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Electroless Etching of ZnSe in Aqueous Ferricyanide Solutions

An Electrochemical Study

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ABSTRACT

Using electrochemical and *in situ* luminescence measurements we show that ferricyanide ions are reduced at n-type ZnSe electrodes by hole injection into the valence band of the semiconductor. At negative potentials the holes recombine with electrons and electroluminescence is observed. At the open-circuit potential, the injected holes are used for the oxidation and dissolution of the semiconductor. This electroless etching reaction is under mixed diffusion/kinetic control at 20°C, but becomes diffusion controlled at higher temperature.

Introduction

With the current interest in optoelectronic devices based on the zinc chalcogenides, including blue-emitting lasers,^{1,2} a need has arisen for a range of etchants for various applications of these materials. While wet etching of III-V semiconductors has been extensively studied, II-VI materials have received much less attention. One can distinguish two modes of etching at the open-circuit potential: chemical and electroless.³ Chemical etching is based on a localized exchange of electrons between surface bonds and the etching agent in solution, resulting in the dissolution of surface atoms. Since no free charge carriers are involved in this process, the rate of chemical etching is not dependent on potential. Typical chemical etching agents for III-V semiconductors include two-electron oxidizing agents such as the halogens (Br₂, Cl₂, I₂), H₂O₂, and hypochlorite.⁴ De Wit and Kelly have shown that CdS is also etched chemically in aqueous Br₂ solution⁵ while hypochlorite is an interesting chemical etching agent for ZnSe.⁶ Electroless etching requires an oxidizing agent capable of being reduced by hole injection into the valence band of the semiconductor.⁷ The holes are used for the oxidation and dissolution of the solid. At the open-circuit potential (U_{oc}), the rates of these two electrochemical reactions are equal. However, since etching involves free charge carriers (holes), the anodic etch rate can be changed by an externally applied potential. Electroless etching of III-V semiconductors has been reviewed by a number of authors.^{4,8,9} Of the II-VI materials only CdTe has been studied in detail. Iranzo Marin *et al.* have investigated the etching of CdTe in acidic Ce⁴⁺ solutions.¹⁰ In this article we consider the electroless etching of ZnSe.

In early work on ZnSe¹¹ Williams performed capacitance, photovoltage, and photocurrent measurements in 1 M HCl solution and found results typical of a wide band-gap n-type semiconductor. Photoanodic etching was observed at positive potentials. The position of the valence bandedge of the semiconductor is important for the choice of oxidizing agent for an electroless etchant. Impedance measurements by Wang *et al.*¹² show the flatband potential of n-ZnSe to be -2.5 V vs. the standard calomel electrode (SCE) at pH 14. This would place the valence bandedge at about 0.1 eV below the redox energy of the SCE. Oxidizing agents with a redox potential more positive than this value could inject holes into the valence band. Simple redox systems are generally preferable and a possible choice is ferricyanide (Fe(CN)₆³⁻); Lemasson and Gautron¹³ have shown that Fe(CN)₆³⁻ is cathodically reduced at n-ZnSe at pH 14, and they suggested a hole injection mechanism

If the bandedges of ZnSe shift in the usual manner as a function of pH¹⁴ then Ce⁴⁺ is a candidate for an acidic etchant.

* Electrochemical Society Active Member.

The oxidation of ZnSe either under anodic conditions¹² or by an oxidizing agent such as H₂O₂¹⁵ invariably leads to formation of a solid layer of selenium on the surface. This blocks the surface and suppresses the etching reaction.¹⁶ Wallace *et al.*¹⁷ show that sulfite can be used to remove Se

Alternatively, CN⁻ ions can complex Se

The use of such complexing agents introduces further restrictions. They can only be applied at neutral or high pH (especially in the case of CN⁻) and in combination with relatively weak oxidizing agents; otherwise, the complexing agent is itself oxidized. Considering these various requirements we decided that the alkaline ferricyanide system with excess cyanide might prove an interesting etchant for ZnSe. Since electroless etching involves two electrochemical reactions, cathodic reduction of the oxidizing agent and anodic oxidation of the semiconductor, it was logical to use electrochemical methods to study the mechanism.

The cathodic reduction of Fe(CN)₆³⁻ at n-ZnSe was studied at various pH values by cyclic voltammetry using a rotating disk electrode (RDE). To determine whether holes were being injected during the reduction reaction, light emission from the electrode was measured; holes recombining radiatively with the majority carriers, give rise to electroluminescence. Smiley *et al.* have observed electroluminescence when peroxydisulfate is cathodically reduced at n-ZnSe.¹⁸ Rotating ring-disk electrode (RRDE) measurements were used to follow the formation of the reduced component, Fe(CN)₆⁴⁻; this is useful for electroless etching conditions when the total current passing through the electrode is zero. The results of the RRDE measurements were compared with the results of etching experiments. Finally, impedance measurements served to locate the position of the valence bandedge of the semiconductor in the various solutions.

Alkaline Fe(CN)₆³⁻ solutions have been widely used for electroless etching of both metals and semiconductors.^{19,20}

Experimental

High resistivity ZnSe wafers cut from a single crystal, about 1 mm thick, were heated at 800°C in a reducing atmosphere (H₂/N₂ 1:3) enriched with Zn vapor. A donor density of about 10¹⁶ cm⁻³ was achieved in this manner. An ohmic contact was made by soldering In on the sample at 300°C in a reducing atmosphere (H₂/N₂ 1:3). The surface area of the disk electrode exposed to the electrolyte was 0.13 cm². The ring-disk electrodes had a ZnSe disk and a Pt ring. The experimentally determined collection efficiency was 30%. Before use, the electrodes were etched in a 2% Br₂/methanol solution.

The electrochemical cell contained the working electrode, a Radiometer SCE as reference and a large area platinum counterelectrode. All potentials are referred to

SCE. The electrochemical measurements were carried out with a Wenking POS73 potentiostat. For the ring-disk electrode experiments an EG&G PAR 366A bipotentiostat was used and for the electrical impedance measurements an EG&G PAR 273A electrochemical interface together with a Solartron SI 1255 frequency response analyzer. The electroluminescence was detected with a Perkin-Elmer MPF44B fluorescence spectrophotometer together with a Tektronix TDS 240 digitizing oscilloscope. The etch depth was determined using a Tencor Alpha-Step 500 surface profiler.

The electrolyte solutions contained reagent grade chemicals dissolved in distilled water. Unless otherwise stated, the measurements were performed at room temperature (about 20°C).

Results

Cyclic voltammetry.—In Fig. 1 the current density-potential ($j-U$) curve is shown for an n-ZnSe electrode in a solution containing $10^{-2} M K_3Fe(CN)_6$ of pH 14. The onset of the cathodic current is at $-1.5 V$. A current plateau is reached at $-1.9 V$. Since the plateau is not observed in $Fe(CN)_6^{3-}$ -free solution, the current can be attributed to the reduction of the oxidizing agent. A plot of the limiting current *vs.* the square root of the rotation rate of the electrode yielded a straight line which, when extrapolated, passed through the origin (see inset of Fig. 1). This shows that the cathodic reduction of $Fe(CN)_6^{3-}$ is, in this case, diffusion controlled. The diffusion coefficient calculated from these results was $8 \times 10^{-6} cm^2/s$, which is in reasonable agreement with the literature value.²¹ At more negative potentials the cathodic current increases again with an onset at $-2.2 V$. This is due to hydrogen evolution. A slight hysteresis in the current-potential curve is observed on the return scan (not shown) to positive potential.

Figure 2 shows results for n-ZnSe in a $10^{-2} M Fe(CN)_6^{3-}$ solution of pH 6. A plateau is not observed in the current-potential curve for the scan to negative potential. Instead, the current begins to increase strongly at $-1.7 V$ and hydrogen is evolved. A plateau appears in the return sweep and the limiting current, which is similar to that of the measurements in alkaline electrolyte (Fig. 1), is again directly proportional to the electrode rotation rate. Obviously, $Fe(CN)_6^{3-}$ is not reduced before the onset of hydrogen evolution in the scan to negative potential. Severe hysteresis is obvious in the current-potential curve.

Electroluminescence.—Light emission could be observed visually when $Fe(CN)_6^{3-}$ was reduced cathodically at n-ZnSe at pH 14 and pH 6. At fixed potential the intensity however decreased with time. A stable emission could

Fig. 1. Current density-potential curve of an n-ZnSe electrode in a $10^{-2} M K_3Fe(CN)_6$, $0.1 M NaCl$, $1 M NaOH$ solution; rotation rate 900 rpm, scan speed 50 mV/s. The inset shows the limiting cathodic current as a function of the square root of the electrode rotation rate.

Fig. 2. Current density-potential curve of an n-ZnSe electrode in a $10^{-2} M K_3Fe(CN)_6$, $0.1 M NaCl$ solution of pH 6; rotation rate 900 rpm, scan speed 50 mV/s.

be obtained by using a block voltage and switching between cathodic and anodic limits. Figure 3 shows the spectrum of the emitted light measured at pH 6 on alternating the potential between $-3 V$ (for 50 ms) and $0 V$ (for 600 ms); at this pH the highest emission intensity in potentiodynamic measurements was found at $-3 V$ (see below). Two emission bands are clear, a narrow band with a maximum at 2.7 eV, due to band-band emission, and a broad band at 1.9 eV, due to emission via a bandgap state. The ratio of the intensities of the bands depended somewhat on the pretreatment of the electrode. The spectrum is similar to that reported by Smiley *et al.* for peroxydisulfate reduction,¹⁸ although the short wavelength emission is relatively stronger in our measurement. Smiley *et al.* have shown that the spectral distribution of the photoluminescence and of the electroluminescence of n-ZnSe are similar. The observation of band-band emission in these electroluminescence experiments means that holes must be injected into the valence band from the oxidizing agent in solution.

Figure 4 shows the potential dependence of the emission measured at 630 nm for an n-ZnSe electrode whose potential was scanned at 100 mV/s in a $0.1 M Fe(CN)_6^{3-}$ solution of pH 14. The corresponding current density-potential curve is also given. In the scan to negative potential the emission onset is observed in the current plateau for $Fe(CN)_6^{3-}$ reduction. The intensity goes through a maximum and decreases further during the return scan to positive potential.

The emission in the experiment at pH 6 was considerably weaker (by a factor of 25) than in the pH 14 case. The onset of electroluminescence was at $-2.8 V$ in the scan to negative potential and the light emission, though reduced in intensity, was observed in the return scan up to $-2 V$. As

Fig. 3. Spectral distribution of the electroluminescence emission at $-3 V$ of an n-ZnSe electrode in $0.1 M K_3Fe(CN)_6$, $0.1 M NaCl$ solution of pH 6; rotation rate 2500 rpm. The potential was switched between $-3 V$ (for 50 ms) and $0 V$ (for 600 ms).

Fig. 4. The potential dependence of the current density (solid line) and of the electroluminescence intensity at 630 nm (dashed line) for an n-ZnSe electrode in a 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M NaCl, 1 M NaOH solution; scan speed 100 mV/s.

for the pH 14 case, the intensity-potential curve showed strong hysteresis.

Rotating ring-disk voltammetry.—In Fig. 5 the results of RRDE measurements are shown for 10^{-2} M $\text{Fe}(\text{CN})_6^{3-}$ solution of pH 14. The current density of the n-ZnSe disk electrode was measured as a function of potential while the potential of the Pt-ring electrode was held constant at 0.6 V; at this value $\text{Fe}(\text{CN})_6^{4-}$ formed at the disk can be oxidized to $\text{Fe}(\text{CN})_6^{3-}$ at the ring. The limiting cathodic current due to $\text{Fe}(\text{CN})_6^{3-}$ reduction at the disk is accompanied by a limiting anodic ring current whose magnitude is that expected on the basis of the collection efficiency of the ring-disk configuration. As the disk current goes to zero at positive potentials, the ring current drops to about half its limiting value but then remains constant up to high positive potentials. Clearly $\text{Fe}(\text{CN})_6^{3-}$ is being reduced in the potential range in which the total current of the system is zero. This means that an oxidation reaction must also be occurring. This reaction is very likely oxidation of ZnSe, i.e., ZnSe is undergoing electroless etching in this solution.

A Koutecky-Levich plot²² of the reciprocal of the ring current density vs. the reciprocal of the square root of the electrode rotation rate, in the electroless potential range, yielded a straight line (Fig. 6 curve a). Reduction of $\text{Fe}(\text{CN})_6^{3-}$ and, consequently, etching of ZnSe are at positive potentials under mixed diffusion/kinetic control. The rate constant for the reduction reaction, as ascertained from the intercept on the current axis, was 1.8×10^{-3} cm/s.

The kinetics of the surface reactions change when the temperature of the solution is raised. Results are shown in

Fig. 5. Current density-potential curve of an n-ZnSe disk/Pt ring electrode in a 10^{-2} M $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M NaCl, 1 M NaOH solution; rotation rate 900 rpm. The disk potential was scanned at 50 mV/s while the Pt-ring was held at 0.6 V. The dashed line represents the disk current density, the solid line the ring current normalized with respect to the disk surface area.

Fig. 6. Koutecky-Levich plots for the reduction of $\text{Fe}(\text{CN})_6^{3-}$ at an n-ZnSe disk [held at 0 V (SCE)] based on the current of the Pt-ring which was held at 0.6 V (SCE) in a 10^{-2} M $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M NaCl, 1 M NaOH solution at (a) 20°C, (b) 85°C.

Fig. 7. For potentials at which $\text{Fe}(\text{CN})_6^{3-}$ is cathodically reduced at a diffusion limited rate ($U < -1.8$ V) at ZnSe, the anodic ring current is markedly larger at 85°C than at 20°C, because of the increase in diffusion coefficient due to a decrease in viscosity of the solution with increasing temperature. The ring current is in the 85°C case constant over the whole potential range. Reduction of $\text{Fe}(\text{CN})_6^{3-}$ is obviously diffusion controlled, even at potentials more positive than U_{oc} . This is clear from the Koutecky-Levich plot (b) in Fig. 6; the straight line passes through the origin indicating a very large rate constant for hole injection, in contrast to the result at 20°C.

Figure 8 shows the RRDE results for an $\text{Fe}(\text{CN})_6^{3-}$ electrolyte solution of pH 6. The considerable hysteresis observed in the disk current-potential curve is mirrored in the ring current. The $\text{Fe}(\text{CN})_6^{4-}$, produced at the disk in the return scan to positive potentials, is oxidized at the ring. In contrast to the experiment at pH 14, the ring current goes to zero as the disk current decreases to zero at around -1.5 V. We can conclude that at the open-circuit potential and at more positive potentials $\text{Fe}(\text{CN})_6^{4-}$ is not being formed.

Etching.—Open-circuit etching experiments were performed to confirm that ZnSe undergoes electroless dissolution in $\text{Fe}(\text{CN})_6^{3-}$ solution of pH 14. A partly masked electrode was rotated in solution, and the etched depth at the mask edge was measured with the surface profiler. Figure 9 shows that for a solution containing 10^{-2} M $\text{Fe}(\text{CN})_6^{3-}$ the etched depth is a linear function of the time, giving over a long period a constant etch rate of 4 $\mu\text{m}/\text{h}$. For these extended experiments it was essential to have excess CN^-

Fig. 7. Ring current-potential curves of an n-ZnSe disk/Pt ring electrode in a 10^{-2} M $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M NaCl, 1 M NaOH solution; rotation rate 900 rpm. The disk potential was scanned at 50 mV/s while the Pt-ring was held at 0.6 V. Results are shown for two temperatures.

Fig. 8. Current density-potential curves of an n-ZnSe disk/Pt ring electrode in a 10^{-2} M $K_3Fe(CN)_6$, 0.1 M NaCl solution of pH 6; rotation rate 900 rpm. The disk potential was scanned at 50 mV/s while the Pt-ring was held at 0.6 V. The dashed line represents the disk current density, the solid line the ring current normalized with respect to the disk surface area.

in solution; otherwise, a reddish layer of elemental Se was formed which blocked the surface and prevented etching.

Similar experiments at pH 6 showed clearly that ZnSe is not etched at open-circuit potential at the lower pH.

Impedance measurements.—Impedance measurements were made with n-ZnSe at 10 kHz under depletion conditions. Linear Mott-Schottky plots were obtained, which upon extrapolation gave the flatband potential U_{FB} . The results obtained in indifferent electrolyte solution and in solution containing $Fe(CN)_6^{3-}$ are given in Table I.

In 1 M NaCl solution U_{FB} becomes more negative as the pH is increased from 1.6 to 14. The flatband value at pH 14 agrees with that reported by Wang *et al.*¹² Cathodic prepolarization of the electrode at potentials at which hydrogen was evolved caused a negative displacement of the Mott-Schottky plot (and thus of U_{FB}) measured at positive potential.

From Table I it is clear that for a given pH the addition of $Fe(CN)_6^{3-}$ to the solution leads to a negative shift of the flatband potential, with the magnitude of the effect depending on the concentration of the oxidizing agent. At fixed $Fe(CN)_6^{3-}$ concentration, the trend in U_{FB} as a function of pH is the same as for indifferent electrolyte. The flatband potential measured in $Fe(CN)_6^{3-}$ solution was also found in a subsequent measurement in indifferent electrolyte solution indicating a “permanent” change in the electrode surface. Etching in Br_2 /methanol solution was required to restore the electrode to its “pre- $Fe(CN)_6^{3-}$ condition.”

Fig. 9. The time dependence of the etch depth of an n-ZnSe disk at the open-circuit potential in a 10^{-2} M $K_3Fe(CN)_6$, 0.1 M KCN, 1 M NaOH solution; rotation rate 900 rpm.

Table I. Flatband potential of n-ZnSe electrodes in aqueous electrolyte solutions.

Solution	pH 1.6	pH 6	pH 14
1 M NaCl	-1.70	-2.15	-2.45
10^{-2} M $K_3Fe(CN)_6$	—	-2.30	-2.60
10^{-2} M $K_3Fe(CN)_6$	-2.20	-2.45	-2.80

Discussion

The change in the flatband potential of n-ZnSe to more negative values as the pH of the indifferent electrolyte solution is raised (Table I) follows the trend normally found for compound semiconductor electrodes.¹⁴ These Mott-Schottky measurements were performed under depletion conditions at positive potentials and the flatband potential therefore reflects the “oxidized” surface. Our measurements show that when the electrode is prepolarized at negative potentials and the Mott-Schottky plot is measured in a scan to positive potential, a more negative flatband value is obtained. An analogous effect has been previously reported for GaAs with the “reduced” surface giving a more cathodic U_{FB} value than the “oxidized” surface.²³

The negative shift of the flatband potential due to the presence of $Fe(CN)_6^{3-}$ in solutions of all three pH values (see Table I) is somewhat surprising. Since ZnSe is not etched at lower pH, this effect cannot be due to oxidation/dissolution of the semiconductor. Rubin *et al.* have shown that when n-CdS is brought into contact with $Fe(CN)_6^{3-/4-}$, a cadmium ferri/ferrocyanide ($CdFe(CN)_6^{2-/1-}$) surface complex results.²⁴ The fact that, in the present case, a displaced flatband value is found in a subsequent measurement in indifferent electrolyte solution could indicate the formation of an equivalent Zn complex. An etch treatment in Br_2/CH_3OH solution is needed to restore U_{FB} to a value typical of a measurement in indifferent electrolyte solution. The presence of a zinc cyanide complex would give rise to a negatively charged surface. The resulting change in the Helmholtz potential would then displace U_{FB} to negative potentials.

The position of the bandedges of ZnSe can be deduced from the flatband potential. Energy level diagrams are shown in Fig. 10 for solutions of pH 14 (a) without and (b) with 10^{-2} M $Fe(CN)_6^{3-}$. The distribution functions of the $Fe(CN)_6^{3-/4-}$ couple are also shown. A reorganization energy of 0.65 eV is assumed.^{25,26} A limited overlap of the empty states of the redox system and the filled states in the solid can be expected on the basis of the impedance measurements at positive potentials in $Fe(CN)_6^{3-}$ solution (case (b), Fig. 10). Hole injection from the oxidizing agent is possible and, considering the weak overlap, it is not surprising that the rate of this reaction is kinetically limited. The potential range ($U \geq U_{OC}$) corresponds to strong depletion.

Fig. 10. Schematic representation of the empty and filled states of the $Fe(CN)_6^{3-/4-}$ couple in solution in relation to the valence and conduction bands of n-ZnSe in an electrolyte of pH 14; (a) without $K_3Fe(CN)_6$, (b) with 10^{-2} M $K_3Fe(CN)_6$.

The surface electron concentration is very low. The holes are held at the surface by the electric field and the semiconductor is oxidized and dissolves. As the potential is made more negative, the electric field decreases and the surface electron concentration increases. The injected holes recombine with electrons, and a cathodic current is observed. This current becomes diffusion limited. The rate of reduction is higher than at positive potentials, as is obvious from the ring current of the RRDE measurement (Fig. 5). This is very likely due to a slight upward shift of the bandedges on going from positive to negative potentials (as seen in the impedance measurements). Radiative recombination and electroluminescence are observed toward the end of the cathodic current plateau confirming hole injection into the valence band. Although hole injection begins at more positive potential (at the onset of the cathodic current), the onset of emission is only observed at -2.2 V (see Fig. 4). This is probably due to effective surface recombination caused by the strong band bending, which holds the holes at the surface. Quenching of the electroluminescence at more negative potentials (Fig. 4) may be due to nonradiative surface recombination caused by cathodic decomposition of the semiconductor or to hydrogen absorption giving rise to nonradiative recombination centers in the solid.

The negative shift of the flatband potential and the corresponding upward displacement of the bandedges resulting from $\text{Fe}(\text{CN})_6^{3-}$ in solution is obviously favorable for the hole injection reaction (compare cases (a) and (b) of Fig. 10). While hole injection at positive potentials is under mixed diffusion/kinetic control at room temperature (Fig. 6 curve a), the kinetics become more favorable as the temperature is raised. At 85°C (Fig. 7) the reduction of $\text{Fe}(\text{CN})_6^{3-}$, and thus the oxidation and dissolution of the semiconductor, are diffusion-controlled (Fig. 6 curve b). This may be due to a slight positive shift of the Nernst potential and a broadening of the distribution function for the oxidized species at higher temperature; this gives rise to a better overlap of the empty redox states with filled valence band states.

The more positive flatband potential (and thus lower valence bandedge) at pH 6 accounts for the absence of hole injection at positive potentials and in the scan to negative potentials (Fig. 8). However, since the bandedges shift upward under cathodic polarization, electroluminescence is detected at negative potential and a diffusion-limited $\text{Fe}(\text{CN})_6^{3-}$ reduction current is observed on the return sweep. The bandedges, however, return to a lower energy at positive potentials and hole injection ceases. No etching is observed at or more positive than the open-circuit potential.

The etching experiments carried out at room temperature at U_{oc} (Fig. 9) confirm hole injection from $\text{Fe}(\text{CN})_6^{3-}$. By comparing the rate of dissolution with the rate of reduction of the oxidizing agent (from RRDE measurements) we can determine the dissolution valence, i.e. the number of charge carriers required to dissolve one ZnSe entity. For the conditions shown in Fig. 9 (10^{-2} M $\text{Fe}(\text{CN})_6^{3-}$, pH 14, 900 rpm) a value of 3.7 is estimated. This can be compared with values of 2.4 to 3.3 reported by Wang *et al.*¹² for the photoanodic oxidation of ZnSe in alkaline solution containing sulfite; in their case the dissolution valence increased with increasing current density. Various reactions are possible for the electrochemical oxidation of ZnSe in alkaline solution

The Se^0 must be removed from the surface by CN^- (or sulfite) as shown in Eq. 2 and 3. Alternatively, selenium may also be electrochemically oxidized

Our experimentally determined value of 3.7 suggests that in alkaline $\text{Fe}(\text{CN})_6^{3-}$ solutions containing cyanide a combination of two reaction paths may be occurring.

Conclusions

The observation of strong electroluminescence at negative potentials and of electroless etching at the open-circuit potential shows that at pH 14 $\text{Fe}(\text{CN})_6^{3-}$ is reduced at n-type ZnSe by a hole injection mechanism. The dependence of the rate of hole injection on applied potential and pH is consistent with what one expects from the energy level diagrams as deduced from impedance measurements.

These results show that alkaline $\text{Fe}(\text{CN})_6^{3-}$ solutions containing cyanide to complex elemental selenium may prove interesting for the etching of ZnSe devices. By changing the temperature one can have either kinetically or diffusion limited dissolution, as required for anisotropic and isotropic etching, respectively.

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