Surface charging effects during photoanodic dissolution of n-GaAs electrodes

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Fig. 13. Annealing temperature dependence of the (111) peak intensity.

are changed by annealing; (iv) several elements of the annealing atmosphere are introduced into the phosphor. However, these models were rejected for the following reasons.

Removing zinc oxide on the phosphor surface by etching does not impair life. ESR and thermoluminescence measurements indicate that the trap density (sulfur vacancy density) is not varied by annealing in air. Variations in Cu and Br content and the particle size by annealing in air are small. Various atmospheres are efficient for improving life.

Therefore, the reason for improvement in life by annealing is considered to be not the above facts (i)-(iv), but structural changes in the EL phosphor particles.

Upon annealing, the x-ray diffraction (111) peak intensity decreases, and deterioration activation energy increases from 0.3 to 0.45 eV. Reference (5) reports that the (111) peak intensity of x-ray diffraction is closely related to EL maintenance. Life tends to improve with a decrease in the (111) peak intensity in the case of fractionation, etching, and ball milling. This suggests phosphor crystal quality is closely related to life.

On the other hand, Ref. (10) reports that the deterioration activation energy of unannealed ZnS:Cu, Br phosphors is about 0.3 eV, which is equal to the activation energy of Cu diffusion in ZnS.

From these results, the reason why the annealed phosphor has a long life may be considered to be that the crystal quality is changed by annealing, which prevents Cu diffusion. In addition, it appears that quenching after annealing accelerates the change of phosphor crystal quality.

On the other hand, the reason why air and NH₃ atmospheres are more effective than N₂ or sulfur atmospheres for EL life improvement cannot be explained by the authors.

Summary

Annealing EL phosphor at temperatures from 700° to 1000°C for more than 1 hr in NH₃ or air and quenching was found to be most effective for life improvement. For example, phosphor annealed in air at 900°C for 2 hr had a half-life of more than 3000 hr (initial brightness = 100 nt). Variations in sulfur vacancy density, dopant content, and phosphor particle size by annealing are small, but x-ray diffraction peak intensity was changed, and the activation energy of deterioration was increased from 0.3 to 0.45 eV by annealing. The reason the annealed and quenched phosphor has a long life may be that the crystal quality is changed.

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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

Key words: semiconductor, interfaces, impedance, photoconductivity.

is an important step in the fabrication of many semiconductor devices (1, 2) while corrosion of n-type electrodes constitutes a serious problem in photoelectrochemical solar cells (3). It has been suggested that

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} - $10^{18}/\text{cm}^3$, were obtained from MCP Electronics, England. Mechanochemically polished electrodes with a diameter of 3 mm, were etched at room temperature in H_2SO_4 (98%)/ H_2O_2 (30%)/ H_2O (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 $7.1 \times 10^{-2} (\text{cm}^2)$ 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 H_2SO_4 was used as a measure of the photon density. An intensity N_{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 measurements, which were performed at room temperature. EDTA refers to ethylenediamine tetraacetic acid; its disodium salt, designated Na_2 EDTA, was used in the present work.

Results and Discussion

Film formation: photocurrent results.—The shape of the photocurrent-potential curve of an n-GaAs electrode in 0.1M Na_2 EDTA, 0.1M NaClO_4 solution at pH 5 was similar to that found in NaClO_4 solution without EDTA: in both cases the onset potential for photocurrent flow was -0.8V and the current reached its limiting value at approximately -0.6V . 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_{ph} , measured at $+0.50\text{V}$ in 0.1M Na_2 EDTA, 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_{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

Fig. 1. Photocurrent transients for n-GaAs at $+0.50\text{V}$ (SCE) in 0.1M Na_2 EDTA, 0.1M NaClO_4 , pH 5 at photon densities $N_{\text{ph}} = 0.75$ [curve (a)]; 1.5 [curve (b)]; 2.8 [curve (c)], and 4.9 a.u. [curve (d)].

Fig. 2. Steady-state photocurrent of n-GaAs at $+0.50\text{V}$ (SCE) as a function of photon density (a) 0.1M Na_2 EDTA, 0.1M NaClO_4 , pH 5; (b) as (a) but without Na_2 EDTA; (c) as (a) but with 0.1M Fe^{II} EDTA added.

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^{II} 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 the photocurrent. This explains why the current in the limiting photocurrent range is independent of light intensity and applied potential. On the basis of this constant photocurrent and the time required to dissolve the surface film in the dark, and assuming a molecular weight and density typical of a

Fig. 3. Recovery of the photocurrent after film formation at $+0.50\text{V}$ (SCE). The photocurrent transient was recorded until a steady-state current was attained. The light was switched off and the electrode kept at $+0.50\text{V}$ in the dark for the time shown, before illumination was recommenced ($N_{\text{ph}} = 5 \text{ a.u.}$).

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 ΔV_{FB} , the displacement of the flat-band (FB) potential.

Fig. 4. Mott-Schottky curves (10 kHz) for n-GaAs in 0.1M Na_2EDTA , 0.1M NaClO_4 , pH 5 in the dark (curve a) and with illumination: $N_{\text{ph}} = 0.35$ [curve (b)]; 0.65 [curve (c)]; 2.0 [curve (d)]; and 3.2 a.u. [curve (e)].

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 ($\Delta V_{\text{FB}} \approx 0.22\text{V}$) at higher light intensity.

If the capacitance of the film-covered electrode, measured under illumination, is due mainly to the

Fig. 5. The influence of light ($N_{\text{ph}} = 5$) on the current and impedance (10 kHz) of n-GaAs at $+0.50\text{V}$ (SCE) in 0.1M Na_2EDTA , 0.1M NaClO_4 , pH 5.

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_{sc} 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_{if} 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, $Z_{re} (= R_s)$ and $Z_{im} (= 1/\omega C_s)$, 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_{if} is built up at the GaAs/film interface. The semiconductor band bending is reduced by ΔV_{sc} and a corresponding potential ΔV_{ox} appears over the surface film (dashed lines).

Fig. 6b. Equivalent circuit for an illuminated n-GaAs electrode with surface film.

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_2EDTA , 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 I.

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

$$\frac{1}{Z_{re} - R_e} = (R_L C_{sc}^2) \omega^2 + \frac{(C_{if} + C_{sc})^2}{R_L C_{if}^2} \quad [1]$$

$$\frac{\omega Z_{im}}{Z_{re} - R_e} = \left\{ \frac{R_L C_{sc} (C_{sc} + C_{ox})}{C_{ox}} \right\} \omega^2 + \frac{(C_{if} + C_{sc}) (C_{if} + C_{sc} + C_{ox})}{R_L C_{ox} C_{if}^2} \quad [2]$$

R_e can be obtained from the high frequency limit of Z_{re} in the dark. It follows from these equations that plots of $1/Z_{re} - R_e$ and $\omega Z_{im}/Z_{re} - R_e$ as a function of ω^2 should give straight lines. In Fig. 8, the second of these functions is plotted for a film-covered electrode at a photon density $N_{ph} = 2$ 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 kHz) 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 $C_{ss} \gg C_{sc}$. 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 the gradual increase in C_{sc} 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 with the illuminated MOS device (10). We further note a dependence of R_L on light intensity

Fig. 8. The results shown in curve (d) of Fig. 7 plotted according to Eq. [2], as described in the text.

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

Case	N_{ph} (a.u.)	R_L (k Ω)	C_{sc} (nF)	ΔV_{sc} (= $-\Delta V_{ox}$)
a	dark	≈ 500.0	5.8	—
b	0.35	400.0	6.0	(0.10) ¹
c	1.1	10.8	8.1	0.88
d	2.0	4.8	9.2	1.08
e	3.2	2.7	10.1	1.21
f	5.7	1.6	10.7	1.27
g	11.4	0.8	11.1	1.31

¹ An anodic film is not formed ($\Delta V_{sc} = -\Delta V_H$).

$$R_L \propto N_{ph}^n \quad \text{with } n \approx -1.1$$

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_{sc} 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 values 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} -f 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

$$Q_{sc} + Q_{if} = Q_{ox} \quad [3]$$

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

$$V = V_{sc} + V_{ox} + V_H + V' \quad [4]$$

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 $N_{ph} = 11$ a.u.

V (SCE)	0.00	0.50	1.00
R_L (Ω)	7.6×10^2	7.7×10^2	7.5×10^2
C_{sc} (nF)	11.1	11.1	11.0
C_{ox} (nF)	3.2×10^2	1.9×10^2	1.4×10^2

the potential difference associated with the reference electrode. If V_{FB} is defined as the value of V at which $V_{sc} = V_{ox} = 0$, then V_{FB} is the measured value of V for an extremely thin film at FB condition and

$$V_{ox} = V - V_{FB} - V_{sc} \quad [5]$$

Introducing the linear film capacitance $C_{ox} = Q_{ox}/V_{ox}$ we obtain

$$C_{ox}(V - V_{FB} - V_{sc}) = Q_{sc} + Q_{if} \quad [6]$$

The potential drop across the depletion layer V_{sc} can be calculated from the measured value of C_{sc} (see Table I) via the Mott-Schottky relation (15)

$$C_{sc} = \left(\frac{\epsilon_0 N_D e}{2} \right)^{1/2} \left(V_{sc} - \frac{kT}{e} \right)^{-1/2} \quad [7]$$

in which ϵ 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. Values for the change in band bending ΔV_{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_{if} , stored at the interface, can be calculated. The values of Q_{if}/e range from approximately $5 \times 10^{12}/\text{cm}^2$ to $3 \times 10^{13}/\text{cm}^2$ 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 ($C_{sc} \ll C_H$). Consequently, the change in V_{sc} and Q_{sc} , caused by illumination, can be calculated directly from the measured C_s 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 potential ($\Delta V_H = -\Delta V_{sc}$). In order to obtain the corresponding interface charge density

$$C_H \Delta V_H = \Delta Q_{sc} + Q_{if} \quad [8]$$

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

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 ($i_{ph} \propto N_{ph}$), 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-

not escape to solution at a sufficient rate; and as C_{ox} is considerably smaller than C_H , the surface film can accommodate a more substantial rearrangement of the surface potential ($-\Delta V_{sc} = \Delta V_{ox} \approx Q_{if}/C_{ox}$) for a given value of Q_{if} . We shall return to these points later. Although the interface charge could, in this case, be located in an inversion layer, various indications seem to favor an interface state interpretation here also. The interface charge densities found when a surface film was present are quite similar to those for a film-free electrode at slightly lower intensity. The same intermediate states are expected in both cases. In the latter case, a deep depletion and not an inversion condition is found to prevail. In addition, apparent Fermi level pinning sets in at low values of the band bending [curves (d) and (e) of Fig. 4] at which the surface majority carrier concentration is still very high; this makes an explanation based on inversion unlikely and leads us to conclude that interface states dominate over inversion. On the other hand, inversion is important in determining the capacitance of the illuminated MOS transistor (11, 12). However, the interface state density for the MOS device is reported to be more than two orders of magnitude lower than that indicated in the present work (20). Another significant difference is, of course, that the oxide thickness is not constant in this work but increases with applied potential, even up to high potentials (9).

In the above discussion we have suggested, as other workers have also done (5, 6, 16), that the interface states can act as intermediates in the dissolution reaction. It is therefore of interest to examine the experimental impedance results in terms of the kinetics of the charging of such states, in order to obtain information on the importance of surface charging for the dissolution reaction. Although the light-induced change in V_{sc} , and thus in V_H or V_{ox} as shown in Fig. 6, is expected to be a complex function of minority carrier generation, trapping, recombination, and faraday rates, we can use a simple reaction scheme to illustrate the possible effect of these parameters. This scheme is suggested by analogy with models already described in the literature (3, 4, 18); in the present case, the intermediate is considered to be positively charged

We assume that all holes, generated by light at a rate g in step 1, reach the semiconductor surface where they may be trapped at states S . These states very likely involve surface imperfections such as steps or dislocations. The hole trapping reaction is considered to be reversible. The charged states can be discharged by electrons in step 3. Reaction of a charged intermediate S^+ in step 4 with a second hole and the nucleophilic reagent X^- from solution is followed by the dissolution of a GaAs entity.

Such a scheme can be described by the following equations (19)

$$\frac{dp_s}{dt} = g - k_p p_s N (1 - f) + k_r N f - k_f p_s N f \quad [9]$$

$$N \frac{df}{dt} = k_p p_s N (1 - f) - k_r N f - k_f p_s N f - k_n n_s N f \quad [10]$$

$$n_s = n_o \exp(-eV_{sc}/kT) \quad [11]$$

in which n_s and p_s are the surface concentrations of electrons and holes, n_o 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

$$V_{sc} = V - V_{FB} - \Delta V_H \quad [12a]$$

with

$$\Delta V_H \approx eNf/C_H \quad (\Delta Q_{sc} < Q_{if}) \quad [12b]$$

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

$$\Delta V_H = (V - V_{FB}) + \frac{kT}{e} \ln \left(\frac{g - j_F}{k_n n_o N f} \right) \quad [13]$$

For a chosen value of f , ΔV_H can be calculated from Eq. [12b], and the faraday flux j_F ($= 2k_p p_s N f$) can be obtained using p_s from Eq. [9]. Inserting these values into Eq. [13], we obtain the corresponding value of $V - V_{FB}$. In this way, ΔV_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

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{\epsilon \epsilon_0 N_D e} \right) \left(V - V_{FB} - \frac{eNf}{C_H} - \frac{kT}{e} \right) \quad [14]$$

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, ΔV_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 $V - V_{fb}$ [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 ($eNf/C_H \approx 0$ in Eq. [14]). In previous work (4), we found this to be essentially the case for photoanodic dissolution of n-GaAs in H_2SO_4 solution.

Fig. 9. Calculated band bending V_{sc} as a function of applied potential $V - V_{FB}$. $n_o = 10^{17}/\text{cm}^3$, $N = 5 \times 10^{13}/\text{cm}^2$, $k_p = 10^{-7} \text{ cm}^3/\text{sec}$, $k_n = 10^{-9} \text{ cm}^3/\text{sec}$, $k_f = 10^{-9} \text{ cm}^3/\text{sec}$, $k_r = 10^4/\text{sec}$. Curve (a) refers to electrode in the dark or at very low light intensity. Curves (b), (d), (e): $g = 10^{15}/\text{cm}^2 \text{ sec}$; curve (c): $g = 5 \times 10^{15}/\text{cm}^2 \text{ sec}$. Curves (b), (c): $C_H = 20 \mu\text{F}/\text{cm}^2$; curve (d): $C_H = 3.5 \mu\text{F}/\text{cm}^2$. For curve (e), see the text.

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 ($> 10^{13}/\text{cm}^2$ 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_H 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 ΔV_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. 4) 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 and the film capacitance decreases. This tends to accentuate the effect shown in curve (d), and the apparent pinning of 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_{ox} ($d_{ox} = \alpha V_{ox}$ with $\alpha = 2.5 \text{ nm/V}$). This allows us to calculate Q_{ox} , and by taking this value to be (approximately) equal to (eNf) , f can be calculated and consequently, V_{sc} . The constant value of V_{sc} suggested in curve (e) implies a C_{sc} value which is independent of applied potential.

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 EOS 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, which is very likely responsible for the fast changes in C_s and R_s when the light is switched off, may give information on the nature of the surface states. The simple reaction scheme, proposed here, emphasizes again the importance of surface charge trapping (4) and recombination (18) for the kinetics of photoanodic reactions,

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 H_2SO_4 solution might be due to a higher oxide solubility at low pH. We have seen 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 (8, 13).

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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 ($^3\text{P}_{2,1}$ O and $^1\Delta$ O₂) 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 photoresist (0.5 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 $^1\Delta$ 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 an 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-

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