the $p(T)$ curves in the equilibrated and in the preilluminated conditions should be observed as a result of a change in the compensation ratio, as reported in [11]. On the other hand this change was not observed in [10] and our experiments also show only a very small variation of the order of 0.01 eV. Using the same model of [11] it can be shown that the acceptor band in our samples is quite narrow, less than 0.025 eV and that the variations are probably due to a real change in the acceptor level [17].

As the PPC decay time is much greater than the measurement time (see Fig. 3 below), it is possible to assume, also for preilluminated samples, a constant concentration of ionized donor during data acquisition up to room temperature. Eq. (1) can thus be used to fit both the equilibrated and preilluminated curves of Fig. 1. The use of this equation even for the doped samples will be discussed in Section 4.

The results of the fits performed on the equilibrated samples are reported in Table 1. It can be seen that the chlorine doping has the following consequences: the activation energy is reduced, both the donor and acceptor concentrations are increased as well as the compensation ratio N_A/N_{D^+} . The decrease of the activation energy of $p(T)$, observed in our samples, is probably related to the different resistivity of the materials as already reported in the past [18].

To check the correctness of these numbers we have also performed several capacitance–voltage (C–V) measurements to obtain the concentration of the net fixed charge, N_{fix} . This charge is obtained using the Schottky relation:

$$N_{\text{fix}}(x) = \frac{C^3}{e\epsilon A^2} \left(\frac{dC}{dV} \right)^{-1} \quad (2)$$

where C is the capacitance of the junction, e is the module of electron charge, ϵ is the dielectric constant of Cu₂O, about $7\epsilon_0$, V is the applied voltage bias, $A=0.5\text{ cm}^2$ is the active device area and $x=\epsilon A/C$ is the distance from the Cu₂O/metal interface.

The value of N_{fix} for large x is an estimate of the quantity $N_A - N_{D^+}$ [19]. Since the acceptor level is about at 0.3 eV from the top of the valence band and has a fast response, we can assume that under reverse bias $N_{A^-} = N_A$. Therefore we can obtain $N_A - N_{D^+}$ from the C–V measurements and we find that it is in agreement with the value obtained from the fit of carrier concentration vs. temperature. For example in Fig. 2 the charge profile for a Schottky junction based on the doped S98 substrate is shown. The value of $N_A - N_{D^+}$ is about $7 \times 10^{14} \text{ cm}^{-3}$ which is in good agreement with the values reported in Table 1.

3.2. Persistent photo-conductivity decay

In this section we report the measurements of the decay time constants of the PPC in the doped substrates, comparing them to those of the undoped ones.

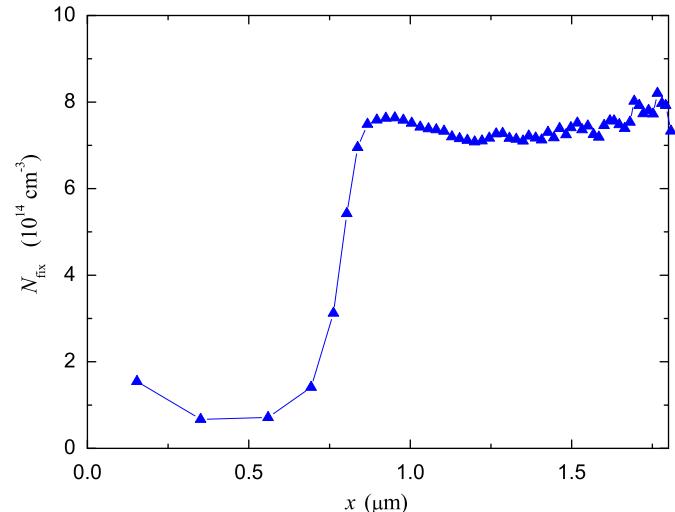


Fig. 2. Net fixed charge N_{fix} profile of the doped substrate S98 obtained by C–V measurement on an Al/Cu₂O Schottky junction. The constant value of N_{fix} far from the interface is an estimate of $N_A - N_{D^+}$ and is consistent with the value obtained from the conductivity vs. temperature fit.

The preillumination of the sample was done as described above: illuminating the photo-conductor until its photo-conductivity reached its maximum value. The light was then switched off and the decay transient of PPC was monitored at the same temperatures as the illumination.

All transients show an exponential behavior both for doped and undoped samples. Experimental data for the S94, undoped, and S98, doped, are reported in Fig. 3 together with the exponential fit. The results of the fit are summarized in Table 2. We note that PPC decay time constants in doped samples are about one order of magnitude larger than in the intrinsic case, with a similar activation energy.

In agreement with the conductivity measurements discussed in the previous section, the results show that the persistent photo-conductivity effect is greatly reduced in Cl-doped samples. At the same time the photo-conductivity is much smaller: while in intrinsic substrates the conductivity increment under illumination is about 700% of the dark value, this increment is only 10% in doped samples.

4. Discussion of conductivity data

A chlorine atom can enter the lattice in two different ways: at an interstitial site (Cl_i), introducing an acceptor level, or in a substitutional position for oxygen (Cl_o), resulting in a donor level. The latter configuration can also be seen as a way for the chlorine to reduce the concentration of the simple intrinsic defect V_O (a double donor).

The neutrality condition states:

$$p + [\text{D}^+] + [\text{Cl}_o^+] = [\text{V}_{\text{Cu}}^-] + [\text{Cl}_i^-]. \quad (3)$$

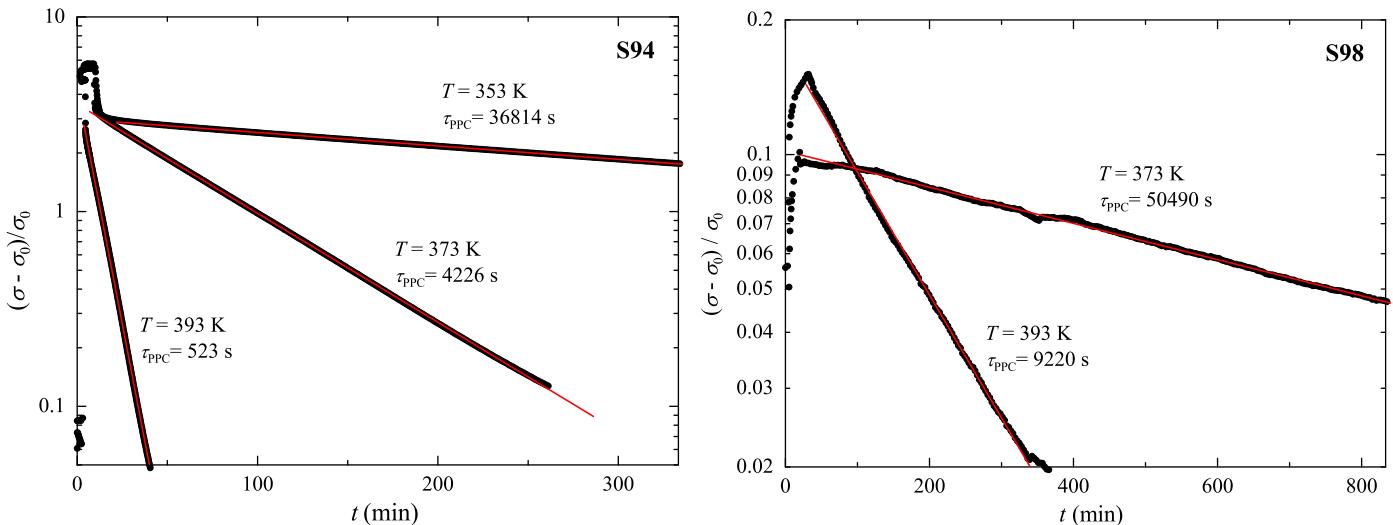


Fig. 3. PPC decay for the undoped S94 and the doped S98 samples. The black circles represent the experimental data while the red lines correspond to the exponential fits. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Persistent photo-conductivity decay time constants, τ_{PPC} , at different temperatures. The values are obtained by an exponential fit of the experimental data. E_{PPC} and τ_0 are respectively the slope and the prefactor of the activated behavior of $\tau_{\text{PPC}}(T)$.

Sample	τ_{PPC} (s)			E_{PPC} (eV)	τ_0 (s)
	393 K	373 K	353 K		
S94	523	4226	36814	1.17	6.9×10^{-13}
S97			53613		
S98	9220	50490		1.07	1.56×10^{-10}

where D^+ represents the intrinsic donor concentration (V_O or the complex ($V_O - V_{Cu}$)).

This charge neutrality condition is in general not compatible with the simple expression shown above (Eq. (1)). However the fit of the $p(T)$ data of the doped samples with the simple expression is still good. Therefore we hypothesize that it should be possible to divide the defects into two groups according to the difference between their energy levels and Fermi level ($E_i - E_F$). The former group contains levels with $E_i - E_F \gg kT$, so that their charge does not depend on temperature and it is described by the N_{D^+} value while the latter contains levels with $E_i - E_F \ll kT$, whose charge changes with temperature and it is described by N_A .

Since both N_A and N_{D^+} increase with chlorine doping, the simplest explanation of our data is that chlorine ions act both as interstitial acceptors, with an energy level very close to the V_{Cu} one, and also as substitutional donors. Therefore we propose to identify N_A with $[V_{Cu}] + [Cl_i]$ and N_{D^+} with $[D^+] + [ClO^-]$.

Another effect is that the PPC is greatly reduced. We are therefore induced to believe that chlorine passivates the intrinsic donors responsible for PPC.

Moreover the PPC effect connected to the residual V_O concentration shows a time decay about one order of magnitude greater than that observed in the undoped samples. According to our model based on defect complexes [9], the time constants should be roughly inversely proportional to the V_{Cu}^- concentration. In order to estimate the residual $[V_{Cu}^-]$ we can invoke the self-compensation mechanism [20,21]: while the neutral defect formation energy is independent of Fermi level, the formation energy of charged intrinsic acceptors increases linearly with

decreasing E_F and therefore

$$[V_{Cu}^-]_{\text{dop}} = [V_{Cu}^-]_{\text{undop}} \frac{p_{\text{undop}}}{p_{\text{dop}}} \quad (4)$$

Since the hole concentration in doped samples is more than one order of magnitude larger than that in the undoped ones, the τ_{PPC} increase is consistent with this hypothesis.

These arguments indicate that chlorine strongly reduces the concentration of both intrinsic defects. Therefore the data from Table 1 can be interpreted in such a way that in the doped substrate S98, the chlorine has produced roughly 8×10^{14} acceptors and 10^{14} donors per cubic centimeter.

5. Solar cell quantum efficiency: the role of excitons

Having improved the conductivity of Cu_2O samples by chlorine doping, it was natural to check if these substrates could produce better solar cells with reduced series resistance and increased fill factor. We made several devices based on Schottky junctions, as described in Section 2. Unfortunately their efficiency did not improve as expected since the short circuit current was reduced.

To understand the reason for this decrease, we performed quantum efficiency (QE) measurements on both doped and undoped cells (see Fig. 4). The measurements showed a reduced performance at long wavelengths of devices made with doped substrates.

The simplest explanation for these results is a shorter lifetime of photogenerated electrons, which could simply be attributed to the action of chlorine impurities as recombination centers as already proposed by Olsen [14].

We analyzed the long wavelength data of the external QE, between 500 and 650 nm, with the expression [14]

$$QE(\lambda) = T(\lambda) \left(1 - e^{-\alpha(\lambda)W} \frac{1}{1 + \alpha(\lambda)L_n} \right) \quad (5)$$

where $T(\lambda)$ is the transmittance of the bilayer ZnS/Cu , $\alpha(\lambda)$ is the absorption coefficient of the cuprous oxide [22] and L_n is the electron diffusion length.

The fits of the quantum efficiency reported in Fig. 4 were performed using a constant value of $T(\lambda)$ and the values of W obtained by C-V measurements. The electron diffusion lengths

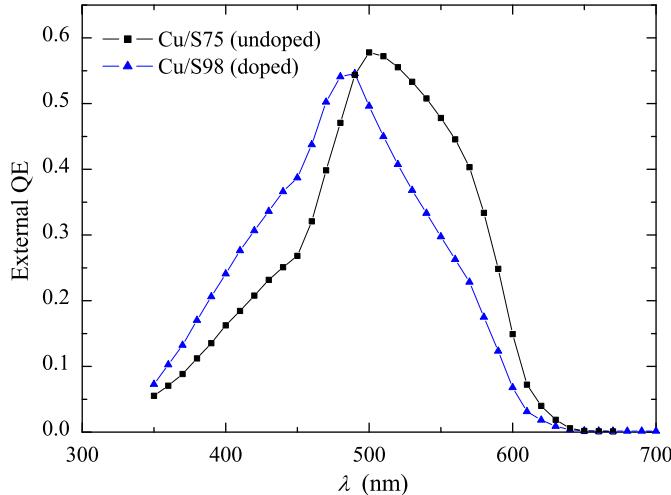


Fig. 4. External quantum efficiency for Cu/Cu₂O Schottky junction solar cells based on S75 undoped substrate (squares) and on S98 chlorine doped substrate (triangles). The resistivity of the substrates are $\rho(\text{S75}) = 1250 \Omega\text{cm}$, $\rho(\text{S98}) = 255 \Omega\text{cm}$.

were determined to be $L_n = 5 \mu\text{m}$ for the undoped device and $L_n = 1 \mu\text{m}$ for the doped device.

The simple electron lifetime τ_n was calculated using the relation $L_n = \sqrt{D_n \tau_n}$, where D_n is the electron diffusion coefficient which is given by $D_n = \mu_n kT/e$. The mobility μ_n at room temperature was estimated rescaling the hole mobility by the ratio of the effective masses, $m_h/m_e \approx 0.58$, obtaining a value of $D_n \approx 1.3 \text{ cm}^2/\text{s}$. Using this number, the electron lifetime was found to be about 190 ns for the undoped substrate and 8 ns for the doped one.

However, since the exciton binding energy ΔE_{exc} in Cu₂O is quite large (139 meV for the threefold degenerate orthoexciton state and 150 meV for the paraexciton) [23] and since their formation should be favored in the doped material (see Eq. (6) below), we investigated a possible contribution of excitons to transport and recombination mechanisms [24]. It must be noted that the excitonic gap of the material is 1.95 eV (635 nm) for the orthoexciton and therefore, for energies lower than the real band gap (2.09 eV corresponding to 593 nm), the absorbed photons produce excitons and not free carriers.

Thus we cannot exclude the hypothesis that the charge transport is also due to diffusion of excitons which are dissociated by the electric field when they reach the edge of the depletion region. In this case, if we assume a smaller diffusion length for excitons, their greater concentration in doped devices could explain the decrease of the QE.

To date there are no clear measurements of diffusion coefficient and lifetime of excitons in cuprous oxide at room temperature. An extrapolation of the Trauernicht data [25] gives a value of $D_{\text{exc}}(300 \text{ K}) \approx 10 \text{ cm}^2/\text{s}$ at 300 K. The room temperature exciton lifetime shows a huge variability, from about 1 ns to about 1 μs depending on the sample quality [23,26]. Using these values we obtain $1 \mu\text{m} \lesssim L_{\text{exc}} \lesssim 30 \mu\text{m}$ which are compatible with those found from our fits of QE, even assuming exciton diffusion as the dominant collection mechanism.

Nonetheless we can exclude an important exciton contribution to the transport mechanism considering the ratio between exciton and electron density (n_{exc} and n respectively) under illumination. Assuming that these two populations are in quasi-equilibrium and following the treatment of Combescot [27] we have

$$\frac{n_{\text{exc}}}{n} = \frac{p}{n^*} \quad (6)$$

with

$$n^* = \left(\frac{2\pi m_e m_h k T}{m_{\text{exc}} h^2} \right)^{3/2} e^{-\Delta E_{\text{exc}}/kT} \quad (7)$$

where $m_e = 0.98 m_0$, $m_h = 0.58 m_0$ and $m_{\text{exc}} = 3 m_0$ are the effective masses of the electron, hole and exciton respectively [28–30]. Since $\Delta E_{\text{exc}} = 139 \text{ meV}$, we obtain $n^* \approx 5 \times 10^{15} \text{ cm}^{-3}$ at 300 K. Considering that for our samples $p \approx 10^{14} \text{ cm}^{-3}$, Eq. (6) gives an exciton concentration which is only 4–5% of photogenerated minority carriers. It must be noted that the removal of the quasi-equilibrium assumption would further reduce this ratio (see Appendix A). Therefore, even assuming an electron diffusion length much smaller than that of excitons, it is very unlikely to have a dominant contribution of the excitons to the QE.

Now, we investigate whether the reduction of electron lifetime in the doped samples can be explained by the fact that excitons introduce an alternative recombination channel for electrons. This effect could be more important in doped samples because the larger density of holes leads to a greater probability of exciton formation. The lifetime of minority carriers produced by photons with $E_{\text{ph}} > 2.09 \text{ eV}$, can be expressed in terms of an effective lifetime that takes two recombination channels into account (see Appendix A)

$$\tau_n^{\text{eff}} = \tau_n \frac{1/b + \tau_{\text{exc}} n^*}{1/b + \tau_{\text{exc}} n^* + \tau_n p} \quad (8)$$

where b is the binding coefficient of an electron-hole pair to form an exciton, τ_{exc} is the exciton lifetime and τ_n is the electron lifetime in the absence of excitons. The value of b in Cu₂O is not known; the binding coefficient was investigated both theoretically [31] and experimentally [32] in silicon only and it was found that $b \approx 3 \times 10^{-7} \text{ cm}^3/\text{s}$ at room temperature. As stated above, the variability range of the exciton lifetime is $1 \text{ ns} \lesssim \tau_{\text{exc}} \lesssim 1 \mu\text{s}$.

Using Eq. (8) we can show that the effect of excitons cannot explain the reduction in the effective electron lifetime in doped samples. First of all we have to consider that τ_n is always greater than τ_n^{eff} and therefore $\tau_n > 200 \text{ ns}$. Considering that in doped samples p is at most 10^{14} cm^{-3} , even in the worst case of $\tau_{\text{exc}} = 1 \text{ ns}$ and $b \gg 3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ ($\tau_{\text{exc}} b n^* \gg 1$), we would obtain $\tau_n^{\text{eff}} > 50 \text{ ns}$.

Therefore it seems very unlikely that the exciton formation can be the dominant recombination channel for electrons. Thus the decrease of the device QE caused by doping is very likely related to the action of chlorine as a recombination center. Obviously a measurement of exciton lifetime in our samples would be necessary to confirm this conclusion.

6. Conclusions

In this paper we have analyzed the chlorine doping of Cu₂O. A decrease in the resistivity of about one order of magnitude was observed between the best undoped and doped samples.

The typical metastability effect observed in Cu₂O, the persistent photo-conductivity, commonly attributed to the presence of oxygen vacancies, was greatly reduced in the doped substrates. This suggests that the chlorine can passivate the intrinsic donors, most likely acting as a substitutional ion for oxygen.

Free carrier vs. temperature measurements showed that both acceptor and donor concentrations increase. This suggests that chlorine acts as an interstitial acceptor, with an energy level close to that of the copper vacancy, and as a substitutional donor also.

However, the solar cells made with doped substrates showed a lower efficiency. From the analysis of their QE, a reduction of the electron lifetime was observed. This is likely due to recombination centers introduced by chlorine doping. We have also considered

the possible contribution of excitons both to transport and recombination mechanisms, showing that their effects are most likely to be negligible.

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Appendix A. Exciton and electron lifetime

We derive Eq. (8) presented above under the hypothesis of illumination with photons of energy greater than 2.09 eV. In this case we can neglect the generation term in the exciton rate equation. In the low injection approximation we have

$$\begin{cases} \frac{dn}{dt} = G_n + n_{\text{exc}}\alpha_{\text{diss}} - \frac{n}{\tau_n} bnp, \\ \frac{dn_{\text{exc}}}{dt} = + bnp - \frac{n_{\text{exc}}}{\tau_{\text{exc}}} - n_{\text{exc}}\alpha_{\text{diss}}, \end{cases} \quad (9)$$

where G_n is the generation rate of free electron–hole pairs, α_{diss} is a coefficient related to the dissociation probability of an exciton, b is the binding coefficient of an electron and a hole (*non-geminate formation*) and τ_{exc} is the exciton lifetime.

From the principle of detailed balance, equating the rate of exciton formation and dissociation at equilibrium ($bnp = n_{\text{exc}}\alpha_{\text{diss}}$) and using Eq. (6), we obtain

$$\alpha_{\text{diss}} = bn^* \quad (10)$$

that holds in general.

In the steady state we can define an effective electron lifetime τ_n^{eff} which includes both non-radiative recombination and recombination via excitonic states:

$$G_n = \frac{n}{\tau_n^{\text{eff}}} \quad (11)$$

Solving the system (9) in the steady state, we obtain the following expression for τ_n^{eff} :

$$\tau_n^{\text{eff}} = \tau_n \frac{1 + \tau_{\text{exc}}\alpha_{\text{diss}}}{1 + \tau_{\text{exc}}\alpha_{\text{diss}} + \tau_n bp} = \tau_n \frac{1 + \tau_{\text{exc}}bn^*}{1 + \tau_{\text{exc}}bn^* + \tau_n bp}. \quad (12)$$

It can be easily seen that τ_n^{eff} increases with τ_{exc} and τ_n , whereas it decreases as p increases.

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