Transient photocurrent response of p-Si/0·5 M H₂SO₄ interface

K G ANURADHA and A Q CONTRACTOR

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India

Abstract. An experimental study of the transient photocurrent response of p-Si/0·5 M H₂SO₄ interface is presented. The results have been analysed in terms of a theoretical model wherein surface states are assumed to be present at a discrete level E_s and communicate exclusively with the semiconductor. The results indicate substantial Fermi level pinning at this interface. Influence of surface oxide films and Pt deposition on the transient response is also discussed.

Keywords. Transient photocurrent response; photoelectrochemistry; surface states.

1. Introduction

The efficiency of PEC systems depends chiefly on the relative kinetics of the component processes like transport of minority charge carriers in the semiconductor, charge transfer across the interface and recombination. The rates of surface recombination and charge transfer via surface states are determined by the thermal velocity of charge carriers and by the capture cross-sections and density of surface states. By transient photocurrent analysis it is possible to get information on relaxation of charge carriers into surface states.

There are several theoretical treatments of the relaxation of minority carriers (Gartner 1959; Nishida 1980; Albery *et al* 1981; Kelly and Memming 1982; Peter *et al* 1984). The events following the photogeneration of charge carriers are not very clear and the various theories proposed to evaluate the influence of these processes on the photocurrent-voltage characteristics not only suffer from lack of convincing experimental verification but also fail in many instances to explain all the anomalies observed in real systems.

It is known that there are recombination losses due to mid-gap states. In general the calculation of the minority carrier flux at the surface is considered in terms of recombination in three distinct regions. Recombination in the neutral region is described by first order kinetics (Gartner 1959). Recombination in the space charge region is considered either in terms of second order kinetics with the approximation that quasi-Fermi levels are flat (Sah *et al* 1957; Reichman 1980) or in terms of first order kinetics (Albery *et al* 1981). Treatment of recombination at the surface is complicated by the possible charge transfer to redox species in solution via surface states. As a simplification one can consider that surface states either communicate with the semiconductor or with the electrolyte. Nishida (1980) discussed the two limiting cases. Peter *et al* (1984) derived expressions for the flux of minority carriers in terms of the excess minority carrier density in surface states. They assumed that surface states are present at a discrete level E_s and communicate exclusively with the semiconductor. We have analysed our data for p-Si/0·5 M H₂SO₄ interface in terms of this model.

2. Experimental

Figure 1 illustrates the experimental set-up used for recording transient photocurrents. p-Si single crystal wafers of resistivity $0.3-0.5\,\Omega$ cm obtained from M/s Bharat Electronics Limited were used without further polishing. The specimens were mounted on a copper disc after rubbing GaIn alloy to obtain an ohmic contact and fixed inside a teflon holder. All samples were treated in HF for a few minutes to obtain an oxide-free surface. The electrode was fitted inside a three-compartment glass cell provided with a quartz window. A Pt foil counterelectrode and a saturated calomel reference electrode were used. A scanning potentiostat (PAR model 362) was used for controlling the potential. Light was chopped using either a camera shutter of speed $1/1000$ s or a light chopper (PARC model 196) and data were stored on a digital storage oscilloscope (Phillips model PM 3310) and recorded on an X-Y recorder. The current output was amplified through a pre-amplifier (PARC model 113) and used as an external trigger. All photo current vs potential plots were taken at a scan rate of 50 mV/sec. Oxide films were grown in-situ by potentio-dynamic sweeps to various anodic potential limits. The thickness of the oxide film is proportional to the anodic potential limit of the sweep. Platinum was deposited galvanostatically and deposition of 10 monolayers results in a surface decorated with microscopic islets of the metal (Szklarczyk *et al* 1984).

3. Results and discussion

Figure 2 shows the I-V and some of the transients recorded with the electrode held at different potentials. There is a gradual change in the shape of the transients from the onset to the limiting current region. The exponential decay almost disappears near the limiting current region.

Figure 3 shows the model used in interpreting the experimental data. Considering a set of surface states of density N_s located at an energy E_s above the Fermi level, charge transfer and recombination processes which can be considered are illustrated. g is the flux of minority carriers into the surface and j_p is the flux of holes. The rate constants for electron and hole capture by the surface levels are k_n and k_p respectively and k_0 is the rate constant for interfacial electron transfer. The net time-dependent photocurrent due to the reaction of minority carriers is j_{photo} (t). τ is the relaxation time of the minority carriers which is chiefly determined by the concentration of
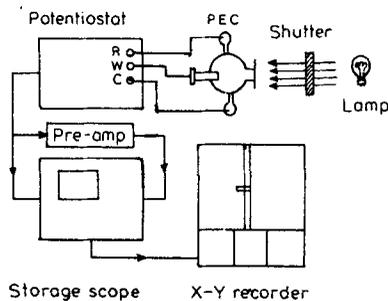

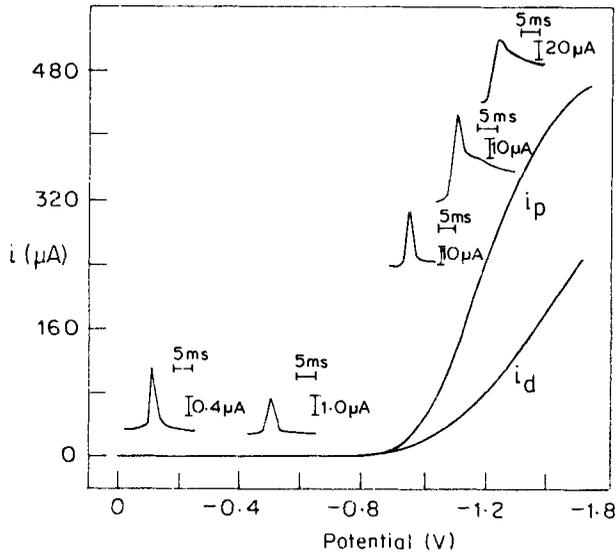**Figure 1.** Block diagram of the experimental set-up.

Figure 2. I-V recorded for oxide-free surface at a scan rate of 50 mV per sec. The insets read from left to right; dark→light transients recorded at -0.1 V, -0.5 V, -0.9 V, -1.0 V and -1.1 V respectively.
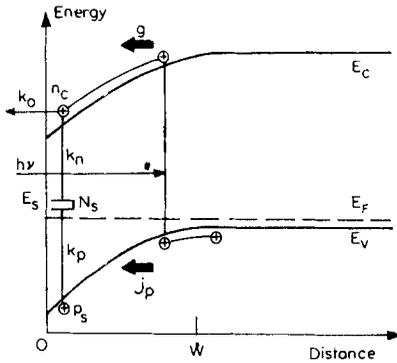

Figure 3. Model of recombination at semiconductor/electrolyte interface.

majority carriers at the surface.

$$\tau = (k_p \, p_s)^{-1},\tag{1}$$

where k_p is the rate constant for hole capture and p_s is the density of holes at the surface. The transient photocurrent is given by the expression

$$j_{\text{photo}}(t) = g\left[\, 1 - \frac{1 - \exp - (t/\tau)}{1 + k_0/k_n N_s(1 - f_0)}\,\right],\tag{2}$$

where f_0 is the trap occupancy in the dark. The steady state photocurrent follows from equation (2) in the limit $t \to \infty$

$$j_{\text{photo}}(\infty) = g\left[\, 1 - \frac{1}{1 + k_0/k_n N_s(1 - f_0)}\,\right].\tag{3}$$

The photocurrent decay can be written in the convenient dimensionless form

$$\frac{j_{photo}(t) - j_{photo}(\infty)}{j_{photo}(0) - j_{photo}(\infty)} = \exp - (t/\tau), \tag{4}$$

and τ is given by the slope of

$$\log \left[\frac{j_{photo}(t) - j_{photo}(\tau)}{j_{photo}(0) - j_{photo}(\tau)} \right] \text{ vs time plot.}$$

Figure 4 shows such a plot for an oxide-free surface. The data were obtained using a mechanical light chopper with a chopping speed of 20 Hz. The data from transients obtained at 0 V and -0.9 V vs SCE are shown in figure 4. They are typical of the behaviour in the range 0 to -1.1 V vs SCE. It is seen that the experimental results are in fair agreement with equation (4). Since τ is determined by the density of majority carriers at the surface τ should increase as the band-bending is increased.

$$\tau = (k_p p_s)^{-1} = \left[\sigma_p v_p p_0 \exp(-|e|\Delta\phi/kT) \right]^{-1}, \tag{5}$$

where σ_p is the capture cross-section for holes, v_p is the thermal velocity and $\Delta\phi$ is the potential drop in the space charge region. According to this equation if the total potential drop occurs in the space-charge region then a plot of $\ln \tau$ vs electrode potential should be a straight line with a slope of $[-(|e|/kT)]^{-1}$ equal to 59 mV per decade. Figure 5 shows a plot obtained for the oxide-free surface. A slope of 643 mV per decade is obtained which indicates a much less sensitive potential
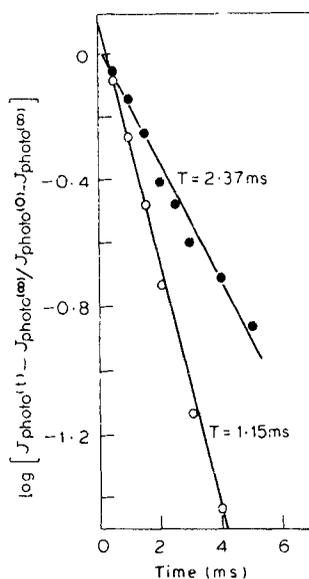

Figure 4. A typical plot for an oxide-free surface. Open circles represent transient at -0.9 V and closed circles represent transient at 0 V.
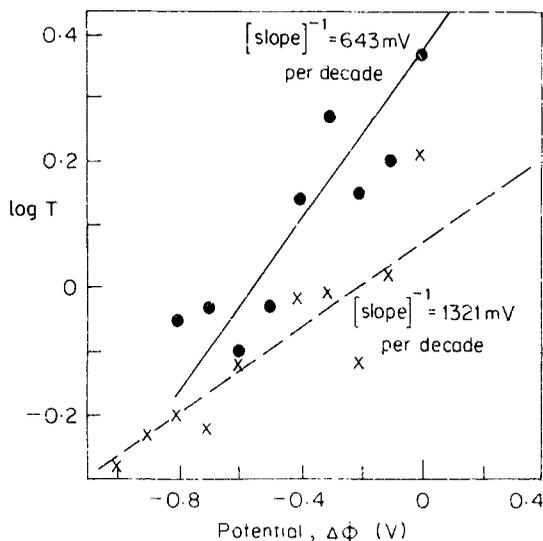
Figure 5. Dependence of log τ on potential. Closed circles represent oxide-free surface and crosses represent oxide-covered surface.
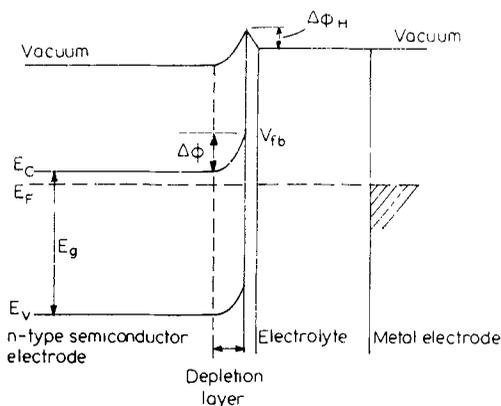

Figure 6. Illustration of potential drop in the semiconductor ($\Delta\phi$) and in the Helmholtz layer ($\Delta\phi_H$) at n-type semiconductor electrolyte junction.

dependence of τ than that predicted by equation (5). Since τ is measured as a function of electrode potential rather than the band-bending ($\Delta\phi$), effects due to fermi level pinning may become important and the variation of τ with potential may be expected to be less rapid.

$$V - V_{fb} = \Delta\phi + \Delta\Delta\phi_H. \tag{6}$$

V and V_{fb} are the electrode potential and the flat band potential respectively. $\Delta\phi_H$ is the potential drop in the Helmholtz double layer (figure 6)

$$\Delta\Delta\phi_H = (^{SC}\Delta^S\phi)_v - (^{SC}\Delta^S\phi)_{fb}, \tag{7}$$

where $^{SC}\Delta^S\phi$ is the galvani potential drop in the double layer at V and flat band respectively (Bockris and Uosaki 1978). Only when $\Delta\Delta\phi_H$ goes to zero we can expect

a slope of 59 mV per decade. In the extreme case where due to surface state charging the entire potential drop occurs on the solution side, the band-bending in the space charge region remains constant. In this case τ would essentially be independent of the electrode potential. It appears from figure 5 that in the case p-Si/0·5 M H_2SO_4 interface the surface is not completely metallized though there is substantial fermi level pinning. Bard *et al* (1980) and Bocarsly *et al* (1980) have reported evidence for fermi level pinning in p-Si.

Thin films of oxide on the surface are known to have negative effects on the I-V characteristics. However with p-InP a thin film of indium oxide results in passivation of surface states and improvement of photo-electrochemical performance (Heller *et al* 1981). Thus it will be of interest to examine the influence of oxide formation on the photocurrent transients. The decay times, τ, observed on an oxide-covered surface are shown in figure 5. The oxide film was formed in situ by scanning the potential to +1·0 V vs SCE. It is assumed that there is no significant reduction of the oxide atleast until −1·0 V vs SCE. This seems to be reasonable as repeated transients recorded at −1·0 V show no change. The results shown in figure 5 indicate that for an oxide-covered surface τ is even less sensitive to potential than on an oxide-free surface. Thus the oxide resulted in further pinning of the fermi level, which is in agreement with the observations at III-V semiconductors (Spicer *et al* 1980). The influence of oxide film thickness on the decay time was also investigated. Table 1 shows the decay times observed with various oxide film thickness. The decay times are fairly insensitive to film thickness which also shows that the τ values are not controlled by the RC component of the oxide. A careful examination of the photo-current transients revealed that the charge under the transients has a systematic potential dependence. It is not clear at this stage how this charge is to be interpreted but it may be thought to give some estimate of the number of recombination centres. Figure 7 shows the charge obtained by integrating the transient photocurrent and correcting for the steady-state photocurrents. The charge is generally of the order of a microcoulomb and this corresponds to a surface coverage of less than 1% assuming a single electron transfer per site. The charge is therefore too small to represent an adsorption process. The behaviour of the oxide-covered surface parallels the behaviour of the oxide-free surface, but exhibits a larger charge. This seems to support the earlier conclusion of oxides contributing surface states. A similar conclusion may be inferred from figure 8 which shows that the charge increases with increased oxide coverage.

Effects of metal layers at the surface have been studied extensively (Butler and Ginley 1983; Contractor *et al* 1983; Contractor and Bockris 1987; Heller 1981).

Table 1. Relaxation time τ as a function of oxide film thickness.

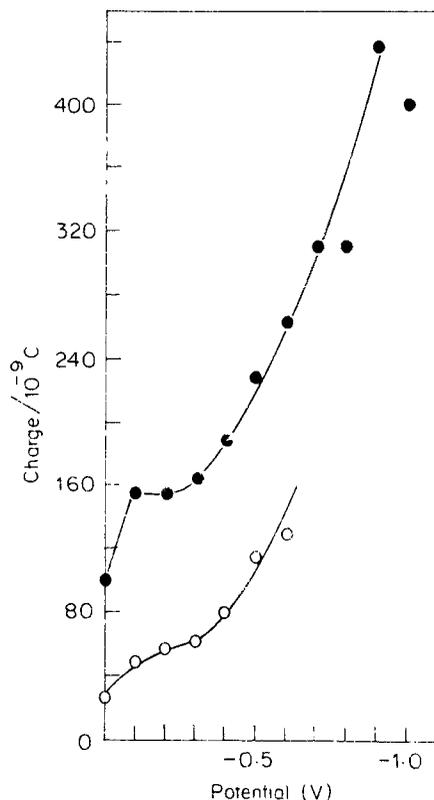| Oxide film thickness in arbitrary units	τ/ms
1	1·21
2	0·94
3	0·92
4	0·88
5	1·08
6	0·92

Figure 7. Charge under the transients as a function of potential. Closed circles represent oxide-covered surface and open circles represent oxide-free surface.

Metals like Pt are known to catalyse the hydrogen evolution reaction. The influence of metal layers on the semiconductor surface has been interpreted in several ways. These can be briefly classified as: (i) modification of the Schottky barrier (Heller *et al* 1982), (ii) passivation of surface states or charge transfer mediation by states created close to the band edges (Butler and Ginley 1983; Heller 1981) and (iii) a true catalytic effect resulting from higher exchange current density at the metal/solution interface (Contractor *et al* 1983). It was therefore thought worthwhile to investigate the influence of such metal layers on the photocurrent transients. Figure 9 shows the dependence of log τ on potential for a surface decorated with platinum islets. The amount of platinum deposited corresponds to ten monolayers. The log τ vs potential plot yields a slope of 485 mV per decade as compared to 643 mV for Pt-free surface. This is perhaps an indication of a change in surface state profile upon platinum deposition.

4. Conclusion

These preliminary studies show that information on the relaxation parameters can be obtained from the analysis of the photocurrent transients. The surface when modified by formation of oxide films or deposition of platinum shows a change in
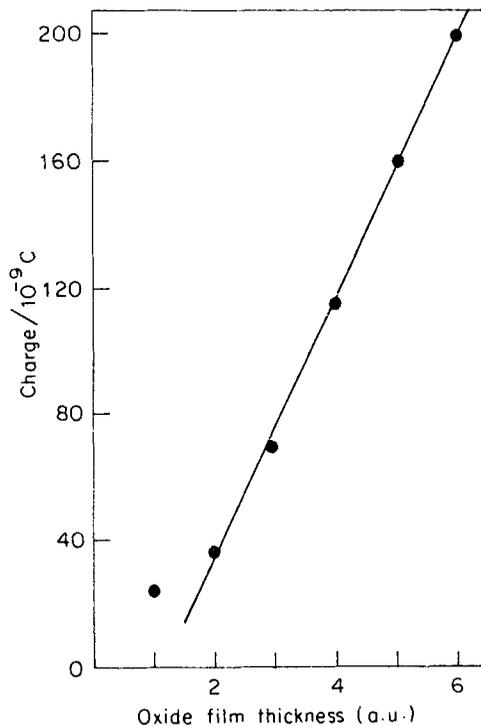
Figure 8. Charge under the transient as a function of oxide film thickness.
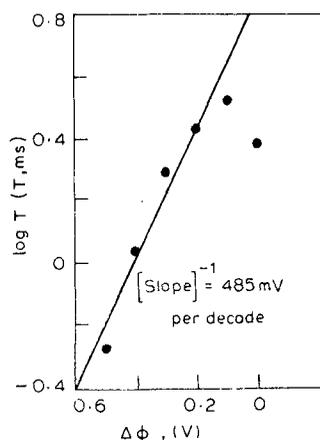

Figure 9. Potential dependence of $\log \tau$ for the surface decorated with 10 monolayers of Pt.

surface state profile. These studies when complemented with data from other techniques may result in a more precise description of the interface.

Acknowledgement

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