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The impedance of surface recombination at illuminated semiconductor electrodes

A non-equilibrium approach

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ABSTRACT

The impedance of surface recombination at illuninated n-type semiconductor electrodes is calculated regarding non-equilibrium charge distributions. The occupancy of the surface states, as well as the hole distribution in the valence band, are calculated from charge exchange processes between the surface states and the conduction and valence bands of the semiconductor. It appears that deep lying surface states can be emptied completely at large irradiation intensities. When saturation occurs, the impedance is found to deviate strongly from its equilibrium value. However, in general saturation does not occur and the surface states are occupied almost in accordance with Fermi–Dirac statistics, even at high illumination intensities. Apparently, unless saturation occurs, the impedance for recombination at semiconductor/electrolyte interfaces deviates only to a very small extent from its equilibrium value, and can be interpreted using simple expressions for the equivalent circuit elements. Consequently, the surface state density, the energetic position in the bandgap and kinetic parameters of dark or illuminated semiconductor surfaces can be obtained from impedance data. Hence, impedance spectroscopy is a valuable tool in the study of surface properties of semiconductor/electrolyte interfaces.

INTRODUCTION

Although the classical theory of semiconductor/electrolyte interfaces, as reviewed by Gerischer [1], does account for many observed effects, a more sophisticated model is required for a detailed understanding of the response of such systems to electrical perturbations or optical excitations. In particular, the quality of the semiconductor surface seems to play a vital role in many observations [2]. For most systems studied an appreciable number of sub-bandgap electronic states, located at the surface of the semiconductor, are present. Such interface or surface states can be categorized into ordinary surface states, which are an intrinsic property of the semiconductor/electrolyte interface, and optically induced surface states. These

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latter states are absent at dark semiconductor/electrolyte interfaces, and are created when light is switched on, and photocreated minority carriers arrive at the interface. Especially for n-type semiconductors, optically induced surface states are often related to photoanodic decomposition processes of the semiconductor. Reaction intermediates which are involved in this process form the chemical origin of this type of surface state.

Impedance spectroscopy is used successfully in the study of surface states [3–16]. With this technique, the presence of surface states can be observed "in situ" for dark or illuminated semiconductor electrodes. The surface state capacitance and resistance obtained experimentally are usually interpreted assuming the surface states to be in thermodynamic equilibrium. In that case the interpretation of the experimental data is rather straightforward, and a clear distinction between ordinary and optically induced surface states can be made. Moreover, the surface state density, their energetic position and kinetic parameters can be obtained. Obviously, for surface states which are in thermodynamic equilibrium, impedance spectroscopy is a very powerfull technique and can be applied in the analysis of, for instance, the photoanodic decomposition mechanism at illuminated n-type semiconductor electrodes. However, the assumption that at illuminated semiconductor electrodes the surface states are also in equilibrium has not been justified so far. In the present study we not only present the justification for this assumption, but also predict the possible occurrence of saturation in case of deep lying surface states at high illumination intensities. The onset of saturation is shown to lead to distorted asymmetric surface state capacitance versus voltage curves.

The kinetics of indirect recombination phenomena in semiconductors via inter-band electronic states was modelled in 1952 by Hall [17], and by Shockley and Read [18]. In their model, inter-band states are able to accept electrons from the conduction band and holes from the valence band. Trapped electrons or holes can be excited thermally. During an indirect recombination process, the charge distributions in the conduction and valence bands, as well as in the inter-gap states are assumed to follow equilibrium statistics. Brattain and Bardeen [19] adapted the Shockley and Read model to account for indirect recombination via inter-band states located specifically at the semiconductor surface. An excellent review of indirect recombination phenomena in the semiconductor bulk or specifically at the surface is presented by Many et al. in ref. 20.

Nicollian and Goetzberger [21] studied the trapping of majority carriers at n-Si/SiO_2 interfaces. They derived the impedance associated with charge trapping by inter-band surface states, and found a series RC equivalent circuit as a model for their system. The surface states were assumed to be in equilibrium with the conduction band, and the charge distribution in this band was assumed to follow equilibrium, non-degenerate Boltzmann statistics. In their approach, the presence of minority carriers is neglected.

In order to explain the occurrence of a large difference between the photocurrent onset and the flatband potential in n-type GaAs electrodes, Kelly and Notten [22] abandoned equilibrium statistics for illuminated semiconductor electrodes. The minority carriers, in their case holes, were no longer distributed in the valence band according to Boltzmann statistics. In addition, these authors allowed for a Faraday current associated with photochemical etching of the semiconductor via surface state reactions.

For illuminated semiconductor electrodes, Vanmaekelbergh and Cardon [23] calculated the equivalent circuit associated with recombination via inter-band surface states regarding non-equilibrium conditions. A different equivalent circuit from that derived by Nicollian and Goetzberger was found. In particular, they found the circuit to comprise RC p R s, where p stands for a parallel and s for a series connection. In their approach, the occupancy of the surface states is determined entirely by the charging kinetics.

Additional theoretical treatments of the impedance of semiconductor/electrolyte interfaces for equilibrium, and non-equilibrium systems can be found in refs. 24–31. In the framework of the newly developed technique of modulated light intensity photocurrent spectroscopy, theoretical descriptions of non-equilibrium semiconductor electrodes have been reported [32–34].

In this paper we report on the calculation of the impedance of indirect recombination via surface states in a generalized non-equilibrium approach. With our model we are able to simulate numerical values for the surface state resistance, capacitance, and time constant. It appears that the surface states are either in equilibrium or completely empty. Only in a very small potential region is the surface states occupancy found to be an intermediate between these two extremes.

THE SURFACE STATE EQUIVALENT CIRCUIT

When a semiconductor is brought into contact with an electrolyte, charge redistribution between the semiconductor and the electrolyte occurs. In the semiconductor, three different regions can be distinguished:

(i) The semiconductor bulk. The part of the semiconductor in which steady electrical fields are unable to penetrate. In any circumstance charge neutrality prevails here.

(ii) The space charge region. A region just below the surface in which steady electrical fields can penetrate and an excess of positive or negative charge may be present.

(iii) The semiconductor surface. The region of the semiconductor where the crystal lattice terminates, and where adsorbed species, for instance, from the electrolyte create energy levels that may be located within the forbidden zone.

At the surface of a semiconductor, electronic states, or "surface states", are assumed to be present with an energy E_{ss} within the bandgap, i.e. $E_c < E_{ss} < E_v$, where E_c and E_v are the energy of the conduction and valence band, respectively. The surface state density is denoted N_{ss}.

If an electron or hole moves from the bulk into the space charge region and flows towards the surface, an electron must pass through the external circuit to restore the neutrality of the semiconductor bulk. Hence the electrical current from the bulk into

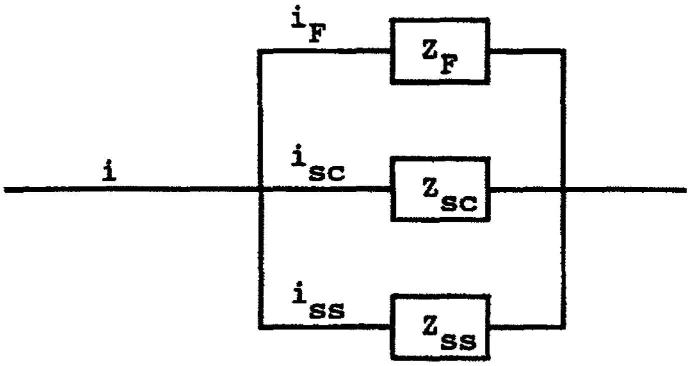

Fig. 1. Charge flow diagram for a semiconductor with surface states.

the space charge region towards the surface equals the measurable current in the external circuit. If electron–hole recombination in the bulk and in the space charge region can be neglected, the electrical current from the bulk towards the surface comprises three additive contributions. The first contribution is the Faradaic current, i_F, and is caused by the occurrence of charge exchange between the conduction or valence band of the semiconductor and electro-active species in the electrolyte. The second contribution is the current due to the charging or discharging of the space charge region of the semiconductor: i_{sc}. The third contribution is the current due to the charging or discharging of the surface states: i_{ss}. The total current can thus be written as $i = i_F + i_{sc} + i_{ss}$.

In terms of an equivalent circuit the process of charge flow from the bulk into the space charge region towards the surface can be represented by the scheme presented in Fig. 1, where the Faradaic impedance Z_F is often resistive: $Z_F = R_F$; the space charge impedance Z_{sc} is capacitive: $Z_{sc} = (j\omega\ C_{sc})^{-1}$; and the surface state impedance Z_{ss} for an electrode at equilibrium with only majority carriers being present is found to be a series RC circuit: $Z_{ss} = R_{ss} + (j\omega\ C_{ss})^{-1}$ [21]. Figure 2 represents the equivalent circuit for this case.

Our current interest is to derive the surface recombination impedance of an electrode which is not necessarily in equilibrium but may be in any time-independent (steady) state. In particular, we focus on an n-type semiconductor electrode

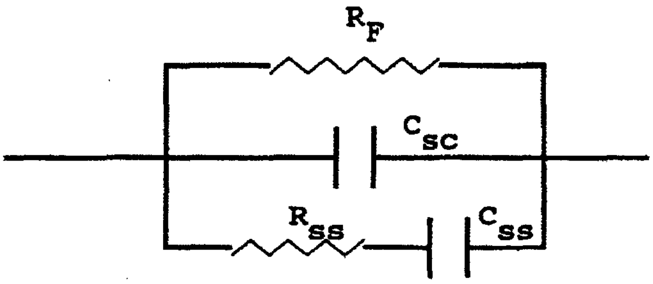

Fig. 2. Equivalent circuit for a semiconductor electrode at equilibrium with only majority carriers.

that is potentiostated and irradiated with light of sufficient energy to generate electron–hole pairs in the bulk and in the space charge region.

When the surface states are electron donors the following reaction takes place at the surface: $ss \rightarrow ss^+ + e^-$. The electron is injected either into the conduction band or into the valence band (hole capture). So, the surface states are assumed to exchange charge only with the bands of the semiconductor and not directly with electroactive species in the electrolyte. This assumption may limit the application of the present model but is being made in order to simplify the calculations considerably. The density of filled surface states [ss] is denoted n_{ss}, the density of empty surface states $[ss^+]$ is denoted p_{ss}. The total surface state density is $[ss] + [ss^+] = n_{ss} + p_{ss} = N_{ss}$.

If surface states at different energies are present, the charging current of these states can be split into a sum of currents, each of which accounts for the charging of a mono-energetic surface state: $i = i_{ss,1} + i_{ss,2} + \cdots + i_{ss,m}$, where m is the number of mono-energetic surface states. Here, however, we shall consider surface states all having the same energy level, i.e. E_{ss}.

The current in the external circuit due to the discharging of surface states is given by the equation:

$$i_{ss} = -eA\mathrm{d}n_{ss}/\mathrm{d}t = eA\mathrm{d}p_{ss}/\mathrm{d}t \tag{1}$$

where A is the surface area. From here on we set A equal to 1 cm^2 and thus change from currents to current densities. The minus sign accounts for the direction of the current. When n_{ss} increases in time, electrons will flow from the bulk towards the surface states, which means that the electrical current flows from the surface to the bulk. Such a current will be given a negative sign.

For extrinsic semiconductors with doping levels of 10^{16} cm^{-3} or higher, the density of the majority carriers exceeds the density of the minority carriers considerably. When the semiconductor is illuminated, additional charge carriers are generated. The relative change in minority carrier density is much larger than the relative change in the majority carrier density. In agreement with the work of Kelly and Notten [22], the majority carriers, i.e. electrons, are assumed to remain in equilibrium even at high irradiation intensities. Their surface density, n, varies with the potential drop across the space charge region, ΔV_{sc}, according to

$$n = n_{\mathrm{bulk}} \exp[-e\Delta V_{sc}/kT] \tag{2}$$

The photogenerated minority carriers, i.e. holes, will not be in equilibrium, and their distribution is determined entirely by the kinetics of the charging of the surface states. Charge exchange between the valence band and electroactive species in the electrolyte has been disregarded. However, when a photoanodic Faradaic charge exchange between the valence band and the electrolyte does take place, the surface hole density, p, is reduced, which can be considered as a reduction of the effective hole generation. In other words, when the hole density at the surface is lowered due to an additional Faradaic hole consuming process, the concomitant loss of holes can be compensated for by increasing the irradiation intensity.

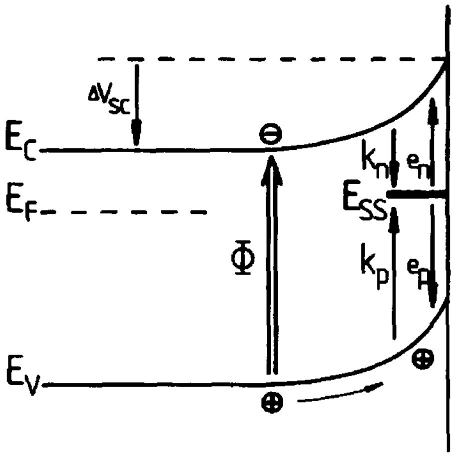

Fig. 3. Band diagram for an n-type semiconductor at depletion with mono-energetic surface states.

When the present model is compared to the model proposed by Vanmaekelbergh and Cardon [23], three generalizations should be noted. Firstly, the present model does not neglect the occurrence of thermal emission of charge carriers trapped in the surface states. Secondly, the contribution of minority carriers to the surface state impedance is included, and thirdly we did not neglect any terms in the linearization procedure of the charging current. These generalizations make it possible to consider the situation of equilibrium as the limiting case for zero irradiation intensity.

The number of electrons captured from the conduction band per unit area per second is proportional to both the empty surface state density and the conduction band electron density at the surface. The proportionality constant, k_n, can be thought of as being the product of the electron capture cross section of the empty surface states and the (thermal) velocity of the conduction band electrons. The number of electrons that are emitted thermally from filled surface states into the conduction band per unit area per second is proportional to the number of filled surface states with a proportionality constant, e_n. For the capture and excitation of holes, similar proportionality relationships hold. Hence the rate of filling or emptying of the surface states comprises four additive contributions which are presented in Fig. 3 and give rise to the following general rate equation.

$$\mathrm{d}n_{ss}/\mathrm{d}t = -\frac{1}{e} i_{ss}(t) = nk_n p_{ss} - e_n n_{ss} - pk_p n_{ss} + e_p p_{ss}$$

With $N_{ss} = n_{ss} + \mathrm{p}_{ss}$, we obtain

$$\mathrm{d}n_{ss}/\mathrm{d}t = -(nk_n + pk_p + e_n + e_p)n_{ss} + (nk_n + e_p)N_{ss} \tag{3}$$

which has the solution:

$$n_{ss}(t) = a \exp[-bt] + c \tag{4}$$

with

$$a = n_{ss}(t=0) - n_{ss}(t=\infty)$$
$$b = nk_n + pk_p + e_n + e_p$$
$$c = N_{ss}(nk_n + e_p)/(nk_n + pk_p + e_n + e_p)$$

At steady state:

$$\lim_{t\to\infty} n_{ss}(t) = \bar{n}_{ss} = N_{ss}(nk_n + e_p)/(\bar{n}k_n + \bar{p}k_p + e_n + e_p)$$

At thermodynamic equilibrium, a detailed charge balance holds which leads to the following equations:

$$\begin{aligned} e_n &= k_n n^\circ p_{ss}^\circ / n_{ss}^\circ \\ e_p &= k_p p^\circ n_{ss}^\circ / p_{ss}^\circ \end{aligned} \tag{5}$$

From these equations we define $e_n \equiv k_n n_1$ and $e_p \equiv k_p p_1$. As can be verified easily

$$n_1 = N_c \exp[-(E_c - E_{ss})/kT]$$

and

$$p_1 = N_v \exp[-(E_{ss} - E_v)/kT]$$

and the following equation holds:

$$n_1 p_1 = n^\circ p^\circ \tag{6}$$

When the expression for e_n and e_p are substituted into eqn. (3) the general surface state occupancies are obtained:

$$\bar{n}_{ss} = N_{ss}\frac{\bar{n}k_n + p_1 k_p}{k_n(\bar{n} + n_1) + k_p(\bar{p} + p_1)} \tag{7a}$$

$$\bar{p}_{ss} = N_{ss} - \bar{n}_{ss} = N_{ss}\frac{n_1 k_n + \bar{p}k_p}{k_n(\bar{n} + n_1) + k_p(\bar{p} + p_1)} \tag{7b}$$

In order to the measure the impedance as a function of the electrode potential, a time independent voltage ($\bar{V}$) is applied with a sinusoidal, time dependent, small amplitude voltage ($\tilde{V}$): $V = \bar{V} + \tilde{V}$ superimposed on this steady potential.

$$\tilde{V} = |\tilde{V}|\sin(\omega t) \qquad \text{with } |\tilde{V}| < 25 \text{ mV}$$

The first order current response to this stimulus will be the superposition of a steady current and a sinusoidal time dependent current:

$$i = \bar{i} + \tilde{i} \qquad \text{with } \tilde{i} = |\tilde{i}|\sin(\omega t + \phi)$$

The impedance (Z) is defined as: $Z \equiv \tilde{V}/\tilde{i} = (|\tilde{V}|/|\tilde{i}|)\exp[-j\phi]$

Since only small amplitude sinusodial voltages are applied, the generation of higher harmonics in the current response can be disregarded. Moreover, any harmonic but the fundamental will normally be filtered out by a frequency response analyzer. To evaluate the current response, a first order Taylor expansion centered around the steady current $\bar{i}(\bar{V})$ will be appropriate

$$i_{ss}(V) = i_{ss}(\bar{V}) + (\mathrm{d}i_{ss}/\mathrm{d}V)_{V=\bar{V}}(V - \bar{V}) \tag{8}$$

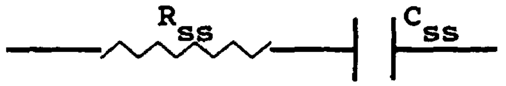

Fig. 4. The equivalent circuit representing charging and discharging of the surface states either for dark or irradiated semiconductor electrodes.

Since the number of surface states is finite, the charging current, i_{ss}, is a transient and must be zero when the steady state is reached, i.e.

$$i_{ss}(\bar{V}) = \bar{i}_{ss} = 0$$

$$\tilde{i}_{ss}(V) = (\mathrm{d}i_{ss}/\mathrm{d}V)_{V=\bar{V}}\tilde{V}$$

and

$$\tilde{i}_{ss}/\tilde{V} = (\mathrm{d}i_{ss}/\mathrm{d}V)_{V=\bar{V}} \equiv Y_{ss}$$

The linearized current equation is derived in the appendix and the generalized surface state admittance obtained is given by eqn. (9):

$$Y_{ss} = -e\left[k_n\bar{p}_{ss}\left(\frac{\mathrm{d}n}{\mathrm{d}V}\right)_{V=\bar{V}} - k_p\bar{n}_{ss}\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)_{V=\bar{V}}\right] \times\left[1-\left[1+j\omega\left(k_n(\bar{n}+n_1)+k_p(\bar{p}+p_1)\right)^{-1}\right]^{-1}\right] \tag{9}$$

The surface state admittance can be related to a series *RC* circuit. Usually *R* is denoted the surface state resistance (R_{ss}) and *C* the surface state capacitance (C_{ss}). The product R_{ss} C_{ss} represents the surface state time constant τ_{ss}.

The equivalent circuit representing the charging and discharging process of the surface states is given in Fig. 4. By correlating the theoretical surface state admittance and the admittance of the equivalent circuit, analytical expressions for R_{ss} and C_{ss} are obtained, i.e.

$$R_{ss} = -e^{-1}\left[k_n\bar{p}_{ss}\left(\frac{\mathrm{d}n}{\mathrm{d}V}\right)_{V=\bar{V}} - k_p\bar{n}_{ss}\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)_{V=\bar{V}}\right]^{-1} \tag{10a}$$

$$C_{ss} = -e\frac{k_n\bar{p}_{ss}\left(\frac{\mathrm{d}n}{\mathrm{d}V}\right)_{V=\bar{V}} - k_p\bar{n}_{ss}\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)_{V=\bar{V}}}{k_n(\bar{n}+n_1)+k_p(\bar{p}+p_1)} \tag{10b}$$

From these expressions we obtain for the time constant,

$$\tau_{ss} \equiv R_{ss}C_{ss} = \left[k_n(\bar{n}+n_1)+k_p(\bar{p}+p_1)\right]^{-1} \tag{10c}$$

When the semiconductor is irradiated with photons of sufficient energy, electron–hole pairs are created in the bulk and in the space charge region. When depletion of the majority carriers exists, a fraction of the photoholes will reach the surface due to either diffusion (in the bulk), or the influence of the internal electrical field (in the space charge region). The photo-generated hole flux will be denoted "*g*". The density of valence band holes per unit area, $\mathscr{P}$, increases in time due to the flow of optically generated holes, g, and due to thermally excited holes from the surface states, and decreases due to hole capture by the surface states. Hence, when optical energy is put into the system, the charge distribution at the semiconductor surface deviates from equilibrium. To incorporate this process into the model, the following rate equation is introduced

$$(\mathrm{d}\mathscr{P}/\mathrm{d}t) = g - k_\mathrm{p}(pn_\mathrm{ss} - p_1 p_\mathrm{ss}) \tag{11}$$

At steady state $(\mathrm{d}\mathscr{P}/\mathrm{d}t) = 0$ and hence

$$\bar{p} = g/k_\mathrm{p}\bar{n}_\mathrm{ss} + p_1 p_\mathrm{ss}/\bar{n}_\mathrm{ss} \tag{12}$$

When expressions (7a,b) for $\bar{n}_\mathrm{ss}$ and $\bar{p}_\mathrm{ss}$ are combined with expression (12), the analytical forms of the occupancy of the surface states are obtained.

$$\bar{n}_\mathrm{ss} = (\bar{n} + n_1)^{-1}[N_\mathrm{ss}\bar{n} - g/k_\mathrm{n}] \tag{13a}$$

$$\bar{p}_\mathrm{ss} = (\bar{n} + n_1)^{-1}[N_\mathrm{ss}n_1 + g/k_\mathrm{n}] \tag{13b}$$

Obviously, the state occupancy $\bar{n}_\mathrm{ss}$ can be saturated at high irradiation intensities. If $g/k_\mathrm{n} > N_\mathrm{ss}\bar{n}$, all surface states are occupied by holes, i.e. $\bar{n}_\mathrm{ss} = 0$.

For g equal to zero, the statistics of the surface state occupation are found to follow the Fermi–Dirac distribution, which means that in the dark situation equilibrium exists.

$$\bar{n}_\mathrm{ss}(g = 0) = n_\mathrm{ss}^\circ = N_\mathrm{ss}[1 + \exp[(E_\mathrm{ss} - E_\mathrm{F})/kT]]^{-1} \tag{14}$$

From equation (7a,b) a relation between the kinetic constants k_n and k_p can be derived

$$k_\mathrm{n} = k_\mathrm{p}\left[\frac{\bar{p}_\mathrm{ss}p_1 - \bar{n}_\mathrm{ss}\bar{p}}{\bar{n}_\mathrm{ss}n_1 - \bar{p}_\mathrm{ss}\bar{n}}\right] \tag{15}$$

In order to calculate $(\mathrm{d}p/\mathrm{d}V)_{V=\bar{V}}$, its total differential must be evaluated:

$$\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right) = \left(\frac{\mathrm{d}p}{\mathrm{d}n_\mathrm{ss}}\right)\left(\frac{\mathrm{d}n_\mathrm{ss}}{\mathrm{d}V}\right) + \left(\frac{\mathrm{d}p}{\mathrm{d}p_\mathrm{ss}}\right)\left(\frac{\mathrm{d}p_\mathrm{ss}}{\mathrm{d}V}\right) + \left(\frac{\mathrm{d}p}{\mathrm{d}g}\right)\left(\frac{\mathrm{d}g}{\mathrm{d}V}\right) \tag{16}$$

In must be noted that n_ss and p_ss are not independent variables. Moreover, it is reasonable to neglect the potential dependence of g. With both considerations implemented, the differential of p reduces to:

$$\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right) = \left(\frac{\mathrm{d}p}{\mathrm{d}p_\mathrm{ss}}\right)\left(\frac{\mathrm{d}p_\mathrm{ss}}{\mathrm{d}n}\right)\left(\frac{\mathrm{d}n}{\mathrm{d}V}\right) \tag{17}$$

Calculation of the derivatives yields

$$\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)_{V=\bar{V}} = -[\bar{n}_\mathrm{ss}(\bar{n} + n_1)]^{-2} \times \left[N_\mathrm{ss}^2 n_1 p_1 + \frac{g^2}{k_\mathrm{n}k_\mathrm{p}} + gN_{ss}\left[\frac{p_1}{k_\mathrm{n}} + \frac{n_1}{k_\mathrm{p}}\right]\right]\left(\frac{\mathrm{d}n}{\mathrm{d}V}\right)_{V=\bar{V}} \tag{18}$$

The surface state capacitance

First we shall evaluate the expression for the surface state capacitance. When eqn. (15) is substituted into eqn. (10b) we find:

$$C_{ss} = -e\frac{g}{k_n k_p}\frac{k_n \bar{p}_{ss}(dn/dV)_{V=\bar{V}} - k_p \bar{n}_{ss}(dp/dV)_{V=\bar{V}}}{N_{ss}(\overline{np} - n_1 p_1)} \tag{19}$$

For $g = 0$, equilibrium exists and we obtain

$$C_{ss}(g=0) \equiv C^{\circ}_{ss} = (e^2/kT)(n^{\circ}_{ss} p^{\circ}_{ss}/N_{ss}) \tag{20a}$$

With the equilibrium expressions for n°_{ss} and p°_{ss} substituted we obtain

$$C^{\circ}_{ss} = (e^2/4KT)N_{ss}(\cosh[(E_{ss} - E_F)/2kT])^{-2} \tag{20b}$$

The equilibrium surface state capacitance derived here is identical to the expression found by Nicollian and Goetzberger [21].

When the semiconductor is irradiated, minority carriers approach the surface. The non-equilibrium surface state capacitance, $C_{ss}(g)$ can be obtained by substitution of eqn. (18) into eqn. (19) and with the use of eqns. (2) and (6), C_{ss} is found to be

$$C_{ss}(g) = \frac{e^2}{kT}\frac{\dfrac{g\overline{np}_{ss}}{k_p}\left[1 + \dfrac{g^2 + gN_{ss}(n_1 k_n + p_1 k_p) + N_{ss}^2 n^{\circ} p^{\circ} k_n k_p}{\bar{n}_{ss}\bar{p}_{ss}(\bar{n} + n_1)^2 k_n^2}\right]}{N_{ss}(\overline{np} - n^{\circ} p^{\circ})} \tag{21}$$

The surface state resistance

In order to calculate the surface state resistance we substitute eqn. (18) into eqn. (10a) and use eqn. (2).

For $g = 0$, equilibrium exists and for this case R_{ss} reads

$$R_{ss}(g=0) \equiv R^{\circ}_{ss} = \left[(e^2/kT)(k_n p^{\circ}_{ss} n^{\circ} + k_p n^{\circ}_{ss} p^{\circ})\right]^{-1} \tag{22}$$

If there are no holes present at the semiconductor surface, which is approximately true for n-type semiconductors in the dark, and no holes are being injected from the electrolyte, $p^{\circ} = p_1 = 0$, and R°_{ss} reduces to the expression found by Nicollian and Goetzberger [21]

$$R^{\circ}_{ss}(p^{\circ} = p_1 = 0) = \left[(e^2/kT)k_n p^{\circ}_{ss} n^{\circ}\right]^{-1} \tag{23}$$

If the semiconductor is irradiated the non-equilibrium surface state resistance $R_{ss}(g)$ is found to be

$$R_{ss}(g) = \left[\frac{e^2}{kT}\bar{n}k_n \bar{p}_{ss} \times \left[1 + \frac{g^2 + gN_{ss}(k_n \bar{n}_{ss} + k_p \bar{p}_{ss}) + N_{ss}^2 n^{\circ} p^{\circ} k_n k_p}{\bar{n}_{ss}\bar{p}_{ss}(\bar{n} + n_1)^2 k_n^2}\right]\right]^{-1} \tag{24}$$

The surface recombination time constant

The surface recombination time constant $\tau_{ss}(g)$ $(=R_{ss}(g)C_{ss}(g))$ can easily be obtained from the previous results, i.e. in the dark:

$$\tau_{ss}=\tau_{ss}^{\circ}=\left[k_{n}(n^{\circ}+n_{1})+k_{p}(p^{\circ}+p_{1})\right]^{-1} \tag{25}$$

If $p^{\circ}=p_{1}=0$:

$$\tau_{ss}^{\circ}(p^{\circ}=p_{1}=0)=\left[k_{n}(n^{\circ}+n_{1})\right]^{-1} \tag{26}$$

which is identical to the expression found by Nicollian and Goetzberger [21].

For an illuminated semiconductor, the non-equilibrium $\tau_{ss}(g)$ is expressed by

$$\tau_{ss}(g)=\frac{g}{k_{n}k_{p}}\frac{1}{N_{ss}(\overline{np}-n^{\circ}p^{\circ})} \tag{27}$$

RESULTS AND DISCUSSION

Before the impedance of surface recombination at illuminated, non-equilibrium semiconductor electrodes is discussed, we would first like to summarize the route by which this impedance has been calculated.

We started our model by investigation of the transient surface state charging current, i.e. eqn. (1), and derived a kinetic expression in the form of a differential equation, i.e. eqn. (3). This equation was solved for $\lim t\to\infty$, and the steady occupancy was obtained (eqns. 7a,b). In order to calculate the current response to a sinusoidal time dependent small-amplitude voltage, a first order Taylor expansion, centered around the steady current $\bar{i}_{ss}(\bar{V})$, was performed (eqn. 8). The surface state admittance was a direct result of this expansion and could be modelled with a series RC circuit (eqn. 9). Expressions for the passive circuit elements were obtained, i.e. eqns. (10a–c). At this point all results were direct consequences of the current eqns. (1) and (3), and the fact that i_{ss} represents a transient with $\bar{i}_{ss}(\bar{V})$ being zero. To incorporate the energy input into the system, which causes the deviation from equilibrium, we introduced a second fundamental expression (eqn. 11). This expression accounted for the hole flux towards the surface as a consequence of bandgap irradiation. By calculating the steady state solution, an expression for the steady hole density at the surface was found, i.e. eqn. (12). This expression was substituted into the steady surface state occupancies (eqns. 7a,b) to give the analytical forms (eqns. 13a,b), and was differentiated to potential (eqns. 16 and 17) to yield eqn. (18). Upon substitution of eqns. (13a,b) and (18) into eqns. (10a–c) and by using eqns. (2), (6) and (15), the final results were obtained, i.e. eqns. (21), (24) and (27). In order to avoid very lengthy expressions for C_{ss}, R_{ss} and τ_{ss}, the parameters $\bar{p}$, $\bar{n}_{ss}$ and p_{ss} are still present in the final results. These parameters, however, can easily be eliminated by substitution of eqns. (12) and (13a,b), respectively.

To understand the non-equilibrium expressions for the surface state equivalent circuit elements, we first take a closer look at the occupancy of the surface states, i.e. eqns. (13a,b). $\bar{n}_{ss}$ is the density of occupied surface states and its numerator $N_{ss}\,\bar{n} - g/k_n$ has an exponential potential dependence via $\bar{n}$. At high irradiation intensities, g/k_n may become equal or even larger than $N_{ss}\bar{n}$. Then $\bar{n}_{ss}$ will be zero, indicating that all surface states are empty and the surface states can no longer respond to the sinusoidal stimulus. Hence, if $g/k_n \geqslant N_{ss}\bar{n}$, then $\tilde{i}_{ss} = 0$ and $Y_{ss} \to 0$ ($R_{ss} \to \infty$ and $C_{ss} \to 0$). The potential where saturation occurs is given by

$$\Delta V_{sc}^{sat} = (kT/e)\, ln(N_{ss} n_{bulk} k_n/g) \tag{28}$$

If $\Delta V_{sc} < \Delta V_{sc}^{sat} - \delta$, then $N_{ss}\bar{n} - g/k_n$ can be approximated by $N_{ss}\bar{n}$ for δ as small as about 50–100 mV. Thus, for every applied potential being at least about 50–100 mV more negative than the saturation potential, the occupancy of the surface states is given by its equilibrium value.

In order to evaluate the complicated expressions for the non-equilibrium surface state capacitance, resistance and time constant, numerical simulations have been performed. In these simulations the hole-generation term, g, is calculated from the well known Gärtner–Butler equation [35–37], while hole diffusion into the depletion region has been disregarded

$$g = \Phi_0(\lambda)\left[1 - \exp\left[-\alpha(\lambda) W_0 (\Delta V_{sc} \mp kT/e)^{1/2}\right]\right] \tag{29}$$

in which $\alpha(\lambda)$ is the absorption coefficient at λ nm, and W_0 the width of the space charge region at $\Delta V_{sc} = 1 + kT/e$.

The parameters and their values used in the simulations presented in Figs. 5–7) are: $k_n = 10^{-5}$ cm^3 s^{-1}, $k_p = 10^{-8}$ cm^3 s^{-1}, $N_c = N_v = 10^{19}$ cm^{-3}, $N_{ss} = 10^{13}$ cm^{-2}, $n_{bulk} = 10^{17}$ cm^{-3}, $E_c - E_v = 2.0$ eV, $E_c - E_{ss} = 0.4$ eV and $\alpha(\lambda)W_0 = 1$.

Since the donor states are charged positively when empty, and are neutral when occupied, the electron capture process is enhanced by the electrostatic, Coulomb, interaction, and the hole capture process is not. Hence, it is reasonable to assume the capture constant of the conduction band electrons, k_n, to be much larger than the capture constant of the valence band holes, k_p.

The surface state capacitance

In Fig. 5 the surface state capacitance is plotted versus the band bending for various irradiation intensities. From this figure it is clear that $C_{ss}(g)$ is nearly independent of the light intensity except for the occurrence of saturation. Saturation causes asymmetric $C_{ss}(g)$ curves $C_{ss}(g) \to 0$ for $\Delta V_{sc} \to \Delta V_{sc}^{sat}$. In the absence of saturation $C_{ss}(g) \approx C_{ss}^{\circ}$ and is defined by eqn. (20b), i.e.

$$C_{ss}^{\circ} = (e^2/4kT) N_{ss} (\cosh[(E_{ss} - E_F)/2kT])^{-2} \tag{20b}$$

C_{ss}° reaches a maximum, $C_{ss}^{\circ\,max}$, when the cosh function reaches its minimum, i.e. $\cosh[(E_{ss} - E_F)/2kT] = 1$. At this potential the Fermi level coincides with the surface state energy level and $f^{\circ} = (1 - f^{\circ}) = 1/2$. At the maximum, C_{ss}° reads

$$C_{ss}^{\circ\,max} = (e^2/4kT) N_{ss} \tag{30}$$

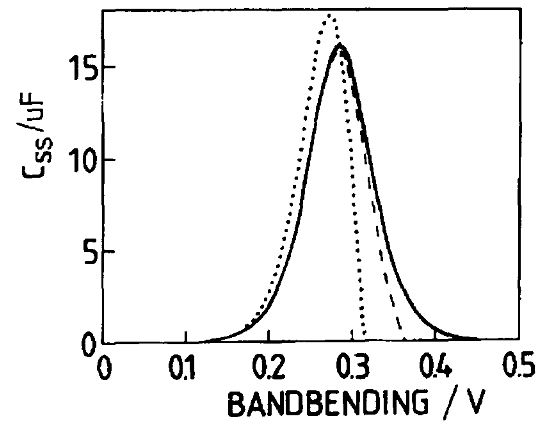

Fig. 5. The surface state capacitance versus the band bending for the dark situation (———) and for bandgap illumination with intensities of $\Phi_0(\lambda) = 10^{19}$ (— — —) and 10^{20} (· · · · · ·) cm^{-2} s^{-1}.

Obviously, the maximum in the C_{ss} versus V plot is related directly to the surface state density.

The surface state resistance

In Fig. 6 the surface state resistance is plotted logarithmically versus the band bending for different light intensities. If saturation is absent, $R_{ss} \approx R_{ss}^{\circ}$ and R_{ss}° starts to increase exponentially when the Fermi level crosses the surface state energy level E_{ss}. In Fig. 6 it is seen that $R_{ss} \approx R_{ss}^{\circ}$ except for the region where $\Delta V_{sc} \approx \Delta V_{sc}^{sat}$. In this region $R_{ss} \to 0$ for $\Delta V_{sc} \to \Delta V_{sc}^{sat}$.

The surface recombination time constant

In Fig. 7 the surface recombination time constant is plotted versus the band bending for different light intensities. In the dark $\tau_{ss} = \tau_{ss}^{\circ}$ and increases sharply

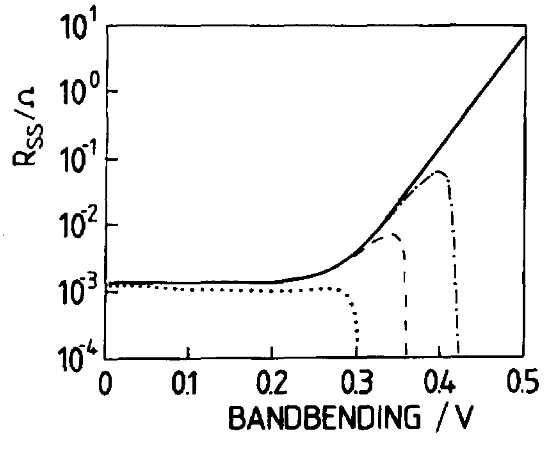

Fig. 6. The surface state resistance plotted logarithmically versus the band bending for an electrode in the dark (———) or illuminated with $\Phi_0(\lambda) = 10^{18}$ (— · — · —), 10^{19} (— — —) and 10^{20} (· · · · · ·) cm^{-2} s^{-1}.

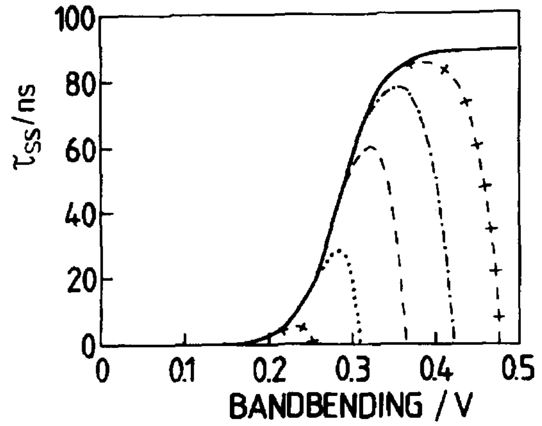

Fig. 7. The recombination time constant versus the band bending for an electrode in the dark (———) or illuminated with $\Phi_0(\lambda)=10^{17}$ (+ – + – +), 10^{18} (– · – · –), 10^{19} (– – –) 10^{20} (······) and 10^{21} (+ + + + +) $cm^{-2}\ s^{-1}$.

when the Fermi level sweeps from negative to more positive potentials through the surface state energy level. For $q\Delta V_{sc} \ll E_{ss}$, or $q\Delta V_{sc} \gg E_{ss}$, τ_{ss}° is potential invariant. If the electrode is irradiated, τ_{ss} shows a maximum. The position of this maximum is not related to the position of the surface states, but is determined exclusively by the position of the saturation potential ΔV_{sc}^{sat}.

CONCLUSIONS

The impedance of surface recombination at dark or illuminated semiconductor electrodes can generally be modelled with a series *RC* circuit, which parallels the space charge capacitance, and the Faradaic resistance. Vanmaekelbergh and Cardon [23] derived a more complicated equivalent circuit with an additional resistance shunting the surface state capacitance. Their equivalent circuit is a direct consequence of the simplifying assumptions used. As we have shown, a more generalized approach employing the full basic equations leads to a less complicated equivalent circuit.

Numerical simulations of the non-equilibrium surface state recombination capacitance, resistance and time constant as a function of the potential drop across the depletion region show that deep lying surface states can be emptied completely at large illumination intensities. The saturation potential, as has been specified in eqn. (28), is the proper parameter that determines the occurrence of saturation. It expresses the position in the forbidden zone below which (n-type) or above which (p-type) the surface states are fully emptied, i.e. saturated for given N_{ss}, n_{bulk}, g, and k_n values. High light intensities combined with slow electron trapping (n-type) and a small donor density will favour the occurrence of saturation for a given density of surface states.

However, in general saturation does not occur and the surface states remain near to equilibrium even at strongly illuminated semiconductor electrodes. Hence, the surface state capacitance is a simple $\cosh^{-2}$-shaped function for monoenergetic surface states and with eqn. (30), the surface state density N_{ss} can be determined unambiguously.

Ordinary surface states are unaffected by the occurrence of optical generation of minority carriers, and their density and energetic position can be obtained either in the dark or at illuminated semiconductor electrodes. However, for optically induced surface states, the density, N_{ss}, is a function of the light intensity. Whenever optically induced surface states are related to the presence of intermediates of a photoanodic decomposition process of the semiconductor, a characteristic relationship between the limiting photocurrent and the maximum of the C_{ss}° peak must be expected. Hence, the impedance of surface recombination at illuminated semiconductor/electrolyte interfaces provides fundamental information about surface recombination via either ordinary surface states or optically induced surface states, and elucidates the competition between the various possible charge flow pathways.

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APPENDIX

The first order Taylor expansion of i_{ss} centered around the steady state potential $\bar{V}$ is given by eqn. (8)

$$i_{ss}(V) = i_{ss}(\bar{V}) + (\mathrm{d}i_{ss}/\mathrm{d}V)_{V=\bar{V}}(V - \bar{V}) \tag{A1}$$

Combining eqn. (1) with eqn. (3) and employing eqn. (5) leads to

$$i_{ss}(V) = e\left[k_n(n + n_1) + k_p(p + p_1)\right]n_{ss} - eN_{ss}(nk_n + p_1k_p) \tag{A2}$$

The parameters n, p, n_{ss}, (p_{ss}) are all potential dependent.

The derivative of $i_{ss}(V)$ is given by:

$$\begin{aligned}(\mathrm{d}i_{ss}/\mathrm{d}V) = &-e\left[k_n(N_{ss} - n_{ss})(\mathrm{d}n/\mathrm{d}V) - k_pn_{ss}(\mathrm{d}p/\mathrm{d}V)\right]\\ &+ e\left[k_n(n + n_1) + k_p(p + p_1)\right](\mathrm{d}n_{ss}/\mathrm{d}V)\end{aligned} \tag{A3}$$

Since $i_{ss} = \bar{i}_{ss} + \tilde{i}_{ss}$ and $\bar{i}_{ss} = 0$; $\tilde{i}_{ss}(V) = (\mathrm{d}i_{ss}/\mathrm{d}V)_{V=\bar{V}}\tilde{V} \Rightarrow Y_{ss} = \tilde{i}_{ss}/\tilde{V} = (\mathrm{d}i_{ss}/\mathrm{d}V)_{V=\bar{V}}$. Equation (1) offers an alternative expression for i_{ss}, and in order to eliminate the unknown potential derivative of n_{ss}, we write:

$$i_{ss} = \tilde{i}_{ss} = -e\left(\frac{\mathrm{d}n_{ss}}{\mathrm{d}t}\right) = -e\left(\frac{\mathrm{d}n_{ss}}{\mathrm{d}V}\right)\left(\frac{\mathrm{d}V}{\mathrm{d}t}\right) = \left(\frac{\mathrm{d}i_{ss}}{\mathrm{d}V}\right)_{V=\bar{V}}\tilde{V} \tag{A4}$$

$\tilde{V}$ has a harmonic time dependence, i.e. $(\mathrm{d}V/\mathrm{d}t) = \mathrm{j}\,\omega\,\tilde{V}$.

When we substitute this harmonic time dependence of V together with eqn. (A3) into eqn. (A4), the derivative of $\bar{n}_{ss}$ is found to be

$$\left(\frac{\mathrm{d}n_{ss}}{\mathrm{d}V}\right)_{V=\bar{V}} = \frac{k_n \bar{p}_{ss}(\mathrm{d}n/\mathrm{d}V)_{V=\bar{V}} - k_p \bar{n}_{ss}(\mathrm{d}p/\mathrm{d}V)_{V=\bar{V}}}{j\,\omega + \left(k_n(\bar{n}+n_1) + k_p(\bar{p}+p_1)\right)} \tag{A5}$$

Substituting this expression into eqn. (A3) yields the admittance of the surface states Y_{ss}, which is represented in eqn. (9).

DEFINITION OF SYMBOLS

E_c	conduction band energy
E_v	valence band energy
E_g	semiconductor bandgap energy
E_F	Fermi energy position in the semiconductor bulk
E_{ss}	surface state energy level
N_c	conduction band effective density of states
N_v	valence band effective density of states
N_{ss}	surface state density
n, p	electron and hole volume density at the semiconductor surface
n_{bulk}	electron volume density in the bulk of the semiconductor
$\mathcal{P}$	valence band hole density per unit area
n_{ss}, p_{ss}	filled and empty surface state density
f	surface state occupation function; $n_{ss} = N_{ss} f$
n_1, p_1	electron and hole density when E_F equals E_{ss}
k_n, k_p	electron and hole capture constants
e_n, e_p	surface state electron and hole emission rates
i_F	Faradaic current
i_{sc}, i_{ss}	space charge and surface-state-transient charging currents
ΔV_{sc}	potential drop across the space charge layer
V	applied potential difference
ΔV_{sc}^{sat}	potential drop across the space charge layer at which the surface state starts to saturate
Z_F	Faraday impedance
Z_{sc}	space charge impedance
Z_{ss}, Y_{ss}	surface state impedance and admittance
R_{ss}, C_{ss}	surface state resistance and capacitance
τ_{ss}	surface state recombination time constant
ϕ	phase angle
g	hole flux towards the semiconductor surface
$\alpha(\lambda)$	semiconductor absorption coefficient at λ nm irradiation
W_0	space charge region width at $\Delta V_{sc} = 1 + kT/e$ V
$\Phi_0(\lambda)$	incident radiation flux at λ nm
j	square root of -1

The superscripts °, ¯ and ˜ denote:

A° parameter A at thermodynamic equilibrium
$\bar{A}$ parameter A at steady state
$\tilde{A}$ parameter A at sinusoidal variation

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