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(54) **PHOTO-ELECTROLYTIC CATALYST
SYSTEMS AND METHOD FOR HYDROGEN
PRODUCTION FROM WATER**

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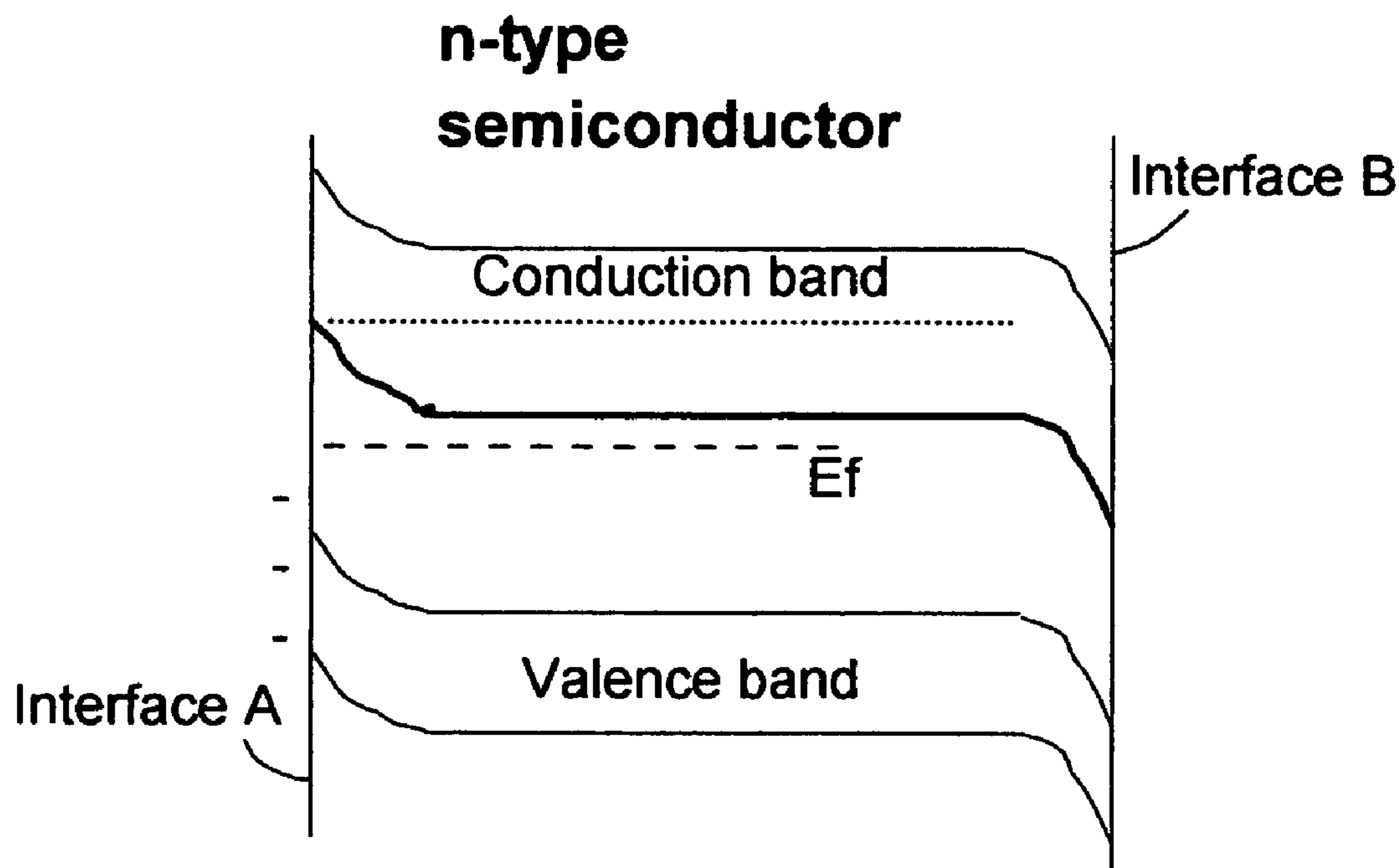
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(57) **ABSTRACT**

A photo-electrolytic catalyst system which comprises two materials: (a) a semiconductor material with a non-zero energy gap E_g which, in response to an incident radiation having an energy greater than E_g , generates electron-hole pairs as charge carriers; and (b) a facilitating material in electronic contact with the semiconductor material to facilitate separation of the radiation-generated electrons from the holes to reduce the probability of charge carrier recombinations. The catalyst makes use of both majority and minority charge carriers to promote photo-electrolysis reactions for producing hydrogen directly from water or an aqueous electrolyte at higher rates and improved efficiencies.



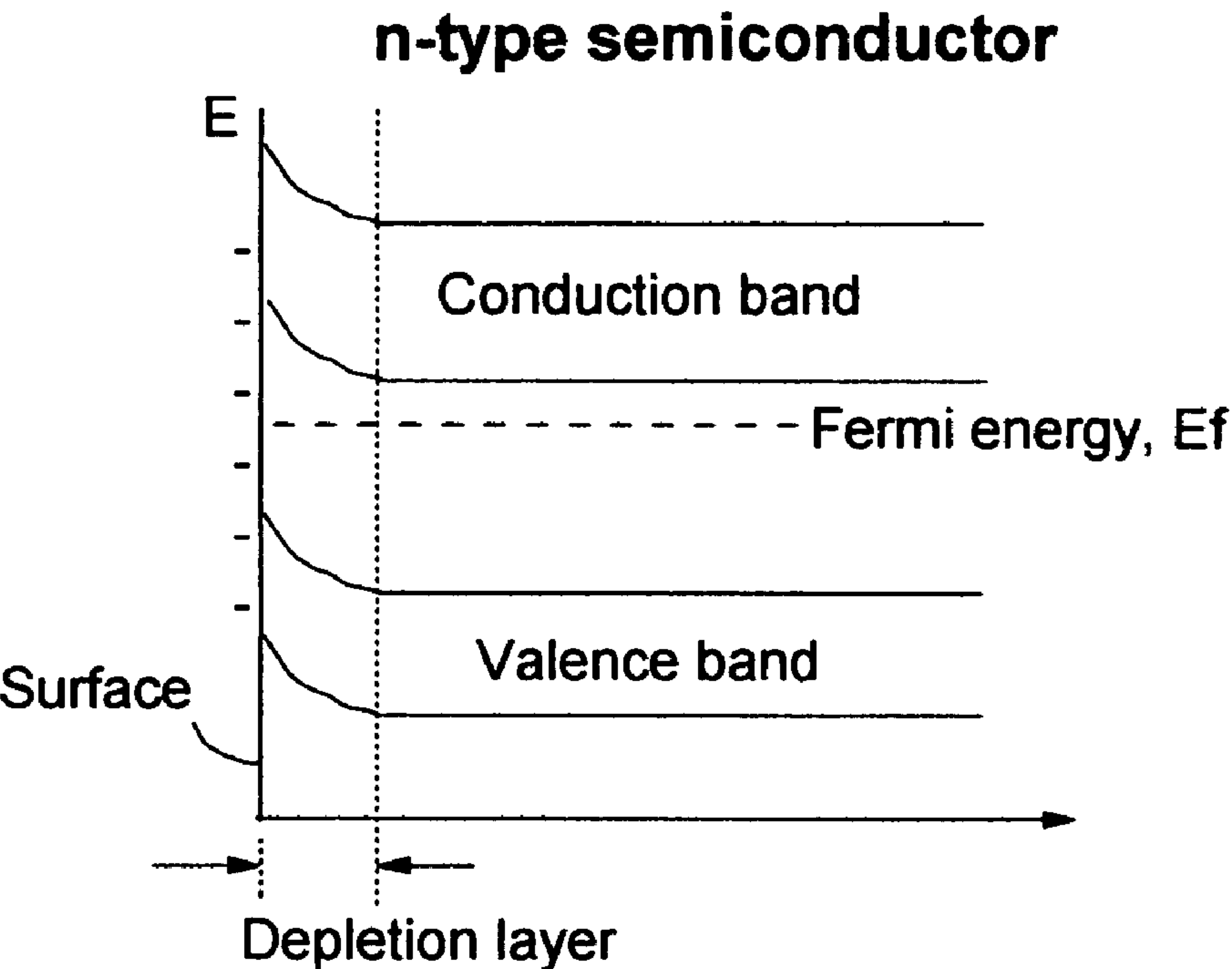


FIG.1A

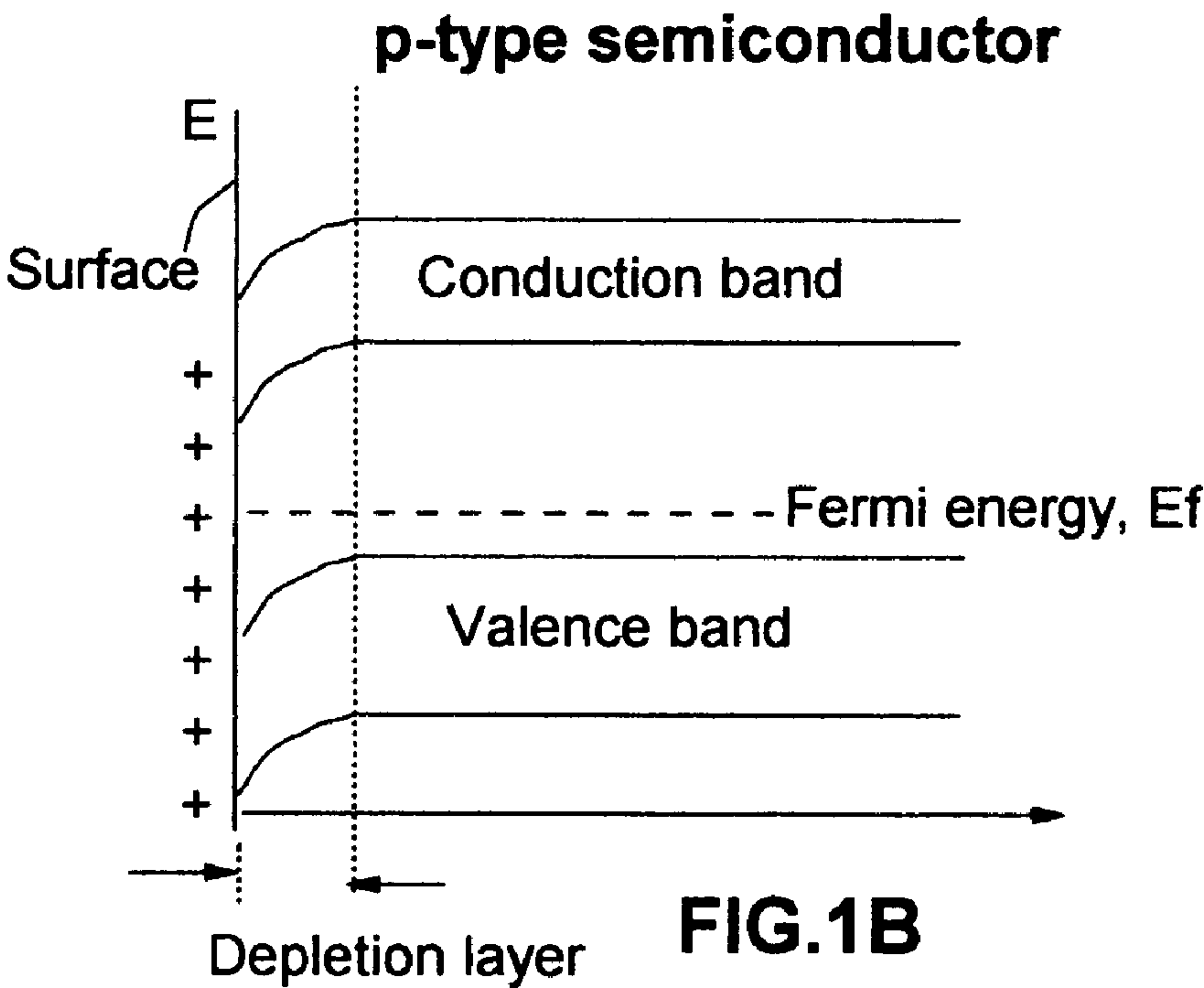


FIG.1B

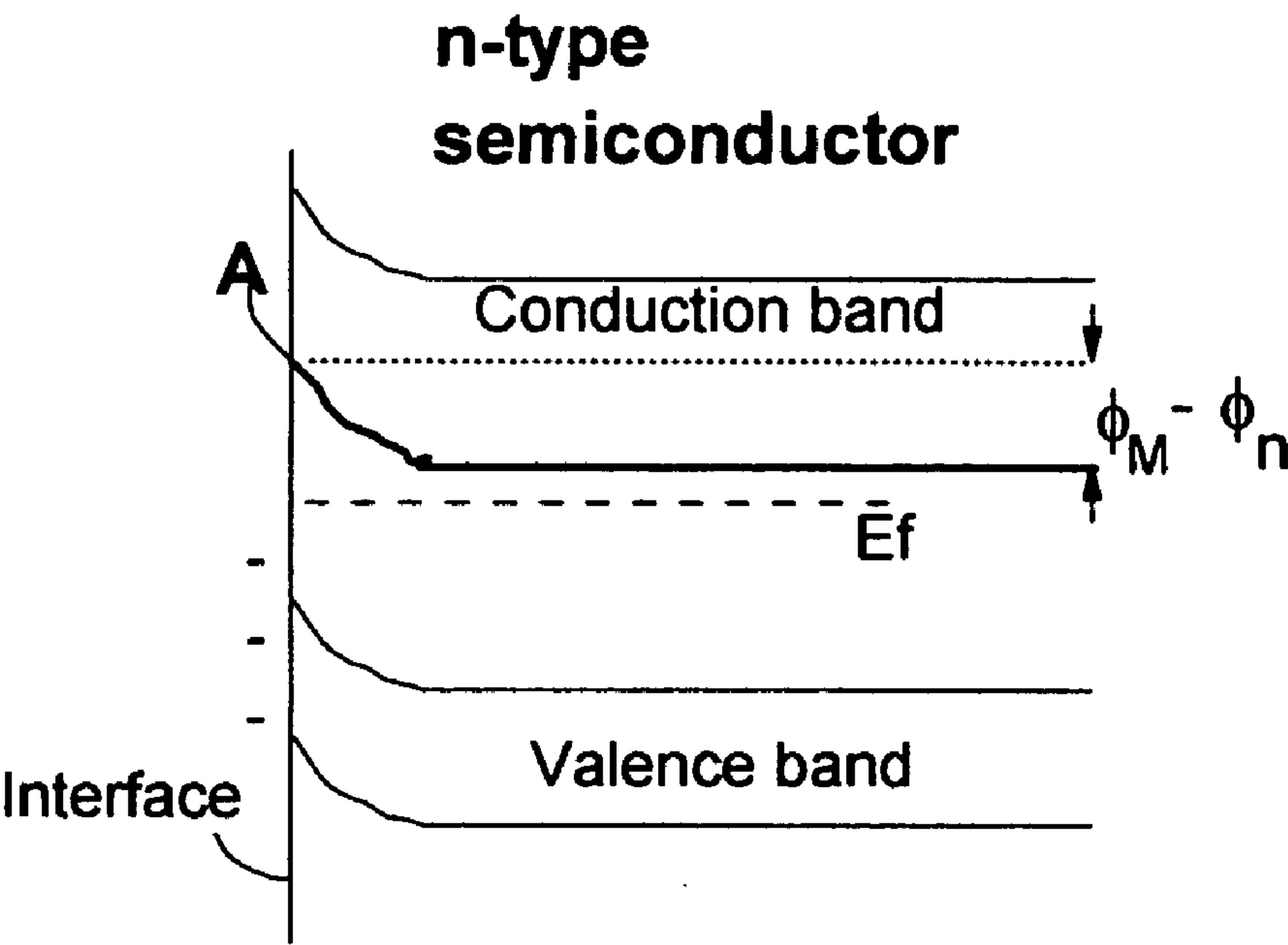


FIG.2A

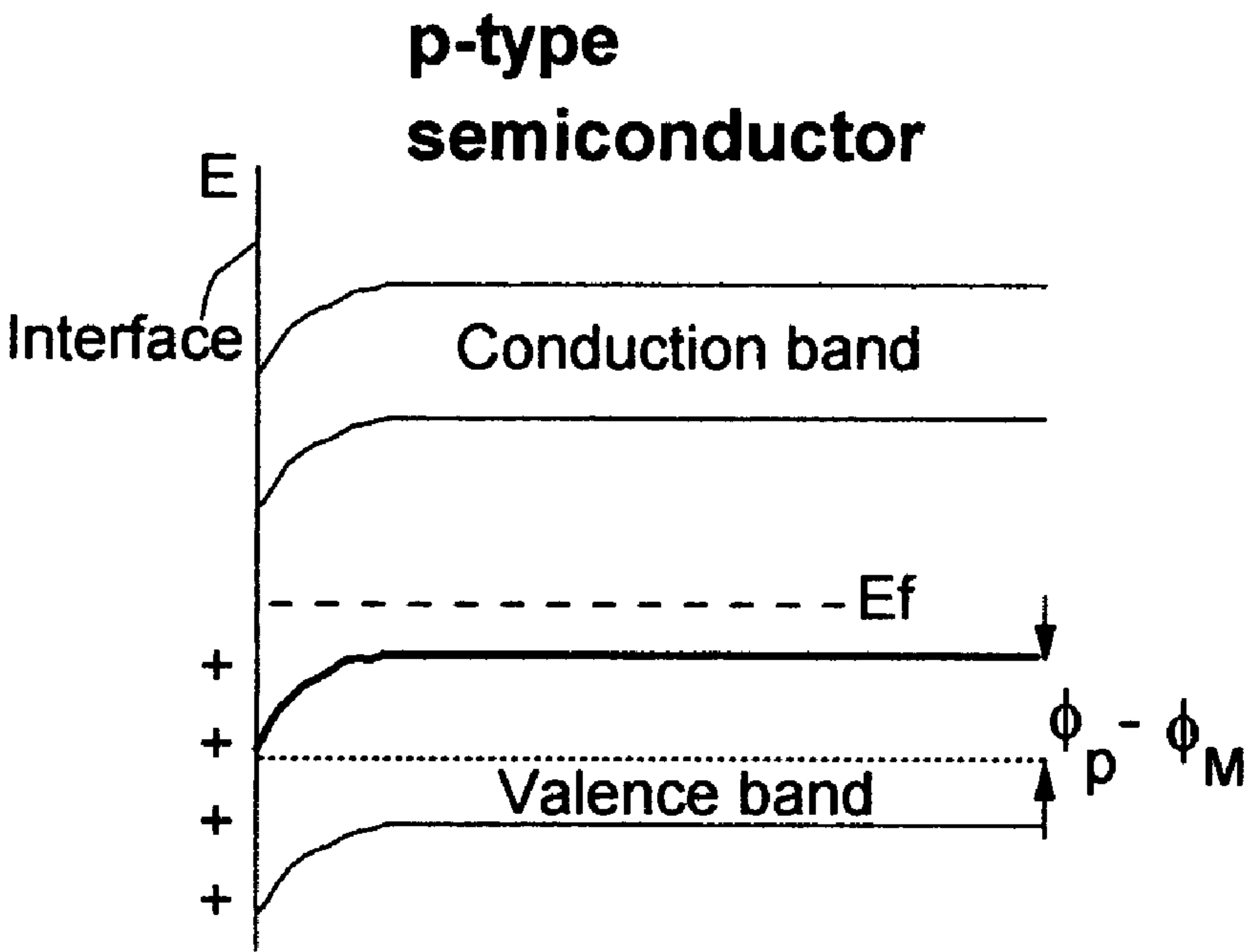


FIG.2B

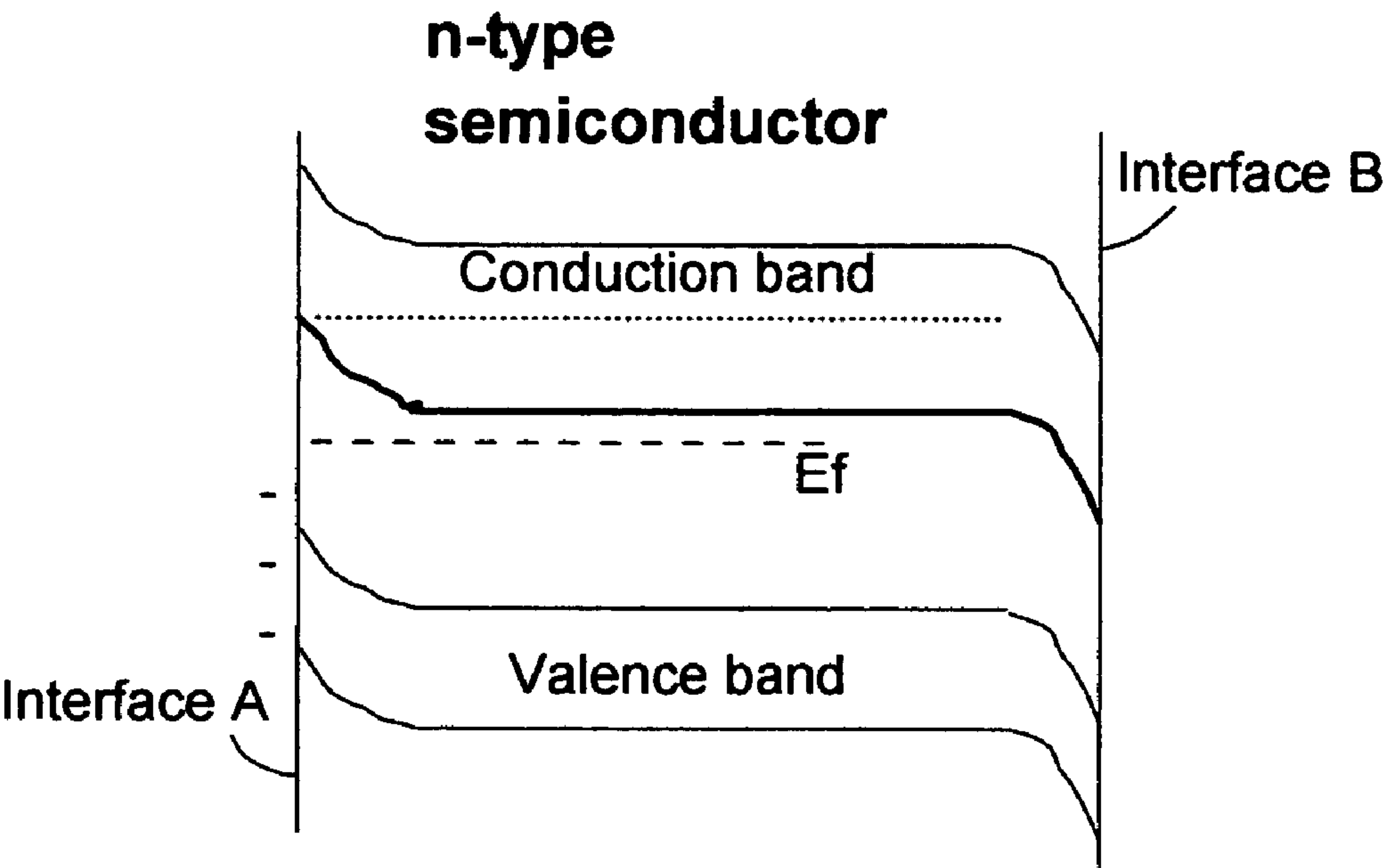


FIG.3A

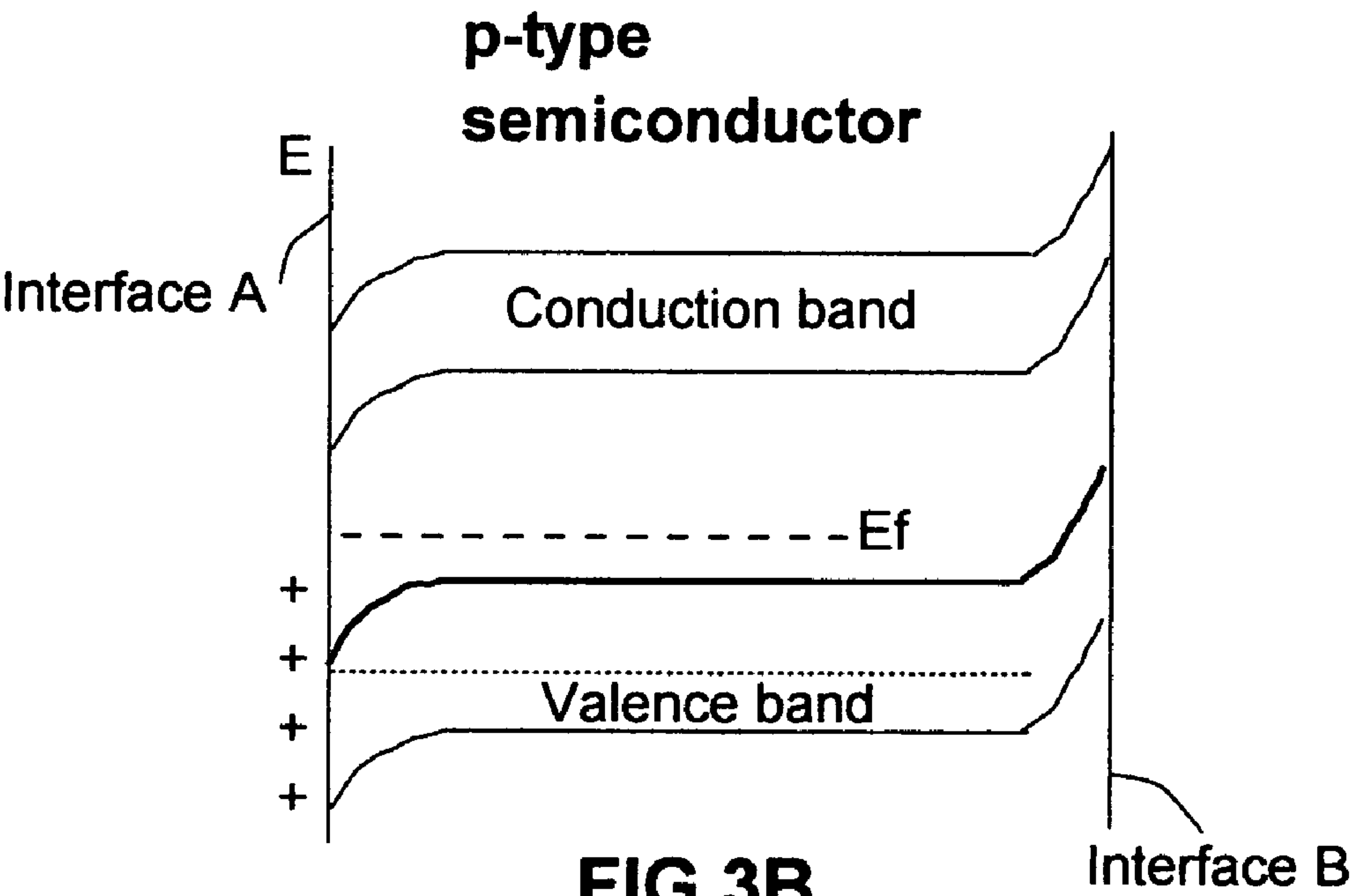


FIG.3B

PHOTO-ELECTROLYTIC CATALYST SYSTEMS AND METHOD FOR HYDROGEN PRODUCTION FROM WATER

FIELD OF THE INVENTION

[0001] This invention provides a photo-electrolytic catalyst system for water splitting to produce hydrogen and oxygen gases. This invention also provides a method of using an improved semiconductor-based photo-electrolytic catalyst to promote solar energy conversion of water or aqueous electrolyte into hydrogen.

BACKGROUND OF THE INVENTION

[0002] A fuel cell converts chemical energy into electrical energy and some thermal energy by means of a chemical reaction between hydrogen-containing fuel and oxygen. As compared to other energy sources, fuel cells provide advantages that include low pollution, high efficiency, high energy density and simple fuel recharge. Fuel cells can be used in electrochemical engines, portable power supplies for various microelectronic and communication devices, standby power supply facilities, power generating systems, etc. Further, fuel cells utilize renewable resources and provide an alternative to burning fossil fuels to generate power.

[0003] For fuel cell applications, hydrogen is the "ultimate fuel." Hydrogen is practically inexhaustible since it is the most plentiful element in the universe (over 95% of all matter). Furthermore, hydrogen is an inherently low cost fuel. Hydrogen has the highest energy density per unit weight of any chemical fuel and is essentially non-polluting since the main by-product of "burning" hydrogen is water. Thus, hydrogen can be a means of solving many of the world's energy related problems, such as global warming, pollution, strategic dependency on oil, etc. Hydrogen can be produced by various processes which split water into hydrogen and oxygen or which oxidize methanol or ethanol into hydrogen and other molecules. The hydrogen can then be stored and transported in a solid state form.

[0004] Hydrogen is produced as a co-product in various industrial processes. For example, hydrogen is produced as a co-product in the electrolysis of aqueous alkali metal halide brines to yield the corresponding alkali metal hydroxide, the halogen, and hydrogen. Hydrogen is also produced as a co-product in the electrolysis of aqueous alkali metal sulfates to yield the alkali metal hydroxide, oxygen, and hydrogen. In all of these industrial processes, electrical power must be applied from an external power supply, across an anode and a cathode of an electrolytic cell, to yield oxygen or halogen at the anode, the alkali metal hydroxide at the cathode, and hydrogen as a cathode co-product.

[0005] The photolysis of water into H_2 and O_2 using solar radiation is an attractive method of producing hydrogen since it involves renewable and non-polluting energy sources: water and sunlight. The conversion of solar energy into chemical energy has the advantage of easy energy storage (in the form of the photo-generated fuel), as compared with solar energy conversion via photovoltaic or photo-thermal processes. An important process for accomplishing the decomposition of water into H_2 and O_2 using solar radiation is photo-electrolysis.

[0006] Photo-electrolytic decomposition of water using a pair of n-type and p-type semiconductor electrodes electri-

cally connected by an electrolyte solution was disclosed by Tchernev in U.S. Pat. No. 3,925,212 (Dec. 9, 1975). Nozik (U.S. Pat. No. 4,094,751, June 13, 1978) disclosed photochemical diodes which use light to drive both endoergic and exoergic chemical reactions such that optical energy is converted into chemical energy. Either Schottky-type (rectifying metal-semiconductor junction) or p-n type diodes were employed to convert water into hydrogen and oxygen gases. In a typical photochemical diode, for instance, the p-type portion and the n-type portion are intimately joined together through an ohmic contact. Gratzel, et al. (U.S. Pat. No. 4,389,290, Jun. 21, 1983) disclosed a photolytic system comprising a darkened half cell and an illuminated half cell in which oxidation and reduction are made to occur. Ayers (U.S. Pat. No. 4,466,869, Aug. 21, 1984) developed a multi-layered photo-electrolytic device to produce hydrogen. This complicated device includes a multiplicity of stacked photoelectric or photovoltaic elements between a substrate and an electrode, a counter-electrode, and an unbiased external circuit. Another complicated, multi-layer photo-electrolytic device is disclosed by Gordon (U.S. Pat. No. 4,650,554, Mar. 17, 1987).

[0007] Photolytic decomposition of water was also accomplished by Khan, et al. (U.S. Pat. No. 4,889,604, Dec. 26, 1989) who used a catalyst system that included a semiconductor of hexagonal crystal structure loaded with a noble metal and a transition metal oxide. The catalyst was suspended in ethylene diamine tetra-acetic acid (EDTA) as a part of the catalyst system. The photo-catalytic method for water decomposition disclosed by Sayama, et al. (U.S. Pat. No. 5,262,023, Nov. 16, 1993) involved bringing an aqueous solution of carbonate into contact with a semiconductor carrying a metal or a metal compound, and irradiating the aqueous solution with light. The photo-catalyst used by Takaoka, et al. (U.S. Pat. No. 5,759,948, Jun. 2, 1998) was composed of titanium oxide particles which have part or the whole of an iron compound supported thereon. A series of photo-catalysts each consisting of a catalytically active ingredient (e.g., Cs and CdS) and a supporting or promoting ingredient (e.g., Ni, Co, Fe, and $K_4Nb_6O_{17}$) were proposed by Park and co-workers (U.S. Pat. No. 5,865,960, Feb. 2, 1999; U.S. Pat. No. 6,017,425, Jun. 25, 2000; U.S. Pat. No. 6,077,497, Jun. 20, 2000; U.S. Pat. No. 6,300,274, Oct. 9, 2001; U.S. Pat. No. 6,297,190, Oct. 2, 2001; U.S. application Ser. No. 09/735,605, filed Dec. 14, 2000). Bipolar electrodes with a semiconductor coating, titanium dioxide doped with iron, was disclosed by Haug, et al. (U.S. patent application Ser. No. 09/783,228, filed Feb. 14, 2001).

[0008] The above inventions have one or several of the following drawbacks: (1) complicated junctions or multiple-layer structures, (2) insufficient photolytic or photo-electrolytic efficiency, (3) slow hydrogen production rate, (4) involving non-water liquid ingredients (e.g., EDTA, acid, strong base, or other potentially hazardous chemicals), and (5) photo-catalysts with unknown operating mechanisms (hence, the resulting efficiency, yield, and rate can only be improved by trial-and-error and cannot be readily or effectively optimized).

SUMMARY OF THE INVENTION

[0009] This invention provides simple (non-complicated) but effective photo-electrolytic catalyst systems which comprise two materials: (a) a semiconductor material with a

non-zero energy gap E_g which, in response to an incident radiation having an energy greater than E_g , generates electron-hole pairs as charge carriers; and (b) a facilitating material in electronic contact with the semiconductor material to facilitate separation of the radiation-generated electrons from the holes to reduce the probability of charge carrier recombinations. The catalysts make use of both majority and minority charge carriers to promote photo-electrolysis reactions for producing hydrogen at higher rates and improved efficiencies.

[0010] The semiconductor material and/or the facilitating material preferably has at least one dimension being smaller than one micron ($1\ \mu\text{m}$) and, further preferably, smaller than or equal to 100 nm. Either or both materials are preferably porous. These two features (small dimensions and high porosity levels) more readily facilitate the separation of the photon-generated electrons and holes and provide larger material-water interface areas where redox reactions occur, leading to more efficient and faster hydrogen production.

[0011] The present invention also provides a method of using these photo-electrolytic catalysts to generate hydrogen gas from water.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] **FIG. 1** (A) Upward bending of energy band curves for an n-type semiconductor and (B) Downward bending of energy band curves for a p-type semiconductor.

[0013] **FIG. 2** (A) Upward bending of energy band curves for an n-type semiconductor at a rectifying contact interface and (B) Downward bending of energy band curves for a p-type semiconductor at a rectifying contact interface.

[0014] **FIG. 3** (A) Upward bending of energy band curves for an n-type semiconductor at a rectifying semiconductor-electrolyte contact interface and downward bending at a semiconductor-facilitating material interface and (B) Downward bending of energy band curves for a p-type semiconductor at a rectifying semiconductor-electrolyte contact interface and upward bending at a semiconductor-facilitating material interface.

DETAILED DESCRIPTION OF THE INVENTION

[0015] A. Basic Operating Mechanisms of the Invented Photo-electrolysis Catalyst Systems

[0016] In conventional photo-electrolysis, light is absorbed in separate, discrete semiconducting electrodes in contact with an electrolyte. Ideally, the absorbed light generates electron-hole pairs within the electrodes which, hopefully, are subsequently separated by the semiconductor-electrolyte junctions. At the cathode and anode, electrons and holes are respectively injected into the electrolyte, thereby inducing reduction and oxidation reactions, respectively. Electrons and holes are known to be strong reducing and oxidizing agents, respectively. Hence, an overall photo-electrolysis reaction is achieved in two steps: (1) electrons and holes are first generated by photo-excitation of electrons across an energy band gap (E_g) of a semiconducting electrode, and (2) the electrons and holes drive chemical reactions in either or both electrodes. In such a photo-chemical process, the possibility exists that this sequence can drive

reactions at more favorable energies than can either direct photolysis or direct electrolysis acting independently.

[0017] In order for such a photo-electrolysis process to work efficiently, the electrons and holes generated must be immediately separated, at least tentatively, from each other to reduce or eliminate electron-hole charge recombinations. In a conventional Schottky-type photo-electrolysis cell (e.g., as disclosed in U.S. Pat. No. 3,925,212), the semiconductor/ohmic contact forms one electrode, while metal forms the second, or counter-electrode. The two electrodes are separated by the electrolyte, being joined externally by an electrical circuit to provide a path for hole and electron transfer, possibly as a means of separating electrons from holes. In a conventional p-n type photo-electrolysis cell, the p-type semiconductor/ohmic contact forms one electrode, while the n-type semiconductor/ohmic contact forms the other electrode. Again, the two electrodes are separated by the electrolyte and are joined externally by an electrical circuit to provide a path for electron and hole transfer.

[0018] In an improved photo-electrolysis system (Nozik, U.S. Pat. No. 4,094,751), either Schottky-type or p-n type photo-chemical diodes were employed to convert water into hydrogen and oxygen gases. Each diode comprises two portions, e.g., in the case of a p-n type diode, the p-type portion provided with an ohmic contact and the n-type portion also provided with an ohmic contact. The two portions are intimately joined or bonded together through the ohmic contacts. The conventional wisdom maintains that, for a p-n photo-chemical diode, the ohmic contact permits recombination of the photo-generated majority carriers in the respective regions of the diode, and thereby allows the minority carriers to be injected into the electrolyte to complete the current path. That is, the photons absorbed in each portion of the p-n photochemical diode create electron-hole pairs; the minority holes (from the n-type portion) and the minority electrons (from the p-type portion) are injected into the electrolyte. The majority electrons and holes must recombine for current continuity to exist, and this can only happen if ohmic contacts are sandwiched between the p- and n-type semiconducting portions of the diode. Such a concept has a serious drawback in that the majority charge carriers (that normally outnumber the minority charge carriers by several orders of magnitude) are all wasted, not given an opportunity to catalyze the respective oxidation and reduction reactions in an aqueous medium.

[0019] Contrary to the teachings of the prior art and in accordance with the present invention, photo-electrolytic catalyst systems are provided which comprise two materials: (a) a semiconductor material with a non-zero energy gap E_g which, in response to an incident radiation having an energy greater than E_g , generates electron-hole pairs as charge carriers; and (b) a facilitating material in electronic contact with the semiconductor material to facilitate separation of the radiation-generated electrons from the holes to reduce the probability of charge carrier recombinations. Such a new photo-electrolysis catalyst system, preferably in the form of a fine powder or a micron- or sub-micron-scale entity, may simply be suspended or dispersed in an aqueous electrolyte. Preferably, the facilitating material has a high surface-to-volume ratio, thus providing a large surface area whereon majority charge carriers can tentatively reside prior to catalyzing respective reduction and oxidation reactions at the facilitating material-electrolyte (water) interfaces. In addi-

tion to the majority charge carriers being capable of catalyzing the chemical reactions, minority charge carriers are capable of being directly injected into the aqueous medium to complete the current path as well as catalyzing the redox reactions.

[0020] The need to have a high surface-to-volume ratio can be achieved by making the catalyst system in small scales or of high porosity. The facilitating material and/or the semiconductor material preferably are (is) micron-scaled and further preferably nano-scaled (<100 nm). The facilitating material is preferably micro-porous or nano-porous, with a large number of micron- or nano-scale pores to accommodate water molecules and to allow the resulting hydrogen and oxygen molecules to escape. These large surface areas provide large facilitating material-water interfaces where reduction/oxidation reactions occur. The present invention also eliminates the need for both large planar electrode systems and external circuitry.

[0021] The hole-electron separation-facilitating material preferably has an attribute in that it can tentatively retain majority charge carriers (e.g., electrons) therein or thereon to give the retained charge carriers improved chances of encountering reactant species and reacting therewith (e.g., $2H_2 + 2e^- \rightarrow H_2$ or $2H_2O + 2e^- \rightarrow 2OH^- + H_2$). For an n-type semiconductor, the facilitating material may preferably comprise a reduction catalyst such as platinum (Pt). For a p-type semiconductor, the facilitating material may preferably comprise an oxidation catalyst such as ruthenium oxide (RuO_2). Although these features are preferred, they are not necessary requirements. For an intrinsic semiconductor, either type or both types of catalysts may be used as a facilitating material.

[0022] B. The Constituent Semiconductor Material

[0023] For the purpose of clearly defining the claims, the term semiconductor refers to a single element-type material such as silicon (Si) or a multiple-element material such as gallium arsenide (GaAs) provided that it has non-zero energy band gap (Eg). A multiple-element semiconductor typically contains at least one metal element. In the present context, any conventionally defined “electrical insulator” such as oxides, nitrides and carbides (despite having a large energy gap, e.g., Eg greater than 3.0 eV) will be considered as a semiconductor. A “metal” refers to an element of Groups 2 through 13, inclusive, plus selected elements in Groups 14 and 15 of the periodic table. Thus, the term “metal” broadly refers to the following elements:

[0024] Group 2 or IIA: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).

[0025] Groups 3-12: transition metals (Groups MB, IVB, VB, VIB, VIIB, VIII, IB, and IIB), including scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), tungsten (W), manganese (Mn), technetium (Tc), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), tungsten (W), manganese (Mn), technetium (Tc), rhenium (Re), iron (Fe), ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd), platinum (Pt), copper (Cu), silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and mercury (Hg).

[0026] Group 13 or IIIA: boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl).

[0027] Lanthanides: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

[0028] Group 14 or IVA: germanium (Ge), tin (Sn), and lead (Pb).

[0029] Group 15 or VA: antimony (Sb) and bismuth (Bi).

[0030] For photo-electrolysis catalyst applications, the metal is preferably selected from the group consisting of aluminum, antimony, bismuth, boron, cadmium, copper, iron, gallium, germanium, indium, lead, titanium, tin, and zinc. Preferably a counter ion element is selected from the group consisting of hydrogen, oxygen, carbon, nitrogen, chlorine, fluorine, boron, iodine, sulfur, phosphorus, arsenic, selenium, tellurium and combinations thereof. These elements may be used to react with a metal to form a compound or ceramic of hydride, oxide, carbide, nitride, chloride, fluoride, boride, iodide, sulfide, phosphide, arsenide, selenide, and telluride, and combinations thereof. The range of compound semiconductor or ceramic materials that can be used as a semiconductor includes, but not limited to, I-VII, II-VI, and III-V compounds. All of these materials can be selectively doped with electron-donors or electron acceptors to produce n-type or p-type semiconductors. Pure, un-doped semiconductors are referred to as intrinsic semiconductors. Table 2 shows some of the preferred semiconductors for use in the invented photo-electrolysis catalyst.

TABLE 1

Selected semiconductor materials.	
n-type	p-type
Miscellaneous	
TiO ₂	Cu ₂ O
CoO	CuS
NiO	
M _x Zn _y O ₂	
MTiO ₃	
ZnO	
Fe ₂ O ₃	
WO ₃	
Si, Te, SiC	Si, Ge, SiC
(M is a transition metal element or rare-earth metal element)	
II-VI compounds	
CdS	CdTe
CdSe	ZnTe
CdTe	ZnSe
III-V compounds	
GaP	GaP
GaAs	GaAs
InP	InAs
AlAs	AlAs
AlSb	AlSb
GaSb	GaSb
InP	

TABLE 1-continued

Selected semiconductor materials.	
n-type	p-type
Mixed crystals of II-VI compounds	
Cd _{1-x} Zn _x S	
Mixed crystals of III-V compounds	
GaAs _x P _{1-x}	GaInP ₂
Cu _x In _y Ga _z Se ₂	
GaIn _{1-x} As	
Al _x Ga _{1-x} As	
Chalcopyrites	Chalcopyrites
Chalcogenides	Chalcogenides
I-III-V ₂ compounds	
CuInS ₂	CuInS ₂
AgInSe ₂	CuGaS ₂
AgInS ₂	CuAlS ₂
CuInSe ₂	CuAlSe ₂
	CuInSe ₂
II-IV-V ₂ compounds	
ZnSiP ₂	ZnSiAs ₂
CdSiP ₂	ZnGeP ₂
CdSnP ₂	ZnSnAs ₂
CdSnAs ₂	ZnSnP ₂
	ZnSnSb ₂
	CdSnP ₂
	CdSnAs ₂
ZMO compounds (Z = alkaline or alkali metal)	
K ₄ Nb ₆ O ₁₇	
Na ₂ Ti ₆ O ₁₃	
K ₂ Ti ₆ O ₁₃	
BaTi ₄ O ₉	

[0031] C. Electron-Hole Separation-Facilitating Materials

[0032] If a semiconductor is in a physical contact with a metal, a rectifying contact (Schottky junction) or an ohmic contact is formed, depending on the type of metal used. Assume that the surface of an n-type semiconductor has somehow been negatively charged, as schematically shown in FIG. 1A. The negative charges repel the free electrons that had been near the surface and leave positively charged donor ions behind (e.g., As⁺). Any electron which drifts toward the surface (i.e., moving in the negative X-direction toward the surface) “feels” this repelling force. As a consequence, the region near the surface has less free electrons than the interior of the solid. This region is known as the depletion layer or space charge region. The repelling force of an external negative charge may be customarily represented by an upward-bending energy band curve near the surface, FIG. 1A. This implies that the electrons like to roll downhill. Similarly, if a p-type semiconductor is somehow positively charged at the surface, the positive charge carriers (holes) are repelled toward the inert part of the material and the band edges are bent downward, FIG. 1B. This represents a potential barrier for holes because the holes have to drift upward in order to come closer toward the surface.

[0033] Assume that a metal with a work function ϕ_M is brought into contact with an n-type semiconductor with a work function ϕ_n , where $\phi_M > \phi_n$, electrons start to flow from the semiconductor “down” into the metal until the Fermi energies of both materials are equal. As a consequence, the metal will be charged negatively and a potential barrier is

formed just as shown in FIG. 1A. This means that the energy bands in the bulk semiconductor are lowered by the amount $(\phi_M - \phi_n)$ with respect to a point A at the metal-semiconductor interface, FIG. 2A. Such a junction is a rectifying contact. Contrarily, if $\phi_M < \phi_n$, the contact will be an ohmic contact and the energy band curves near the metal-semiconductor interface will be down-ward bending.

[0034] Similarly, if a p-type semiconductor (work function ϕ_p) is brought into contact with a metal and $\phi_M < \phi_p$, electrons diffuse from the metal into the semiconductor and, therefore, the surface of the p-type semiconductor is charged positively. A potential barrier ($\phi_p > \phi_M$) is formed just as shown in FIG. 1B. This situation is illustrated by a “downward” potential barrier (for the hole), indicated in FIG. 2B. Contrarily, if $\phi_M > \phi_p$, the contact will be an ohmic contact and the energy band curves near the metal-semiconductor interface will be up-ward bending. When a p-type semiconductor and an n-type semiconductor are brought into contact with each other, a rectifying potential barrier is established.

[0035] The interface between a liquid electrolyte (e.g., water) and a semiconductor is similar to a metal-semiconductor junction and can be an ohmic contact or a rectifying contact, depending upon the relative magnitudes of the work functions as explained above, using FIGS. 1A, 1B, 2A, and 2B. With an n-type ZnO (Eg=3.35 eV) as an example, photo-chemical splitting of water at the water-ZnO interface and the direct conversion of solar energy into chemical energy may be represented as a process in the rectifying metal-semiconductor junction (e.g., at interface A of FIG. 3A) or in one half of a p-n junction. When solar radiation is absorbed in the n-type ZnO, electron-hole pairs are created. The potential gradient established at the depletion zone forces the electrons to drift into the bulk of the semiconductor and likely become wasted (not participating in any chemical reactions). However, the holes drift to the surface of the semiconductor where they may combine with HO⁻ ions or react with H₂O (H₂O+2h⁺→2H⁺+½O₂) and result in the evolution of oxygen gas.

[0036] The present invention provides a facilitating material that “attracts” the photo-generated electrons or promotes the photo-generated electrons to sweep across the “bulk” of the n-type semiconductor and across the facilitating material-semiconductor interface (e.g., interface B of FIG. 3A) so that they have opportunities to combine with H⁺ or react with H₂O at the facilitating material-electrolyte interface to produce hydrogen (e.g., through 2H₂O+2e⁻→2OH⁻+H₂). Without the presence of this facilitating material, these electrons would somehow recombine with the defects or holes in the bulk of the semiconductor and would be wasted. In one preferred embodiment, the semiconductor has one dimension smaller than 1 μm and further preferably has one dimension smaller than 100 nanometers (nm). Preferably, the facilitating material also has a dimension smaller than 1 μm and, further preferably, smaller than 100 nm. Alternatively or additionally, the facilitating material and/or the semiconductor material is porous, being meso-porous (pore size>10 μm), micro-porous (0.1 μm<pore size<10 μm), and/or nano-porous (pore size<0.1 μm). The small dimension(s) of the semiconductor make it easier for the photo-generated charges to readily sweep across the bulk of the semiconductor (the “bulk” itself being so small) with reduced chances of recombinations. A porous semiconductor means a larger surface area to promote hole-water contacts.

Both the small dimension(s) and the pores of the facilitating material mean greater interface areas between the facilitating material and water where desirable hydrogen production reactions can occur.

[0037] In the case of a p-type semiconductor (e.g., an acceptor-doped ZnSe), the corresponding process involves the generation of hole-electron pairs by the absorption of solar radiation. The electrons in this case are forced to drift to the surface while the holes drift to the bulk of the semiconductor. At the semiconductor-water interface (e.g., interface A of FIG. 3B), the electrons are transferred to the electrolyte where they combine with H^+ and cause the evolution of hydrogen. Without the assistance of a facilitating material, the holes would somehow disappear in the bulk through undesired recombinations and would not assist in the water splitting reactions. The facilitating material “attracts” the photo-generated electrons or promotes the photo-generated holes to sweep across the “bulk” of the p-type semiconductor and across the facilitating material-semiconductor interface (e.g., interface B of FIG. 3B) so that they have opportunities to combine with OH^- or react with H_2O at the facilitating material-electrolyte interface to produce oxygen and hydrogen ion (e.g., through $H_2O + 2h^+ \rightarrow 2H^+ + \frac{1}{2}O_2 \uparrow$).

[0038] The overall photoelectro-catalytic splitting of water may be conveniently expressed as:

$$h\nu - 2h^+ + 2e^- \quad (h = \text{Planck's constant, } \nu = \text{frequency of the radiation}) \quad (1)$$



[0039] However, from the perspective of reaction mechanisms, the overall reaction may begin with electrolysis of water:



[0040] The required water redox potential ($\Delta E \approx 1.23 \text{ eV}$) may come from the semiconductor, the facilitating material, or a combination. The resulting ions of OH^- and H^+ may then react with holes and electrons to produce oxygen and hydrogen, respectively:



[0041] It is important to realize that both electrons and holes are essential to completing the above loop of reactions (Eqn.(2)-(6)). Even though one may be interested in collecting hydrogen only, the production of oxygen is indispensable because the production of oxygen (Eqn.(2) or Eqn.(5)) also results in the formation of H^+ ions as a co-product, which is needed for hydrogen production to complete the loop. This is another reason why a facilitating material is desired in the invented photo-electrolytic catalyst system. Further, a small amount of energy is lost to heat and other loss mechanisms and, hence, a potential greater than 1.23 eV (typically >1.6 eV) is required for electrolysis of water. Therefore, a semiconductor with a band gap greater than 1.6 eV is preferred.

[0042] The facilitating material may include an element selected from Group VI and Group VII of the Periodic Table of Elements. The facilitating material may include a transition metal element or a rare earth element. Preferably, the facilitating material may include an element selected from

the group consisting of Fe, Mn, Co, Ni, Cr, and Ti. The above elements were found to constitute very effective facilitating materials.

[0043] In order to make better use of the solar radiations, it is advantageous to combine or mix two or three semiconductor materials together that share with the same facilitating material to form a hybrid photo-electrolytic catalyst system. The two or three semiconductors are preferably of different energy band gaps, covering both UV and visible wavelengths. A semiconductor material or a hybrid combination of two or three semiconductor materials may be in electronic contact with two or more facilitating materials. Preferably, one facilitating material is an electron-drawing material while another one is a hole-drawing material. Such a combination could more effectively facilitate the separation of electrons from holes immediately after they are photo-generated in a semiconductor. When three or more semiconductor materials are combined, they are preferably connected electrically in series. The resulting solid state junctions at the micro- or nano-scale act to reduce semiconductor-electrolyte interface voltage requirements.

[0044] Another preferred embodiment of the present invention is a method for producing hydrogen from water or an aqueous electrolyte. The method comprises suspending photo-electrolytic catalysts as illustrated above in an aqueous electrolyte (including, but not limited to, pure water or sea water) and then illuminating the catalysts with optical energy. The method may further include means of collecting the hydrogen gas produced.

EXAMPLE 1

[0045] A micro-crystalline powder of GaP (average particle size $\approx 0.7 \mu m$) was doped with sulfur to produce an n-type semiconductor. A thin layer of platinum (Pt) was sputter-coated over a portion of individual n-GaP particles to serve as a facilitating material. When such a photo-electrolytic catalyst system was suspended in an aqueous solution, hydrogen was evolved.

EXAMPLE 2

[0046] Materials similar to those in Example 1 were used, but the average particle size of GaP was slightly below 100 nm. When such a photo-electrolytic catalyst system was suspended in the same aqueous solution, hydrogen was much more vigorously evolved.

EXAMPLE 3

[0047] Several samples were prepared for this example. As in Example 2, nano-scaled n-type GaP powder was used, but the facilitating materials were Mn, Fe, Ni, and Co, respectively. When such photo-electrolytic catalyst systems were suspended in the same aqueous solution, hydrogen was vigorously evolved. The solar-to-hydrogen power conversion efficiencies for these samples were found to be in the following order: $Mn \approx Fe > Ni > Co$ (as facilitating materials).

EXAMPLE 4

[0048] Several samples were prepared for this example. As in Example 3, nano-scaled p-type ZnTe powder was used and the facilitating materials were Mn, Fe, Ni, and Co, respectively. When such photo-electrolytic catalyst systems were suspended in the same aqueous solution, hydrogen was

vigorously evolved. The solar-to-hydrogen power conversion efficiencies for these samples were found to be in the following order: $\text{Mn} \approx \text{Fe} > \text{Ni} > \text{Co}$ (as facilitating materials). The efficiencies are slightly lower than those of corresponding catalysts using n-type GaP as the semiconductor material

EXAMPLE 5

[0049] Several samples were prepared for this example. Nano-scaled n-type ZnO powder was used, but the facilitating materials were RuO_2 , IrO_2 , and NiO , respectively. The three oxides are well-known oxidation catalysts. When such photo-electrolytic catalyst systems were suspended in the same aqueous solution, hydrogen was vigorously evolved.

EXAMPLE 6

[0050] Three samples were prepared for this example. As in Example 2, nano-scaled n-type GaP powder was used, but the facilitating materials, MnO , Mn_2O_3 and Mn_3O_4 , respectively, were deposited via reactive sputtering. When such photo-electrolytic catalyst systems were suspended in the same aqueous solution, hydrogen was more vigorously evolved in the samples containing Mn_3O_4 or Mn_2O_3 than in that containing MnO as the facilitating material. This may be understood from the fact that polyvalent ions (such as Mn^{3+}) are more powerful electron-drawing materials than a divalent Mn^{2+} . Furthermore, with a polyvalent ion, reactions similar to the following may occur:



[0051] The present invention provides photo-electrolytic catalysts that are efficient in un-biased water splitting for hydrogen production. No external circuit or electric power is needed, the only energy source is solar radiation or other forms of light. No complex solid state microelectronic devices (such as multi-layer thin-film junctions) are needed.

1. A photo-electrolytic catalyst system for hydrogen production from water, said catalyst system comprising:

- (a) a first semiconductor material with a non-zero energy gap E_{g1} which, in response to an incident radiation having an energy greater than E_{g1} , generates electron-hole pairs as charge carriers; and
- (b) at least a first facilitating material in electronic contact with said semiconductor material to facilitate separation of the radiation-generated electrons from the holes to reduce the probability of charge carrier recombination.

2. The catalyst system as defined in claim 1, wherein both said first semiconductor material and said first facilitating material have at least one dimension being nanometer-scaled, smaller than or equal to 100 nm.

3. The catalyst system as defined in claim 1, wherein at least one of said semiconductor material and facilitating material is porous.

4. The catalyst system as defined in claim 1, 2, or 3, wherein said first facilitating material comprises an electron-drawing atom, molecule, or ion.

5. The catalyst system as defined in claim 1, 2, or 3, wherein said first semiconductor material comprises an element or compound selected from the group consisting of group IV semiconductors, III-V compounds, II-VI com-

pounds, mixed crystals of II-VI compounds, mixed crystals of III-V compounds, I-III-V₂ compounds, I-IV-V₂ compounds, ZMO compounds (where Z=an alkaline or alkali metal and M=a transition metal or rare earth metal element), oxides, phosphides, arsenides, sulfides, selenides, tellurides, chalcogenides, chalcopyrites and combinations thereof

6. The catalyst system as defined in claim 1, 2, or 3, wherein said first semiconductor material has an energy band gap greater than 1.6 eV.

7. The catalyst system as defined in claim 1, 2, or 3, wherein said first facilitating material comprises an element selected from Group VI and Group VII of the Periodic Table of Elements.

8. The catalyst system as defined in claim 1, 2, or 3, wherein said first facilitating material comprises a transition metal element or a rare earth metal element.

9. The catalyst system as defined in claim 1, 2, or 3, wherein said facilitating material comprises an element selected from the group consisting of Fe, Mn, Co, Ni, Cr, and Ti.

10. The catalyst system as defined in claim 1, wherein said first semiconductor material and/or said facilitating material has a dimension smaller than 1 μm .

11. The catalyst system as defined in claim 1, wherein said first semiconductor material and/or said facilitating material is a nano-scaled material with a dimension smaller than 100 nanometers.

12. The catalyst system as defined in claim 1, 2, or 3, further comprising a second semiconductor material with an energy gap E_{g2} different from E_{g1} , wherein said second semiconductor material is in electronic contact with said first facilitating material.

13. The catalyst system as defined in claim 1, 2, or 3, wherein said first semiconductor material is of n-type and said catalyst system further comprises a second semiconductor material of p-type in electronic contact with said first facilitating material.

14. The catalyst system as defined in claim 1, 2, or 3, further comprising a second semiconductor material in electronic contact with said first semiconductor material, wherein said second semiconductor material has an energy gap E_{g2} different from E_{g1} .

15. The catalyst system as defined in claim 14, further comprising at least a third semiconductor material, wherein said first, second and third semiconductor materials are connected in series.

16. The catalyst system as defined in claim 14, further comprising a second facilitating material in electronic contact with said second semiconductor material.

17. The catalyst system as defined in claim 1, 2, or 3, further comprising a second facilitating material in electronic contact with said first semiconductor material.

18. The catalyst system as defined in claim 17, wherein said first facilitating material comprises a reduction catalyst and said second facilitating material comprises an oxidation catalyst.

19. A method for converting optical energy into chemical energy to drive a chemical reaction for producing hydrogen gas from an aqueous electrolyte, said method comprising:

- (A) suspending discrete photo-electrolytic catalysts in said electrolyte; and
- (B) illuminating said catalysts with optical energy to produce hydrogen gas; wherein said catalysts com-

prises (a) a first semiconductor material with a non-zero energy gap E_{g1} which, in response to optical energy, generates electron-hole pairs as charge carriers; and (b) at least a first facilitating material in electronic contact with said semiconductor material to facilitate separation of the optical energy-generated electrons from the holes to reduce the probability of charge carrier recombination.

20. The method as defined in claim 19, further comprising operating means to collect said hydrogen gas produced.

21. The method as defined in claim 19, wherein both said first semiconductor material and said first facilitating material have at least one dimension being nanometer-scaled, smaller than or equal to 100 nm.

22. The method as defined in claim 19, wherein at least one of said semiconductor material and facilitating material is porous.

23. The method as defined in claim 19, wherein said optical energy is provided by solar radiation.

24. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said catalysts further comprise a second semiconductor material with an energy gap E_{g2} different from E_{g1} , wherein said second semiconductor material is in electronic contact with said first facilitating material.

25. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said first semiconductor material is of n-type and said catalysts further comprises a second semiconductor material of p-type in electronic contact with said first facilitating material.

26. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said catalysts further comprise a second semiconductor material in electronic contact with said first semiconductor material, wherein said second semiconductor material has an energy gap E_{g2} different from E_{g1} .

27. The method as defined in claim 24, wherein said catalysts further comprise at least a third semiconductor material and said first, second and third semiconductor materials are connected in series.

28. The method as defined in claim 24, wherein said catalysts further comprise a second facilitating material in electronic contact with said second semiconductor material.

29. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said catalysts further comprise a second facilitating material in electronic contact with said first semiconductor material.

30. The method as defined in claim 29, wherein said first facilitating material comprises a reduction catalyst and said second facilitating material comprises an oxidation catalyst.

31. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said first facilitating material comprises an electron-drawing atom, molecule, or ion.

32. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said first semiconductor material comprises an element or compound selected from the group consisting of group IV semiconductors, II-V compounds, II-VI compounds, mixed crystals of II-VI compounds, mixed crystals of III-V compounds, I-III-V₂ compounds, II-IV-V₂ compounds, ZMO compounds (where Z=an alkaline or alkali metal and M=a transition metal or rare earth metal element), oxides, phosphides, arsenides, sulfides, selenides, tellurides, chalcogenides, chalcopyrites and combinations thereof.

33. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said first semiconductor material has an energy band gap greater than 1.6 eV.

34. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said first facilitating material comprises an element selected from Group VI and Group VII of the Periodic Table of Elements.

35. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said first facilitating material comprises a transition metal element or a rare earth metal element.

36. The method as defined in claim 19, **20, 21, 22** or **23**, wherein said facilitating material comprises an element selected from the group consisting of Fe, Mn, Co, Ni, Cr, and Ti.

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