Photoelectrochemical and photocatalytic processes induced by short-wavelength light

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Photocurrent spectra in the photoelectrochemical studies are conventionally used for determining the bandgap energy (E_g), the type of interband transitions, and sometimes for estimating the minority-carrier diffusion length (L_p) and the rate constant of surface recombination [1-3]. To determine these parameters, the long-wavelength edge of spectrum, which corresponds to interband optical transitions with a minimum contribution of other types of non-actinic absorption (for example, free charge carrier absorption of heavily doped semiconductors [2]), is analyzed. Interest to the long-wavelength edge and sub-bandgap transitions has been also aroused by a steady desire to shift the photoresponse spectrum of photocorrosion-stable wide-bandgap semiconductors towards longer wavelengths.

The short-wavelength part of spectrum has received considerably less consideration. However, this spectral region can be also applied for obtaining useful information [4, 5] and for observation of interesting effects [6]. This report focuses on consideration of such possibilities.

Depending on the nature of a semiconductor under investigation and parameters of a reactive medium, the effects of the short-wavelength light action can be classified as follows.

1. The effects associated with the existence of sub-surface layers on a semiconductor electrode, since the light penetration depth decreases.
1.1. The decrease in photocurrent due to the shift of the main photogeneration region towards outer layers of an electrode, which may be porous, permeable to electrolyte, amorphous or with strongly disturbed structure.
1.2. The appearance of an additional photoresponse from a foreign layer formed as a result of the chemical interaction of electrode surface atoms with species of a reactive medium or the decrease in photocurrent due to the filtering action of a foreign layer which exhibits no photoresponse in given conditions.
1.3. The formation of internal potential barriers at the interface between a disturbed or foreign layer and semiconductor bulk.
2. The increase in the efficiency of separation of photogenerated electron-hole pairs in semiconductors with an extremely low charge carrier mobility due to the transfer of a portion of the excess energy of photons into the kinetic energy of charge carriers.
3. The participation of charge carriers, photogenerated in higher lying sub-bands, in PEC processes (processes involving hot carriers [6]).
4. The increase in importance of the surface recombination due to the gain in the local sub-surface concentration of majority carriers.
5. For nanoporous and nanostructured semiconductors, the influence of the light penetration depth on the efficiency of the majority charge carrier transport from their generation place to a conducting substrate by the dispersive mechanism.
6. For photocatalytic suspension systems, the increase in the contribution of direct photolysis of a pollutant in comparison with the photocatalytic reaction in going to shorter wavelengths of light, which can influence strongly the chemical nature of products.

A typical example of the effect of disturbed and/or foreign layers on the PEC behavior is the appearance of a short-wavelength dip in the photocurrent spectrum of Bi_2O_3 electrodes (n-type semiconductor with a relatively low photocorrosion stability) after the PEC aging (Fig. 1). In this case, a disturbed non-photosensitive layer is formed, which acts as an optical filter absorbing the short-wavelength light. Alternatively, a foreign layer formed can be photoactive, as for instance, thin CdS film forming in the course of the PEC reaction at CdO electrode in solutions containing S^{2-} ions [3, 4]. It should be noted that in both cases, the absorption

spectrum of a foreign or disturbed layer can be reconstructed from the combined photocurrent spectra, and the important optical parameters can be determined.

Within the simplest approximation, it can be assumed that the attenuation of the intensity of incident light (J) and, correspondingly, the decrease in photocurrent (i_{ph}) due to the formation of a disturbed or foreign layer is equal to $k = J_o/J = i/i_{ph} = K \exp(\alpha^* d^*)$, where α^* is the absorption coefficient of the disturbed or foreign layer, d^* is its optical thickness, K is the wavelength-independent constant. Substitution of the conventional expression for the absorption coefficient $\alpha = A_n (\hbar\omega)^{-1} (\hbar\omega - E_g^*)^{n/2}$ in this equation gives

$$\{\hbar\omega \ln[i_{ph}/(i_{ph}^b K)]\}^{2/n} = (A_n d^*)^{2/n} (\hbar\omega - E_g^*),$$

where E_g^* is the bandgap of the disturbed layer, i_{ph}^b is the photocurrent from bare semiconductor electrode, n=1 for direct and n=4 for indirect optical transitions. Extrapolation of the linear portion in $\{\hbar\omega \ln[i_{ph}/(i_{ph}^b K)]\}^{2/n}$ versus $\hbar\omega$ plots to the energy axis allows us to estimate the E_g^*. Using this equation, the optical thickness of the disturbed or foreign layer can be also estimated in some cases [4]. For this purpose, the missing parameters can be obtained from the long-wavelength region of the photocurrent spectrum, where the filtering effect of the disturbed layer is absent.

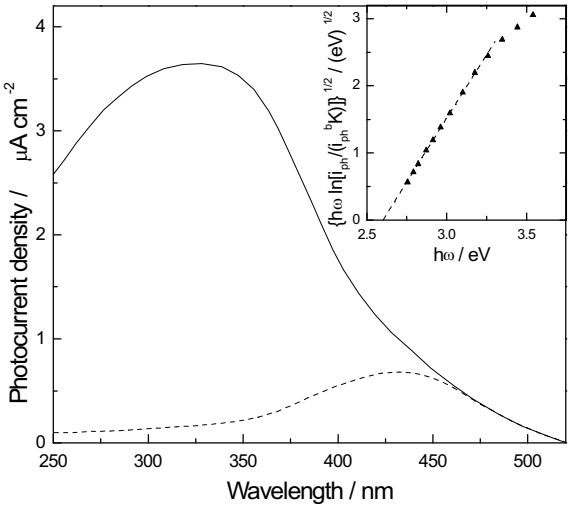

Fig. 1. Photocurrent spectra of Bi_2O_3 electrodes before (——) and after (----) the PEC aging in 0.25 M K_2SO_4. Inset shows the plot for determining the bandgap for outer disturbed layer.

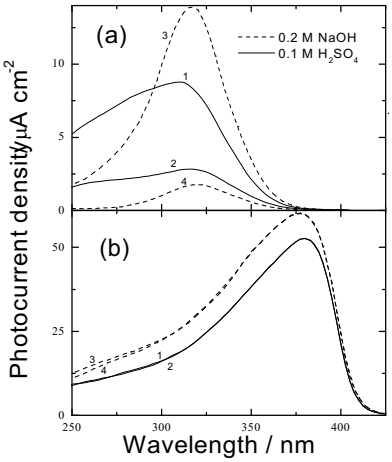

Fig. 2. Photocurrent spectra for (a) nano- and (b) single-crystal TiO_2 electrodes in deaerated acidic and alkaline solutions without (2, 4) and with (1, 3) electrondonor species (glycine).

Different short-wavelength effects manifest themselves especially strongly in the case of ctured electrodes. Therefore, nanostructured TiO_2 electrodes demonstrate an extremely high sensitivity of the short-wavelength edge of photocurrent spectrum to changing the pH of electrolyte and to introducing electrodonor or electroacceptor species in solution as compared with single crystal TiO_2 electrodes, the photocurrent spectrum shape of which remains unchanged (Fig. 2). A complicated superposition of the coordinate dependencies of the e-h pair generation efficiency, the concentration of non-equilibrium (first of all, majority) charge carriers and the concentration of electroactive species in the film pores is mainly responsible for the short-wavelength effects observed for nanostructured electrodes.

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