

SEMICONDUCTOR ELECTRODES. PHOTO-INDUCED ELECTROGENERATED CHEMILUMINESCENCE AND UP-CONVERSION AT SEMICONDUCTOR ELECTRODES

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A photosensitized reduction process, leading to electrogenerated chemiluminescence (ECL) at a p-type silicon electrode in which neither the energy of the light used for sensitization nor the electrical energy input reach the threshold energy for the production of the emitted photon if applied separately, is described and discussed. The main experiment consisted of irradiating a p-type Si electrode, immersed in an acetonitrile solution containing 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (DPACl₂) and held at a potential where DPACl₂ reduction does not occur, with light of energy less than 1.7 eV. The photosensitized reduction of DPACl₂ leads to the production of excited singlet 9, 10-diphenylanthracene and the emission of 3.0 eV light.

1. Introduction

The electrochemical behavior of a semiconductor (SC) electrode in contact with an electrolyte solution is generally influenced by the energy and intensity of the light at the interface. The action of light may promote production of holes in the valence band and electrons in the conduction band of the SC (for light of energy greater than the SC band gap energy) thus perturbing the space charge region at the SC/solution interface and initiating faradaic processes, as well as electron transfer reactions of excited states of solution species [1, 2]. Thus, there has been much recent interest [3, 4] in using illuminated SC electrodes not only to enable one to carry out processes which do not occur in the dark because of the rectifying nature of the SC/solution interface, but also to perform photosensitized electron transfer processes at lower electrode potentials (i.e., less positive for oxidations and less negative for reductions) than the reversible (dark) thermodynamic values as would be observed at an inert metal (e.g., platinum) electrode. This "negative overpotential" at an illuminated SC electrode as compared to a reversible metal electrode is a consequence of the partial conversion of light energy to electronic energy, so that an electron transfer reaction can be accomplished with less applied electrical energy.

Electrogenerated chemiluminescence (ECL) involves the conversion of electrical energy to light via the electrogeneration of reactants (usually radical anions, A⁻, and cations, D⁺) in a well-purified organic solvent; the annihilation reaction between A⁻ and D⁺ produces excited states and emission of photons [5, 6]. In ECL the free energy of the annihilation reaction, and thus the difference in standard potentials for the generation of A⁻ and D⁺, must be larger than a certain threshold value which corresponds to the electronic energy of the excited state with respect to the ground state. The excited state can also be produced, of course, by optical excitation with light of energy greater than that of the excited state. We report here an optical-electrochemical experiment in which ECL is produced at an SC electrode under illumination, and in which the electrical and photoexcitation energies are coupled to produce sufficient energy for the emitted photons (i.e., neither the electrical potential nor the exciting light alone had sufficient energy to produce the emission). The main experiment used to illustrate this coupling involved the photosensitized transfer of electrons from p-type single crystal silicon under excitation with light of about band-gap energy (< 1.7 eV) to produce ECL from 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (DPACl₂) at about 3.0 eV.

2. Experimental

A conventional three-electrode ECL cell and associated electrochemical apparatus and techniques were employed [5-7]. The working electrode was a single crystal of p-type silicon (0.05 ohm cm) of area 0.75 cm² with the 2:1:1 plane exposed to the solution, 1 mM DPACl₂ and 0.1 M tetra-*n*-butyl-ammonium perchlorate (TBAP) in acetonitrile (ACN). The excitation source was a 500-watt tungsten lamp whose output was filtered by three consecutive filters: 3 mm ESCO-4811 (red), Kodak 65 (green), and Kodak 29 (red), which resulted in a beam containing only a very little visible light, in the red region of the spectrum, and mostly near infrared radiation. The emitted blue ECL was passed through a 3 mm ESCO blue filter and detected with a photomultiplier (Dumont 6467). Solutions were prepared in a glove box (Vacuum Atmospheres, Inc., Hawthorne, Cal.) from purified solvent and reagents and transferred into a sealed electrochemical cell.

3. Results

The electrochemical and ECL behavior of DPACl₂ at Pt and Si electrodes is shown in fig. 1. DPACl₂ shows emission characteristic of 9,10-diphenyl-anthracene (DPA) fluorescence upon reduction [8]. While the mechanism of this reaction has not been established with certainty, the excited DPA is most probably formed by reaction of DPA⁻, produced at the second reduction wave, with an intermediate species formed during the reduction of DPACl₂ by DPA⁻ (e.g., DPACl[•]) [9]. The potentials and shape of the first reduction wave, the reduction of DPACl₂ to DPA, depend upon Pt electrode pretreatment and solution conditions [8,9]; the second wave, however, represents the nernstian one-electron reduction of DPA to DPA⁻, and its peak potential at Pt is very close to the thermodynamically predicted value. At a Pt electrode then, light is emitted at potentials of the second wave (figs. 1a and a'). At an Si electrode in the dark the waves are displaced to more negative potentials and only a small amount of emission is observed (figs. 1c and c'). Under illumination with red and near infrared radiation, however, the reduction waves are shifted in a positive direction and blue ECL occurs (figs. 1b and b'); note that the emission commences at potentials about 250 mV positive of where it oc-

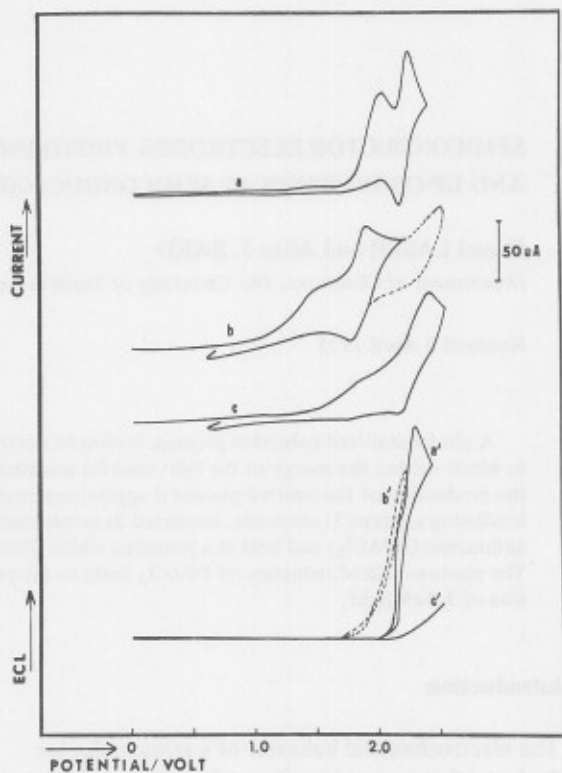


Fig. 1. Cyclic voltammetry (CV) and ECL of DPACl₂. (a) CV-Pt electrode, (b) CV - illuminated p-type Si electrode, (c) CV - p-type Si electrode in the dark; (a'), (b'), (c') are the corresponding ECL emissions. The solution contained 1 mM DPACl₂ and 0.1 M TBAP in ACN; scan rate, 50 mV/s.

curr at Pt. The transient profile of photocurrent and ECL emission at p-type Si under illumination is shown in fig. 2. The decay with time represents decreases in the flux of reactant to the electrode by diffusion. The spatial distribution of the emission corresponds to that of the exciting light. Usually ECL takes the shape of the electrode with emission occurring in a very thin layer close to the electrode surface. For photo-induced ECL, the active portion of the electrode is that of the exciting light beam. To demonstrate this effect, the beam of a krypton laser (674.3 nm) was used to induce ECL at a large area (ca. 2 cm²) p-type Si electrode held at -2.5 V. The ECL originated only at the point where the beam struck the electrode; by pulsing the electrode potential from -1.0 to -2.5 V at a high enough frequency (10 Hz) to minimize lateral divergence due to diffusion, a focused point of ECL could be obtained.

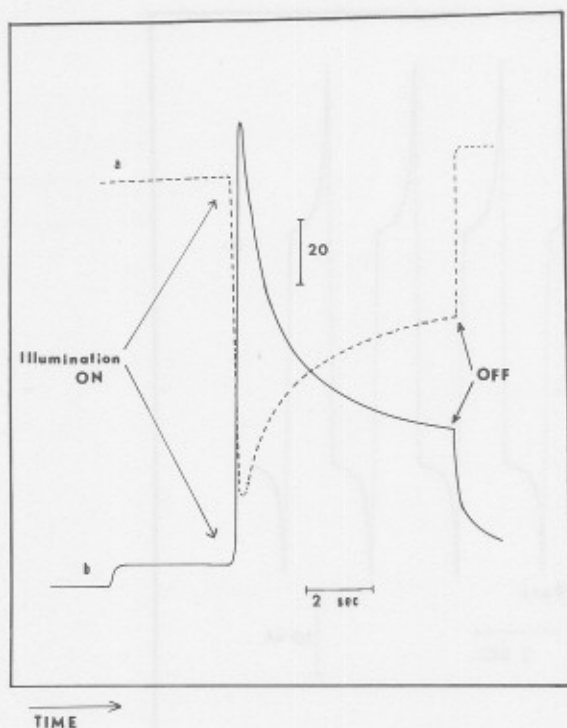


Fig. 2. Transient upon illumination of p-type Si electrode. (a) DPACl_2 reduction current (dashed line); (b) ECL emission (solid line). Electrode potential, -2.5 V; solution, as in fig. 1.

Similar behavior was observed at other small band-gap p-type semiconductors, such as GaAs and InP. The ECL of DPACl_2 for a p-type InP electrode pulsed between -0.0 and -2.5 V to obtain time-independent behavior similar to conventional ECL is shown in fig. 3.

4. Discussion

Models for exchange of minority carriers in SC electrodes under illumination have been proposed elsewhere [1, 13]. The basic energetic considerations for electron transfer between a semiconductor and solution are the same as those that apply to metals [10]. The electrochemical potential (i.e., Fermi level) of an electron in the bulk of a moderately doped semiconductor can be closely identified with the energy at the edge of the conduction band (n-type) or valence band (p-type), respectively [11]. The condition for reduction is that this electrochemical potential is higher than

the Fermi level of the electron in solution, represented by the redox potential of the system [1, 12, 13]. By determining the flat band potential of the SC electrode for the same solution with respect to a given reference electrode, a common relative energy scale can be established between the solution redox level and the SC energy levels. The relative position of the electrochemical potentials of an electron in the bulk SC and in solution can be adjusted by changing the inner potential difference between the two phases, i.e., changing the applied potential to the electrode; at a given electrode potential, this difference is independent of electrode material. Thus charge transfer is thermodynamically possible at any SC electrode whenever the electrode potential with respect to a given reference electrode attains the value needed for reversible charge transfer (i.e., as at a Pt electrode). However, the electrochemical potential of an electron at the SC/solution interface may not be changed with respect to the solution by changes in applied potential between solution and bulk SC, because of the potential drop through the SC space charge region. The effect of light at the p-type SC surface can be looked upon as the formation of a new phase (the illuminated region) not in equilibrium with the bulk material and in which the electrochemical potential of the electrons is higher than before illumination. If the electrochemical potential of the electrons is above the solution Fermi level, electron transfer to solution will occur and because the change in electrochemical potential in this illuminated phase is not compensated by a build-up of difference of inner potential between bulk SC and illuminated surface, reductive charge transfer will be observed at less negative applied potentials (which we designate as "negative overpotential"). Experimentally the "negative overpotential" at an illuminated SC is only a fraction of its band-gap (or input photon energy) and for the same SC at the same irradiation energy depends upon the electrical condition of the SC. For example, oxygen evolution in aqueous solutions at an n-type TiO_2 electrode has a "negative overpotential" of about 1 V, although the band gap and absorbed photons are of 3 eV energy [3]. Iodide oxidation at TiO_2 [14], as well as hydrogen evolution at p-type Si, show only small differences in potential under illumination compared to these same processes at Pt. We recently studied several electrode processes at p-type Si immersed in ACN under red light and found "negative overpoten-

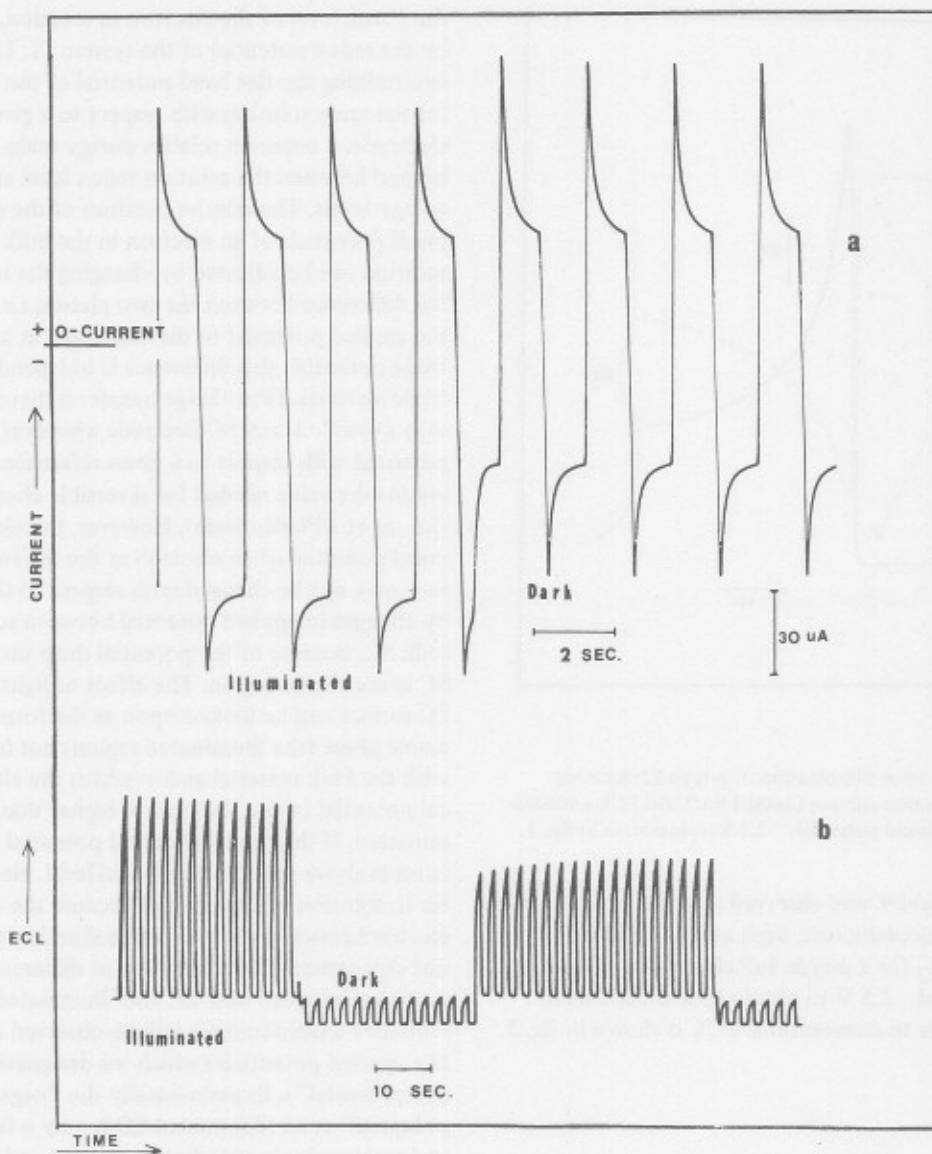


Fig. 3. Current and ECL of DPACl_2 at a p-type InP electrode under pulsed conditions. (a) Current; (b) ECL emission. The electrode was pulsed between 0 and -2.5 V at 0.5 Hz; solution, as in fig. 1.

tials" of 0 to 0.35 V [15]. The magnitude of this "negative overpotential" (or photovoltage for a faradaic process) depends upon the rate of electron transfer between solution and SC, the rate of electron-hole recombination, and the mass transfer rates of the carriers; an approximate model for photovoltage under constant current conditions has been given by Gerischer [16]. As pointed out in this work, photosensitized reductions

will only be observed when the electrical field in the space charge region is in such a direction that electrons migrate to the interface and holes migrate away from it. The hole concentration at the surface must be kept small to eliminate excited electron/hole recombination either directly in the SC phase or through a redox reaction with solution species (i.e., oxidation of the reduced form just formed by electron transfer). The extent of

band-bending (and the electric field at the interface) depends upon the potential to which the SC electrode must be biased to make it conform to the redox potential of the reducible system of interest. Thus no negative overpotential will be observed for reductions at electrode potentials at or positive of the flat band potential and light will not supply any additional energy to promote these reductions. For systems with more negative redox potentials, the imposed electrode bias will be in a direction sufficient to establish the desired space charge region field, even if the electrode potential is positive of its thermodynamic redox potential. Our previous study of the p-type Si electrode in ACN located the flat band potential (or, approximately, the edge of the valence band) at 0.20 ± 0.10 V versus Ag/Ag^+ [15]. Thus the DPACl_2 and DPA systems are both negative of this potential, and indeed are negative of (i.e., lie above) the conduction band as well. Electrode illumination provides about 0.35 V negative overpotential, a value similar to that observed with several other systems [e.g., tris-bipyridylruthenium (II), $\text{Ru}(\text{bipy})_3^{2+}$].

Similar photoinduced ECL can undoubtedly be carried out with more conventional ECL systems involving alternate generation of A^- and D^+ at an SC electrode under illumination, where generation of one of the species (A^- on a p-type and D^+ on an n-type) is hindered in the dark. This could not be accomplished on p-type Si with, e.g., the $\text{Ru}(\text{bipy})_3^{2+}$ system, however, because of instability and surface alteration of the electrode in the positive potential region. This instability may be a general problem with narrow band gap semiconductor materials. This type of ECL conversion was suggested by Nicholson [17], but apparently was never reduced to practice [18]. This arrangement suggested a thin layer ECL cell composed of a semiconductor electrode and a wire mesh counter electrode. One attempt at constructing such a cell utilizing a p-type Si cathode and an indium oxide coated conducting glass anode spaced 50μ apart with a solution consisting of rubrene in benzonitrile did not show ECL. Twin electrode thin layer ECL cells are known to be difficult to operate, however [7].

An alternate arrangement for photogeneration of ECL would employ an Si solar cell to drive an ECL cell. This solar cell could either be external to the ECL cell which would produce non-localized emission or could be one electrode of the cell. For example, we operated

a commercial Si solar cell (Edmund Scientific, Co., Barrington, N.J.) as an electrode by connecting it through its n-type side while the thin p-type layer was exposed to solution and illumination; a Pt counter electrode was employed. Illumination of the electrode in this case is equivalent to introducing a new voltage source into the working electrode lead, or shifting the working electrode potential with respect to the reference electrode. For the cell connected as described the shift was about 0.5 V in the positive direction (making this arrangement not useful for DPACl_2 ECL). In this case then, illumination caused the dark current to decrease when the electrode potential was adjusted for a cathodic reaction. A pn junction electrode with the n-type material exposed to solution would presumably be useful for photosensitized reductions, but such an electrode was not available to us.

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