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Stepped light-induced transient measurements of photocurrent and voltage in dye-sensitized solar cells based on ZnO and ZnO:Ga

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In order to explain the higher short-circuit current (J_{sc}) with comparable open-circuit voltage (V_{oc}) from dye-sensitized solar cells (DSCs) based on gallium-modified ZnO (ZnO:Ga) porous electrodes, the diffusion coefficient (D) and electron lifetime (τ) in DSCs with and without Ga-modified ZnO were studied by stepped light-induced transient measurements of photocurrent and voltage. In comparison to DSCs based on ZnO electrodes, the ZnO:Ga-based solar cells provided lower D and higher τ values. The results were interpreted according to the transport-limited recombination model, where the Ga modification induced a higher density of intraband charge traps. At matched electron densities, a decrease in V_{oc} from DSCs based on ZnO:Ga was observed, suggesting a positive shift of the ZnO:Ga conduction band edge. The higher J_{sc} can be explained by the positive shift of the ZnO:Ga conduction band edge in addition to the increased roughness factor of the electrode due to the Ga modification. © 2009 American Institute of Physics.

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I. INTRODUCTION

Dye-sensitized solar cells (DSCs) have received significant attention in recent decades due to their respectable efficiency and low cost.^{1,2} The solar cells consist of a dye-adsorbed nanoporous semiconductor electrode immersed in an electrolyte and a Pt counterelectrode. One of the key issues to increase the energy conversion efficiency is to enhance the electron transport in order to overcome the recombination losses inherent with the nanocrystalline film. Since the porous electrode is filled with an electrolyte, the electron transport has been described as a diffusion process due to the presence of cations, which screen the electrons in the electrode.³⁻⁵ The effect of cations on the electron transport has been interpreted in terms of ambipolar diffusion.⁶ Electron diffusion in the nanostructured electrodes of DSCs has been described by a model that takes into account events of trapping by and detrapping from localized trap sites.^{5,7} It has been shown that the traps are located mainly on the nanoparticle surface,⁸ and at interparticle boundaries.⁹ Since charge recombination in DSCs occurs through charge transfer at electrode/dye/electrolyte interface, charge recombination can be retarded by the proper surface modification of the semiconductor oxide¹⁰ or even by doping.¹¹ The use of Al and W as photovoltaic property-enhancing impurities in TiO₂ may cause two effects: a different morphology (and as a consequence a different surface polarity), and a change in the defect content (which affects the charge-transfer kinetics and dye loading).¹¹ Solar cells based on doped TiO₂ electrodes

presented a better performance in comparison to pristine TiO₂ counterpart, evidencing the role of surface polarity and defect charge balancing on surface states.¹¹ An improvement in the incident photon to current conversion efficiency and overall conversion efficiency has also been reported for a DSC based on nitrogen-doped titania.¹²

ZnO has emerged as a versatile material for electrodes in DSCs especially due to facile modification of its morphology, such as different nanostructures:¹³ nanorods/nanowires,¹⁴⁻¹⁶ nanoflowers,¹⁷ nanotubes,^{18,19} and nanotips in addition to gallium-doped zinc oxide (ZnO:Ga or GZO) as the transparent conductor oxide material,²⁰ etc. The *n*-type semiconductor features of ZnO stem from the presence of intrinsic defects, such as oxygen/zinc vacancies, oxygen/zinc interstitials, and complex defects associated with oxygen/zinc vacancies.²¹ In order to enhance the electron transport properties in ZnO nanostructured electrode, Ga³⁺ was used in this work as the impurity ions, as surface modifiers, and/or as dopants. In gallium-modified zinc oxide (ZnO:Ga), Ga³⁺ is expected to cause a little lattice distortion due to the similar Zn²⁺ and Ga³⁺ tetrahedral radii.²² Ga impurities act as a kind of donor in ZnO,²³ thereby affecting the point defect density and surface charge, a behavior probably arising from the different Zn²⁺ and Ga³⁺ ionic charges. Charge balance in ZnO:Ga (Ref. 24) might require a complex equilibrium between oxygen/zinc vacancies and oxygen/zinc interstitials, while the formation of single oxygen vacancies is likely to take place. Since some native defects, e.g., single oxygen vacancies and zinc interstitials, have energy levels close to the ZnO conduction band edge,¹³ the electron density in ZnO would increase up to a certain

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gallium doping level.²⁵ The higher electron density arising from Ga doping²¹ produces many-body effects resulting in the renormalization of the band gap, lowering the band gap energy.²¹ However, the role of Ga doping into ZnO still needs further studies,²¹ especially if the formation of other crystalline phases, such as zinc gallate,^{22,26} takes place. Even though there are many reports on the electron diffusion coefficient (D) and electron lifetime (τ) for electrodes based on TiO₂, little is known about ZnO electrodes. Recently we reported the enhancement of the photocurrent and overall efficiencies in DSCs based on GZO porous electrodes compared to ZnO.²⁷ The aim of this work is to elucidate the higher energy conversion efficiencies of DSCs based on ZnO:Ga by means of stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV).

II. EXPERIMENTAL SECTION

ZnO and ZnO:Ga 1, 3, and 5 at % nanoparticles were prepared in an aqueous solution of zinc nitrate and/or gallium nitrate in the presence of triethanolamine.²⁸ The paste was spread onto the conducting substrate (fluorine-doped SnO₂, Hartford Glass Co. 8–12 Ω/\square) by the doctor blading technique and then sintered at 450 °C for 30 min. The electrodes were sensitized in a 0.5 mmol L⁻¹ ethanolic solution of the complex N719 [cis-bis(isothiocyanato)bis(2, 2'-bipyridyl-4, 4'-dicarboxylate-ruthenium(II) bis-tetrabutylammonium)] for 3 h at room temperature. The electrolyte was 0.5 mol L⁻¹ 4-*tert*-butylpyridine, 0.8 mol L⁻¹ tetrabutylammonium iodide, 0.1 mol L⁻¹ LiI, and 0.05 mol L⁻¹ I₂ in methoxypropionitrile:acetonitrile (50:50 v/v). The counterelectrode was a Pt-sputtered conducting substrate. The DSCs were sealed by using the thermoplastic Himilan (Mitsui-Dupont Polychemicals). Film thickness was ~ 6 μm (measured by the Sloan Technology profiler, Dektak 3) and typical cell area was 0.15 cm². For SLIM-PCV measurements, a diode laser (Coherent, LabLaser, $\lambda=635$ nm) was used for both photocurrent and voltage transients, as described elsewhere.²⁹ Since D and τ exhibit some dependence on dye loading, the amount of dye adsorbed into the porous nanostructured electrodes was measured.³⁰ The dye was desorbed from the porous films by using a 1 mol L⁻¹ NaOH solution (water:ethanol 1:1 v/v), and the dye loading was determined from the absorption spectra of the solution. The J - V curves of the sealed DSCs were measured under AM 1.5 illumination (100 mW cm⁻²) using a solar simulator (Yamashita Denso, YSS-80). The data for J - V curves and SLIM-PCV measurements were the average for at least three identical samples.

III. RESULTS AND DISCUSSION

The porosity of the porous nanocrystalline electrodes increased upon increasing the gallium content, as reported by our group in an earlier paper.²⁷ The increase in roughness factor, that is, a higher actual area per projected area ratio, provided a higher dye loading upon increasing gallium content, which is reflected in a higher short-circuit photocurrent density (J_{sc}), as observed in Table I. However, the increase in roughness factor is not enough to explain the increase in J_{sc}

TABLE I. Roughness factor and parameters from the J - V curves (AM 1.5, 100 mW cm⁻²) measured from sealed DSCs based on 6- μm -thick ZnO and ZnO:Ga electrodes. Average cell area: 0.15 cm².

DSC	Roughness factor (%)	Dye loading (mol cm ⁻²)	J_{sc} (mA cm ⁻²)	V_{oc} (V)
ZnO	274	$<1 \times 10^{-8}$	2.07	0.79
ZnO:Ga 1 at %	365	6×10^{-8}	5.32	0.79
ZnO:Ga 3 at %	389	6.5×10^{-8}	5.56	0.79
ZnO:Ga 5 at %	483	8.1×10^{-8}	6.49	0.79

values. We have recently shown, by transient absorption spectroscopy (TAS) measurements, some evidence for a higher density of dye cations generated for the case of ZnO:Ga electrodes compared to pristine ZnO.²⁷ While it suggests a higher charge injection efficiency in agreement with the higher J_{sc} , the longer electron diffusion length in the ZnO:Ga electrodes could be one of the main reasons for the enhanced J_{sc} .

Typical photocurrent and photovoltage transients from the SLIM-PCV measurements for DSCs based on 6- μm -thick electrodes are shown in Fig. 1. The photocurrent transients from all the DSCs based on ZnO and on ZnO:Ga were similar to the one shown in the inset of Fig. 1. Therefore, all the photocurrent transients measured at different laser intensities in this work could be well fitted by a single-exponential function.²⁹

The higher photocurrent density (J_{sc}) from DSCs based on ZnO:Ga compared to analogous DSCs based on ZnO electrodes may also be observed in Fig. 2. The V_{oc} scales up with the laser intensity, in good agreement with the simplified Butler–Volmer expression.³¹ Besides, for the unmatched electron density condition, the open-circuit photovoltage (V_{oc}) from DSCs based on ZnO:Ga electrodes is smaller than that observed for DSCs based on ZnO electrodes, corroborating our previous work.²⁷

The electron diffusion coefficients in DSCs with and without Ga-modified ZnO electrodes are shown in Fig. 3. The gallium modification brought about a twofold decrease in the values of D . The decrease in D might be a consequence of a higher trap density in ZnO:Ga in comparison to

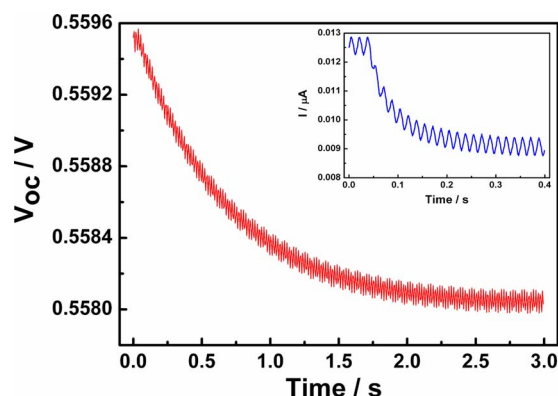


FIG. 1. (Color online) Typical photovoltage transient induced by the stepped laser intensity. The inset shows a typical photocurrent transient from SLIM-PCV measurements. Both photovoltage and photocurrent transients were observed for DSCs based on a ZnO:Ga 3 at % electrode.

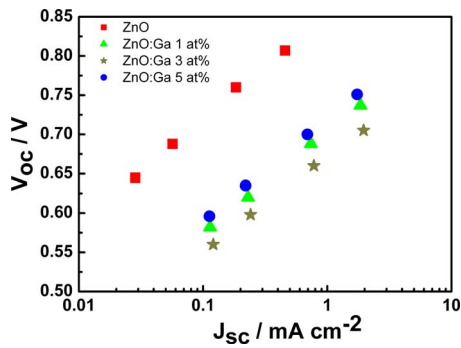


FIG. 2. (Color online) Behavior of V_{oc} and J_{sc} from SLIM-PCV measurements for DSCs based on ZnO and ZnO:Ga 1, 3, and 5 at % electrodes under open-circuit conditions at different illumination intensities. The bottom axis shows J_{sc} values measured under the same laser intensity used for the photovoltage transient measurements.

ZnO electrodes and/or a higher resistance at the interparticle boundaries. The increase in trap density would arise from the higher surface area of ZnO:Ga electrodes compared to that of the ZnO electrode and/or from the introduction of Ga^{3+} as intraband states. Since electrons spend more time in traps, the values of D become smaller. Indeed, measurements from impedance spectroscopy for the same DSCs reported herein evidenced a higher chemical capacitance for DSCs based on ZnO:Ga compared to the ZnO-based analogs.³² Such higher chemical capacitance in ZnO:Ga is believed to arise from the higher surface area, porosity, roughness factor, and point defect density.³²

Additional data from the XPS spectra of ZnO and ZnO:Ga photoelectrodes showed the presence of gallium as Ga^{3+} in ZnO:Ga powder samples by the characteristic binding energies.²⁷ Therefore, it is believed that some of the Ga^{3+} ions seem to substitute for Zn^{2+} ions in the wurtzite hexagonal structure of ZnO (Ref. 27) or occupy the position of zinc vacancies.²¹ However, the possibility of some Ga^{3+} ions acting in the surface modification of ZnO cannot be ruled out.

The electron lifetime values (τ) obtained from photovoltage transients are shown in Fig. 4. In the case of τ , gallium modification provided DSCs with a longer electron lifetime than those in ZnO-based ones, as expected from the D values (Fig. 3). This can be rationalized in terms of diffusion-limited electron lifetimes; that is, trapped electrons do not recombine with I_3^- , and, thus, an increase in trapped time results in a decrease in recombination rate. The results

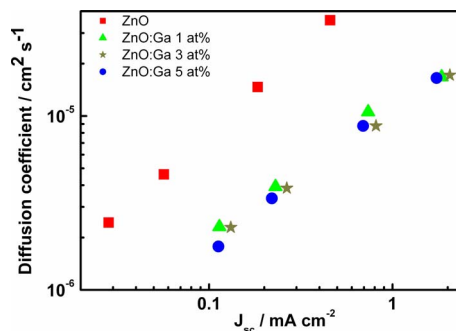


FIG. 3. (Color online) Diffusion coefficient under different illumination intensities from SLIM-PCV measurements in DSCs based on N-719-sensitized ZnO and ZnO:Ga electrodes (film thickness: 6 μm).

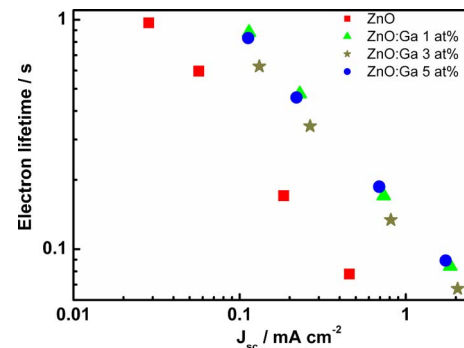


FIG. 4. (Color online) Electron lifetimes determined from photovoltage transients under open-circuit conditions at different illumination intensities. The bottom axis shows J_{sc} values measured under the same laser intensity used for the photovoltage transient measurements.

in Figs. 3 and 4 are also similar to those reported by Kopydakakis *et al.*³³ In their report, Li^+ ions intercalated into the TiO_2 and the cations acted as charge traps, decreasing the electron diffusion coefficient and recombination rate. Another report shows that the decrease in D and the increase in τ with smaller TiO_2 particle sizes were interpreted in terms of a larger film surface area and a higher number of particle boundaries, where charge trap sites are likely to exist.³⁴

Figure 5 shows the V_{oc} as a function of photogenerated electron density. Note that the porosity of the film was not taken into account to determine the electron density. The ZnO:Ga-based DSCs showed a lower V_{oc} at matched electron densities. This might be associated with the positive shift of the conduction band edge (E_{CB}) and the increase in trap density. However, by taking porosity into account to explain the decrease in V_{oc} at matched electron densities, the trap density could be increased by a factor of 6–8. On the other hand, the roughness factor was only doubled. With the results of the decrease in D by a factor of 2, it is not sufficient to explain the lower V_{oc} only by the change in trap density. As mentioned previously, TAS data from our group suggested a higher charge injection yield for the case of ZnO:Ga electrodes.²⁷ This suggests that the conduction band edge of ZnO was shifted positively by the addition of Ga ions. Thus, the lower V_{oc} at the matched electron density is probably caused by both the increase in trap density and the positive shift of the conduction band edge. Table I shows that the V_{oc} was the same regardless of Ga modification under 1

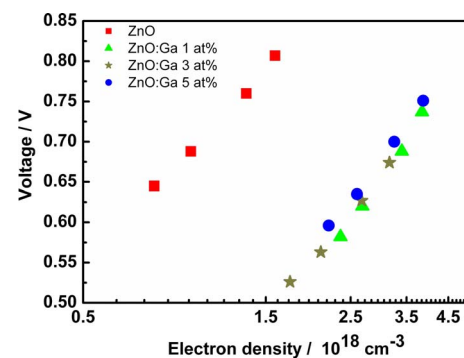


FIG. 5. (Color online) Photoelectron density from ZnO and ZnO:Ga electrodes and the associated photovoltage at different illumination intensities.

sun illumination. This can be well explained by a higher electron density in ZnO:Ga than in ZnO due to the longer electron lifetime of the former.

IV. CONCLUSIONS

The studies of photocurrent and photovoltage transients showed that the electron diffusion coefficients in ZnO electrodes were decreased, while the electron lifetimes were increased, after a gallium modification of the ZnO electrode. This behavior was interpreted according to the increase in intraband charge traps in the nanoporous electrodes. The lower V_{oc} of DSCs using Ga-modified ZnO at matched electron density is probably caused not only by the increased intraband trap density but also by the positive shift of the ZnO:Ga conduction band edge. The higher J_{sc} values observed in ZnO:Ga-based DSCs were assigned to higher charge injection efficiencies, resulting mainly from the positive shift of the ZnO:Ga conduction band edge, in addition to the higher roughness factor of the electrode.

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