Surface Charging Effects during Photoanodic Dissolution of n-GaAs Electrodes

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ABSTRACT

The photoanodic dissolution of n-GaAs was investigated in an electrolyte, 0.1M EDTA solution at pH 5, in which oxide formation can occur at higher light intensity. The effect of illumination and film formation on the charge and potential distribution of the electrode was studied by means of impedance measurements. A model involving positively charged states at the semiconductor/oxide interface is developed to account for the buildup of a high surface charge density during illumination. The importance of surface oxide and interface charge for photoanodic reactions is considered in terms of this model.

Two factors are mainly responsible for the current interest in the dissolution of III-V materials: etching and illumination. The importance of surface oxide and interface charge for photoanodic reactions is considered in terms of this model.

Key words: semiconductor, interfaces, impedance, photoconductivity.
charge localization in surface or interface states may be important in the dissolution of semiconductor electrodes (4–7). Such states may act as intermediates in the dissolution reaction and may, when electrically charged, influence the potential distribution at the electrode/electrolyte interface. The effect of interface states is expected to be modified by the formation of a surface film, which often accompanies dissolution (8).

In the present study of the photoanodic dissolution of n-GaAs, we chose an electrolyte, 0.1M EDTA solution at pH 5, which is known to give rise to oxide formation under illumination (9). Using steady-state and transient impedance measurements, we have observed characteristic surface charging effects during dissolution. On the basis of the influence of light intensity and film formation on the charge and potential distribution of the GaAs electrode, we suggest a model to describe charge localization at the illuminated semiconductor/electrolyte interface and we consider the consequence of surface charging for the photoanodic dissolution reaction.

Experimental

The n-type single-crystal wafers, with (100) orientation and a carrier density in the range \(10^{17}-10^{19}/\text{cm}^2\), were obtained from MCP Electronics, England. Mechanically polished electrodes with a diameter of 3 mm, were etched at room temperature in \(\text{H}_2\text{SO}_4 (98\%)/\text{H}_2\text{O}_2 (30\%)/\text{H}_2\text{O} (3/1/1)\) solution and dipped in concentrated HCl solution prior to use.

Impedance was measured under potentiostatic control in a conventional electrochemical cell using either a General Radio Company 1615 A capacitance bridge or a Solartron 1172 Frequency Response Analyzer with an rms signal of 10 mV. In order to normalize the experimental impedance results with respect to unit area, a conversion factor of \(7.1 \times 10^{-3} (\text{cm}^2)\) must be used. In the mathematical treatment, the corresponding values are given in normalized form. Potentials are quoted with respect to the reference saturated calomel electrode (SCE) in all cases.

For illumination, a Spectra-Physics 1 mW 133 He-Ne laser was used in combination with a light cable. Absolute light intensities were not determined but the limiting photocurrent of an n-GaAs electrode in 1N \(\text{H}_2\text{SO}_4\) was used as a measure of the photon density. An intensity \(N_{\text{ph}}\) with arbitrary unit (a.u.) = 1 corresponds to a limiting photocurrent density of 0.1 mA/cm\(^2\). Neutral filters were used to vary the intensity.

The electrolyte solutions, prepared from reagent grade chemicals, were not stirred during the measurement. The concentration of photon density \(N_{\text{ph}}\) was determined by a light intensity of 0.1 M NaEDTA solution and dipmed in concentrated HCl solution prior to use.

\(\text{Fe}^{2+}\) EDTA solution and dipmed in concentrated HCl solution prior to use.

Film formation: photocurrent results.—The shape of the photocurrent–potential curve of an n-GaAs electrode in 0.1M NaEDTA, 0.1M NaClO\(_4\) solution at pH 5 was similar to that found in NaClO\(_4\) solution without EDTA: in both the cases the onset potential for photocurrent flow was \(-0.8\text{V}\) and the current reached its limiting value at approximately \(-0.6\text{V}\). Although the limiting photocurrent was potential independent in both electrolytes, the presence of EDTA in the solution had a considerable influence on the magnitude of this current. This effect is illustrated in Fig. 1 and 2.

At low light intensity, the anodic photocurrent \(i_{\text{ph}}\) measured at \(+0.50\text{V}\) in 0.1M NaEDTA, 0.1M NaClO\(_4\) solution at pH 5, was constant in time [curve (a), Fig. 1] and its magnitude was directly proportional to the photon density \(N_{\text{ph}}\) as shown in the lower part of curve (a), Fig. 2. At higher light intensity, the photocurrent observed initially was the same as that found in 0.1M NaClO\(_4\) alone [dashed line (b), Fig. 2]. This current, however, decayed after an induction period [curves (b)–(d), Fig. 1]. The induction time decreased as the light intensity was increased. In this case, the steady-state photocurrent was essentially independent of photon density [curve (a), Fig. 2]. The inhibition of the anodic photocurrent could be prevented by adding to the electrolyte a reducing agent (0.1M Fe\(^{2+}\) EDTA) capable of competing with the GaAs dissolution (3) [curve (c), Fig. 2]. At higher light intensity, the competition was incomplete and photocurrent decay was eventually observed.

Such results, found in various electrolytes containing EDTA at pH 5, strongly suggest the formation of a solid film on the electrode. Similar effects were observed by Elliott and Regnault at much higher potentials which gave rise to considerably thicker anodic films (9). Since the original photocurrent transient could be reproduced after film formation by maintaining the electrode at the same potential in the dark (see Fig. 3), it is clear that the surface film dissolves chemically in the electrolyte. Under steady-state conditions, the rate of chemical dissolution determines the magnitude of photocurrent. This explains why the current in the limiting photocurrent range is independent of light intensity and applied potential. On the basis of the constant photocurrent and the time required to dissolve the surface film in the dark, and assuming a molecular weight and density typical of a
GaAs oxide, a thickness of the order of 1.5-5 nm was calculated for the various films described in this work.

Influence of illumination and film formation on the electrode impedance.—The Mott-Schottky plot for an n-GaAs electrode measured in the dark in EDTA solution at pH 5 [curve (a), Fig. 4] was identical to that found in a citrate/NaOH buffer solution of the same pH; $C_s$ is the equivalent series capacitance of the electrode measured, in this case, at 10 kHz. In the dark, a surface oxide, if present on the GaAs electrode, is expected to be very thin. Since the capacitance of the Helmholtz layer is much greater than that of the depletion layer, the change in the externally applied potential $V$ is concentrated in the space-charge region of the semiconductor, and the electrode behaves as a Schottky barrier.

When the electrode was exposed to a low light intensity, a linear plot was again observed [curve (b)] but displaced with respect to the dark [curve (a)]. An increase in light intensity, to a value still not sufficient to cause film formation, gave a further shift in the curve [curve (c)]. Such a parallel displacement of the Mott-Schottky plots would be consistent with hole trapping at the electrode surface (4, 5). The potential across the Helmholtz layer changes by an amount corresponding to $\Delta V_{FB}$, the displacement of the flat-band (FB) potential.

The capacitance of the film-covered electrode, measured under illumination, is due mainly to the presence of the surface film had a dramatic effect on the impedance of the illuminated electrode. This is shown in curve (d) of Fig. 4 for a photon density capable of maintaining a stable film. The steady-state $C_s$ value at 10 kHz became almost independent of the applied potential in a wide range. $C_s$ increased with increasing photon density as shown in curve (e). That these effects are connected with the presence of the surface film can be deduced from transient measurements at 10 kHz (Fig. 5). During the induction period of film formation [see curve (a)], $C_s$ increased somewhat with respect to its dark value [curve (b)]. This change corresponds to the parallel shift in the Mott-Schottky curve of Fig. 4. The capacitance, however, increased markedly as the photocurrent decayed to its steady-state value. A corresponding change was also observed in the equivalent series resistance $R_s$ [curve (c)]. Similar behavior was found at other light intensities, with $C_s$ and $R_s$ following the photocurrent changes closely. It should be noted that, although the surface film dissolved only slowly in the dark (Fig. 3), both $C_s$ and $R_s$ relaxed rapidly when the light was switched off (Fig. 5).

Further evidence that the anodic film formed in EDTA solution is responsible for the impedance results in curves (d) and (e) of Fig. 4 is provided by measurements in an EDTA-free electrolyte at pH 5. As already mentioned, the photocurrent in the absence of EDTA was stable and directly proportional to light intensity up to the highest values used (Fig. 2). In this case, illumination also gave a shift in the Mott-Schottky curve similar to that shown in curves (b) and (c) of Fig. 4. However, the displaced curve remained parallel to the dark curve even up to the highest photon densities; the change in FB potential tended to a limiting value ($\Delta V_{FB} \approx 0.22V$) at higher light intensity.

If the capacitance of the film-covered electrode, measured under illumination, is due mainly to the
space-charge layer of the semiconductor, then the potential independent $C_s$ values in curves (d) and (e) of Fig. 4 imply a considerably reduced but almost fixed band bending. Such an apparent pinning of the Fermi level could result from a buildup of charge at the GaAs-oxide interface. A fast decay of this interface charge would account for the rapid relaxation of the electrode impedance when the light is switched off.

The results reported above therefore suggest that charge is stored at the GaAs surface during photoanodic dissolution. It is obvious that the model of a Schottky barrier, which describes the electrode under depletion conditions in the dark and at low light intensity, does not hold for an illuminated electrode with surface film. Before further considering the effect of illumination on the charge and potential distribution at the interface, we first examine a model for the film-covered electrode. We then use the results to discuss the nature of the interface charge and its role in the dissolution reaction.

Model for the film-covered electrode under illumination.—The behavior of the electrode with photoanodic film, described in the previous section, resembles, in certain respects, that of the illuminated MOS transistor (10-12). In order to treat our results, we shall therefore use an analogous electrolyte oxide semiconductor (EOS) model [Fig. 6(a)], with additional features involving a "leaky" insulator and hole trapping in interface states. A similar approach has been used qualitatively by Morrison and co-workers (8, 13) for photoanodic reactions at n-type Si electrodes.

The equivalent circuit for such a model is shown in Fig. 6b. In the theory describing the illuminated MOS transistor (11), the depletion layer capacitance $C_{dc}$ is the high frequency limit, characterized by the fact that minority carriers cannot respond to the small a-c measuring signal; the low frequency semiconductor capacitance $C_s$ describes the storage capacity of the minority carriers in the interface region, for the case in which the carriers are in quasi-equilibrium; $R_L$ takes into account the generation/recombination resistance between the two bands and gives information on the path through which minority carriers are supplied to the surface region; $C_{ox}$ and $R_e$ refer, respectively, to the film capacitance and the solution plus bulk semiconductor resistance.

In the present case, a small d.c. flows during illumination. This means that the space charge and surface film capacitances must be shunted by a large (nonlinear) faraday resistance. This resistance, which could be deduced from measurements at low frequency, had a value in excess of $5 \times 10^5 \Omega$. For simplicity, it has been omitted from Fig. 6b as it is not important for the impedance measurements at higher frequency discussed here.

In order to test the applicability of such a model for the present EOS case, we measured the frequency dependence of the electrode impedance at various light intensities. The real and imaginary components, $Z_{re} (= R_d)$ and $Z_{im} (= 1/\omega C_{ox})$, are plotted in Fig. 7.

![Fig. 6a. EOS model for illuminated n-GaAs. $E_c$ and $E_v$ (solid lines) refer to conduction and valence bands in the dark. As a result of illumination, a positive charge density $Q_{ph}$ is built up at the GaAs/film interface. The semiconductor band bending is reduced by $\Delta V_{SC}$ and a corresponding potential $\Delta V_{OX}$ appears over the surface film (dashed lines).](image)

![Fig. 6b. Equivalent circuit for an illuminated n-GaAs electrode with surface film.](image)

![Fig. 7. The frequency dependence of the real ($Z_{re}$) and imaginary ($Z_{im}$) components of the impedance of n-GaAs at +0.50V (SCE) in 0.1M Na$_2$ EDTA, 0.1M NaClO$_4$, pH 5 in the dark (curve a). Remaining curves (b)-(g) refer to illuminated electrode at increasing light intensity. $N_{ph}$ values are given in Table 1.](image)
in the frequency range 500 Hz-10 kHz, for an electrode without a surface film in the dark and at low light intensity [curves (a) and (b), respectively], and at increasing light intensity for an electrode with an anodic film [curves (c)-(g)]. The light intensity clearly has a significant effect on the impedance of the film-covered electrode.

An analysis of the equivalent circuit yields the following equations

\[ \frac{1}{Z_{eq} - R_0} = \left( R_L C_{sc} + C_{ox} \right) \omega^2 + \frac{(C_{if} + C_{sc})^2}{R_L C_{if}^2} \]  

\[ \frac{\omega Z_{im}}{Z_{eq} - R_0} = \left\{ \frac{R_L C_{sc} (C_{if} + C_{sc})}{C_{ox}} \right\} \omega^2 + \frac{(C_{if} + C_{sc}) (C_{if} + C_{sc} + C_{ox})}{R_L C_{ox} C_{if}^2} \]  

\[ \frac{Z_{im}/Z_{eq} - R_0}{\omega^2} = \frac{R_L C_{sc} (C_{if} + C_{sc})}{C_{ox}} \omega^2 + \frac{(C_{if} + C_{sc}) (C_{if} + C_{sc} + C_{ox})}{R_L C_{ox} C_{if}^2} \]  

\[ R_L \text{ can be obtained from the high frequency limit of } Z_{eq} \text{ in the dark. It follows from these equations that plots of } 1/Z_{eq} - R_0 \text{ and } \omega Z_{im}/Z_{eq} - R_0 \text{ as a function of } \omega^2 \text{ should give straight lines. In Fig. 8, the second of these functions is plotted for a film-covered electrode at a photon density } N_{ph} = 2 \text{ a.u. Excellent linearity is observed over a range of two orders of magnitude. This was also the case for Eq. [1]. Some deviation from such ideal behavior was found at lower frequency } (< 2 \text{ kHz}) \text{ at the highest light intensities.} \]

It was not possible to obtain the four unknown circuit elements directly from Eq. [1] and [2]. In order to get an estimate of the various capacitances, we assumed that the oxide thickness is directly proportional to the potential drop across the oxide (15). Using a proportionality constant for the potential dependence of the film thickness in the range 1.5-4.0 nm/V, as expected for anodic films on GaAs (15), we showed that \( C_{ox} \gg C_{sc} \). This latter condition was subsequently used to calculate a self-consistent set of impedance parameters. The intercept and slope of the plot of Eq. [1] yield \( R_L \) and \( C_{sc} \), and \( C_{ox} \) can then be obtained from Eq. [2]. The most striking aspect of this analysis is the very significant decrease in \( R_L \) and \( C_{ox} \) with increasing photon density (Table I). The latter result supports the suggestion made in the previous section that illumination decreased the band bending. This is also found by the gradual increase in \( C_{ph} \) with increasing photon density (Table I). The latter result supports the suggestion made in the previous section that illumination decreased the band bending. This is also found.

Table II. Influence of photon density \( N_{ph} \) on the parameters \( R_L, C_{ox} \), and \( \Delta V_{sc} \) measured at \( +0.50 \text{V (SCE)} \)

<table>
<thead>
<tr>
<th>Case</th>
<th>( N_{ph} ) (a.u.)</th>
<th>( R_L ) (kOhm)</th>
<th>( C_{ox} ) (nF)</th>
<th>( \Delta V_{sc} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>dark</td>
<td>500.0</td>
<td>5.8</td>
<td>0.0</td>
</tr>
<tr>
<td>b</td>
<td>0.36</td>
<td>400.0</td>
<td>8.1</td>
<td>0.10</td>
</tr>
<tr>
<td>c</td>
<td>1.1</td>
<td>10.8</td>
<td>9.2</td>
<td>0.88</td>
</tr>
<tr>
<td>d</td>
<td>3.0</td>
<td>27.7</td>
<td>10.1</td>
<td>1.21</td>
</tr>
<tr>
<td>e</td>
<td>3.3</td>
<td>27.7</td>
<td>10.1</td>
<td>1.21</td>
</tr>
<tr>
<td>f</td>
<td>5.7</td>
<td>10.6</td>
<td>10.7</td>
<td>1.27</td>
</tr>
<tr>
<td>g</td>
<td>11.4</td>
<td>11.1</td>
<td>11.1</td>
<td>1.21</td>
</tr>
</tbody>
</table>

\[ R_L \propto N_{ph}^n \text{ with } n \approx -1.1 \]

similar to that found for the MOS transistor (11, 12). In the MOS case, this dependence has been accounted for theoretically by the Shockley-Read recombination model (11).

Table II shows that, at constant light intensity, \( C_{ox} \) and \( R_L \) change only slightly with applied potential in the limiting photocurrent range. The film capacitance \( C_{ox} \) decreases with increasing potential; this indicates an increase in film thickness, as might be expected for electric field dependent film growth (14). Except at low potential, \( C_{ox} \) is approximately an order of magnitude smaller than the generally accepted value of the Helmholtz capacitance; omitting \( C_H \) from the circuit of Fig. 6 involves, however, some error in the \( C_{ox} \) determination. If we assume a dielectric constant of 8 for the surface film (15), the measured \( C_{ox} \) values indicate a film thickness ranging from 1.5 to 4 nm, in reasonable agreement with those already estimated.

For electrolytes without EDTA, the impedance spectra of the electrode illuminated up to high intensity resembled those of the EDTA system in the dark or at very low light intensity (Fig. 7, curves (a) and (b)). The \( Z_{im} \) plots were linear between 1 and 10 kHz with a slope of -1. The equivalent \( R_L \) term was very large and decreased only slightly on illumination, in contrast to the very considerable decrease in the EDTA case (Table I). In the absence of an anodic film, recombination is not important as hole transfer to the solution remains effective even at high photon density.

Potential and charge distribution.—By using the results of the impedance analysis from the previous section and following a procedure very similar to that adapted by Frese and Morrison (15), information can be obtained concerning the potential and charge distribution at the semiconductor/film interface. If we denote the charge density in the depletion region of the semiconductor by \( Q_{sc} \) and that at the interface by \( Q_{if} \), without, for the moment, considering whether this is located in an inversion layer or in interface states, then

\[ Q_{sc} + Q_{if} = Q_{ox} \]  

where \( Q_{ox} \) is the charge density on the outer surface of the oxide. The potentiostatically fixed potential difference \( V \) between the GaAs and the reference electrode is given by

\[ V = V_{sc} + V_{ox} + V_H + V' \]  

where \( V_{sc}, V_{ox} \), and \( V_H \) refer to the potential drop across the space charge region, the surface film, and the Helmholtz layer, respectively, and \( V' \) allows for

Table II. Influence of electrode potential on impedance parameters measured at \( N_{ph} = 11 \text{ a.u.} \)

<table>
<thead>
<tr>
<th>V (SCE)</th>
<th>0.00</th>
<th>0.50</th>
<th>1.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_L ) (kOhm)</td>
<td>7.6 \times 10^7</td>
<td>7.7 \times 10^7</td>
<td>7.5 \times 10^7</td>
</tr>
<tr>
<td>( C_{ox} ) (nF)</td>
<td>11.1</td>
<td>11.1</td>
<td>11.0</td>
</tr>
<tr>
<td>( C_{if} ) (nF)</td>
<td>1.9 \times 10^8</td>
<td>1.9 \times 10^8</td>
<td>1.4 \times 10^8</td>
</tr>
</tbody>
</table>
states do not seem unlikely since anodic dissolution shown that a considerable charge accumulates at the lar manner. The capacitance measured at high fre-

tion is observed [curves (b) and (c), Fig. 4] and the solution reaction (iph cc Nph), a deep depletion condi-

tions can be calculated from the measured value of Csc (see Table I) via the Mott-Schottky relation (15)

\[ C_{sc} = \left( \frac{\varepsilon N_D e}{2} \right)^{1/2} \left( \frac{V_{sc} - kT}{e} \right)^{-1/2} \]  

in which \( \varepsilon \) is the dielectric constant and \( N_D \) the donor density of the semiconductor. Using Eq. [5], \( V_{ox} \) can now be calculated as a function of light intensity. Van de Waals for the change in band bending \( \Delta V_{sc} \) which results from illumination, are given in Table I and confirm the trend already discussed. The decrease in \( V_{sc} \) is, of course, compensated by an increase in \( V_{ox} \) \((- \Delta V_{sc} = \Delta V_{ox})\) as shown schematically in Fig. 6. Since the depletion layer charge \( Q_{sc} \) can be estimated for a given value of \( V_{sc} \) from an integrated form of Eq. [7] and since \( C_{ox} \) and \( V_{ox} \) are known, the charge density \( Q_{sc} \) stored at the interface, can be calculated. The values of \( Q_{sc}/\varepsilon \) range from approximately 5 \( \times \) 10^{12}/cm^2 to 3 \( \times \) 10^{13}/cm^2 at the highest light intensity for the film-covered electrode.

We can deal with the lower light intensity case involving a very thin surface film \( (C_{ox} > C_{H}) \) in a similar manner. The capacitance measured at high frequency is almost identical to the depletion layer capacitance \( (C_{sc} < C_{H}) \). Consequently, the change in \( V_{sc} \) and \( Q_{sc} \) caused by illumination, can be calculated directly from the measured \( C_{sc} \) values of the Mott-Schottky plots [e.g., curves (a)-(c) of Fig. 4]. Since the applied potential is fixed, a change in \( V_{sc} \) must, in this case, be compensated by a change in the Helmholtz potentials \( (\Delta V_{H} = -\Delta V_{sc}) \). In order to obtain the corresponding interface change density

\[ C_{H-VH} = \Delta Q_{sc} + Q_{H} \]  

we assume, by analogy with other electrodes under comparable conditions, a value of 20 \( \mu F/cm^2 \) for \( C_{H} \); this necessary since the Helmholtz capacitance cannot be measured directly in this case. It is clear from curves (a)-(c) of Fig. 4 that \( Q_{H} \) increases with increasing light intensity. The limiting value of \( Q_{H}/\varepsilon \), for a photon density just below that required to form an anodic film, was of the order of 3 \( \times \) 10^{13}/cm^2.

Mechanism of surface charging.—During photoanodic dissolution, holes generated by light move under influence of the electric field in the space-charge region of the semiconductor to the surface where bond breaking occurs (6, 16). In the previous section, we have shown that a considerable charge accumulates at the interface during dissolution and the potential distribution changes significantly. In the absence of a thick surface film, as at low light intensity, excess holes are readily removed from the surface region by the dissolution reaction \( (h_{ph} \propto N_{ph}) \), a deep depletion condition is observed [curves (b) and (c), Fig. 4] and the change in the Helmholtz potential can be attributed to positive charge in surface or interface states. Such states do not seem unlikely since anodic dissolution of a semiconductor involves the rupture of many surface bonds and the formation of radical- and ion radical-like intermediates (4, 6, 16, 17).

The presence of an anodic film, as formed at higher light intensity, can have two important effects: dissolution is inhibited so that holes created by light can-
\[ n_s = n_e \exp(-eV/kT) \]  

in which \( n_s \) and \( n_e \) are the surface concentrations of electrons and holes, \( n_e \) is the bulk electron concentration, \( N \) is the interface state density, \( f \) is the fraction of states occupied by a hole, and the \( k \) terms refer to the various rate constants. Since the applied potential may be located in the space-charge layer and in the Helmholtz layer, it follows that the band bending under illumination \( V_{SC} \) is given by

\[ V_{SC} = V - V_{FB} - \Delta V_H \]  

with

\[ \Delta V_H = eNf/CH \quad (\Delta Q_{ox} \ll Q_{it}) \]  

In these expressions, \( C_H \) and \( V_H \) must be replaced by \( C_S \) and \( V_{Sc} \) when the surface film becomes dominant \((C_{ox} < C_H)\). Equations [9]-[12] yield under steady-state conditions

\[ \Delta V_H = (V - V_{FB}) + \frac{kT}{e} \ln \left( \frac{g - j_p}{h_n n_0 N_f} \right) \]  

For a chosen value of \( f \), \( \Delta V_H \) can be calculated from Eq. [12b], and the Faraday flux \( j_p = (2kpsf/Nf) \) can be obtained using \( p_f \) from Eq. [9]. Inserting these values into Eq. [13], we obtain the corresponding value of \( V - V_{FB} \). In this way, \( \Delta V_H \) or \( V_{Sc} \) (see Eq. [12a]) can be calculated as a function of the applied potential \( V - V_{FB} \) for a given set of kinetic parameters. On inserting the value for \( V_{Sc} \) from Eq. [12] into Eq. [7], we get the modified Mott-Schottky expression for the illuminated case

\[ \frac{1}{C_{sc}^2} = \left( \frac{2}{eN_f e} \right) \left( V - V_{FB} - \frac{eNf}{C_H} \right) \]  

In Fig. 9, the band bending under illumination, calculated using an arbitrary set of rate constants for the dissolution reaction and for electron and hole capture \((19)\), is plotted as a function of applied potential. When \( V - V_{FB} \) is small, the degree of occupation of the interface states is limited, \( \Delta V_H \) is negligible, and \( V_{Sc} \) increases linearly with applied potential. At low interface state density or at very low light intensity, this continues to high values of \( V - V_n \) [curve (a), Fig. 9]; the holes are removed by the dissolution reaction. The Mott-Schottky curve measured under illumination does not differ from the dark case \((eNf/C_H \approx 0 \text{ in Eq. [14]}\). In previous work \((4)\), we found this to be essentially the case for photoanodic dissolution of n-GaAs in H2SO4 solution.

At higher light intensity, the interface states begin to fill as \( V_{Sc} \) increases and the electron concentration at the surface is reduced. If the value of \( N \) is appreciable \((> 10^{13} \text{cm}^{-2}\text{cm}^{-3})\) in this case, the potential in the Helmholtz layer increases and \( V_{Sc} \) tends to level off [curve (b), Fig. 9]. When the steady-state occupancy is attained, characteristic of the particular photon density, \( V_{Sc} \) remains constant, \( V_{Sc} \) again increases, and deep depletion may result. At higher light intensity, a larger steady-state \( f \) value is expected and a correspondingly larger \( \Delta V_H \) shift is calculated [curve (c), Fig. 9]. From Eq. [14], it follows that the parallel shift in the \( V_{Sc} \) plots, caused by illumination, must lead to an equivalent displacement of the Mott-Schottky curves; this is indeed found with the EDTA system at low intensity (Fig. 9) and with the EDTA-free electrolyte in the complete intensity range. Nakato et al. (17) report similar effects with n-GaP electrodes, while we have made similar observations with n-GaP and n-Cds \((4)\).

The value of \( C_H \) used in the examples so far, was typical of that for a normal Helmholtz layer. The effect of an increased capacitance, as for the case when a surface film is present on the electrode \((C_{ox} < C_H)\), is clear from curve (d). The film is about 2 nm thick, in this case, and we have again assumed that dissolution is not kinetically inhibited. The surface barrier height is held almost constant over a much wider potential range \((\approx 0.6 \text{V})\) as the potential across the surface film builds up. For the EDTA case at higher light intensity, the limiting photocurrent is independent of photon density as a result of film formation [curve (a), Fig. 2]. In addition, the film thickness increases with increasing potential in this case, and we have again assumed that dissolution is not kinetically inhibited. The oxide thickness can be directly proportional to \( V_{Sc} \), and the Fermi level is expected to extend over an even wider potential range. In order to get a rough estimate of the band bending in this case [curve (e)], we again assumed the oxide thickness to be directly proportional to \( V_{Sc} \), and the Fermi level is expected to extend over an even wider potential range. In order to get a rough estimate of the band bending in this case [curve (e)], we again assumed the oxide thickness to be directly proportional to \( V_{Sc} \), and the Fermi level is expected to extend over an even wider potential range. In order to get a rough estimate of the band bending in this case [curve (e)], we again assumed the oxide thickness to be directly proportional to \( V_{Sc} \), and the Fermi level is expected to extend over an even wider potential range.

Conclusions

In this paper, evidence is presented to show that a relatively high charge density is localized at the n-GaAs/EDTA-electrolyte interface during photoanodic dissolution. An EDS model, involving the formation of positively charged interface states during illumination, is proposed for this system. The model can account for the parallel displacement of the Mott-Schottky plots at lower light intensity and the drastic changes in the electrode impedance when thicker oxide films are formed at higher photon densities.

It is clear that measurements of the type described in this work may be useful in obtaining information on the mechanism of photoanodic dissolution. For example, if the reverse reaction in the hole trapping step 2 is disregarded, then it can be shown that the parallel displacement of the Mott-Schottky curves becomes independent of light intensity. If, on the other hand, a second hole is not involved in the dissolution step 4, then the displacement should be a linear function of the light intensity. Neither of these observations is in agreement with the experimental results. A study of the relaxation of the interface charge and the dependence of charged interface state density at very low light intensity. Neither of these observations is in agreement with the experimental results. A study of the relaxation of the interface charge and the dependence of charged interface state density at very low light intensity. Neither of these observations is in agreement with the experimental results.
especially in the low quantum efficiency-potential range.

The role of oxide films may be considerable, even when they are not thick enough to act as a tunnel barrier for holes. Such films may serve to stabilize surface intermediates by shielding them from solution; the reason why charging effects are less pronounced in H₂SO₄ solution might be due to a higher oxide solubility at low pH. We have shown that the film may significantly influence the potential distribution when charge is stored at the interface [compare curves (b) and (d) of Fig. 9]. Finally, the considerable surface charging observed in the present work implies, of course, a shift in the semiconductor bandedges with respect to the solution. This aspect has important consequences for the stabilization of n-type electrodes by means of competitive oxidation of reducing agents, as discussed by Madou et al. for n-type Si (6, 18).

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Application of EPR Spectroscopy to Oxidative Removal of Organic Materials

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ABSTRACT

Oxidative species produced in a microwave discharge (P₂, O and ∆₁O₂) have been detected, and some of their reactions with organic solids characterized using a gas phase electron paramagnetic resonance (EPR) spectrometer assembled for that purpose. It has been shown that O atoms rather than excited-state oxygen molecules are the primary reactive species responsible for removal. Also, the O atom oxidation of phenolformaldehyde polymers and graphite has been investigated. The recombination kinetics of O atoms in this flow system can be described by an exponential decay equation involving both wall- and gas-phase collisional recombinations. This allows the signal observed downstream of the reaction to be interpreted as an indication of the gas-solid reaction rate and thus allows the determination of the activation energies of removal of photoreastic (0.3 eV) and graphite (0.45 eV). These experiments have established EPR as a useful analytical tool in the development of gaseous cleaning and other, analogous processes, such as etching.

Reactive species produced in a gas-phase discharge readily attack many materials and may be used to etch or clean surfaces in integrated circuit processing (1-2). The major long-lived and potentially reactive species produced in a molecular oxygen discharge are oxygen atoms (ground state) and ∆₁ excited-state molecular oxygen. These, along with the parent ground-state molecular oxygen, can be detected quantitatively using electron paramagnetic resonance (EPR) spectroscopy.

We have assembled and characterized a gas-phase EPR spectrometer and used it to study the production and reactions of oxygen discharge products with organic materials. Interpretation of the EPR data, which are taken downstream from the production and reaction sites, requires an understanding of how the signal varies as a function of the distance downstream. This, in turn, requires a verification of the recombination kinetics of O atoms, both homogeneous (gaseous collisions) and heterogeneous (wall collisions). In these ways we have established EPR as an analytical technique for the study of oxidation (or etching) reactions and have obtained useful information for the development of gaseous cleaning techniques for hybrid integrated circuit processing. This work has been done to show the usefulness of EPR as a useful analytical tool for the study of cleaning and etching processes.

Experimental

Our EPR spectrometer is a typical balanced-bridge design, operating at 9.6 GHz and using 100 kHz mag-