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The Minority Carrier Recombination Resistance: A Useful Concept in Semiconductor Electrochemistry

J. E. A. M. van den Meerakker, J. J. Kelly, and P. H. L. Notten

Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands

ABSTRACT

The impedance characteristics for redox reactions involving minority carrier recombination at semiconductor electrodes differ markedly from those involving majority carriers. In this work, holes were generated in the valence band of n-GaAs by illumination or injection from solution. A recombination resistance is used to characterize the process by which these holes recombine with electrons from the conduction band. This resistance is shown to be independent of the method of hole generation, the pH of the solution, and the nature of the injecting species, but dependent on the generation rate.

In semiconductor electrochemistry, it is of considerable importance to know which of the bands in the solid is involved in the reaction with a redox system in solution. For example, an oxidizing agent may be reduced either by electron capture from the conduction band or by hole injection into the valence band. On the basis of the standard potential of the redox system and the flatband potential of the semiconductor, it is generally obvious which of the two bands is important. However, the situation becomes more complex when an unstable intermediate is involved in the charge-transfer reaction (1) or when charging of an inversion layer or of surface states causes a considerable change in the Helmholtz potential and thus in the position of the semiconductor bandedges (2). In such cases, more sophisticated methods are often necessary to elucidate the reaction mechanism.

In a previous paper (3), we described how, in the photoanodic dissolution of an n-GaAs electrode, hole transfer to the solution was inhibited by an oxide film on the electrode surface. We showed an analogy between the impedance characteristics of this electrolyte-oxide-semiconductor (EOS) system, with enhanced minority carrier recombination, and that of an illuminated MOS device. The concept of a "recombination resistance" was used in the description of the recombination of the minority carriers created by illumination. The dependence of this resistance on light intensity was very similar to that found for the Si MOS transistor (4).

In principle, it should be possible to use such a concept more generally in semiconductor electrochemistry for cases in which recombination of minority carriers is important, irrespective of how these carriers are created. In this work, we describe the generation of holes in the valence band of n-GaAs by two methods, injection from solution and illumination, and we consider the effect of this generation and subsequent recombination on the impedance characteristics of the electrode. A comparison with results involving hole injection into p-GaAs, for which recombination can be disregarded, emphasizes the significance of the recombination resistance. We suggest that this concept may be useful, in certain cases, for deciding which type of charge carrier in the solid is determining for the electrochemical reaction.

Impedance of GaAs Electrodes under Depletion Conditions

In order to clarify what we mean by the recombination resistance, we shall first briefly consider the creation, recombination, and Faraday reactions of minority carriers in n-GaAs under depletion conditions.

Hole reactions at GaAs electrodes.—Under depletion conditions, the extent of the band-bending at the electrode surface determines what happens to holes injected from an oxidizing agent in solution into the valence band of n-GaAs. At relatively large band-bending [Fig. 1(a)], the holes are held at the surface by the electric field, and rupture of surface bonds occurs; the injection is compensated by dissolution of the GaAs, and the resultant net current is very small (5). At lower band-bending, the injected holes can recombine with electrons either at the surface or within a diffusion length of the surface [Fig. 1(b)]. A net cathodic current, carried by electrons in the bulk, is observed in this case.

In an n-type semiconductor, minority charge carriers can also be created by light. In this case, dissolution gives an anodic (photo-) current whose magnitude is determined by the light intensity [Fig. 1(c)], while recombination results in a net zero current [Fig. 1(d)].

Holes, injected under depletion conditions into a p-type GaAs electrode move away from the surface under influence of the electric field [Fig. 1(e)]. This hole-flow through the valence band of the solid is registered as a cathodic current. Recombination is, of course, not important in this case.

Equivalent circuits for GaAs electrodes.—Myamlin and Pleskov (6), using the analogy with MOS devices (7), propose a complete equivalent circuit for the impedance of an n-type semiconductor electrode under depletion conditions. In Fig. 2, the situation is shown for the case in which the recombination rate in the space-charge layer equals zero. C_D , C_S , and C_I are the capacitances of the depletion layer, the surface states, and the inversion layer, respectively. The Helmholtz capacitance C_H replaces the oxide capacitance of the MOS transistor. $R_{n,D}$ and $R_{p,D}$ are the resistances which characterize the transfer of elec-

Fig. 1. Band diagrams for a semiconductor electrode under depletion conditions. (a) and (b) refer to hole injection (inj.) into an n-type electrode. At large band bending, (a) dissolution (diss.) dominates, while at moderate band bending, (b) recombination (rec.) dominates. (c) and (d) are the analogous cases when holes are generated by light. (e) shows hole injection into a p-type electrode.

trons and holes through the depletion layer, while $R_{n,s}$ and $R_{p,s}$ represent the transfer of electrons from the conduction band and of holes from the valence band to surface levels. R_B is the bulk semiconductor resistance. The impedance Z_r describes the generation and recombination of holes and their flow rates in the region of quasi neutrality in the bulk adjacent to the space-charge layer (7). Finally, if an electrochemical reaction occurs at the electrode, current flow through the surface must be taken into account. i_n and i_p represent the electron and hole currents.

In this work, we are mainly interested in the case in which recombination within the space-charge layer is dominant, i.e., the recombination rate is very high. Here the current in the space-charge layer changes from a predominantly electron current at the bulk side to a predominantly hole current near the surface. It becomes meaningless then to represent the current flow through the depletion layer by separate impedances for holes and electrons. The complex impedance Z_r together with $R_{n,D}$ and $R_{p,D}$ can therefore be replaced by a frequency-independent resistance R_D (7) [Fig. 3(a)]. Since, for the

Fig. 2. Equivalent circuit for an n-type semiconductor under depletion or inversion conditions with zero recombination rate in the space-charge layer.

hole injection experiments described here, the rate of reduction of the oxidizing agent may be diffusion controlled, a Warburg impedance W is introduced into the hole injection path.

The equivalent circuit given in Fig. 3(a) is too complex for practical use, but can be further simplified. Pierret and Sah have shown (8) that the resistance R_D is essentially determined by the recombination process in the space-charge region. We now assume that one of the interface capacitances, C_I or C_S , is dominant, and we represent it by C_{if} [Fig. 3(b)]. If inversion can be disregarded, which is very likely to be the case here, then the space charge and surface resistances can be combined into a single recombination resistance which we denote by R_r . Alternatively, when surface states are unimportant, then inversion may determine the interface capacitance C_{if} . If the impedance is measured using a rotating disk electrode at potentials at which reduction of the oxidizing agent is completely diffusion limited, then the Warburg impedance becomes purely resistive and has a very high resistance value (R_w). For measuring frequencies in the range 1-10 kHz, this part of the circuit may be omitted and current will flow through the Helmholtz capacitance. Finally, on combining the electrolyte and bulk semiconductor resistances R_e and R_B into a term $R_{e,B}$, we obtain the simplified circuit shown in Fig. 3(b). This circuit also covers the generation/recombination case in which minority carriers are created by light instead of injection. The circuit is, in fact, the circuit deduced from composite impedance theory by Pierret and Sah for the illuminated MOS transistor without external current flow (8) and used by us for the GaAs EOS system; in the present case, the oxide capacitance is replaced by C_{if} .

For a p-type electrode under depletion conditions, the recombination resistance R_r appears in the current path for electrons. Since holes are being injected from solution [Fig. 1(e)], the Warburg impedance is found in the current path for majority carriers. Mott-Schottky measurements with p-GaAs show no evidence of surface state or inversion effects under depletion conditions in the dark. Since minority carrier processes are not important, a circuit equivalent to that shown in Fig. 2 can be simplified to one containing C_D , C_{if} , R_w , and $R_{p,D}$. The Helmholtz capacitance should be much larger than that of the depletion layer, and $R_{p,D}$ is negligible with respect to R_w . So, a simple circuit results: the depletion layer capacitance C_D is short-circuited by a large resistance R_w and is connected in series to the solution/bulk semiconductor resistance $R_{e,B}$.

Fig. 3. (a) Equivalent circuit for an n-type semiconductor under depletion or inversion conditions with infinite recombination rate in the space-charge layer. (b) Simplified circuit of a, when the generation rate is diffusion controlled.

In order to characterize the recombination resistance R_r , we measured the frequency dependence of the impedance of an n-GaAs electrode in which holes were created by illumination or injected from Ce^{IV} or $\text{Fe}(\text{CN})_6^{3-}$ ions in solution. Current-potential curves were used to distinguish the regions in which recombination and dissolution were dominant, and the results were compared with those of hole injection into p-GaAs.

Experimental

The GaAs single-crystal wafers were obtained from MCP Electronics, England, and had the 100 orientation. The n-type material was Si doped ($8.6 \times 10^{16} \text{ cm}^{-3}$) and had a resistivity of $0.019 \Omega\text{-cm}$. The p-type wafers were Zn doped ($8.4 \times 10^{17} \text{ cm}^{-3}$) and their resistivity was $0.042 \Omega\text{-cm}$. The diameter of the rotating disk electrodes made from these materials was 4 mm. Prior to use, all electrodes were etched at room temperature in a mixture of $\text{H}_2\text{SO}_4(98\%)$ - $\text{H}_2\text{O}_2(30\%)$ - $\text{H}_2\text{O}(3-1-1)$ and dipped in a 6N HCl solution.

The measurements were made in a conventional electrochemical cell using a platinum disk as a counter-electrode and a saturated calomel electrode (SCE) as a reference. All potentials are given with respect to this SCE. Impedance measurements were done under potentiostatic control with the aid of a Solartron 1172 Frequency Response Analyser and an rms signal of 10 mV. For illumination, a Spectra Physics 1 mW 133 He-Ne laser was used in combination with a glass fiber light cable. The penetration depth of this light is small compared to the diffusion length of holes in n-GaAs.

All solutions were prepared with reagent-grade chemicals and deoxygenated using a nitrogen flow. The measurements were performed at room temperature.

Results

Current-potential measurements.—The reduction of Ce^{IV} at pH 0 and $\text{Fe}(\text{CN})_6^{3-}$ at pH 14 occurs at GaAs electrodes by means of hole injection into the valence band (9). The reduction reaction is diffusion controlled in a wide potential range, as is clear from the current-potential curves measured at p-GaAs [dashed lines in Fig. 4(a)]. An identical limiting current is found at n-GaAs [solid lines in Fig. 4(a)] at potentials more negative than -0.60V . In this range, which corresponds to moderate band bending [Fig. 1(b)], holes injected into the electrode recombine with electrons from the conduction band. At more anodic potentials, the band bending increases, the electron concentration at the surface is greatly reduced, and dissolu-

tion competes with recombination [Fig. 1(a)]. At potentials more positive than -0.35V , all holes injected into the electrode are used for the dissolution reaction, and the current tends to zero. The current-potential curves for $\text{K}_3\text{Fe}(\text{CN})_6$ at pH 14 are similar to those given in Fig. 4(a) but are displaced by approximately 0.8V on the potential axis as a result of the higher pH.

Minority carriers can also be created in n-GaAs by illumination in an inert electrolyte [Fig. 1(c) and (d)]; in this case, the current-potential characteristics are "reversed" [Fig. 4(b)]. Efficient recombination at negative potentials results in very low current. At more positive potentials, the increased electric field at the surface ensures an efficient separation of charge carriers, and a photoanodic current resulting from dissolution is found. The ranges in which recombination or dissolution dominates are exactly the same as in the previous case. From these current-potential curves, the potential range can be deduced in which recombination of minority carriers is important. This is, of course, determined by the nature and the density of the recombination centers at and near the electrode surface and is therefore sensitive to the state of the electrode. The kinetics of the oxidation reaction involving the minority carriers (dissolution of GaAs in this case) are also important. In the present case, we have available a potential range of a few tenths of a volt, in which recombination dominates.

An important parameter in this work is the minority carrier generation rate I_g , which can be assessed from the limiting currents. In the case of illumination, this is given by the limiting photocurrent and is directly proportional to the light intensity. For hole injection from solution, the diffusion-controlled reduction current determines I_g ; its value can be varied by changing the concentration of the oxidizing agent in the solution and the rotation rate of the electrode [Fig. 4(a)].

Impedance measurements.—The equivalent circuit shown in Fig. 3(b) should be valid for n-GaAs when recombination is dominant. An analysis of this circuit gives two equations

$$\frac{1}{Z_{re} - R_{e,B}} = \frac{(C_D + C_{if})^2}{R_r C_{if}^2} + R_r C_D^2 \omega^2 \quad [1]$$

$$\frac{-\omega Z_{im}}{Z_{re} - R_{e,B}} = \frac{(C_D + C_{if})(C_D + C_{if} + C_H)}{R_r C_{if}^2 C_H} + \frac{R_r C_D(C_D + C_H)}{C_H} \omega^2 \quad [2]$$

in which Z_{re} and Z_{im} are the real and imaginary components of the complex impedance. $R_{e,B}$ could be obtained from the high frequency limit of Z_{re} . Plots of $1/(Z_{re} - R_{e,B})$ and $-\omega Z_{im}/(Z_{re} - R_{e,B})$ as a function of ω^2 should give straight lines. For all cases involving efficient recombination, we indeed found this to be the case. An example is shown in Fig. 5 for $\text{Ce}(\text{SO}_4)_2$. This implies that our assumptions with respect to the circuit of Fig. 3(a) are correct, and that the impedance behavior of n-GaAs can be represented by the simplified circuit of Fig. 3(b), when the recombination process dominates.

As C_D is negligible compared to C_H , R_r and C_D could be deduced from the slope of the lines in Fig. 5. The recombination resistance, R_r , depends strongly on the generation rate. Figure 6 summarizes the results both from the illumination and hole injection experiments. The slope of this log-log plot is approximately -1.1 . The most striking aspect of these results is that R_r is independent of the method of minority carrier generation (by illumination or injection from the solution). It is also independent of the species which injects the holes, the pH of the solution, and the potential in the recombination range.

The values of C_D measured during injection increased with decreasing potential, as might be expected. These values, however, were somewhat higher than those measured in an indifferent electrolyte in the dark, and showed an increase with increasing generation rate.

Since R_r and C_D are known, C_{if} could be calculated from the intercept of the plot of Eq. [1]. Its value varied from

Fig. 4. (a) Current-voltage curves of p-type (dashed lines) and n-type (solid lines) GaAs at different rotation speeds (300, 1500, 3000, and 5000 rpm) in $0.05\text{M Ce}(\text{SO}_4)_2/1\text{N H}_2\text{SO}_4$ solution. (b) Photocurrent of n-GaAs in $1\text{N H}_2\text{SO}_4$ solution.

Fig. 5. Impedance results, plotted according to Eq. [1] and [2] for n-GaAs in 5.10^{-4} M $\text{Ce}(\text{SO}_4)_2$ /1N H_2SO_4 solution at -0.70 V (SCE) and 100 rpm. $\omega = 2\pi f$, where f is the measuring frequency in Hz.

approximately $0.1 \mu\text{F} \cdot \text{cm}^{-2}$ at very low injection rates to $15 \mu\text{F} \cdot \text{cm}^{-2}$ at the highest rates.

The impedance behavior of a p-GaAs electrode was, of course, totally different. It was consistent with a capacitance (C_D) shunted by a very large resistance (R_w), as expected. Recombination is not important in this case. For n-GaAs under conditions in which dissolution dominates (at potentials more positive than -0.35 V), recombination also does not occur. In this situation, the impedance picture was similar to that for p-GaAs.

Discussion

These results show clearly the importance of recombination for the impedance characteristics of GaAs electrodes. In the absence of such recombination, as when holes are injected into p-GaAs or when dissolution ac-

Fig. 6. Recombination resistance as a function of the generation rate for n-GaAs. $\text{Ce}(\text{SO}_4)_2$ /1N H_2SO_4 solutions at different $\text{Ce}(\text{SO}_4)_2$ concentrations and rotation speeds at -0.60 V (∇), -0.65 V (Δ), or -0.70 V ($\triangle$) vs. SCE. $\text{K}_3\text{Fe}(\text{CN})_6$ /1N NaOH solutions at different $\text{K}_3\text{Fe}(\text{CN})_6$ concentrations and rotation speeds at -1.50 V vs. SCE ($\circ$). 0.5 M K_2SO_4 solution at pH = 5.0 under illumination at -1.00 V vs. SCE ($\square$). 1N H_2SO_4 solution under illumination at -0.70 V vs. SCE ($\blacksquare$).

counts for all holes introduced into n-GaAs, the depletion layer capacitance is shunted by a large Warburg-type impedance. On the other hand, when recombination within the space-charge layer or at the surface is important, the impedance of the electrode resembles that of the MOS and EOS devices (3, 4). This impedance is characterized by a capacitance associated with charge storage at the electrode/electrolyte interface and by a resistance which describes the recombination of minority carriers in the valence band with electrons from the conduction band [Fig. 3(b)].

The relatively large values of C_{if} found at higher injection rates indicate a considerable charge localization at the interface. This is supported by the increased value of the space-charge capacitance C_D relative to the value found when injection does not occur. This points to a shift in potential from the space-charge layer of the semiconductor to the Helmholtz layer. This change can be calculated from Mott-Schottky theory and used to determine the interface charge density (3). On assuming a value of $20 \mu\text{F} \cdot \text{cm}^{-2}$ for C_H , we obtain charge densities ranging from $6.10^{12} \text{ cm}^{-2}$ at low injection rates to $3.10^{13} \text{ cm}^{-2}$ at the highest injection rates used.

The recombination resistance R_r , measured here at potentials at least 0.2 V positive with respect to the flatband potential, depends on the minority carrier generation rate but not on the method of generation. Since R_r is also insensitive to the electrode pretreatment and the pH and composition of the electrolyte, we may conclude that it is mainly determined by recombination not at the surface but in the space-charge layer; R_r is thus an intrinsic property of the material. The recombination resistance is therefore not coupled directly to the interface capacitance. This is also supported by the fact that such a coupling would lead to a time constant τ ($= R_r C_{if}$) in the range 0.1 – 1 ms, which is much too high to account for the very efficient recombination occurring in this case.

Pierret and Sah have developed a quantitative model for the band-to-band communication in illuminated MOS devices under depletion and inversion conditions (8). Their treatment is based on Shockley-Read theory assuming a single-level recombination center. The theory is valid at low injection levels (8), i.e.

$$\frac{\Delta p}{n_i} < \exp \frac{|E_i(\text{bulk}) - E_F|}{kT} \quad [3]$$

where Δp is the deviation from the equilibrium minority carrier concentration as induced by light, n_i is the intrinsic carrier concentration, and E_i and E_F are the intrinsic and equilibrium Fermi levels, respectively. If the injection level is low, the model is obviously applicable to the present case in which the electrode is illuminated in an indifferent electrolyte at potentials negative with respect to the photocurrent-onset potential; in this range, recombination is dominant so that no external current flows [Fig. 1 (d)]. From Eq. [3] it is clear that the condition of a low injection level is indeed satisfied in the present case ($\Delta p < 10^{17} \text{ cm}^{-3}$, i.e., $\Delta p < n_0$); light intensities were such that the photocurrent was linearly dependent on photon density (10). Sah has shown (11) that, for an extrinsic semiconductor, the nonequilibrium equivalent circuit for the case involving external current flow is identical to the equilibrium case with regard to carrier trapping, recombination, and generation, provided the steady-state carrier concentrations are considered instead of the equilibrium values. This means that the recombination model for the illuminated MOS device (8), also involving steady-state carrier concentrations, must be applicable to hole injection from solution when recombination of minority carriers dominates [Fig. 1 (b)]. Pierret and Sah derive an expression for the recombination resistance on the basis of a transition, within a narrow spatial region in the space-charge layer, from a predominantly hole current at the surface to an electron current in the bulk. This resistance is shown to be potential independent in a wide range. The relationship between the recombination resistance and the generation rate is deter-

mined by the nature of the recombination center. For an efficient level located near midgap with approximately equal capture cross sections for electrons and holes, an inverse square root dependence is predicted ($R_r \propto 1/\sqrt{I_g}$). An inverse linear dependence ($R_r \propto 1/I_g$), as found in the present work, indicates a dominant recombination center somewhat displaced from midgap and with a ratio of capture cross sections considerably different from unity. A similar dependence was found for the Si MOS device and the GaAs EOS system (3, 4).

In this work, we have only considered the two extreme cases: negligible and complete recombination. For an n-GaAs electrode at potentials in the intermediate range at which the anodic photocurrent and cathodic reduction current increase to their limiting values, the recombination resistance increases and the impedance picture becomes more complicated (12). Nevertheless, the presence of a recombination resistance in the equivalent circuit is a clear indication that minority carriers are responsible for the electrochemical reaction. In a subsequent paper, we shall show how this approach can be used to obtain information concerning a more complex reduction reaction at GaAs (13).

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Epitaxial Growth and Characterization of β -SiC Thin Films

P. Liaw^{*1} and R. F. Davis

Department of Materials Engineering, North Carolina State University, Raleigh, North Carolina 27695-7907

ABSTRACT

Crack-free monocrystalline β -SiC films having very smooth final surfaces may be reproducibly grown at 1600 K and 760 torr on (100) Si substrates using SiH_4 and C_2H_4 and H_2 if the Si is initially reacted with the C_2H_4 alone. This initial step produces a buffer layer which reduces the mismatches in expansion coefficients and lattice parameters and thus allows the subsequent growth of the β -SiC film to a thickness exceeding 5 μm . It is necessary to heat the Si wafers from room temperature to the reaction temperature in a C_2H_4 and H_2 environment rather than preheating the substrates to the reaction temperature. An off-axis orientation of the Si in excess of approximately 3° results in a very rough final growth surface on the β -SiC film.

Silicon carbide (SiC) possesses a unique combination of properties which are not available from other more common semiconductor materials. In addition to its high thermal conductivity and melting point, extreme hardness and excellent resistance to chemical attack and mechanical damage, it is also characterized by a range of high energy bandgaps [2.2-3.3 eV, depending on the structure type; (see following discussion and Ref. (1) and (2))] and a high saturated drift velocity [2.27×10^7 cm/s (3-5)], which are particularly important for electronic applications. As such, this material has, for several years, been considered the leading candidate material for future employment in thin film solid-state electronic devices which would be subjected to high temperatures or high frequencies or high power loads or a combination of these severe conditions.

Silicon carbide may exist in one particular crystallographic structure, if grown under carefully selected and controlled conditions. However, as a result of its low stacking fault energy, this material frequently occurs as a collection of several slightly different one-dimensional polymorphs or "polytypes" having different stacking sequences along the directions perpendicular to the closest packed planes. Alpha SiC forms in more than 140 identified hexagonal or rhombic polytypes, whereas, β -SiC possesses only the cubic zinc blende structure. An excel-

lent review of these polytypes and their formation has recently been published by Jepps and Page (6).

The common occurrence of the β polytype as a product of vapor and liquid growth processes, its transformation to one or more of the alpha forms at high temperatures and its recent commercial availability have caused it to be considered almost as a separate material. Because of its small bandgap (2.3 eV) and ease of growth at relatively low temperatures, the β form is currently considered the most desirable polytype for microelectronic applications.

The previous (1956-1973) major research periods concerned with the growth of SiC as an electronic material concentrated heavily on very high temperature sublimation-condensation (Lely) processes which formed an unreproducible variety of alpha polytypes within each crystal. Solution growth via the reaction of molten Si with its graphite container was a common method of growing β -SiC; however, these crystals were invariably small and highly twinned and therefore of little use for electronic applications. Chemical conversion of the Si surface and chemical vapor deposition (CVD) processes were also employed. However, the results in terms of thickness, single crystallinity, and/or device quality of the films were not sufficient to engender continued substantial funding of this research. For an essentially complete record of these earlier studies, the reader is referred to the published proceedings of the three previous SiC conferences (7-9) and their bibliographies.

Research in SiC for semiconductor applications has continued, albeit at a reduced level of effort, with positive

^{*}Electrochemical Society Active Member.

¹Present address: Advanced Micro Devices, Sunnyvale, California 94088.