SEMICONDUCTING OXIDES IN CONTACT WITH PASSIVE METALS

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Semiconducting oxides in contact with metals exert influence on the passive behavior of metals. The electrode potential of semiconducting oxides appears around their flat band potential, which generally is more cathodic (negative) for n-type oxides and more anodic (positive) for p-type oxides than the corrosion potential of metals. When a semiconducting oxide and a metal get in touch with each other, the mixed electrode potential comes somewhere between the metal corrosion potential and the oxide flat band potential.

EFFECTS OF SEMICONDUCTING OXIDES ON THE PASSIVE BEHAVIOR OF METALS

The presence of p-type oxides shifts the potential of passive metals in the anodic direction, which is particularly enhanced by radiation-excitation or photoexcitation of the oxides. It may occur, as a result, that, when being in contact with p-type oxides, a passive metal shifts its potential beyond the passivity-breakdown potential to cause a localized mode of corrosion. Furthermore, the radiation-excited electrons make it thermodynamically possible for the cathodic water reduction to occur on the p-type oxide, provided that the conduction band level is higher than the hydrogen reaction level. This cathodic hydrogen evolution on the oxide may be coupled with the anodic metal dissolution at the passivity-breakdown sites. Localized corrosion (pitting, crevice corrosion, SCC) thereby will go running even in the absence of oxygen.

In case of n-type oxides the situation is exactly reverse to that of p type oxides. The metal potential shifts in the cathodic direction and, if it exceeds the hydrogen potential, cathodic hydrogen evolution will occur on the passive metal. The radioexcited holes also make it thermodynamically possible for the anodic oxygen evolution to occur on the n-type oxide, provided the oxide valence band level is lower than the oxygen reaction level. This anodic oxygen evolution on the oxide may be coupled with the cathodic hydrogen evolution on the passive metal surface. This type of the local cell generated under irradiation will increase the probability of hydrogen damage of the passive metals.

IRRADIATION

As for the radiation effects on metallic corrosion, we have so far been paying attention merely to radiation-damaged solid-state defects and radiolytically produced oxidizing substances in water such as hydrogen peroxides, which is one of the substances that lead to passivity breakdown. Besides, however, we have to keep our eyes on the radiation-excited electrons and holes which have high reducing and oxidizing capacities in solid oxides.

The extremely high energy radiation of the order of MeV does not affect directly the corrosion processes. The secondary low energy radiation however produces in semiconducting oxides excited electrons and holes whose energy (a few eV) is of the same order of magnitude as that of the corrosion reactions, and consequently, these excited electrons and holes affect directly the corrosion processes as mentioned above.

CONCLUSION

During the long-term storage, p-type oxides such as nickel oxides may be formed, for instance, as deposits of passive corrosion debris on the waste package. There will, then, arises a possibility for the breakdown of passive films to occur.

To keep the waste package away from the passivity breakdown, the surface coating of n-type oxides such as titanium oxides on the passive metal package will be effective.

SEMICONDUCTING OXIDES IN LONG-TERM CORROSION OF PASSIVE METALS

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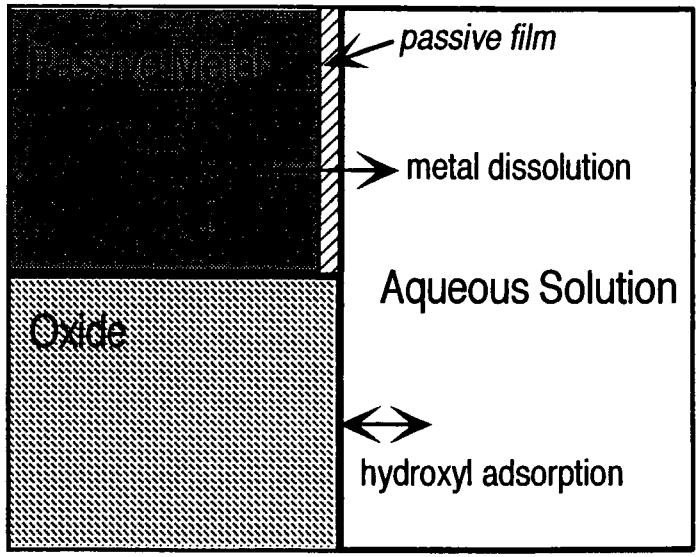
Metallic Corrosion

Oxides in Contact with Metals Affects Passive Metal Corrosion.

Passive Metals and Semiconducting Oxides



Metal: Corrosion Potential, E_{corr}

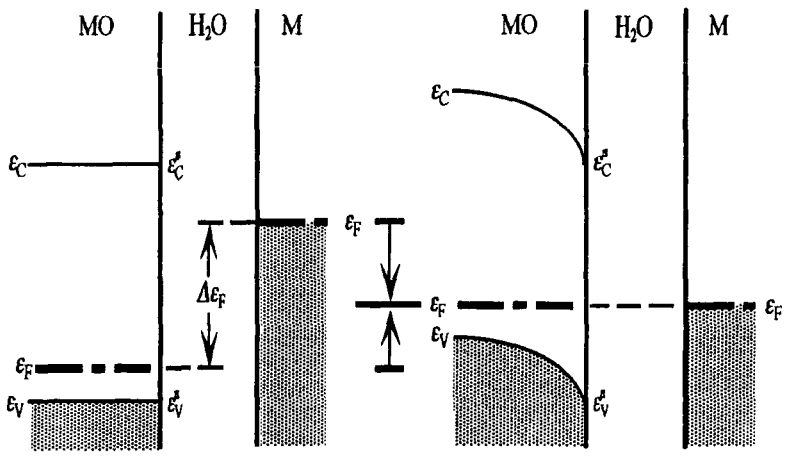
Oxide: Flat Band Potential, E_{fb}

Metal-Oxide in Contact: Mixed Potential, E_{mixed}

Metals in Contact with p-Type Oxides

E_{corr} is More Cathodic Than E_{fb}.

Before Contact; After Contact;

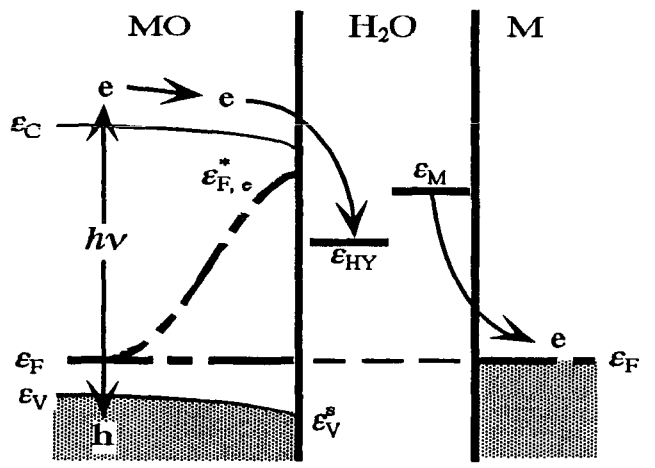


Electronic level diagram for M and p-type MO.

ıen being Excited by Radiation in particular, 'ype Oxides may Raise the Electrode Potential Passive Metals beyond the Passivity- ɜakdown Potential.

Metals in Contact with p-Type Oxides

Cathodic Reactions of Excited Electrons



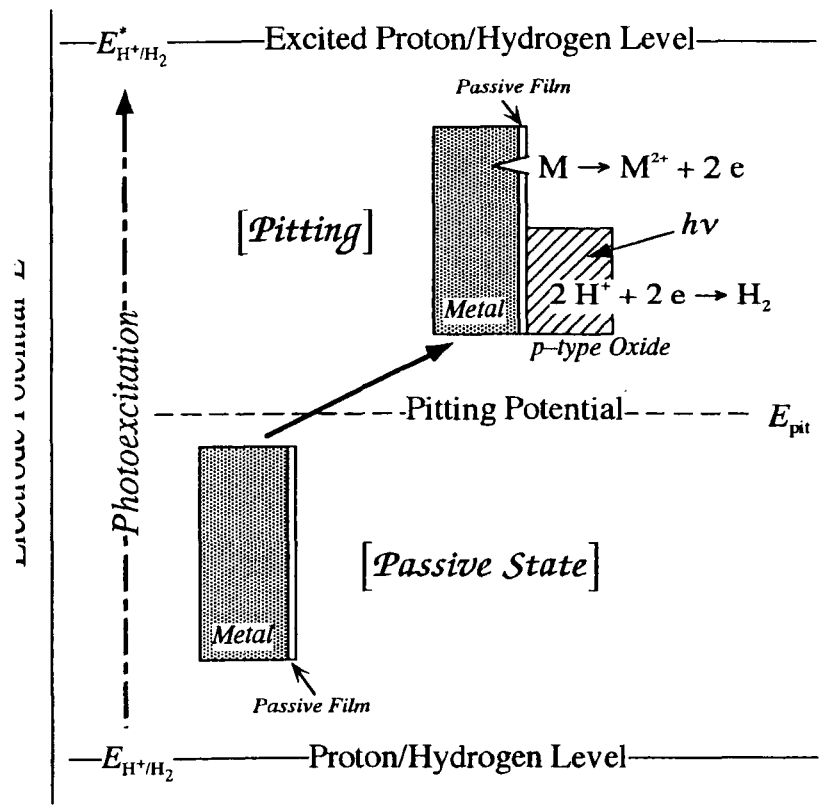
The Excited Electrons Cathodically Reduce Water to Produce *Hydrogen on the Oxide Surface* ($\varepsilon_C > \varepsilon_{HY}$);

$$2\,H^+_{aq} + 2\,e_M \rightarrow H_2 \;,$$

Which may Couple with the Anodic Metal Dissolution at the Passivity Breakdown Sites.

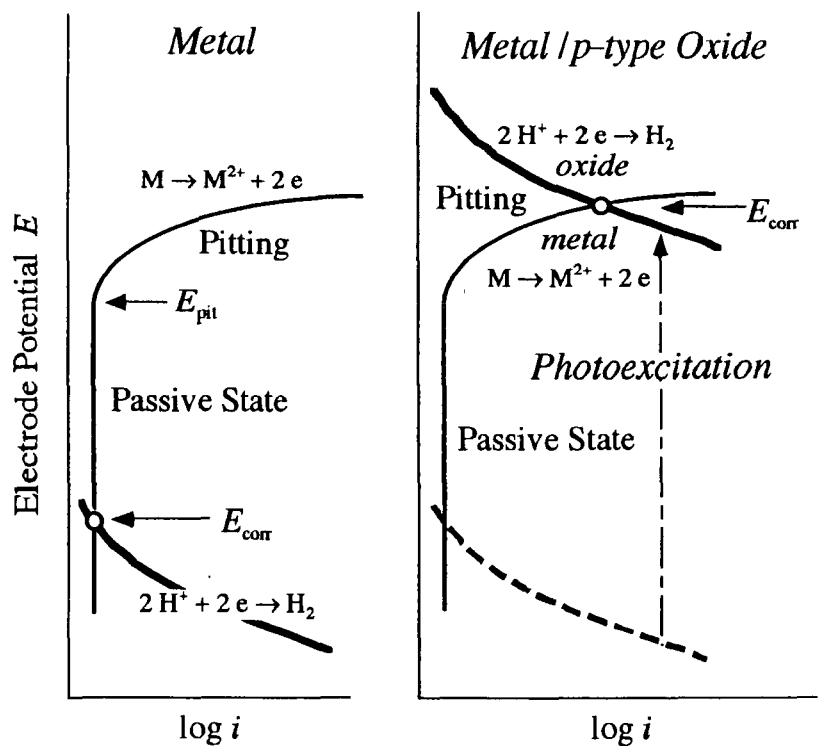
orrosion of Passive Metals in Contact with p-Type Oxides under Excited Conditions.

A Pitting Mood of Metal Dissolution may be Coupled with both the Cathodic Oxygen Reduction on Metals and the Excited-Hole-duced Cathodic Hydrogen Reaction on p-Type Oxides.



Corrosion of Passive Metals in Contact with p-Type Oxides under Excited Conditions in the Absence of Oxygen.

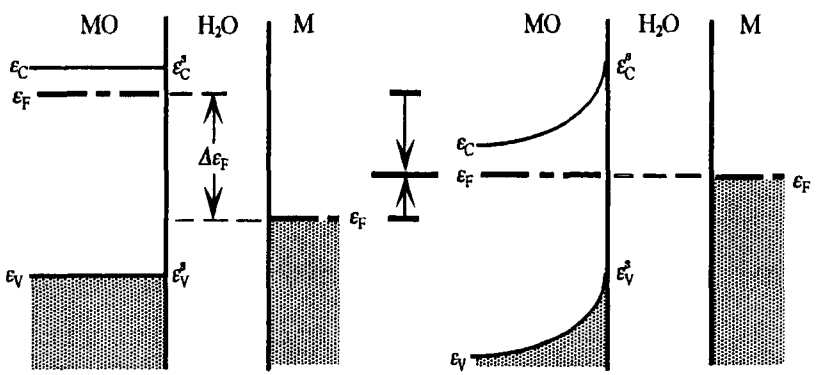
Polarization Curves of Passive Metals with and without Photoexcited p-Type Oxides in Contact. (*Pitting Corrosion*)



Metals in Contact with n-Type Oxides

E_{corr} is More Anodic Than E_{fb}.

Before Contact; After Contact;

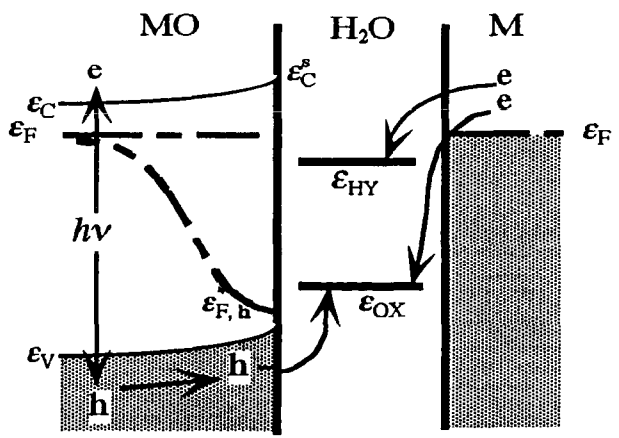


Electronic level diagram for M and n-type MO.

hen being Excited by Radiation in particular,
Type Oxides may Keep the Electrode Potential
wer Than the Passivity-Breakdown Potential.

Metals in Contact with n-Type Oxides

Anodic Reactions of Photoexcited Holes



(*c*)

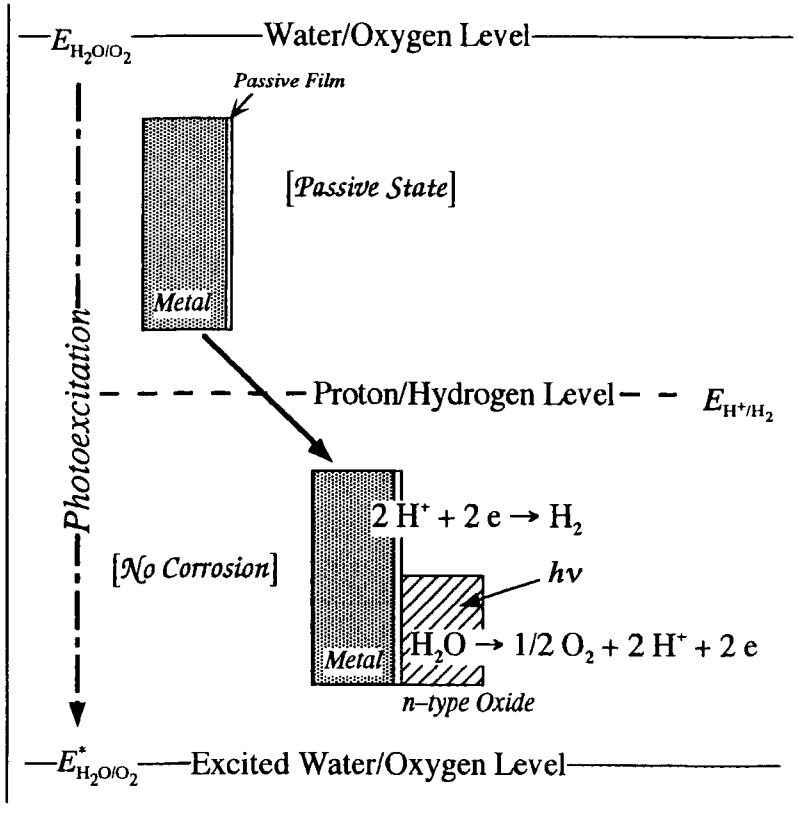
The Excited Holes Anodically Oxidize Water to Produce *Oxygen on the Oxide Surface* ($\varepsilon_V < \varepsilon_{OX}$);

$$2\,H_2O + 4\,h_{redox} = O_2 + 4\,H^+_{aq}.$$

Which may Couple with the *Cathodic Oxygen* ($\varepsilon_{corr} > \varepsilon_{HY}$) *or Proton* ($\varepsilon_{corr} < \varepsilon_{HY}$) *Reduction on the Metal Surface*; Proton Reduction may Increase Hydrogen Damage.

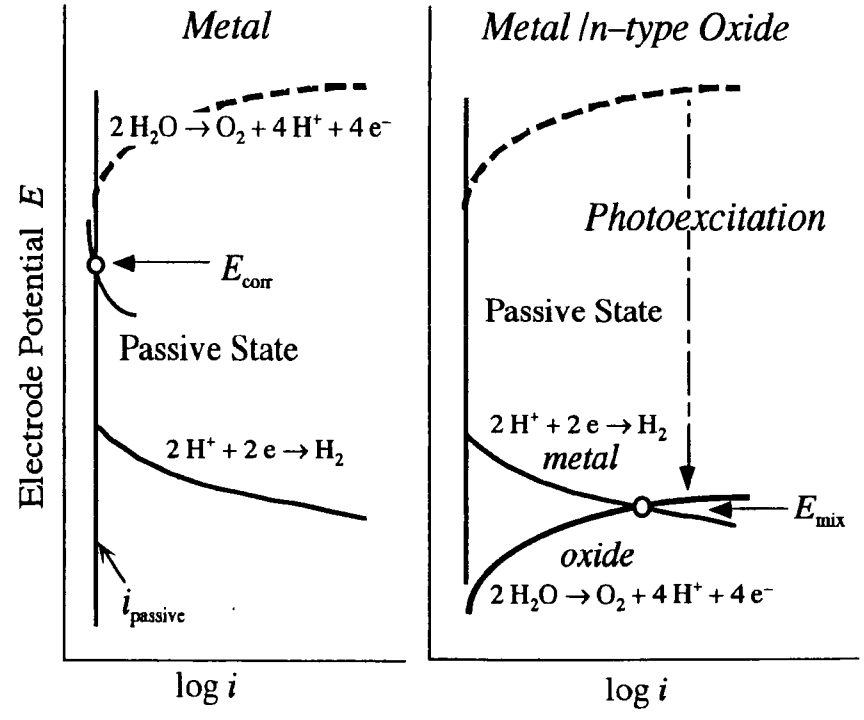
orrosion of Passive Metals in Contact with ·Type Oxides under Excited Conditions.

The Anodic Oxygen Reaction on n-Type Oxides may be Coupled with the *Cathodic Hydrogen Reaction on Metals.* (*Hydrogen Embrittlement*)



Corrosion of Passive Metals in Contact with n-Type Oxides under Excited Conditions.

Polarization Curves of Passive Metals with and without Photoexcited n-Type Oxides in Contact. (*Hydrogen Damage*)



Notes on the Semiconducting Oxides

P-Type Oxides on Metals Shift the Corrosion tential in the Anodic Direction and may Cause loride-Breakdown of Passive Films.

Under Radiation Cathodic Proton Reduction y Occur on p-Type Oxides ($\varepsilon_{CB} > \varepsilon_{HY}$), Which Coupled with Localized Anodic Metal solution at the Passivity Breakdown Sites.

N-Type Oxides on Metals Shift the Corrosion tential in the Cathodic Direction and Prevent ssivity Breakdown.

Under Radiation Anodic Oxygen Evolution y Occur on n-Type Oxides ($\varepsilon_{VB} < \varepsilon_{OX}$), Which y be Coupled with Cathodic Proton Reduction ducing Hydrogen on the Passive Metal face ($\varepsilon_{corr} < \varepsilon_{HY}$), thereby Increasing the bability of Hydrogen Damage.

Conclusions

1. P-Type Oxides on Passive Metals Shift the Metal Potential in the Anodic Direction and may Cause Chloride-Breakdown of Passive Films Leading to a Localized Mode of Corrosion.

2. N-Type Oxides Shift the Metal Potential in the Cathodic Direction and Prevent the Passivity Breakdown, though Increasing the Probability of Hydrogen Damage.

3. In Order to Prevent the p-Type-Oxide-Induced Passivity Breakdown, the Coating of n-Type Oxide Layers on the Passive Metal Surface will be Effective.