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Title	Laser spot scanning in photoelectrochemical systems, relation between spot size and spatial resolution of the photocurrent
Author(s)	Eriksson, S.; Carlsson, P.; Holmström, B. et al.
Citation	Journal of Applied Physics, 69(4), 2324-2327 https://doi.org/10.1063/1.348714
Issue Date	1991-02-15
Doc URL	https://hdl.handle.net/2115/20578
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Type	journal article
File Information	JAP69-4.pdf

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Laser spot scanning in photoelectrochemical systems, relation between spot size and spatial resolution of the photocurrent

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(Received 11 June 1990; accepted for publication 2 November 1990)

Laser spot scanning studies of single-crystalline *p*-InSe in contact with a neutral aqueous solution reveal a dramatic difference in lateral resolution between the material "as cleaved" and after platinization by brief dipping in a dilute H_2PtCl_6 solution. A model is developed to explain these observations, and the resolution is calculated as a function of the diffusion coefficient and the life time of minority carriers, and of the charge transfer rate. The improvement of the resolution is found to be due to the increase of the rate of hydrogen evolution at the illuminated semiconductor by Pt catalyst. The model also provides numerical values for the charge transfer rate in the noncatalyzed and the catalyzed cases.

INTRODUCTION

During the last decade a new technique to study the photoelectrochemical (PEC) properties of semiconductor surfaces has been developed, utilizing a spot of highly focused laser light scanned across the surface.[1-7] This technique, known as laser spot scanning (LSS), has opened new possibilities for laterally resolved studies of the effects of illumination at semiconductor-liquid junctions.

In this technique, a laser spot is scanned over the semiconductor surface and the photocurrent is recorded. Photocurrent images can be directly related to surface structures of polycrystalline materials, such as grain boundaries and surface defects, as shown for TiO_2 (Refs. 1 and 5) and for *n*-Si.[3] Studying the effect of surface treatments is greatly facilitated, as different treatments can be made on the same material and then directly examined with the LSS apparatus. The correlation of surface treatment or structural features of the surface with PEC properties has been studied with the LSS technique, for *n* = GaAs, *n*-WSe_2,[4] and for *p*-InSe.[7] PEC etching of pits on CdSe with focused laser light of high intensity might have applications in data storage.[2]

We took a novel approach to the laser scanning microscopy by introducing fiber optics.[7] We let the laser beam focus onto the end of a single mode glass fiber. The other end is fitted with a Selfoc® lens that focuses the outcoming laser light to a small spot. This approach gives a simpler apparatus for the *x*/*y* scanning of the focused light spot across the semiconductor surface. Another benefit of this approach is evident in photoelectrochemical studies. The apparent light source (the end of the fiber) can be moved very close to the semiconductor surface and thus avoiding blurring of the image or damping of the light as the light passes through the electrolyte.

The resolution of LSS is limited by the size of the focused spot of laser light; values down to a few microns are reported.[1,3] However, we found that the spatial resolution was much lower than the spot size.

In this paper we develop a model to simulate the spatial resolution as a function of properties of the semiconductor material (mobility and life time of minority carriers) and of the chemical system (rate of charge transfer from the semiconductor to the solution). Models exist for spatial resolution in solid-state systems under field-free conditions, when studied by light beam induced current, LBIC[8,9] and electron beam induced current, EBIC.[9] Our model is an extension to a PEC system, with a strong field in the depletion layer forcing minority charge carriers to the surface, and an electrochemical step in which charge is transferred across the solid-/liquid interphase.

RESULTS

The fiber optical laser spot instrument has been described previously.[7] Using a HeNe laser and a 4-μm single-mode fiber the theoretical spot size should be about 4 μm. An SEM picture of holes photoetched by our laser spot in a surface of single-crystalline GaAs is shown in Fig. 1. The etched holes have a diameter of 5–7 μm, slightly above the theoretical spot size. Measurement of the light intensity gradient as the spot passes a sharp edge (Fig. 2) indicates a width at half maximum of just above 4 μm.

Such a high resolution is, however, not always obtained

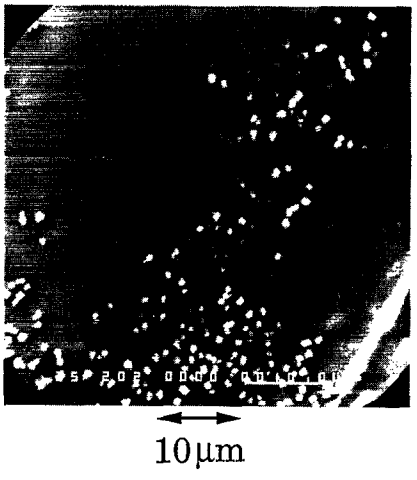

FIG. 1. SEM picture of a photoetched surface of single-crystalline GaAs.

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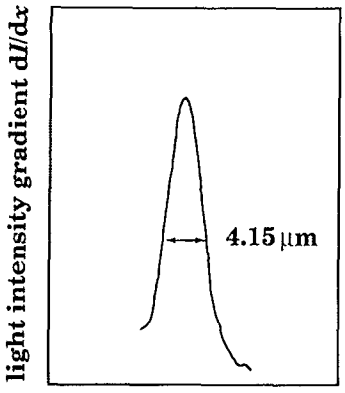

FIG. 2. Light intensity gradient as the laser spot passes a sharp edge.

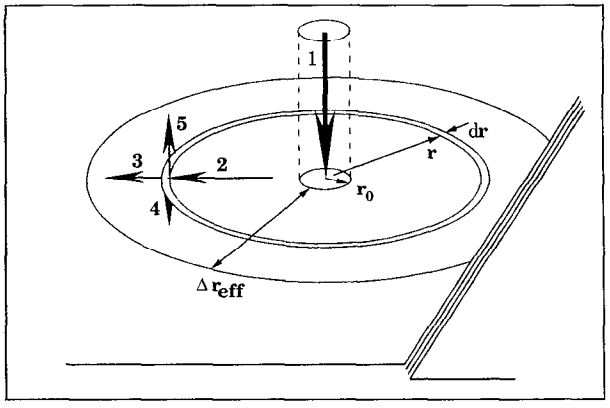

FIG. 4. Schematic diagram of the illuminated area ($r < r_0$) and the charged disk ($r < r_0 + \Delta r_{eff}$), illustrating the elementary processes (1–5) in our model, and showing the truncation of the charged disk when approaching a step in the surface.

in PEC experiments, as exemplified by a study[7] of single-crystalline *p*-InSe in contact with a sodium sulfate solution ($p\mathrm{H} \approx 6.3$). InSe is a layered compound, and steps between adjacent layers are characteristic features of its surface morphology. Figure 3 shows photocurrent images near such steps, for two cases: (a) the material "as cleaved," and (b) after platinization (by dipping in a dilute H_2PtCl_6 solution for 5 min). Steps act as effective recombination centers for charge carriers.[10,11] When the laser spot is scanned across such a step there is at first a gradual decrease of the photocurrent (due to recombination), later followed by a gradual increase. Passing the spot across the step of the platinized surface gave a much more rapid decrease and increase of the photocurrent [Fig. 3(b)] than in the case of the "as cleaved" surface [Fig. 3(a)]. Thus, the lateral resolution is observed to increase dramatically on platinization, other factors being equal.

The photocurrent is proportional to the amount of minority carriers (here CB electrons) present at the surface. As these have a finite lifetime, their concentration is nonzero for some region around the illuminated spot. The concentration in a dark area depends on the lifetime of minority carriers and their diffusion rate. The lifetime depends on the rate of recombination and the rate of charge transfer to the solution (the redox reaction)—the higher these rates, the shorter the lifetime, and the smaller the size of the charged region. In the case discussed here the redox reaction is hydrogen evolution. As this reaction is catalyzed by platinum, the observed improvement in resolution when the surface was platinized can be qualitatively explained as a result of a smaller size of this charged area on the surface (cf. Fig. 4).

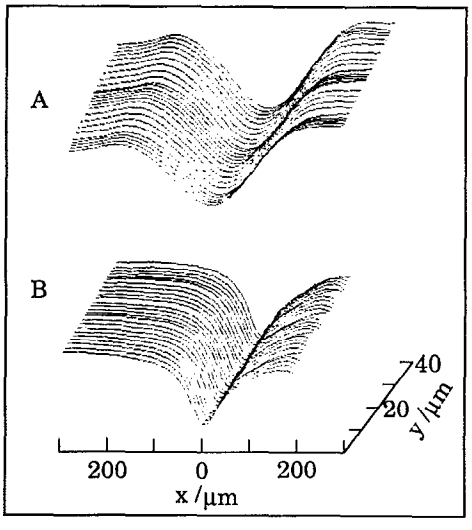

FIG. 3. Photocurrent eight images of single-crystalline *p*-InSe in contact with a sodium sulfate solution; (a) the material "as cleaved," (b) after platinization.

MODEL

We focus our attention to processes taking place in a circular area of the semiconductor surface around the light spot. Although strictly speaking the situation is different on the "front" and the "back" of the moving spot, for a slowly moving spot and in absence of surface structures this distortion is small, and in the following we assume radial symmetry (see Fig. 4). Looking at a small area between circles with radius r and $r + \mathrm{d}r$ we have a set of terms which, assuming steady state, will sum up to zero. Steps 1–4 are "physical" steps, containing parameters related only to the semiconductor under study and the applied bias. The charge transfer to the electrolyte (different for the "as-cleaved" and the platinized sample) is represented by the "chemical" step 5.

(1) Photogeneration $G(r)2\pi r\,\mathrm{d}r$,
(2) Diffusional "in" flux $J(r)2\pi r\,\mathrm{d}r$,
(3) Diffusional "out" flux $-J(r+dr)2\pi r\,\mathrm{d}r$,
(4) Recombination $-\tau^{-1}c(r)2\pi r\,\mathrm{d}r$,
(5) Redox reaction $-k'c(r)2\pi r\,\mathrm{d}r$.

Step 1. In a PEC experiment there is a depletion layer below the electrode surface, with a thickness W which can be varied freely by choosing the electrode bias, and associated with a strong electric field. A circular laser spot generates pairs of charge carriers in a cylindrical region with a characteristic thickness of $1/\alpha$ (where α is the absorption coefficient). In most practical cases, $1/\alpha$ is larger than W. We assume that minority carriers created in the depletion region rapidly migrate to the surface without recombination losses and with negligible sideways diffusion. Minority carriers created beyond W move by diffusion only. We assume that

practically all are lost by recombination. With these assumptions, diffusion perpendicular to the surface does not enter the model, and we are only concerned with minority carriers in a plane at the semiconductor/electrolyte interface.

The generation function $G(r)$ is proportional to the intensity $I(r)$ of the light spot, with a proportionality factor depending on α and varying with the applied bias (i.e., with W). We assume $I(r)$ and thus $G(r)$ to be step functions, going to zero at a specific radius r_0. In the following we only consider the area outside the illuminated spot, $r > r_0$. Using $c(r)$ for the concentration of minority carriers as a function of distance, this amounts to treating $c(r_0)$, the concentration of charge carriers at this light spot edge, as a constant.

Steps 2 and 3. $J(r)$ is the flux of charge carriers through diffusion along the surface. Introducing the diffusion coefficient D and using Fick's law we get

$$J_D(r) - J_D(r + \mathrm{d}r) = D\,\mathrm{d}^2c(r)/\mathrm{d}r^2 \qquad (1)$$

A related quantity is the mobility $\mu \equiv De/kT$.

Step 4. Here τ is the lifetime of excess minority charge carriers in the semiconductor in absence of redox reaction.

Step 5. This is the only chemical step, where k' is the rate constant for electron transfer from the surface to the charge receiving redox species in the solution.

From the resulting homogeneous differential equation, with boundary conditions $c(r) \to 0$ as $r \to \infty$, and $c(r) = c(r_0)$ when $r = r_0$, we get

$$c(r)/c(r_0) = \exp[-(1 - k'\tau)^{1/2}(\Delta r/L)] \qquad (2)$$

where we have introduced $\Delta r \equiv r - r_0$, as well as the diffusion length $\mathrm{L} \equiv (\tau D)^{1/2}$. The relation is shown in Fig. 5 for a range of values for $k'\tau$. As a convenient measure of the size of the charged spot we introduce an "effective radius" $r_{\mathrm{eff}} \equiv r_0 + \Delta r_{\mathrm{eff}}$, satisfying the relation

$$c(r_{\mathrm{eff}})/c(r_0) \equiv \exp(-1). \qquad (3)$$

We now get a relation between Δr_{eff} and $k'\tau$,

$$\Delta r_{\mathrm{eff}}/L = (1 + k'\tau)^{-1/2}, \qquad (4)$$

which is shown in Fig. 6 as a function of $k'\tau$. For $k'\tau \ll 1$, i.e., if the lifetime of the minority carriers is short or charge transfer to the electrolyte is slow, we have $\Delta r_{\mathrm{eff}} = L$. When the charge transfer to the solution is very fast, Δr_{eff} goes towards zero, and the charged spot will have the same "effective" size as the illuminated spot. Clearly large k' values gives a better spatial resolution in LSS experiments.

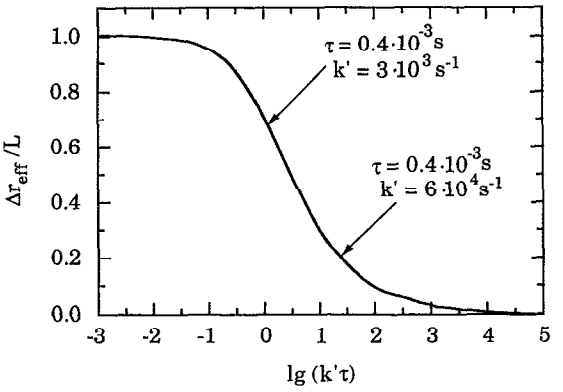

FIG. 6. $\Delta r_{\mathrm{eff}}/L$ as a function of the base 10 logarithm of $k'\tau$. The arrows indicate situations applicable to InSe without and with Pt, resp.

It will be noted that the intensity of the illumination does not enter in our model explicitly, only through the constant $c(r_0)$—the higher the light intensity, the higher the minority carrier concentration at the edge of the spot and elsewhere. The light intensity does not affect the value of Δr_{eff}.

DISCUSSION

To be able to compare our model with experiments we need numerical values for two of the parameters D (or μ), τ, and L for the semiconductor under study.

For p-InSe we have $\tau = 0.2$ to 0.7 ms and $L = 0.4 \pm 0.1$ mm.[12] Inserting these parameters, we can calculate Δr_{eff} for different values of k'. In the limit of $k' \to 0$ we have $\Delta r_{\mathrm{eff}} = L = 0.4$ mm, i.e., a very low resolution. For the example highlighted in Fig. 5, $k' = 6 \times 10^4\ \mathrm{s}^{-1}$, we find $\Delta r_{\mathrm{eff}} = 0.08$ mm. The arrows in Fig. 6 correspond to $k' = 3 \times 10^3$ resp. $6 \times 10^4\ \mathrm{s}^{-1}$ (assuming $\tau = 0.4$ ms).

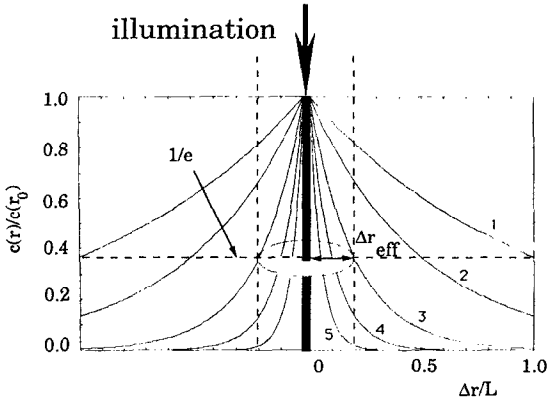

FIG. 5. The concentration of minority carriers as a function of distance, for several values of $(1 + k'\tau)^{1/2}$: 1 (curve No. 1), 2, 5, 10, and 20, and illustrating the definition of Δr_{eff}. For clarity the size of the light spot is exaggerated. For InSe, $L \approx 0.4$ mm and $\tau \approx 0.4$ ms. Curve No. 3 would then correspond to $k' \approx 6 \times 10^4\ \mathrm{s}^{-1}$.

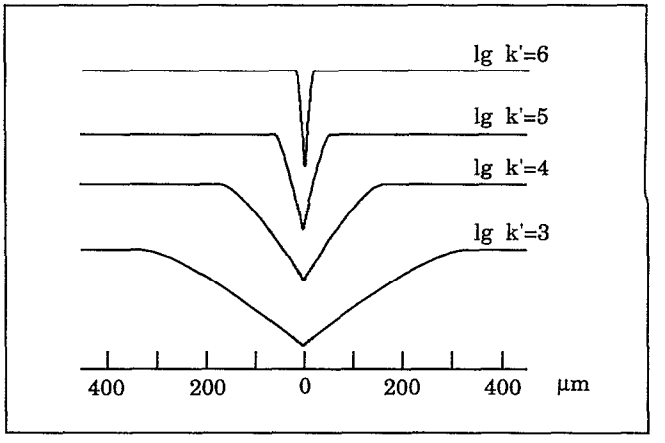

FIG. 7. Variation of the photocurrent (assumed to be proportional to the area of the charged disk) with distance from the step, for a set of k' values, and assuming $\tau = 0.4$ ms.

We can now discuss the decrease in photocurrent when the illuminated spot is moving towards a step in the InSe surface. The recombination rate will be much faster at the step, creating an effective barrier against lateral diffusion of minority carriers. The circular charged area is then gradually truncated (cf. Fig. 4), finally reaching the shape of a semicircle when the center of the light spot is directly at the step. As the light spot moves away from the step, the charged area grows back to its original size, exhibiting a V shaped dip when the light spot moves across the step. Figure 7 shows this behavior for a set of k' values (assuming $\tau = 0.4$ ms, as applicable to InSe).

There is a striking similarity between these "V curves" and the photocurrent curves for the InSe experiments in Fig. 3, and we venture the assumption that the photocurrent is directly proportional to the size of the charged spot. This would indicate a k' value of $3\times10^3\ s^{-1}$ for the "as cleaved" experiment and $6\times10^4\ s^{-1}$ for the platinized electrode. Thus platinization leads to a twentyfold increase in charge transfer rate, which is quite reasonable.[13] From Fig. 6 we then find the corresponding values of the "effective" spot size to be 0.26 and 0.08 mm, respectively. In this particular case, the twentyfold increase in charge transfer rate leads to a threefold decrease in spot size.

A further extension of the model should include the diffusion of minority carriers in the field-free region, and the potential dependence. Further experiments would include other materials, and also work near flat band conditions (i.e., without strong migration). For an isotropic material, excess minority carriers would be distributed over a semisphere with its center at the center of the light spot. For a layered compound like InSe, diffusion is much faster *along* than *between* the layers,[12,14] i.e. the diffusion coefficient $D_\perp$ for minority carriers perpendicular to the c axis is very much higher than the corresponding quantity $D_\parallel$ parallel to the c axis. In such a case the minority carrier semisphere turns into an oblate semi-ellipsoid.

In conclusion we find that our model gives an adequate explanation of our observations of the hydrogen evolution at illuminated p-InSe in absence and presence of Pt, and also provides a quantitative estimate of the improvement in charge transfer rate obtained by the platinization.

ACKNOWLEDGMENTS

This work was supported by the Swedish Board for Technical Development (STU), by the Swedish Natural Science Research Council (NFR), and by the International Scientific Research Program (Joint Research 01044005) of the Ministry of Education, Science and Culture, Japan.

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