Electrolytic decomposition and photodecomposition of compound semiconductors in contact with electrolytes

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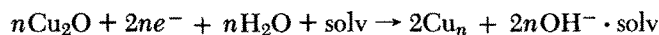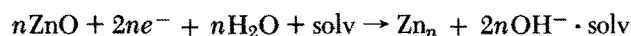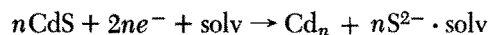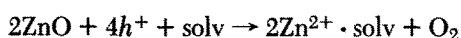*California Institute of Technology, Pasadena, California*

Electrons and holes affect the bond strength of surface atoms. Therefore, in most systems their surface concentration controls the rate of electrolytic decomposition reactions. The thermodynamics of such reactions are characterized by their redox potentials which are equivalent to the Fermi energies of electrons or holes. It is shown that the energy positions of the redox Fermi levels for decomposition with respect to the position of the band edges and the Fermi levels of competing redox reactions, give an immediate indication for the susceptibility of a semiconductor to electrolytic decomposition. This concept is especially useful for the discussion of photodecomposition where the electronic free energy can be described by individual quasi-Fermi levels for electrons and holes. Data are given for the semiconductors ZnO, TiO$_2$, Cu$_2$O, CdS, MoS$_2$, GaP, and GaAs. A model for bond breaking by holes at a kink site of a compound semiconductor is discussed to demonstrate what role the surface bond character plays for the height of activation barriers and how kinetics modify the thermodynamic conclusions on stability.

I. INTRODUCTION

The semiconductor–electrolyte contact has recently found wide interest among physicists because Schottky barriers are easily formed at this type of heterojunction. These Schottky barriers will generate a photovoltage at illumination. Such systems have been studied as converters of solar energy into chemical energy by photoelectrolysis of water[1-4] or as photovoltaic power generators[5-7]; (compare also the papers of a recent conference on electrochemical solar cells, Ref. 8). The greatest obstacle for the practical application of such systems is their susceptibility to photodecomposition. This process occurs if electronic charge carriers, generated by illumination, are accummulated at the surface to such an extent that oxidation or reduction of surface atoms becomes possible.[9] The same type of reaction can be studied in the dark by accummulating majority carriers at the surface with the application of a suitable voltage to the semiconductor electrode.[10-12] It has been found that the reaction rate is proportional to the surface concentration of holes or electrons as long as the electric charge in surface states remains constant[13,14] and the concentration of holes or electrons remains small compared with the effective density of states at the band edges. This agrees with theoretical models for the kinetics of semiconductor electrode reactions.[15] Some examples are given in the following reactions.

$$\text{GaAs} + 6h^+ + 2\text{H}_2\text{O} + \text{solv}$$
$$\rightarrow \text{Ga}^{3+} \cdot \text{solv} + \text{AsO}_2^- + 4\text{H}^+ \cdot \text{solv}$$

$$\text{GaP} + 6h^+ + 3\text{H}_2\text{O} + \text{solv}$$
$$\rightarrow \text{Ga}^{3+} \cdot \text{solv} + \text{H}_2\text{PO}_3^- + 4\text{H}^+ \cdot \text{solv}$$

$$n\text{CdS} + 2nh^+ + \text{solv} \rightarrow n \cdot \text{Cd}^{2+} \cdot \text{solv} + \text{S}_n$$

$$2\text{ZnO} + 4h^+ + \text{solv} \rightarrow 2\text{Zn}^{2+} \cdot \text{solv} + \text{O}_2$$

$$n\text{CdS} + 2ne^- + \text{solv} \rightarrow \text{Cd}_n + n\text{S}^{2-} \cdot \text{solv}$$

$$n\text{ZnO} + 2ne^- + n\text{H}_2\text{O} + \text{solv} \rightarrow \text{Zn}_n + 2n\text{OH}^- \cdot \text{solv}$$

$$n\text{Cu}_2\text{O} + 2ne^- + n\text{H}_2\text{O} + \text{solv} \rightarrow 2\text{Cu}_n + 2n\text{OH}^- \cdot \text{solv}$$
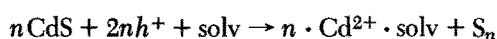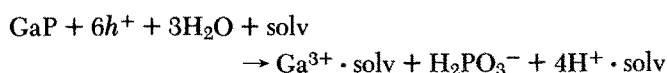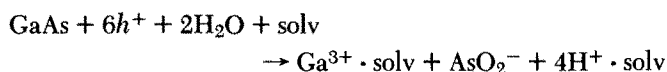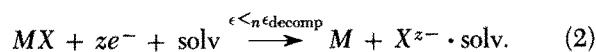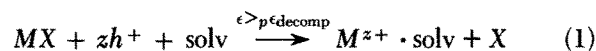
Some thermodynamic aspects of photodecomposition have been discussed elsewhere,[16] but will be repeated here in somewhat different form as the basis for the modifications by kinetics.

II. THERMODYNAMIC ASPECTS

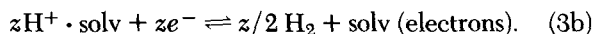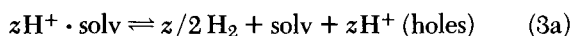### A. Redox potentials of decomposition reactions

Decomposition of a semiconductor by electrolysis can occur either as an anodic or as a cathodic process. Since the electronic reactants are holes in one case, electrons in the other, we shall use two different types of formulations for such reactions. As a simplest example we shall discuss a binary compound semiconductor MX which a wide enough band gap to prevent any considerable rate of thermal generation of minorities. The decomposition reactions can then be formulated as redox reactions as follows:
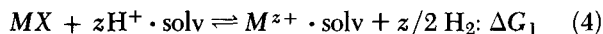
$$MX + zh^+ + \text{solv} \xrightarrow{\epsilon > _p\epsilon_{decomp}} M^{z+} \cdot \text{solv} + X \quad (1)$$

$$MX + ze^- + \text{solv} \xrightarrow{\epsilon < _n\epsilon_{decomp}} M + X^{z-} \cdot \text{solv}. \quad (2)$$

A redox potential can be defined for these reactions denoted by $_p\epsilon_{decomp}$ and $_n\epsilon_{decomp}$. Thermodynamically, for the reactions to proceed as indicated, ϵ must exceed these equilibrium redox potentials, positively for holes, negatively for electrons.

Redox potentials are measured against a reference electrode. To derive their values from thermodynamic data, we
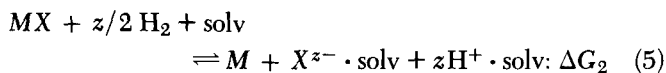
have to obtain a net reaction by adding the electrode reaction of the reference written in the opposite direction, as in Eqs. (3a) and (3b)

$$zH^+ \cdot \text{solv} \rightleftharpoons z/2\,H_2 + \text{solv} + zH^+ \text{(holes)} \qquad (3a)$$

$$zH^+ \cdot \text{solv} + ze^- \rightleftharpoons z/2\,H_2 + \text{solv (electrons)}. \qquad (3b)$$

The free energy difference ΔG for the combination of these reactions gives us the corresponding redox potential. We obtain from Eq. (1) + Eq. (3a)

$$MX + zH^+ \cdot \text{solv} \rightleftharpoons M^{z+} \cdot \text{solv} + z/2\,H_2\colon \Delta G_1 \qquad (4)$$

and from Eq. (2) + Eq. (3b)

$$MX + z/2\,H_2 + \text{solv}$$
$$\rightleftharpoons M + X^{z-} \cdot \text{solv} + zH^+ \cdot \text{solv}\colon \Delta G_2 \qquad (5)$$

The redox potentials of the decomposition reactions (1) or (2) versus the hydrogen electrode are

$$_p\epsilon_{\text{decomp}} = \Delta G_1/zF \qquad (6)$$

and

$$_n\epsilon_{\text{decomp}} = -\Delta G_2/zF \qquad (7)$$

where F is the Faraday constant. Redox potentials can equally be described by the position of the Fermi level E_F in the electrode since this corresponds to the free energy of the electron. If we relate the Fermi energies to the vacuum level, we obtain the following correlation between the redox potential and the Fermi level,

$$E_F = -e_0 \cdot \epsilon + E_{\text{ref}} \qquad (8)$$

where e_0 is the unit electric charge. E_{ref} is the Fermi level of the reference electrode in relation to the vacuum level. For the standard hydrogen electrode as the electrochemical reference system, E_{ref} has a value of $-4.5\ (\pm 0.2)$ eV.[17-19]

Although there is no difference between the free energy of electrons and holes as long as thermodynamic equilibrium is maintained, we shall define the Fermi energies of electrons, $_nE_F$, and holes, $_pE_F$, separately using different reference states for each. This will be useful for the discussion of the nonequilibrium situation under illumination.

$$_pE_F = E_v - f(p) \quad \text{with } p = \text{concentration of holes} \qquad (9)$$

$$f(p) = kT\ln\left(\frac{p}{N_V}\right) \quad \text{for } p \ll N_V \qquad (9a)$$

$$_nE_F = E_C + g(n) \quad \text{with } n = \text{concentration of electrons} \qquad (10)$$

$$g(n) = kT\ln(n/N_C) \quad \text{for } n \ll N_C \qquad (10a)$$

where N_V, N_C are the effective density of states in the valence and the conduction band; E_V, E_C are the energy positions of the respective band edges. At equilibrium, we have $p \cdot n = n_i^2 = N_V \cdot N_C \cdot \exp(E_{\text{gap}}/kT)$ so that $_pE_F = {}_nE_F$.

The merits of these definitions are that the Fermi levels are measured with respect to the position of the band edges at the electrolyte contact. This is a characteristic property of the semiconductor material. These band-edge energies can be determined experimentally.[20,22]

Decomposition reactions can occur if

$$_pE_F < {}_pE_{\text{decomp}} \text{ for reaction (1), and} \qquad (11)$$

$$_nE_F > {}_nE_{\text{decomp}} \text{ for reaction (2).} \qquad (12)$$

A similar discussion of the stability ranges of semiconductors against oxidation by holes has been outlined by Bard and Wrighton.[21]

B. The conditions for decomposition reactions with majority carriers

In semiconductors with a band gap wider than 1 eV, only the majority carriers can cause electrolytic reactions at room temperature in the absence of illumination or other means for the generation of minorities. In principle, the position of the decomposition potential in relation to the position of the band edges at the semiconductor–electrolyte interface, gives direct information about the concentration of the majority carriers at the surface necessary to initiate the decomposition process. Equations (9) and (10) clearly indicate that decomposition becomes possible at relatively low surface concentrations of holes or electrons if $_pE_{\text{decomp}}$ is far above E_V or if $_nE_{\text{decomp}}$ is far below E_C. On the other hand, if $_pE_{\text{decomp}} < E_V$ or $_nE_{\text{decomp}} > E_C$, the respective reactions are possible only in the range of electronic degeneracy at the surface. This range can be reached by applying a high enough anodic voltage to p-type semiconductors or a high enough cathodic voltage to n-type semiconductors.

This discussion shows the importance of measuring the position of the band edges while in contact with an electrolyte. This position depends on the individual semiconductors and to some extent on the composition of the electrolyte. It can be measured by various techniques, especially by the dependence of the capacity on the applied voltage.[15,21-26] Figure 1 gives some examples for some compound semiconductors in aqueous solution. The Fermi levels $E^0_{H_2/H_2O}$ of a hydrogen electrode and $E^0_{O_2/H_2O}$ of an oxygen electrode at the same pH value are introduced for comparison. These Fermi levels correspond to the decomposition potential of water in cathodic and anodic direction at this pH value.

Figure 1 also contains the decomposition potentials for these semiconductors as obtained from thermodynamic data by using Eqs. (6) and (7). The values obtained are only approximate ones since they depend on the final products formed in the electrolyte. This can vary with electrolyte composition and is especially dependent on ions or molecules in solution which interact with the components of the semiconductor by ligand or complex formation.

We see in Fig. 1, that the usual situation found at semiconductors in contact with aqueous electrolytes is $_pE_{\text{decomp}} > E_V$. Therefore, p-type specimens of these materials should easily decompose at rather low surface holes concentrations. This is indeed true for GaAs[27] and GaP[28] where p-type specimens are available. The position of $_nE_{\text{decomp}}$ varies in relation to the band edges. In Cu$_2$O, $_nE_{\text{decomp}}$ is far below E_C, therefore this material can be reduced at very low surface concentrations of electrons.[29] In TiO$_2$ we have the opposite situation with $_nE_{\text{decomp}}$ far above E_C. Such a material can only be reduced electrolytically if a high degeneracy of electrons
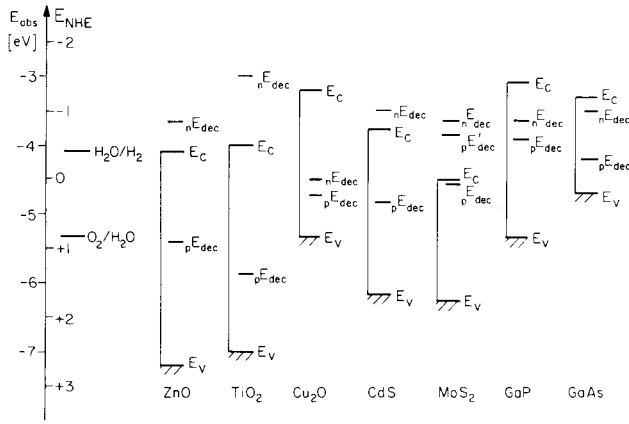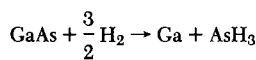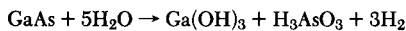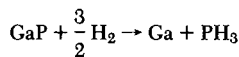
FIG. 1. Position of band edges and decomposition Fermi energies (= decomposition redox potentials) of various semiconductors and of water in absolute (E_{abs}) and electrochemical energy scale (E_{NHE}). Decomposition potentials are calculated from thermodynamic data for the following reaction pairs (first for $_pE_{decomp}$, second for $_nE_{decomp}$)

$$ZnO + 2HCl \rightarrow ZnCl_2 + \tfrac{1}{2}O_2 + H_2$$

$$ZnO + H_2 \rightarrow Zn + H_2O$$

$$TiO_2 + 4HCl \rightarrow TiCl_4 + O_2 + 2H_2$$

$$TiO_2 + 2H_2 \rightarrow Ti + 2H_2O$$

$$Cu_2O + H_2O \rightarrow 2CuO + H_2$$

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O$$

$$CdS + 2HCl \rightarrow CdCl_2 + 2S$$

$$CdS + H_2 \rightarrow Cd + H_2S$$

$$MoS_2 + 2H_2O \rightarrow MoO_2 + 2S + 2H_2\ (= {_pE_{dec}})$$

$$MoS_2 + 2H_2O \rightarrow H_2MoO_4 + 2H_2SO_4 + 5H_2\ (= {_pE'_{dec}})$$

$$MoS_2 + 2H_2 \rightarrow Mo + 2H_2S$$

$$GaP + 6H_2O \rightarrow Ga(OH)_3 + H_3PO_3 + 3H_2$$

$$GaP + \frac{3}{2}H_2 \rightarrow Ga + PH_3$$

$$GaAs + 5H_2O \rightarrow Ga(OH)_3 + H_3AsO_3 + 3H_2$$

$$GaAs + \frac{3}{2}H_2 \rightarrow Ga + AsH_3$$
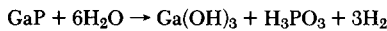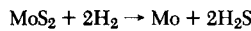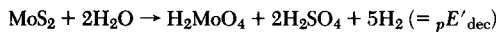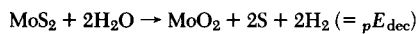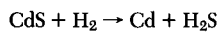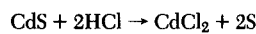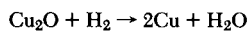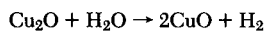
Band edge positions are taken from our own measurements and from Ref. 25, adjusted for pH = 7. Uncertainty of data is in the order of ±0.2 eV.
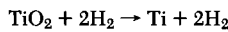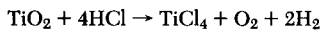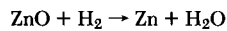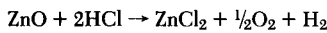
can be obtained at the surface. However, in many cases this is not possible because other reactions can compete successfully with the decomposition of the semiconductor by the majorities. If these reactions are fast enough, the electronic free energy at the surface will not exceed the critical values for decomposition. In this way a semiconductor can be stabilized, as we shall discuss in the next section.

C. Decomposition of the semiconductor in competition with other redox reactions

Electrons and holes can react with any redox system which is present in the electrolyte. All species in the solution can in principle be reduced or oxidized and particularly the solvent itself may undergo redox reactions. Therefore, the electrolytic decomposition reactions of the solvent molecules limit the range of accessible redox potentials in an electrolyte. A

semiconductor can not be decomposed by electrolysis if its decomposition potential is far enough away from the decomposition potential of the solvent. The real situation— which is modified by kinetics, as we shall discuss later—can only be judged by including the decomposition potentials of the solvent into the stability consideration. This is done in the following two figures which represent the typical situations we can meet. As a reference state, the flat band situation is used in these pictures because this best characterizes the particular semiconductor.

Figure 2 shows all possible cases for a p-type semiconductor. In Fig. 2(a), the flat band potential is below the decomposition potential. The semiconductor here will be unstable if the decomposition potential of the solvent is below that of the semiconductor as indicated by $_pE_{solv}$. It would be stabilized by faster solvent decomposition if $_pE_{solv}$ were located above as indicated in this picture by $_pE'_{solv}$. Decomposition of the semiconductor can definitely be prevented only by cathodic polarization as shown in Figure 2.1b.

Figures 2(c) and (d) show the case where the semiconductor is stable at the flat band potential [Fig. 2(c)] and can only be decomposed by anodic polarization leading to degeneracy of holes at the surface [Fig. 2(d)]. The stability can be improved by easier solvent decomposition (case with $_pE'_{solv}$).

Figure 3 represents the respective situation for cathodic reactions with electrons. In Fig. 3(a), the flat band potential is above $_nE_{decomp}$ and decomposition is thermodynamically possible. To prevent this one has to apply some anodic polarization [Fig. 3(b)]. Whether or not the semiconductor can be stabilized by decomposition of the solvent will depend on its decomposition potential. If this is represented by $_nE_{solv}$ there is no protecting it. Protection is possible if the solvent decomposition potential is located at $_nE'_{solv}$.

Figure 3(c) and (d) shows the case where the semiconductor is stable at the flat band potential [Fig. 3(2a)] and can only be decomposed by cathodic polarization leading to degeneracy of electrons at the surface [Fig. 3(d)]. The decomposition of the solvent and its effect on the semiconductor decomposition is the same as discussed above.
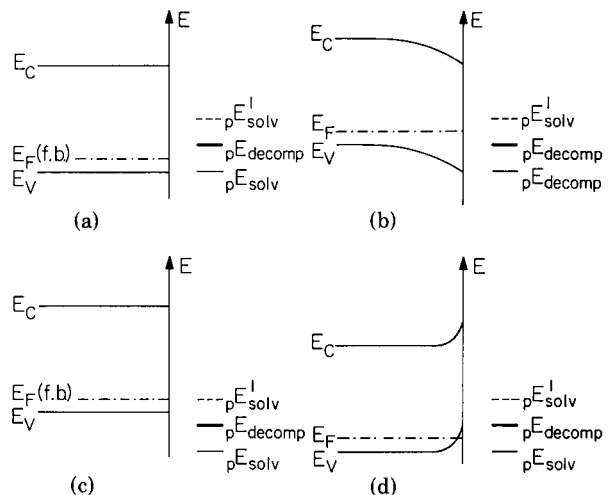

FIG. 2. Energy correlations for decomposition reactions with holes at p-type semiconductors: case 1—unstable at flat band potential; case 2—stable at flat band potential.
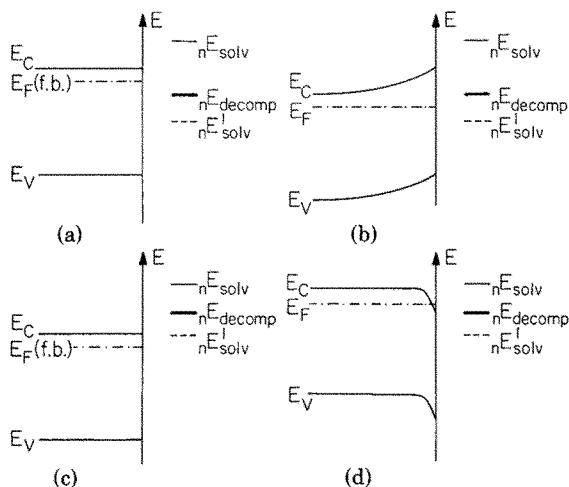
FIG. 3. Energy correlations for decomposition reactions with electrons at n-type semiconductors: case 1—unstable at flat band potential; case 2—stable at flat band potential.

C. Photodecomposition

Illumination has the consequence for electrolytic reactions in that minority carriers are generated and one must now take into account their reactions also. They occur far from thermodynamic equilibrium and can cause photodecomposition.[9,15,30]

In spite of large deviations from real electronic equilibrium one can describe the driving forces of electrons and holes by quasi-thermodynamic quantities as long as an equilibrium distribution is maintained over the electronic energy levels of that particular energy band in which they exist. Since energy relaxation within one energy band is much faster than recombination between the conduction and valence band, this is a widely applicable approximation at normal illumination intensities.

This presumed, the free energies of electrons and holes in an illuminated semiconductor can be characterized by their quasi-Fermi levels E_F^* and expressed with the exclusion of degeneracy by

$$_nE_F^* = E_C + kT\ln(n^*/N_C) \text{ for electrons} \qquad (13)$$

$$_pE_F^* = E_V - kT\ln(p^*/N_V) \text{ for holes} \qquad (14)$$

where n^* and p^* are the local concentrations of electrons and holes in the steady state of illumination. For electrode reactions, it is the surface concentrations n_s^* and p_s^* which control the driving forces.

Equations (13) or (14) will always be applicable to the minorities at normal illumination intensities since recombination will prevent their concentration reaching the range of degeneracy. This means that the position of the band edges sets a limit for the energies which can, under illumination, be reached by the quasi-Fermi level of the minorities. The position of the decomposition Fermi level in relation to the position of the band edges therefore gives an immediate indication of the stability of a semiconductor electrode against electrolytic photodecomposition.

Figure 4 gives a summary of the principal situations which can be expected for semiconductor electrodes in contact with

electrolytes.[16] Unfortunately, the absolute stable situation described by Fig. 4(a) seems not to exist in contact with aqueous electrolytes, nor does the situation given in Fig. 4(d). Therefore, all semiconductors seem to be thermodynamically susceptible to anodic photodecomposition in aqueous solutions.

The quasi-Fermi level of the majorities will always remain close to its equilibrium level in the bulk even at illumination. Only E_F^* of the minorities will deviate largely from this equilibrium value. Therefore, we primarily have to discuss the properties of minority carriers to characterize the conditions of photodecomposition. However, we also have to consider the competition of other reactions as discussed in the previous section for the majorities.

For this purpose, two rather extreme situations are plotted in Figs. 5 and 6 for illuminated semiconductor–electrolyte interfaces in the absence of any electrolysis by majority carriers. Under these circumstances, the quasi-Fermi levels of majorities and minorities approach their respective band edges. Figure 5 shows this for an n-type semiconductor, Fig. 6 for a p-type one, both are at electrode potentials close to the flat band situation. The path of the quasi-Fermi energies in the illuminated space charge layer is qualitatively indicated in these figures with the assumption that the minorities are consumed at the surface by an electrolytic process.

The n-type semiconductor of Fig. 5 is stable against cathodic decomposition [case Fig. 3(c)] and the p-type semiconductor of Fig. 6 is stable against anodic decomposition [case Fig. 2(c)]. On the right-hand side of Figs. 5 and 6, various possible positions of the decomposition Fermi levels for the semiconductor and for the electrolyte are shown in cases a, b, and c.

We can now systematically compare the different cases. A stable situation will be found if the requirements of Figs. 5(a) or 6(a) are fulfilled. Only the electrolyte will react in these cases with the minorities. In cases Figs. 5(b) and 6(b), decomposition of the semiconductor is possible, but might be prevented by the thermodynamically preferred reaction of minorities with the electrolyte. Cases Figs. 5(c) and 6(c) indicating a preferential decomposition of the semiconductor, are the least favorable situations. We shall see, however, that
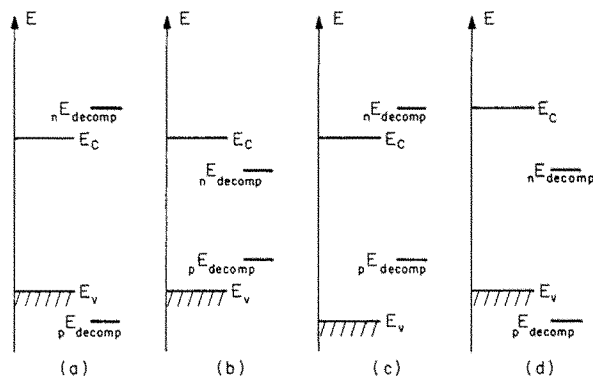

FIG. 4. Energy correlations between band edges and decomposition Fermi levels, characterizing susceptibility to photodecomposition. (a) Stable; (b) unstable, (c) susceptible to anodic photodecomposition, (d) susceptible to cathodic photodecomposition.
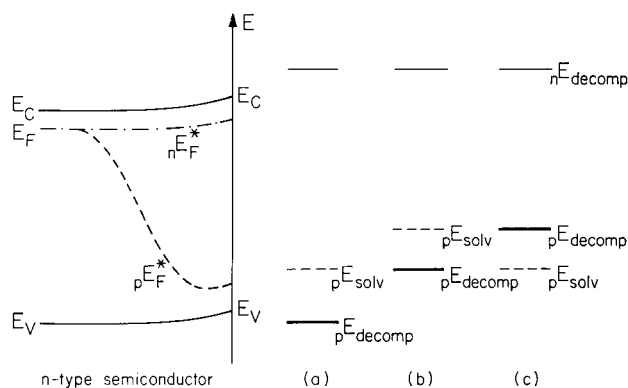
FIG. 5. n-type semiconductors and their susceptibility to photodecomposition by holes in competition with solvent oxidation: (a) stable; (b) metastable, protected by solvent; (c) unstable.

even in cases where thermodynamics show a very unfavorable picture, kinetics can considerably change the situation.

The Fermi levels for decomposition which characterize the reactivity of the solvent in Figs. 5 and 6 have to be understood in a wider sense as the Fermi energies at which redox reactions with the electrolyte become possible. They can also represent redox couples intentionally added to the electrolyte. For kinetic reasons, redox couples with the fastest electron transfer rates are the most efficient as competitive reactants and are therefore especially valuable for the protection of semiconductors.

III. KINETIC ASPECTS

A. Single steps in a decomposition reaction

Since atoms at the surface of a crystal are bonded to several neighbor atoms, a decomposition reaction can only proceed in several steps each having a different rate constant. To make the consequences of such a reaction mechanism for the stability of semiconductors clear we shall pursue this process for a simplified two-dimensional model of a crystal surface. This model shows all the basic features and can easily be transferred to a three-dimensional lattice.

Lattice decomposition begins usually at a kink site. Fig. 7 represents a model of a MX crystal with M being the more electropositive and X the more electronegative component. CdS, ZnO, or GaAs could serve as examples. The two surface molecules at the kink site are marked by dark lines. In order to demonstrate the difference in electronegativity, it is assumed that the X atoms have lone electron pairs in their nonbonding surface electron orbitals while the M atoms have a vacant orbital which interacts with a nucleophilic ligand L. Figs. 7(a)–(d) demonstrates the first four steps of an oxidation reaction in which the component M will leave the lattice as an ion M^{2+} and the X atom will recombine to X_2 molecules. Each of these reaction steps proceeds by interaction of the surface atoms of a kink site with a hole and a nucleophilic ligand L in the electrolyte. L will often be the polar solvent molecule itself.

This series of drawings also indicates schematically the electronic orbitals involved in these steps and the electron

distribution over these orbitals. The obvious assumption is that the presence of a hole will cause the electron density around the X atom to decrease if the valence-band states in such crystals can predominately be attributed to electron orbitals of these atoms. This must weaken the bond to the neighboring M atom and will increase its tendency to interact with electron donors from the electrolyte. This assumption has been made and leads to stage b of Fig. 7.

A second hole will now preferentially be captured at this site where the M atom is attached by a single bond to the surface. This hole, together with another interacting ligand will break the last bond of this M atom. This will then leave the crystal surface as an M^{2+} ion as indicated in Fig. 7(c).

In the configuration of Fig. 7(c), the bonds of the other M-atom in this kink site configuration will be weakened and electrons can easily be removed by holes from such bonds. One can also describe the bonds around the remaining two X atoms of the kink site energetically as electrons in surface states which are located above the valence-band edge. They form therefore efficient traps for holes. After two more holes are trapped there, the second M atom can leave the surface as an M^{2+} ion and the two X atoms will remain at the surface in a weakly bound radical state. This is shown in Fig. 7(d).

If the interaction between these two X atoms is strong enough, they will recombine and form a molecule which leaves the surface. In this way, the initial situation of Fig. 7(a) is reinstituted. This occurs in the oxidation of ZnO and CdS. In the case of GaAs and GaP, such a recombination does not occur. Instead, the lasting bonds of the more electronegative component need also holes and have to interact with more components of the solvent to be broken so that finally both components of the semiconductor leave the surface in an oxidized state. Such a reaction proceeds via a very complex mechanism which can hardly be imagined in any realistic way. For a principal discussion of the net reaction such details are not important. We learn from Fig. 7 that the bond breaking in a kink site of a semiconductor occurs in a series of redox steps with single holes, which might have quite different reaction rates.

It should be mentioned that the electronic oxidation steps attributed exclusively to holes in Fig. 7 could in principle also be performed by electron injection into the conduction band.[9]
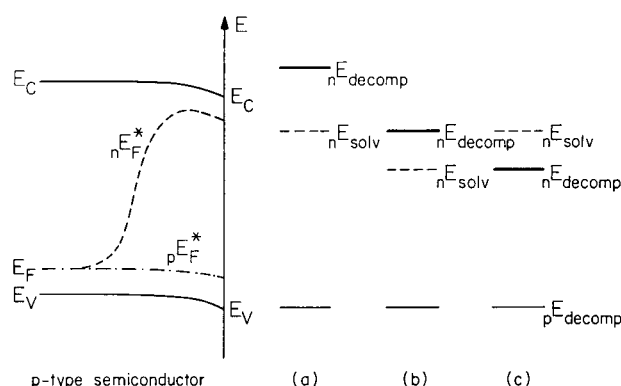

FIG. 6. p-type semiconductors and their susceptibility to photodecomposition by electrons in competition with solvent reduction: (a) stable; (b) metastable, protected by solvent reduction; (c) unstable.
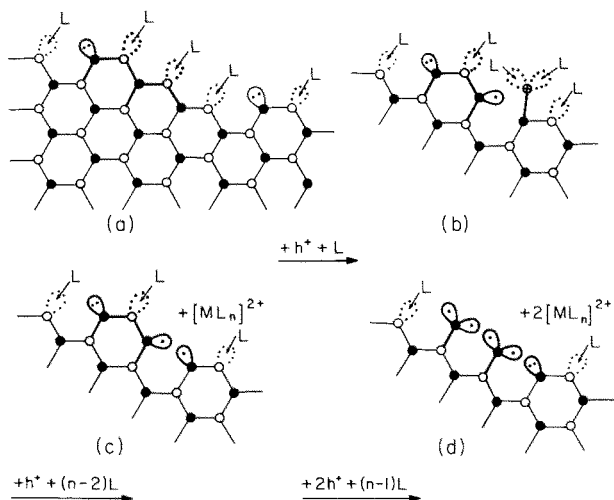
FIG. 7. Mechanism of compound semiconductor oxidation by holes in two-dimensional representation. Four steps in the bond breaking at a kink site of an MX crystal in the reaction: $2MX + 4h^+ + 2nL \rightarrow 2[ML_n]^{2+} + X_2$. Open circle: M atom (more electropositive). Filled circle: X atom (more electronegative). L: nucleophilic ligand from solution. (a) kink site at step in crystal plane; (b) first bond breaking; (c) second bond breaking with removal of one M^{2+} ion from surface; (d) third and fourth bond breaking with removal of second M^{2+} ion from surface, leaving two X atoms in a radical state ready for recombination.
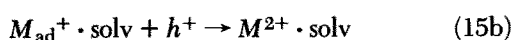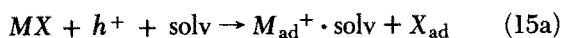
This means unpaired electrons in surface bonds might have a high enough energy that they can reach the conduction band by thermal excitation. This is a normal reaction mode in case of Germanium[31] but occurs at GaAs only to a negligible extent[32] and is not found at semiconductors with a wider band gap.

A fully analogous description can be applied to the cathodic reduction in single steps by electrons.[9,15] Since no principally different insight can be obtained from the cathodic reactions and much less is known experimentally about them, their kinetics will not be discussed here.

B. The rate determining step and its influence on the stability

All single reaction steps discussed above have different rate constants and different free energy consumption. This modifies our previous thermodynamic stability considerations which were based on the free energy changes in the overall reaction and therefore averaged over all single steps, electrochemical and chemical ones. The step with the highest free energy consumption and the highest activation barrier will control as the rate determining step what really occurs. Even without taking into account activation barriers one can see how drastically this might affect the semiconductor stability. The following example will demonstrate this.

We consider the reaction of Fig. 7 and assume that the reaction path can be described—neglecting structural details of the semiconductor surface—by the following sequence of steps,

$$MX + h^+ + \text{solv} \rightarrow M_{ad}^+ \cdot \text{solv} + X_{ad} \quad (15a)$$

$$M_{ad}^+ \cdot \text{solv} + h^+ \rightarrow M^{2+} \cdot \text{solv} \quad (15b)$$

$$X_{ad} + X_{ad} \rightarrow X_2 \quad (15c)$$

The index ad means an adsorbed state, interacting strongly with the surface.

We assume that the first step needs the highest free energy as driving force; this will be the most frequently met situation. This means the decomposition potential $_pE_a$ for the first reaction step must be exceeded to start the reaction. In Fig. 8, we have attributed the individual redox potentials ϵ_a and ϵ_b with the respective Fermi levels of holes $_pE_a$ and $_pE_b$ to the reactions (15a) and (15b) respectively. The free energy change in reaction (15c) shall be ΔG_c. These quantities are interrelated by the equation

$$2\,_pE_{\text{decomp}} = {_pE_a} + {_pE_b} - \Delta G_c/2F \quad (16)$$

Figure 8 demonstrates how such a splitting of the overall decomposition potential can modify the susceptibility of a semiconductor against photodecomposition. Comparing this figure with Fig. 5 one sees immediately that the semiconductor characterized by Fig. 8 will not be decomposed at this illumination intensity because the first oxidation step needs a higher free energy of holes. At the very least, the decomposition will go on at a much smaller rate.

Such a stabilization effect can be enhanced by the presence of an activation barrier for the individual reaction steps, especially if it is high for the slowest step. Some idea about the height of such reaction barriers can only be obtained from an analysis of specific models for individual systems. The model of Fig. 7 has indicated the importance of the interaction between the electronic orbitals, in which the holes are located, and the reactants from solution. Besides the energy position of the electronic states and the concentration of the electronic reactants (their free energy) it is the overlapping of the interacting electronic wave functions which controls the height of the activation barriers. If there is very little overlapping, the barrier will be particularly high.

In this respect very interesting materials have recently been studied by Tributsch, who investigated the electrochemical behavior of layer compounds like MoS and MoSe.[33,34] It turned out that photogenerated holes in these crystals do not affect the metal–chalcogenide bond seriously although thermodynamics would easily permit decomposition as Fig.
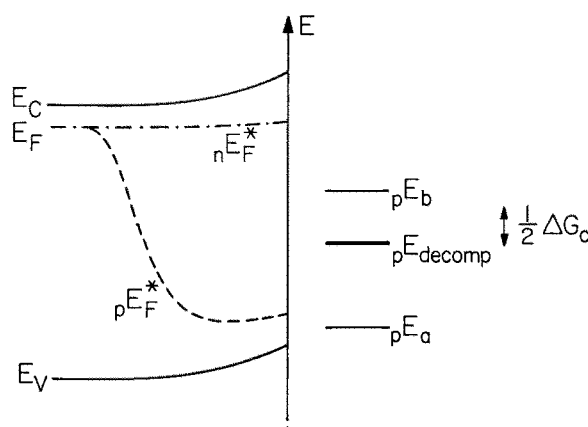

FIG. 8. Decomposition Fermi levels of overall reaction and of individual redox steps in the process, $2MX + 4h^+ + \text{solv} \rightarrow 2M^{2+}\text{-solv} + X_2$ with the mechanism: (a) $MX + h^+ + \text{solv} \rightarrow M^+\text{-solv} + X_{ad}$; (b) $M^+_{ad}\text{-solv} + h^+ \rightarrow M^{2+}\text{-solv}$; (c) $X_{ad} + X_{ad} \rightarrow X_2$.

1 has shown. Holes in these systems are energetic enough to oxidize species in solution if suitable electron donors are present. They can even oxidize water. This, however, has the result that the radical-like oxidation products, as OH, attack the sulfur or selenium layer and oxidize them finally up to even sulfate or selenate. This reaction behavior agrees with the assumption that very little interaction between electronic orbitals is necessary to permit electron transfer[35,36] but much more interaction is needed to obtain chemical effects.

This last example can also be taken as an indication that chemical modifications of the surface can be performed without significantly effecting electron transfer reactions with noninteracting species. This could be important for the development of electrochemical solar cells.

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