

Hole Injection and Etching Studies of GaAs Using the Scanning Electrochemical Microscope

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Received March 2, 1990. In Final Form: April 13, 1990

A scanning electrochemical microscope (SECM) was used as an analytical tool to study the etching of GaAs surfaces. Hole injection from several electrogenerated oxidants to n-type, p-type, and undoped GaAs was examined by the feedback mode of the SECM. Assignment of the process as a hole injection from the oxidized form of the redox couple into the valence band and assignment of the energy of the valence band edge in the semiconductor were made by studying the behavior of the feedback current at various pHs and with different redox couples. The nature of the dopant strongly affected the etching process. n-GaAs and undoped GaAs were etched by using the feedback mode while p-GaAs was completely resistive toward etching. The differences between n-GaAs and p-GaAs are explained in terms of semiconductor-electrolyte interactions.

Introduction

A scanning electrochemical microscope (SECM) was used in this study to modify, i.e., to etch, a semiconductor as well as to analyze semiconductor surface processes. The motivation for this research is mainly to demonstrate that the SECM can be applied not only as an imaging and a modifying technique, *vide infra*, but also as an analytical tool to study surfaces. We show that this method, because of its unique properties as a micromodifying technique, reveals etching selectivity between n-type and p-type GaAs.

Semiconductor-electrolyte interactions have been intensively studied¹⁻³ because of their importance in photoelectrochemical systems. An understanding of the processes involved in charge transfer between electroactive species and semiconductors is needed to design efficient heterogeneous photochemical devices as well as to improve their stabilization against degradation. In addition to numerous experimental results, the theory of charge transfer at the semiconductor/electrolyte interface has been developed.⁴⁻⁶ The theory bridges solid-state physics and electrochemistry and is based on charge transfer between the bands of the solid and the orbitals of electrolyte species, as described by electron-transfer theory. Hole injection from the oxidized form of a redox couple into the valence band of a semiconductor is one of these charge-transfer processes and is of particular interest as being the primary step associated with etching (decomposition) of the semiconductor. Hole injection has been the subject of many publications⁷⁻⁹ and has been studied by electrochemical and photochemical techniques,

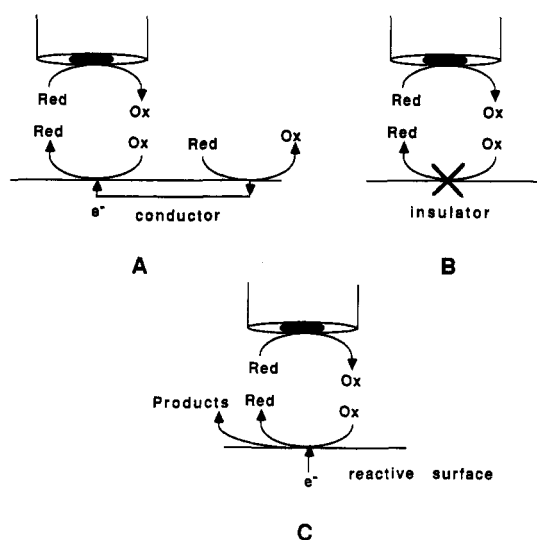


Figure 1. Scheme of the principles of the feedback mode: (A) approaching a conductor; (B) approaching an insulator; (C) approaching a reactive surface.

such as rotating disk electrode voltammetry and electroluminescence. These studies led to a better understanding of the hole injection process and subsequent etching process and at the same time contributed to our model of the semiconductor/electrolyte interface.

Among a variety of semiconductors, gallium arsenide has been extensively used as a substrate for these studies,^{8,9} because of its small band gap and its relative low (less positive) energy of the valence band edge, which makes it suitable for study in aqueous solutions.

Recently, we demonstrated¹⁰ that the scanning electrochemical microscope (SECM) can be successfully applied to the high-resolution etching of semiconductors like GaAs. In an SECM experiments (Figure 1), an oxidized species (Ox) is generated electrochemically from a solution containing only the reduced form of the redox couple (Red) at an ultramicroelectrode (UME) that is held very close (of the order of the electrode diameter) to an unbiased surface. The oxidized species diffuses to the surface where it transfers a hole to the unbiased surface. This results in two effects—an electrochemical reaction takes place at a very localized spot on the surface, and the

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reduced form of the redox couple is regenerated. Due to the regeneration of Red at the surface, an enhancement of the current at the UME is observed compared to the current when the electrode is far from the substrate; i.e., a positive feedback current results. Since the increase in the current depends on the distance of the UME from the surface, the magnitude of the steady-state current at the UME can be employed to determine and control the UME-surface distance.

The SECM has been used in this feedback mode for high-resolution metal deposition¹¹ and high-resolution etching of metals¹² and semiconductors.¹⁰ In addition, the SECM has been used by this laboratory to image a variety of surfaces¹³ including conductors, insulators, and biological samples.¹⁴ We report here the utilization of the SECM as an analytical tool to study semiconductor-electrolyte surface processes. Hole injection, etching, and oxide layer growth were examined with different types of GaAs by using the SECM. The results obtained show that SECM can be utilized not only to probe reactions at the semiconductor/electrolyte interface but also to accomplish selective etching.

Experimental Section

The SECM has been described in detail previously.^{13,15} The Teflon cell contained a Pt counter electrode, a saturated calomel reference electrode (SCE), and the substrate that was attached to the cell bottom. The UME was mounted on the z-piezoelectric inchworm while the cell was attached to the x-y stage. A Model 173 potentiostat and a Model 175 programmer (Princeton Applied Research, Princeton, NJ) were used to bias and to program the UME. The profiles of the etching patterns were determined with an Alpha-step 200 profilometer (Tencor Instruments, Mountain View, CA), and the electron micrographs were taken with a scanning electron microscope (SEM, JEOL, JSM-35C).

Undoped GaAs was obtained from Texas Instruments. n-GaAs (silicon doped, $1.6 \times 10^{18} \text{ cm}^{-3}$) and p-GaAs (zinc doped, $1 \times 10^{19} \text{ cm}^{-3}$) were purchased from Litton (Morris Plains, NJ) while p-GaAs (zinc doped, $9.8 \times 10^{17} \text{ cm}^{-3}$) was obtained from Crystal Specialties (Colorado Springs, CO). Several epitaxially grown (1 μm) p-GaAs (zinc doped, 3×10^{17} – $1 \times 10^{19} \text{ cm}^{-3}$) over undoped GaAs were generously provided by Prof. B. Streetman.

Tris(1,10-phenanthroline)iron(II) chloride, $\text{Fe}(\text{phen})_3\text{Cl}_2$, was prepared by dissolving stoichiometric amounts of ferrous sulfate and 1,10-phenanthroline in water. Excess sodium chloride was added to precipitate the product, which was further washed with small amounts of water and recrystallized from hot water. Tris(4,4'-bipyridine)cobalt(II) chloride, $\text{Co}(\text{bpy})_3\text{Cl}_2$, was instantaneously formed upon mixing stoichiometric solutions of cobalt chloride hexahydrate and 4,4'-bipyridine in acetone. The product was washed with acetone and dried under vacuum before use. Hexammineruthenium(II) dichloride, $\text{Ru}(\text{NH}_3)_6\text{Cl}_2$, was purchased from Alfa Products (Danvers, MA). Milli-Q reagent water (Millipore) was used for preparing the aqueous solutions.

Platinum (25- or 50- μm diameter) UMEs sealed in a glass capillary were fabricated as described previously.¹⁵ The GaAs substrates were pretreated in an etching solution (8:1:1 H_2SO_4 : H_2O : H_2O_2) for 10 min and then rinsed with water before use. The aqueous solutions used in the SECM cell consisted of 1–10 mM redox couple and 0.1 M electrolyte (either KOH, HCl, or potassium phosphate buffer (pH 2.0–12.0)). Since several experiments conducted in complete darkness showed no differ-

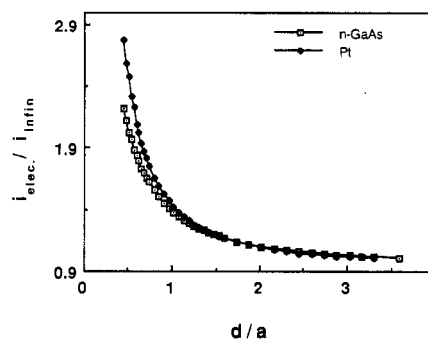


Figure 2. Normalized feedback current vs the normalized distance (d , distance, a , UME radius) upon approach of a platinum electrode to an n-GaAs surface in a 5.4 mM $\text{Fe}(\text{phen})_3^{2+}$, 0.1 M HCl solution. Tip potential +1.0 V vs SCE.

ence with those carried out under dim illumination, all the experiments described here were carried out under dim light.

In a typical experiment, the UME was brought close ($\sim 0.5 \text{ mm}$) to a surface of GaAs, and then the buffer solution containing the redox couple was added. The current was recorded as a function of time while the UME approached the surface (at a speed of 1.3 or 2.3 $\mu\text{m/s}$), and the results were used to generate a current-distance curve.¹⁶ In an etching experiment, the UME was left biased at a constant distance above the surface, and the current as a function of time was recorded and integrated to yield the charge that passed through the UME. Oxide layer growth measurements were performed as follows. The UME was brought to a certain distance from the surface, and then the potential was turned off and the UME was backed slightly away from the surface before moving it to another spot. Finally, the UME was brought to the same distance prior to performing the chronoamperometric experiments.

Results

Etching of n-Type GaAs with $\text{Fe}(\text{phen})_3^{3+}$. When the SECM is operated in the feedback mode, the steady-state current of the UME is examined as it approaches an unbiased surface. The steady-state current of a disk UME, i_∞ , when the electrode is far from the surface, is given by

$$i_\infty = 4nFDCr \quad (1)$$

where n is the number of electrons transferred per molecule, F is the Faraday constant, D is the diffusion coefficient of the electroactive species, C is its concentration, and r is the UME radius.

However, this relation does not hold when the UME approaches a surface. Figure 2 shows the behavior of the steady-state current when a 25- μm -radius UME biased at 1.0 V vs SCE in a 5.4 mM $\text{Fe}(\text{phen})_3^{2+}$, 0.1 M HCl solution approached an n-GaAs surface. The current increased because of regeneration of the reduced form of the redox couple, $\text{Fe}(\text{phen})_3^{2+}$ at the n-GaAs surface so that a positive feedback current was observed. The theory for the feedback current has been established for only two extreme cases.¹⁶ One is for a conductive substrate, where complete regeneration takes place on the surface, and the other is for an insulator, where no electron transfer occurs between the redox couple and the surface (Figure 1A,B). A detailed examination of the feedback current with n-GaAs shows that it essentially exhibits conductive properties, when $\text{Fe}(\text{phen})_3^{2+/3+}$ is used as a redox couple (Figure 2). This implies that electron transfer from the n-GaAs to $\text{Fe}(\text{phen})_3^{3+}$, which is equivalent to hole injection into the semiconductor, is very fast. When the UME was biased at 1.0 V and held for several minutes close (within several microns) to the surface, a positive feedback current was

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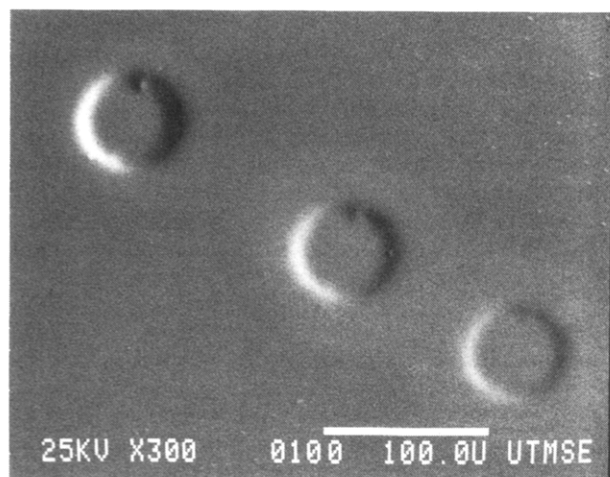
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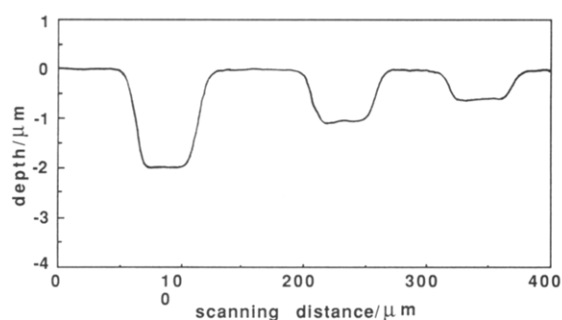
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A



B

Figure 3. SEM picture (A) and the profile (B) of n-GaAs etched for 5, 10 and 20 min with a 50- μm Pt UME held approximately 10 μm above the surface, in 5.4 mM $\text{Fe}(\text{phen})_3^{2+}$, 0.1 M HCl at a potential of 1.0 V vs SCE.

maintained, and an etching spot was formed (Figure 3). The parameters that affect the profile of the etching pattern have been described in our previous report¹⁰ and include the distance between the UME and the surface, the charge that passes through the UME, and the chemistry involved in the different steps of the etching process.

Undoped and p-Type GaAs with $\text{Fe}(\text{phen})_3^{3+}$. To determine the effect of doping on the electron-transfer reaction, undoped and p-GaAs were also studied. In both cases, the feedback current behavior was similar to that found with n-GaAs. Furthermore, increasing the concentration of $\text{Fe}(\text{phen})_3^{2+}$ up to 0.2 M did not show any deviation from the conductor response with p-GaAs. This suggests that the electrons transferred to the oxidized form of the redox couple originated in the GaAs valence band. This conclusion is also in accordance with semiconductor electrode theory, as discussed below. A better overlap is expected between the energy levels of the oxidized (+3) species in solution and the valence band; this overlap increases the probability of efficient charge transfer.

However, while etching always followed the observation of positive feedback current in n-type and undoped GaAs, p-GaAs was not etched at all, despite the appearance of a positive feedback current. Even when $\text{Fe}(\text{phen})_3^{3+}$ was generated at the UME as it was held several microns above the p-GaAs surface for 1 h ($\sim 10^{-4}$ – 10^{-3} C passed through the UME), no changes of the p-GaAs surface were detected. Thus, although holes are efficiently injected into the valence band of p-GaAs, surface etching does not occur. The level of doping did not affect these findings. p-GaAs

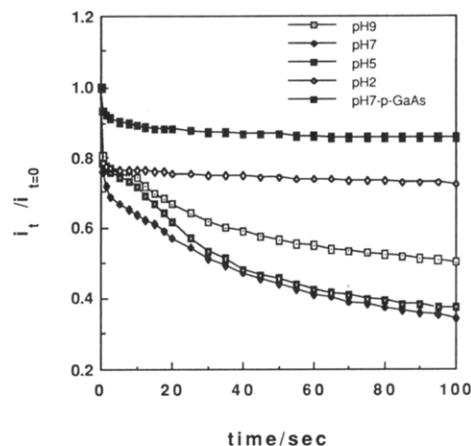
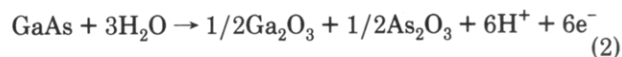


Figure 4. Chronoamperometric measurements made over n-GaAs with a 50- μm Pt UME ($E = 0.95$ V vs SCE) left 8 μm above the surface in a 5 mM $\text{Fe}(\text{phen})_3^{2+}$ /50 mM phosphate buffer solution.

was not etched when the level of doping was varied from 3×10^{17} to 1×10^{19} cm^{-3} . The resistance of p-GaAs toward etching was also confirmed by the fact that the positive feedback current was very stable as compared to that of n-GaAs. With the latter, the positive feedback current consistently decreased as a function of time, when the UME was held close to the surface. This decrease is presumably due to morphological changes of the n-GaAs surface that affect the flux of the regenerated species rather than to an increase of the UME–surface distance because of the etching.

Effect of pH. Changes in the magnitude of the positive feedback current were found, when the hole injection process was carried out at different pH values. Oxidation of GaAs must follow hole injection to result in GaAs etching. GaAs is oxidized to form Ga_2O_3 and As_2O_3 (eq 2) or other insoluble products which are electrochemically inactive. These oxides dissolve in either acidic or basic solutions (eq 3),¹⁷ but the dissolution of oxidized GaAs does not occur at neutral pH¹⁸



Oxide layer formation was followed with the SECM by studying the changes in the steady-state current with the UME close to the surface of n-GaAs. Note that in absence of changes in the surface of the substrate the UME current rapidly attained a constant steady-state current, while the steady-state current decreased upon formation of an oxide layer. In other words, the behavior of n-GaAs changed from conductive to insulating as the oxide layer thickened. In a series of experiments, the decrease in the feedback current as a function of time and pH was examined. From these measurements, we conclude that the rate of the oxide layer formation is highest near pH 7 (Figure 4). On the other hand, the steady-state current with p-GaAs was not affected by a change in pH (Figure 4). The current did not decrease as a function of time even at pH 7, indicating that although holes are injected efficiently into p-GaAs they do not lead to oxidation of the surface with the formation of a blocking oxide layer.

Effect of Different Etchants. A number of other one-electron redox couples were applied as etchants using the

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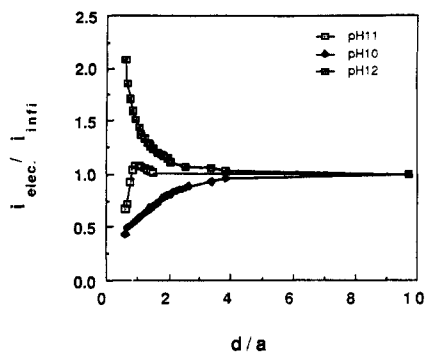


Figure 5. Feedback current of a 50- μm Pt UME in a 10 mM $\text{Ru}(\text{NH}_3)_6^{2+}/0.45$ M phosphate buffer upon approach to a n-GaAs surface at different pH values.

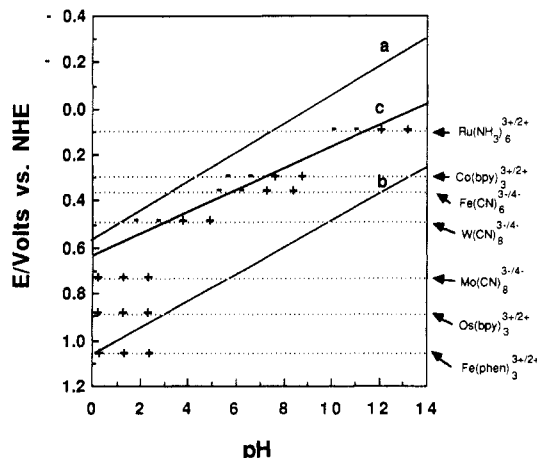


Figure 6. Magnitude of the feedback current for oxidation processes at the tip with various redox couples at different pH values with n-GaAs substrate. The dotted lines represent the redox potential of the different couples: (+) positive feedback current and etching, (-) insulating behavior and no etching. (a) The valence band edge according to Gomes and Cardon.¹⁹ (b) The valence band edge reported by Memming.²⁰ (c) Experimental results obtained in this study.

same approach, where the oxidized form of the redox couple was generated at an UME and diffused to the GaAs surface. When a positive feedback current was detected, the electrode was held within a few microns of the surface for a longer time (typically 5–20 min). The results obtained with all couples were the same as those found with $\text{Fe}(\text{phen})_3^{3+/2+}$: a positive feedback current with n-GaAs or undoped GaAs always resulted in etching, whereas p-GaAs showed positive feedback, but the surface did not reveal any noticeable change.

Interesting results were obtained when the feedback current was examined with different redox couples at different pHs. For instance, when $\text{Ru}(\text{NH}_3)_6^{2+}$ ($E^{\circ'} = -0.14$ V vs SCE) was oxidized at the UME at pH 12, a positive feedback was detected, indicating that holes were injected into the n-GaAs. At pH 11, the feedback current deviated from ideal conductor behavior, although a slight positive response was still observed. Decreasing the pH to 10 caused behavior characteristic of an insulator (Figure 5). In other words, decreasing the pH gradually slowed the rate of hole injection into n-GaAs. Similar experiments were carried out with the other redox couples, which spanned a range of $E^{\circ'}$ values of +0.10 to +1.06 V vs NHE. Figure 6 summarizes the changes of the feedback current as a function of pH for various redox couples. For each couple at a given pH, a plus sign indicates that etching was observed and a minus sign indicates insulating behavior and no etching. Note that the redox potential of the

couples used were independent of pH. A straight line with a slope of ~ 50 mV/pH was obtained through the points, where the feedback current changed from conductive to insulating behavior. This line represents the threshold potential for hole injection into the valence band of n-GaAs at a given pH and can be assigned as the energy of the upper edge of the valence band. Indeed, the experimental values of the valence band are in good agreement with the values reported by Gomes and Cardon¹⁹ but are shifted by 0.3–0.4 eV from those reported by Memming.²⁰

With the $\text{Fe}(\text{CN})_6^{4-/3-}$ couple, there was some deviation from the line (Figure 6). This can be understood in terms of oxide film formation at pH 7. Although the concentration of the couple was low (2 mM) to avoid immediate blocking upon formation of an oxide layer, the feedback current decreased almost instantaneously when the biased UME approached the surface of n-GaAs at a pH < 6. Similar behavior with a line at about the same location was found for the same experiment carried out with undoped GaAs. Similar experiments with p-GaAs, however, gave different results. A continuous positive feedback current was observed, even for couples with less positive standard potentials at lower pH values. For example, $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ showed a positive feedback current down to pH 8 and $\text{Fe}(\text{CN})_6^{4-/3-}$ to pH 3; a negative feedback current was obtained with p-GaAs but at more acidic pHs. In other words, an efficient hole injection occurs from an oxidant like $\text{Ru}(\text{NH}_3)_6^{3+}$ to p-GaAs at pHs where no hole injection is detected with n-GaAs. As with $\text{Fe}(\text{phen})_3^{3+/2+}$, no etching of p-GaAs accompanied this positive feedback current with these couples. However, when a piece of p-GaAs was immersed in a solution containing the oxidized form of the redox couple, e.g., $\text{Fe}(\text{CN})_6^{3-}$ in alkaline solution, etching of the surface was clearly observed. Thus, very different behavior is found with p-GaAs, when the oxidant, $\text{Fe}(\text{CN})_6^{3-}$, is generated locally and most of the p-GaAs is in contact with the reduced form, $\text{Fe}(\text{CN})_6^{4-}$, than when the whole piece is in contact with oxidant.

Only when bromine was electrogenerated at the UME (from 0.1 M HCl containing 10 mM bromide) was p-GaAs etched. Even in this case, the rate of etching of p-GaAs was 3–5 times slower than that of n-GaAs. For example, passage of 4×10^{-5} C through a 50- μm -diameter Pt UME caused the formation of a 2- μm -deep etched pit in n-GaAs, while the same charge resulted in a 0.8- μm -deep pit in p-GaAs. The mechanism for etching of III-V and II-VI semiconductors by bromine is not completely understood. The dissolution of these semiconductors by bromine has been attributed to chemical decomposition rather than to hole injection.²¹ Since a positive feedback current was observed when the electrode (biased at 1.0 V vs SCE) approached a GaAs surface in 10 mM HBr/0.1 M HCl, we believe that the first step does involve regeneration of Br^- from Br_2 , probably via the valence band by bromine.²² However, the steps that follow differ from a typical one-electron redox couple. At this stage, we cannot tell whether bromide ion participates in the dissolution of the surface or bromine itself traps the holes causing the p-GaAs to be etched.

Discussion

To explain the observed behavior, it is necessary to account for the following observations: (1) n-GaAs and

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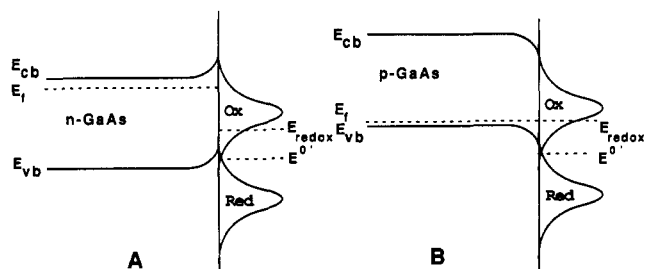


Figure 7. Energy scheme of n-GaAs (A) and p-GaAs (B) immersed in a solution containing the reduced form of a redox couple. E_{cb} , E_{vb} , and E_f refer to the energy of the conduction band, the valence band, and the Fermi level, respectively. E° is the formal potential of the redox couple, and E_{redox} is the initial potential of the solution.

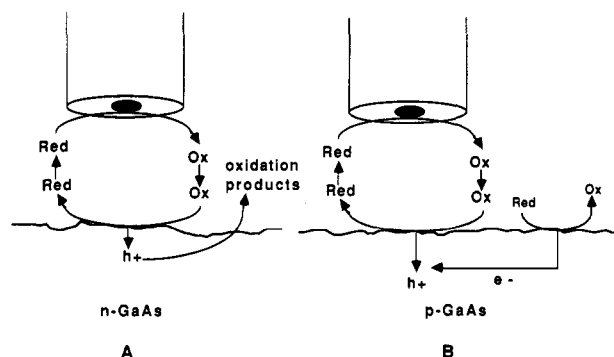


Figure 8. Schematic representation for (A) n-GaAs and (B) p-GaAs etching using the SECM.

undoped GaAs are etched with localized generation of $1 e^-$ oxidants at given pHs, while p-GaAs is not. (2) Even though it is not etched, p-GaAs shows a positive feedback current. (3) p-GaAs is etched by complete immersion in solutions of the same $1 e^-$ oxidants. (4) The effect of pH on the etching of n- and undoped GaAs correlates with previous reports of the energy of the valence band edge of the GaAs. These results can be explained by the energy level diagram shown in Figure 7, which is based on GaAs behavior in which the Fermi level is unpinned and adjusts to the solution Fermi level. Since the initial solution contains only the reduced form of the redox couple, the solution Fermi level initially lies above (negative of) E° . However, localized generation of oxidant moves the local solution Fermi level down (to a more positive potential) and causes injection of a hole into the valence band. The Fermi level at the GaAs surface at this location will move down (toward more positive potentials); the extent of movement depends upon the instantaneous concentration of injected holes. At points on the GaAs surface away from this location, no changes in the semiconductor Fermi level occur. For n-GaAs or undoped GaAs, the bands are bent downward (i.e., the electric field in the space charge region points from the bulk toward the semiconductor surface), so that holes remain at the electrode/solution interface where etching occurs (Figure 8A). At a p-GaAs type semiconductor, the band bending is in the opposite direction, so that holes injected at the surface move into the bulk semiconductor. When oxidant is generated locally, the holes can move away from this location to positions on the surface where they can react with reduced form (i.e., the potential on most of the surface is determined by the reduced form) (Figure 8B). This removal of holes from beneath the tip location must be very rapid on p-GaAs since no etching is observed. Thus, although positive feedback current is seen, etching does not occur. This behavior is different than that found for immersion of the

whole piece of p-GaAs in solution of oxidant, where holes can accumulate at the surface.

This model can also account for the relatively high resolution observed in etching n-GaAs. Injection of holes into n-GaAs tends to compensate for the conduction band electrons and makes the material at the surface more p-type and thus more resistive. This tends to prevent hole migration away from this location and "focuses" the etching beneath the tip. On the contrary, hole injection into p-type material increases the conductivity and promotes hole movement away from the surface.

The variation of feedback current and etching with redox couple and pH can similarly be understood in terms of the location of the valence band edge. Changing the pH results in a shift of the flat band potential for many semiconductors, such as metal oxides and sulfides.²³ These changes are attributed to proton-transfer equilibria on the surface (i.e., protonation of basic sites and deprotonation of acidic sites), which affect the potential drop across the Helmholtz layer. Hence, changing the pH may not affect the sign of the space charge potential, but shifts the band edges. Moreover, we assume that changing the redox couple without changing the pH does not affect the band edges (the redox concentration was kept low relative to the buffer); i.e., the Fermi level is not pinned. In fact, this assumption was confirmed by a set of experiments in which the rate of etching was studied with different redox couples at the same pH. We found that the rate of etching of n-GaAs was independent of the redox potential at a pH where a significant positive feedback current was observed. For example, the same etching profiles were measured with the following oxidants: $Fe(phen)_3^{3+}$ and $Mo(CN)_6^{3-}$ at pH 1 and $Ru(NH_3)_6^{3+}$ and $Fe(CN)_6^{3-}$ at pH 14. These results suggest that the Fermi level is indeed not pinned. Therefore, the changes in the feedback current when varying the pH must have been due to changes in the overlap between the energy states of the oxidized redox species and the valence band (Figure 7). Decreasing this overlap affected the rate of hole injection, as expressed by the feedback current. We might note that GaAs sometimes displays Fermi level pinning (FLP), where the Fermi level position is controlled by a high density of surface states which then equilibrate with the solution redox level.²⁴ Under these conditions, the band edges can move with the E° of the redox couple. While this FLP model can accommodate the results with a single couple, e.g., $Fe(phen)_3^{3+/2+}$, it appears to be inconsistent with the observed correlation of the E° -pH line of Figure 6.

Conclusions

We have demonstrated that SECM can be utilized to study semiconductor surfaces. The feedback current in a SECM experiment provides valuable information regarding the primary charge transfer from a redox couple to the semiconductor. Information about subsequent steps can be obtained by following the feedback current as a function of time while holding the UME at a constant distance near the surface and by measuring the etching profiles. The results, interpreted according to the model of the semiconductor/electrolyte interface, yield the following conclusions: (a) The primary charge transfer from the oxidant to the semiconductor is assigned to be a hole injection into the valence band of GaAs. (b) A threshold

(23) See, for example: (a) Bolts, J. M.; Wrighton, M. S. *J. Phys. Chem.* 1976, 80, 2641. (b) Ginley, D. S.; Butler, M. A. *J. Electrochem. Soc.* 1978, 125, 228. (c) Lohmann, F. *Ber. Bunsen-Ges. Phys., Chem.* 1966, 70, 428. (d) Laflere, W. H.; Cardon, F.; Gomes, W. P. *Surf. Sci.* 1974, 44, 541.

(24) Fan, F.-R.; Bard, A. J. *J. Am. Chem. Soc.* 1980, 102, 3677.

potential for hole injection as a function of pH can be associated with the energy of the valence band edge. (c) Growth of an oxide layer on n-GaAs is pH dependent and prevents further hole injection. (d) Selective etching can be achieved with the SECM in this mode.

Another interesting aspect of this work pertains to the concept of how reactivity of a material can be determined by trace impurity (doping) levels. For example, ppm levels of Zn in GaAs prevented localized etching, because p-type material is produced. Thus, in considering chemical

behavior, the overall electronic properties of the material in addition to its specific chemical properties must be taken into account.

Acknowledgment. The support of this research by a Chaim Weizmann Fellowship to D. Mandler and grants from the Texas Advanced Research Program and the National Science Foundation (CHE 8805685) are gratefully acknowledged. We appreciate helpful comments on this work by Professor Heinz Gerischer.