# Metal cluster enhanced organic solar cells

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## Abstract

An enhancement of the photovoltaic conversion efficiency of an organic solar cell by incorporation of small metal clusters has been reported recently [1]. The enhancement is explained in terms of resonant light absorption in the metal cluster which is accompanied by a strengthened electric field in the vicinity of the particle. It is therefore assumed to be based on an enhanced absorption of the organic dye film. In contrast we will show here that an excited plasmon in a metal cluster is also capable to emit an electron directly in a preferential direction if the particles are placed inside an oriented electrical field like the one existing in the depletion layer of a Schottky junction. Thereby a primary photocurrent is observed in a spectral region without any direct absorption in the organic film. We will present results obtained at a Schottky junction formed at the interface of ITO and zinc phthalocyanine. In order to study the influence of the metal particles we evaporated a thin silver film on top of the ITO substrate and tempered the system in a vacuum, thereby forming small separated silver clusters. We investigated the influence of the silver clusters on the optical extinction spectra and on the short circuit photocurrent spectra of such constructed organic solar cells. The experimental data will be discussed using a qualitative energy diagram. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

A property of a "free" electron gas is its capacity of collective plasma oscillations. These oscillations can occur in the bulk of the material or at the interface between a metal and a dielectric medium. The latter oscillations are therefore called surface plasmons (SP). The physical properties of these plasmons are reviewed in monographs [2,3].

The effect of excited surface plasmons in a *inorganic* semiconductor/metal-Schottky junction has been examined in detail [4–8]. Using the method of attenuated total reflection (ATR) a SP was excited at the metal/air interface. This excited plasmon leads to an increased amount of photoexcited electrons in the metal which are capable to surmount the Schottky barrier and therefore increase the short circuit photocurrent.

The effect of SPs on the short circuit photocurrent ($I_{SC}$) of a Schottky-type *organic* solar cell based on copper phthalocyanine (CuPc) with the cell structure (glass/Al/CuPc/Ag) has also been investigated by several authors [9–13]. An excited surface plasmon in the aluminum interface to CuPc or in the silver interface to air increases ($I_{SC}$). This enhancement was explained with increased absorption of photons in the organic dye layer due to the high electric field strength in the vicinity of the excited SP.

The large enhancement of the electric field related to the oscillating electron plasma can also be used to increase the Raman scattering signal from molecules adsorbed on a metal surface. This surface enhanced Raman scattering (SERS) has also been used to study the Raman spectra of organic dyes [14–16].

In small metal clusters localized plasmon excitations can occur by direct light absorption due to the much simpler selection rules. Here no $k$-selection rule exists. In the system (ITO/metal-clusters/CuPc/In) it has been shown that the incorporation of copper or gold clusters between the ITO and CuPc increases the photocurrent originating from the Schottky-contact at the CuPc/In-contact by a factor of more than two [1]. This effect was explained by an increased photovoltaic conversion efficiency due to resonant light absorption in the metal clusters.

In this paper we examine the influence of excited plasmons in small silver clusters placed directly in a photovoltaic active Schottky-contact formed at the interface of ITO and zinc phthalocyanine (ZnPc).

## 2. Experimental

The ZnPc from Kodak was purified by twofold train sublimation. ZnPc and silver were sublimated on top of an ITO-coated glass substrate from Balzers by vacuum evaporation techniques in an evaporation chamber at $10^{-6}$ mbar. By using appropriate masks sample structures were obtained as shown in Fig. 1. The film thicknesses were 4–10 nm for the silver island layers, around 200 nm for the ZnPc layers and 30 to 50 nm for the silver back contacts. The thicknesses were controlled with a quartz oscillator.
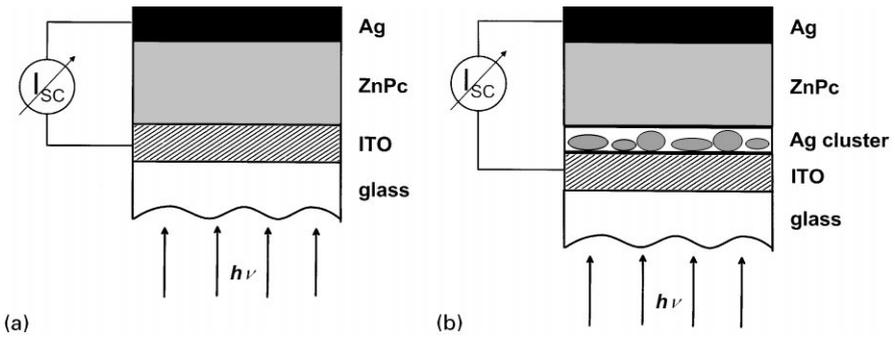
Fig. 1. Sample structures without (a) and with (b) the intermediate silver cluster layer.

The samples were tempered in a vacuum oven at 200°C after the evaporation of the thin silver island film in order to get well separated silver particles on top of the ITO.

The silver island morphology was investigated using the transmission electron microscope (TEM) EM400 from Philips. The extinction spectra were measured with a photometer Cary 3G from Varian and the spectrally resolved $I_{SC}$ was obtained by illuminating the ITO side of the sample with monochromatic light and was monitored by using a Keithley SMU 236 source meter.

## 3. Results

The silver island morphology was studied by TEM. A 4 nm thick silver film was evaporated onto of a carbon covered TEM grid. After the evaporation the silver film consists of densely packed 10–20 nm broad islands (Fig. 2a). The weak contrast of these islands points to very flat particles. After tempering this sample in a vacuum oven for 10 min the islands coalesce and bigger particles with a mean diameter of around 36 nm are formed (Fig. 2b). The island thickness seems to be increased as indicated by the higher contrast.

The tempering changes the film morphology and it is assumed that this happens in more or less the same wax for island films on ITO. This assumption is based on the observation that at the same time pronounced changes of the optical occur. Fig. 3 shows optical extinction spectra of a silver island film on a quartz substrate before and after the tempering. The untreated film shows a very broad extinction band around 2.4 eV. The tempering causes a blue shift of the maximum by 0.7–3.1 eV. Thereby, the half width (HW) of the extinction band decreases from 0.6 to 0.3 eV.

The ZnPc was evaporated on top of the silver island film after tempering. Fig. 4 shows the extinction spectra of the ZnPc-film on ITO with and without the intermediate silver film. In the spectral range where the ZnPc is not absorbing a clear extinction peak originating from the silver island film is observed. Compared with the extinction peak of the tempered silver island in Fig. 3 the extinction peak in Fig. 4 is reshifted due to the increased effective index of refraction in presence of the ZnPc.
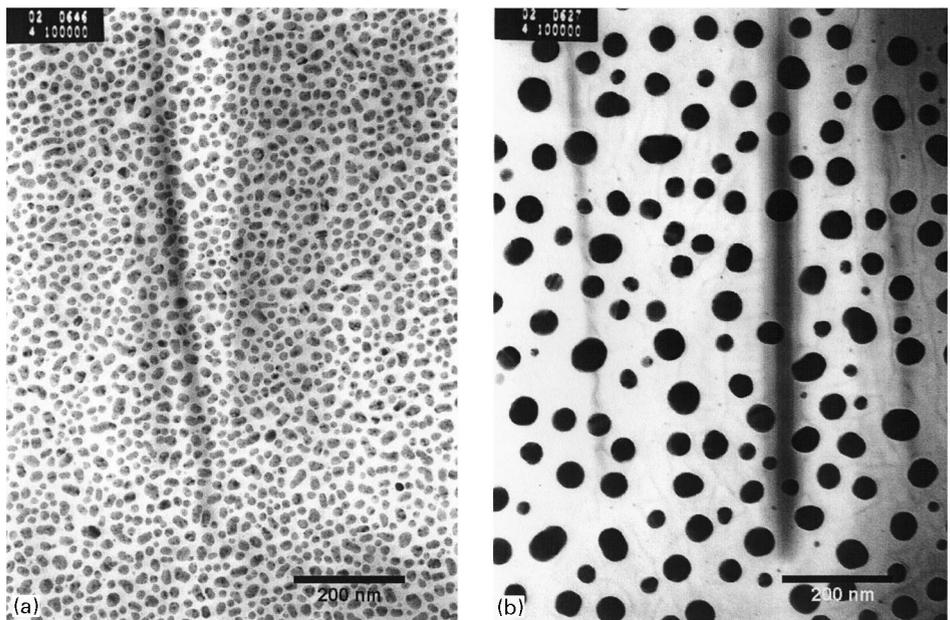
Fig. 2. Morphology of the silver cluster film on a carbon TEM grid before (a) and after (b) the tempering process studied by using TEM.

The $I_{SC}(\lambda)$ of the sample without the intermediate silver particle layer follows mainly the optical extinction of the ZnPc (Fig. 5). From this behavior it is obvious that the short circuit photocurrent is generated close to the interface region of ITO and ZnPc. If the back contact would be the photovoltaically active contact the $I_{SC}$ would not follow the absorption of the ZnPc due to the so-called filter effect and therefore would show maxima in the photocurrent at lower absorption coefficients (compare Ref. [17]).

The incorporation of the silver particles between the ITO and the ZnPc does not affect the position of the active contact. The $I_{SC}(\lambda)$ continues to follow the extinction of the ZnPc. However, with the presence of silver particles in the photovoltaically active contact region an additional local photocurrent maximum occurs between 400 and 550 nm. In this spectral region the ZnPc is not absorbing (see Fig. 4), whereas the metal clusters are. This contribution to the short circuit photocurrent therefore has its origin in the embedded silver particles.

## 4. Discussion

The enhancement of the photocurrent in a spectral region where the ZnPc does not absorb is a clear indication that the electron–hole pair is created in the metal cluster itself.
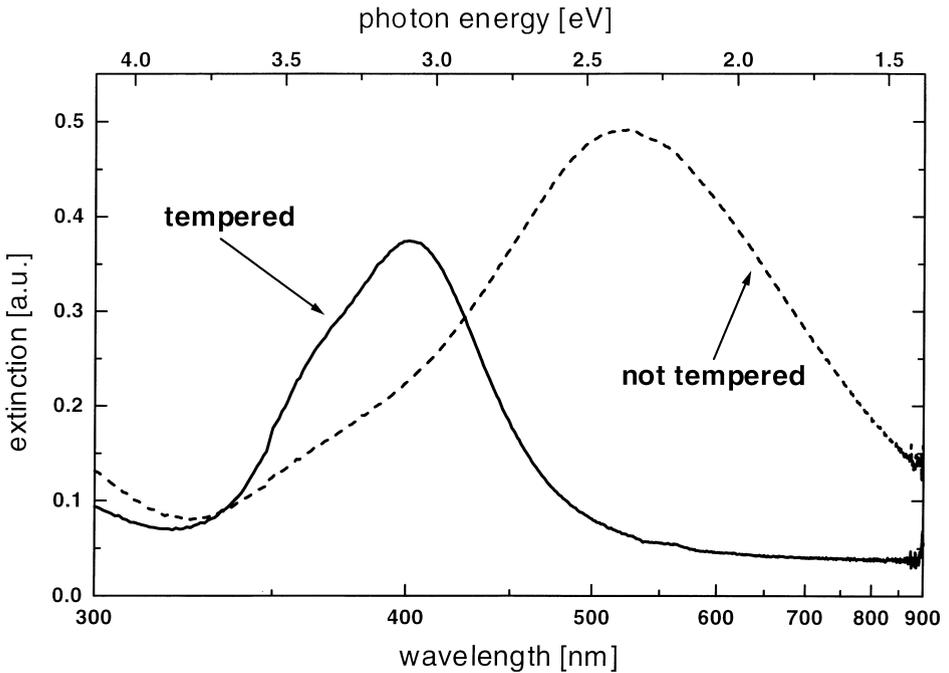
Fig. 3. Optical extinction spectra of a non-tempered and a tempered silver cluster layer on a quartz substrate. The amount of silver corresponds to a 5 nm thick homogenous film as determined with a quartz microbalance.

In our experiment we assume the clusters are located within the space charge region of the ITO/ZnPc contact (Fig. 6). We assume that the collective oscillation of the "free" electron gas transfers energy to one electron. The excited electron can fill an empty state in the ITO, if this electron has a momentum perpendicular to the contact area. This electron transfer can occur either by a direct transfer, ITO and metal are in contact, or by tunneling of the electron from the metal to the ITO through a very thin intermediate ZnPc layer. For the creation of the short circuit photocurrent also the positive charge, empty state, left in the metal particle, has to be filled again with an electron from the valence band of the ZnPc. In other words, as depicted in Fig. 6, a hole has to move from the metal particle to the valence band of the ZnPc. The electrical field of the space charge region drives this charge separation process, especially the transport of the hole in the valenceband of the ZnPc.

Similar studies were performed as photoemission experiments [4–8]. Here, a surface plasmon in samples, metal/n-type semiconductor, was excited using the ATR method. Due to the plasmon excitation an increase of the $I_{SC}$ is observed for photon energies below the band gap of the n-type semiconductor. The origin of this enhancement is explained in terms of increased photoexcitation of metal electrons. If the energy transmitted from the plasmon to one electron is high enough to surmount the barrier of the Schottky contact the electron can be injected into the conduction band
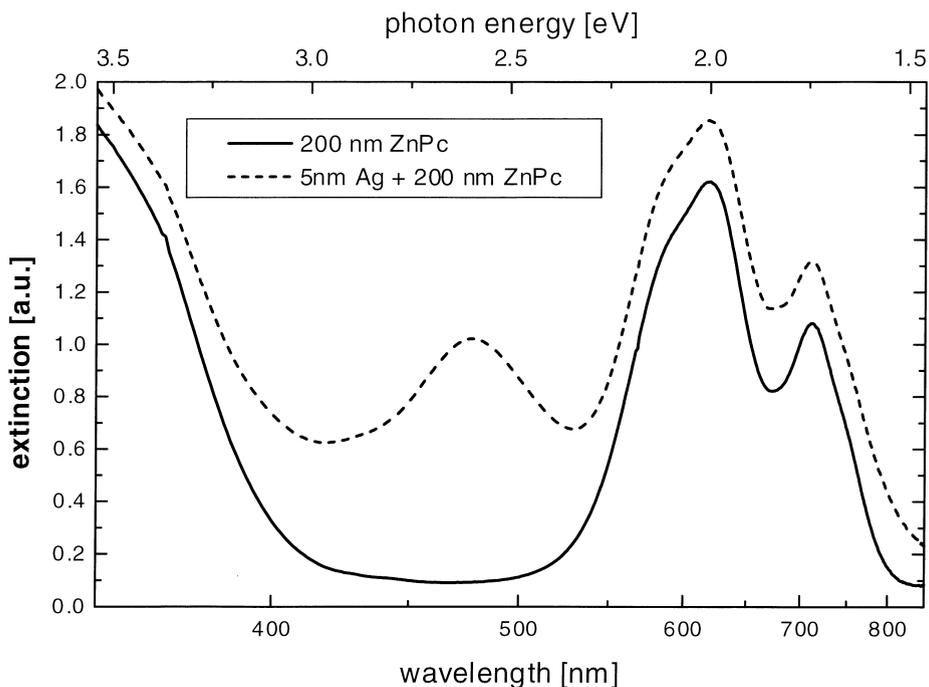
Fig. 4. Optical extinction spectra of a ZnPc layer on a quartz substrate with and without the intermediate silver cluster film.

of the n-type semiconductor. The injected electron is then accelerated towards the bulk of the semiconductor due to the electric field of the depletion layer. In our case the opposite process occurs: after the electron injection into ITO the hole transfer from the metal particle to the valence band of the ZnPc is the key process.

An enhancement of $I_{SC}$ due to an excited surface plasmon in the metal at either the glass substrate/metal or the metal/air interface of a Schottky-type cell has been reported recently [9–13]. Here a sample structure glass-substrate–metal/CuPc/metal has been used. $I_{SC}$ is reported to increase in this case without a pronounced change in the spectrum. Therefore, here the enhancement is explained by an increased absorption in the ZnPc indirectly caused by the excitation of surface plasmons. The calculated electrical field strength at the metal/dielectric medium interfaces are reported to increase by a factor of ten due the excitation of surface plasmons. However, in our opinion this field enhancement is too small to lead to significant changes in the optical constants of the ZnPc due to nonlinear effects. On the other hand, the incident light beam creates surface plasmons if the reflection at the interface changes from normal to total reflection. At this angle also the interference pattern in the thin film system investigated will change. This change in the interference behavior may also explain the increased electric fields at incident angles where the selection rule for surface plasmon excitations is fulfilled. The reported enhancement of the $l_{SC}$ can
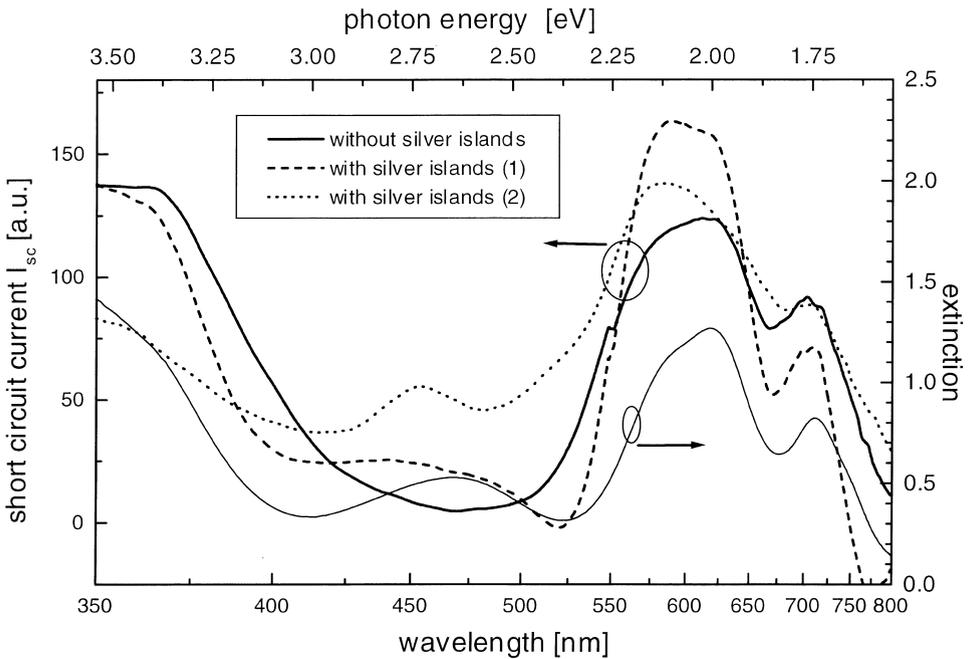
Fig. 5. Short circuit current spectra of an ITO/ZnPc-Schottky contact with ((1) and (2)) and without the embedded silver clusters in comparison with the optical extinction spectrum of the silver cluster containing film. The spectra (1) and (2) were obtained at two samples prepared under slightly different tempering conditions.

therefore in our opinion also be explained without taking any interaction between the dipole field of the oscillating electron gas and the ZnPc into consideration. In SERS investigations the interaction of the spherical plasmon dipole field with an adsorbed molecule increases the intensity of the Raman signal of the latter. Here, the dipole field strength can be several orders of magnitudes higher than the field strength of the incident light [14–16].

An enhancement of $I_{SC}$ due to the incorporation of metal clusters in a sample with the structure, ITO/metal-cluster/CuPc/metal has also been reported recently [1]. In this case the photovoltaically active contact, the rectifying junction, is formed between the CuPc and the metal contact. The incorporation of the metal clusters close to the contact opposite to the Schottky junction is reported to increase $I_{SC}$ by a factor of 2 if copper is used as cluster material, whereas for silver clusters no enhancement was observed. The photocurrent was found to be increased in the whole examined spectral range, showing no correlation with the absorption of the metal cluster film. The increased $I_{SC}$ is again explained with the field enhanced light absorption of the ZnPc and also with photoexcitation of cluster electrons. However, the data presented in Ref. [1] may alternatively be explained by increased dark conductivity and/or photoconductivity due to the incorporation of the metal clusters into an otherwise high resistive
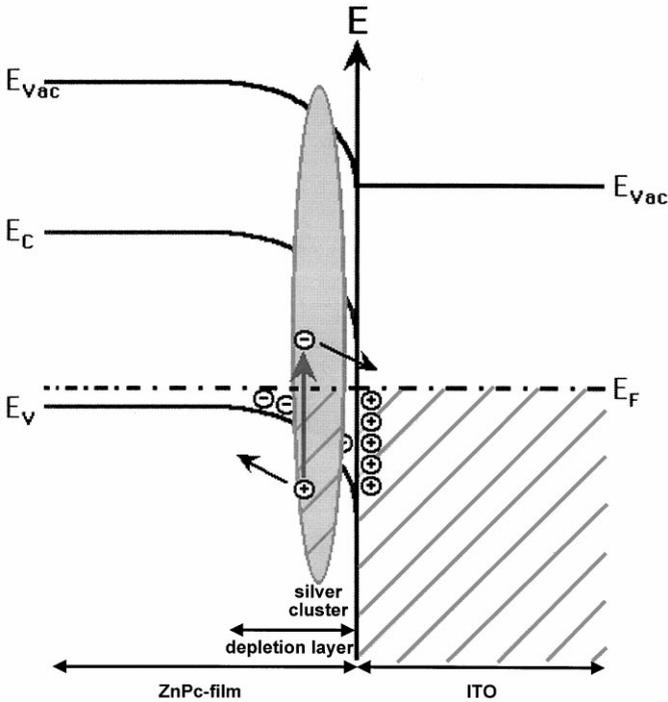
Fig. 6. Schematic energy model showing photoexcitation, charge separation and transport processes in a silver cluster embedded in the depletion layer of an ITO/ZnPc-Schottky contact. ($E_{VAC}$-vacuum level, $E_F$-Fermi level, $E_V$-upper valence band edge, $E_C$-lower conduction band edge).

film as well as by a decreased contact resistance at the ITO/ZnPc interface. These proposed effects could indeed rise $I_{SC}$ independent of the photon energy.

In contrast, in our experiments we found a clear correlation between the optical absorption of the silver cluster film and the $I_{SC}$ (Fig. 5).

The optical properties of the silver cluster layer are strongly dependent on the morphology of the clusters. The extinction maximum of the clusters changes with changing their mean diameter. In the case of silver clusters the extinction is more red shifted with increasing cluster size [17]. In future, a controlled formation of the clusters may lead to a well-defined size distribution and could be used to optimize the absorption of the cluster layer for adjusting the film to the spectrum of the used light source or the sun.

## 5. Summary

We investigated the influence of incorporation of silver metal clusters in the depletion layer of a Schottky contact formed between ITO and ZnPc on its optical and photovoltaic properties. The extinction of the ITO/silver clusters/ZnPc system

was found to be the superposition of the clusters and the ZnPc bulk absorption. The incorporated metal clusters lead to an increase of the short circuit current in a spectral region where the cluster film absorbs but the ZnPc does not. We present a qualitative energy model that is capable to explain the experimental data. The model is based on the assumption that a plasmon-enhanced excitation of an electron takes place inside the metal cluster. The electron is transferred to the ITO electrode while it is replaced by an electron from the valence band of the ZnPc. We assume this charge separation process to be driven by the static electric field of the depletion layer.

## Acknowledgements

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