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Conversion of Sunlight into Electrical Power and Photoassisted Electrolysis of Water in Photoelectrochemical Cells

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In the spring of 1974, Heinz Gerischer spent 3 days with me. Although we planned to compared results on cathodic electroluminescence[1-3] and to discuss recently developed high-energy density lithium inorganic oxyhalide batteries,[4] we spent most of our time discussing the feasibility of a new type of a solar cell based on a semiconductor liquid junction.[5]

Gerischer saw that semiconductor liquid junction cells would be simpler to make than p–n junction cells, because their junction is spontaneously formed when a semiconductor is immersed in a redox couple solution. I recognized that the cells might allow the use of simple polycrystalline semiconductors, instead of single crystals, without the severe penalty in efficiency incurred in p–n junction and other cells.

For production of a p–n junction solar cell,[6] the surface of a p or n type material is doped with atoms that invert the type (p to n or n to p). These atoms are then thermally diffused to the optimal junction depth. Accurate positioning of the junction is essential for cell performance. Since diffusion rates in grain boundaries greatly exceed diffusion in the bulk, it has not been possible to properly position the boundary between the p and n regions in polycrystalline semiconductors. Rapid diffusion of the dopant in grain boundaries often shunted the solar cells; i.e., the dopant traversed the entire depth of the semiconductor at some points, reaching the wrong electrical contact. Because the new cell avoided the need for doping and diffusion, it seemed that it might open the way to the use of simple polycrystalline semiconductors *if* a solution to a second major problem, that of electron hole recombination at grain boundaries, could be found.

To start the program on semiconductor liquid junction solar cells, I joined Bell Laboratories in August 1975. Bell Labs had a long tradition in the field. In 1954 Chapin, Fuller, and Pearson invented the p–n junction silicon solar cell. It was Walter Brattain, coinventor of the transistor, who laid down, in his classical paper with G. C. B. Garrett, the foundations of the physics of the illuminated semiconductor electrolyte junction.[7] Concepts such as the flat band potential,[8] the TiO_2 anode,[9] surface states at semiconductor electrolyte interfaces,[10] and photocorrosion of these interfaces[11] originated at Bell Labs in the 1950s and 1960s and are associated with the names of Boddy, Brattain, Dewald, and Turner.

It is significant that the generation of scientists who founded today's solid-state science and technology, through profoundly familiar with semiconductor–electrolyte junctions, decided to introduce only technologies based on semiconductor–semiconductor (p–n) junctions and on metal–semiconductor (Schottky) junctions. One reason for this was the high capacitance associated with the double layer at the interface, which limited the frequency of potential devices. The devices were, however, not considered even for use in rectifiers and other low-frequency applications because of poor maintenance of their electrical performance. Adsorption of impurities at the interface, passivation, and corrosion changed the electrical behavior, making these, in sharp contrast with other solid-state devices, irreproducible and prone to failure.

When we started our work, only large band gap ($\geq$3 eV) semiconductor electrodes such as n–TiO_2 anodes[9] and photoanodes[12] were known to have reasonable stability. These were unusable for solar conversion, since they absorbed only in the ultraviolet, where there is little solar radiation reaching the surface of our planet. Efficient solar conversion requires materials with bandgaps of 1.3 ± 0.3 eV, i.e., absorption of light to $10\,000 \pm 2500$ Å. As the bandgap drops below 1.0 eV, the photocurrent increases, but the voltage declines and with it the power output and thus the conversion efficiency. If the bandgap exceeds 1.6 eV the photocurrent declines. While the photovoltage may be high, the power output and the efficiency decline. In general, bandgap and stability are correlated: the lesser the bandgap, the lesser the chemical stability, and the existing, stable cells were necessarily inefficient.[13,14]

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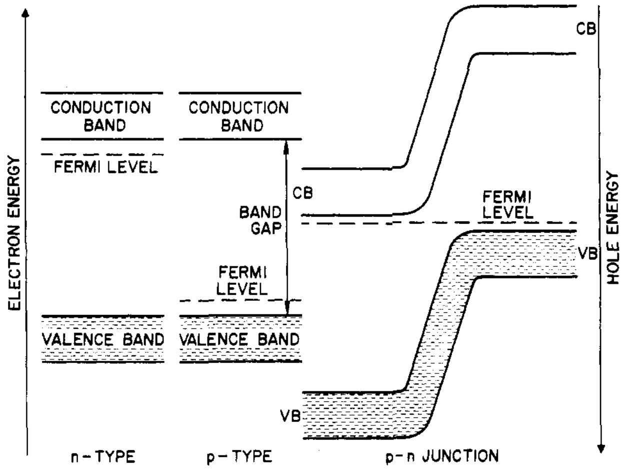

Figure 1. In n-type semiconductors the chemical potential of the electrons, i.e., their Fermi level, is close to the conduction band. In p-type materials, it is just above the valence band. When the p and n regions are joined, i.e., a p–n junction is formed, the Fermi levels of the p and n sides are equalized. This equalizations requires bending of the conduction and valence bands.

Thus, two goals shaped our program on semiconductor–liquid junction solar cells. We wanted to confirm the premise that these cells, in contrast with others, remain efficient when made with small-grained polycrystalline semiconductors of appropriate band gap, and we had to learn the nature of the chemical changes at the semiconductor–electrolyte interface in order to control them.

Principles and Definitions

The concepts behind Chapin, Fuller, and Pearson's classical silicon solar cell[6] are shown in Figure 1 and 2. The basic cell consists of a p–n junction, i.e., a semiconductor having n-doped and p-doped regions, and of electrical contacts to these. While the back contact is continuous, the contact to the front side is a metal grid that passes much of the incident light.

n and p regions differ in the chemical potential of the electrons in the two. Chemists, usually working with solutions and metal electrodes, refer to the chemical potential of electrons as the *redox potential.* Physicists, working with semiconductors and metals, refer to it as the *Fermi level.* It is important to note that the two terms are identical. Here we shall refer to the chemical potential of electrons in solids as their Fermi level and in liquids as their redox potential.

The Fermi level of p-type materials is just above their valence band and of n-type materials just below their conduction band. The higher the concentration of the dopants, the closer the Fermi levels are to the bands.

n- and p-type semiconductors are formed by *doping,* i.e., substituting atoms in the lattice of the semiconductor. If an atom of a lattice has *m* valence electrons and the dopant $m + 1$ valence electrons, one of the electrons will not be accommodated in the valence band (which is, at low temperatures, filled to capacity), and will become an itinerant electron in the conduction band. At increasing densities of electrons in the conduction band the chemical potential of electrons or Fermi level approaches this band and the material becomes n-type. Thus, substitution of some Si atoms by P in silicon, or of Ga atoms by Sn in gallium arsenide makes these materials n type. To make a semiconductor having atoms with *m* valence electrons p type, one dopes the lattice with a dopant having $(m - 1)$ valence electrons. This creates an electron vacancy or *hole* in the valence band. In the presence of holes, i.e., when the valence band is not completely filled, the Fermi level is close to the valence band. Silicon is made p type by substituting some of the Si atoms by Al, and GaAs by substituting some Ga atoms by Zn.

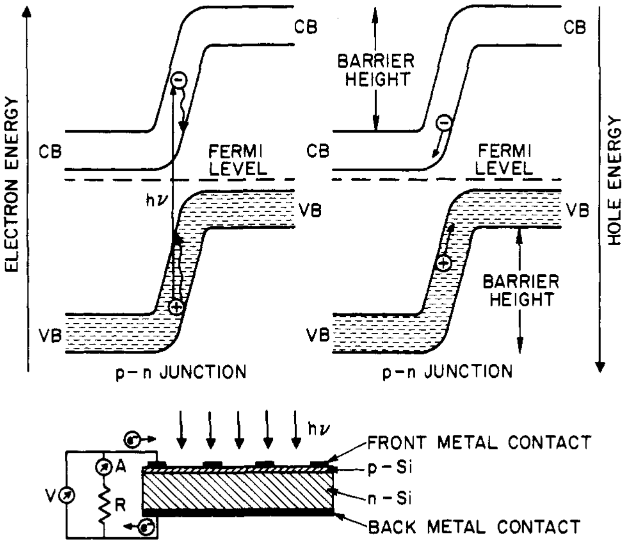

Figure 2. When light is absorbed by a semiconductor with a p–n junction, electrons are promoted from the valence to the conduction band. The holes left in the valence band propagate by being filled with electrons. Simultaneously, this process creates new vacancies. Holes thus move in an electric field in a direction opposite to that of electrons. The electric field associated with the bending of bands at a junction separates the electrons, promoted by light to the conduction band, from the photogenerated holes in the valence band. The electrons move "downhill" while the holes move "uphill". The "uphill" movement of electrons and "downhill" movement of holes are blocked. In the solar cell shown, electrons move from the p to the n region, do useful work in the external circuit, then recombine with holes in the metal stripes covering part of the light exposed face.

Holes propagate in the valence band by capturing nearby electrons, the sites of which now become holes. Thus holes move in an electric field against the direction of the flow of electrons, as if they had a positive charge.

When the surface of p-type silicon is made n type or the surface of n-type silicon is made p type, a p–n junction is formed. Upon illumination the junction acts as a battery or *solar cell.* Electrons flow in the external circuit from the n to the p region through an external resistance in which they do useful work. The chemical potential, or Fermi level, of any two shorted conductors is identical. (Otherwise electrons pour from the high- to the low-potential region.) Since the Fermi level is a property of the material, whether n or p doped, yet in an n-type material the Fermi level is near the conduction band and in a p-type material it is near the valence band, the same potential across the p and n domains can be maintained only by *bending of the conduction and valence bands.* The extent to which the bands must be bent to make the potential the same on the two sides of a junction equals the difference in Fermi levels of the n and p regions. This difference defines the *barrier height,* i.e., the energy barrier that an electron moving in the conduction band from the n to the p region or a hole moving in the valence band from the p to the n region must scale (Figure 2). In ideal solar cells the barrier height represents the upper limit to the photovoltage that can be reached at high irradiance.

The potential difference between the highest energy electrons in the valence band and the lowest energy electrons in the conduction band is the *band gap*. Just as the lowest photon energy required to run a photochemical reaction is represented by the energy difference between the ground and reactive excited state, the band gap represents the lowest photon energy at which a semiconductor-based solar cell will start converting light into electrical energy or into stored chemical energy. Photons promote electrons from the valence band to the conduction band (Figure 2). When thermal equilibrium is reached, the electrons drop to the bottom of the conduction band and travel "downhill" in the electric field associated with the bending of the bands. Thermal equilibration raises the holes to the top of the valence band, where they travel "uphill" in the electric field of the junction. Separation of the electrons from the holes by the junction reduces the rate of their recombination.

In the cell shown in Figure 2, the p region is at the illuminated side of the junction. Electrons travel away from and holes toward the illuminated side. The photocurrent of the cell is determined by the flux of absorbed photons and the quantum yield for formation of separated electron-hole pairs. If electrons and holes recombine before passing through the external circuit, the quantum yield declines. The photovoltage depends on the barrier height. It drops if electrons and holes recombine in the semiconductor without passing through the external circuit.

When a semiconducting photoelectrode and a counterelectrode are immersed in a redox couple solution and shorted to equalize the Fermi level of the semiconductor with the redox potential of the solution, the conduction band (CB) and the valence band (VB) are bent by up to $E_f - E_{redox}$, E_f being the Fermi level of the semiconductor and E_{redox} the potential of the redox couples in solution (Figure 3). This difference, the barrier height, represents the upper limit of the open circuit voltage, V_{oc}, that can be achieved under high irradiance. V_{oc} cannot exceed $|E_f - VB|$ for photoanodes and $|E_f - CB|$ for photocathodes.[5] Solar cells, under a fixed irradiance, operate most efficiently with an external resistance for which the output power reaches a maximum. The maximum power output is a function of the open circuit voltage, V_{oc}, of the short circuit photocurrent, I_{sc}, which is proportional to the quantum yield of oxidation or reduction at the photoelectrode, and of the fill factor, ff, defined as $I_{max}V_{max}/I_{sc}V_{oc}$ where I_{max} and V_{max} are the current and the voltage at the maximum power point. The solar conversion efficiency is, in a electrical power producing solar cell, the ratio of this maximum power and the solar irradiance integrated over the entire solar spectrum. In hydrogen-producing cells the efficiency is the ratio of the electrical power saved in electrolyzing water and the solar irradiance.

The process by which semiconductor liquid junction solar cells convert sunlight into electrical power resembles that of Chapin, Fuller, and Pearson's p–n junction silicon solar cell[6] except that the circuit involves redox reactions at the photoelectrode and at the counterelectrode. These are equal but opposite in direction and thus do not introduce a net chemical change (Figure 3).

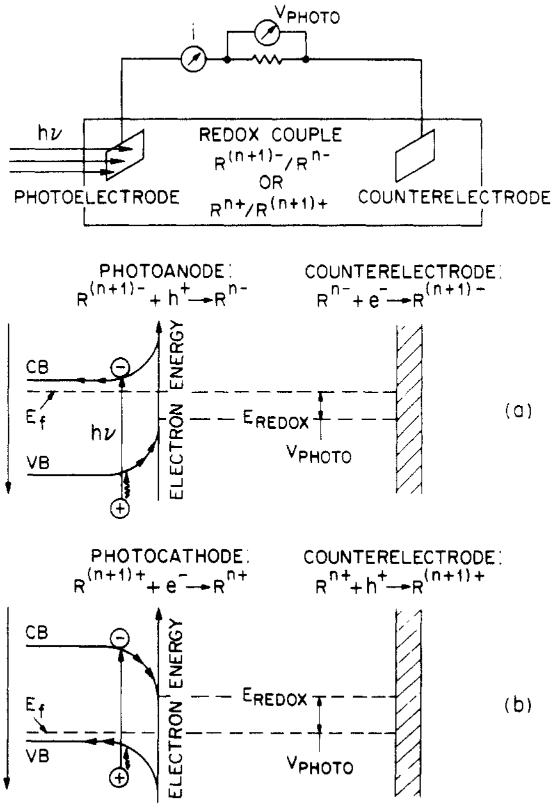

Figure 3. The chemical potential of an electron in a solution, represented by its redox potential, is the rigorous equivalent of a Fermi level in a solid. Instead of forming a junction based solar cell by doping a semiconductor to create p and n regions, one can form a junction by immersing a semiconductor in a redox couple solution. The extent of the bending of the bands, which defines the maximum achievable photovoltage, is the difference between the chemical potential of electrons in the semiconductor (the Fermi level) and the chemical potential of electrons in the solution (the redox potential). If an n-type semiconductor is immersed in an oxidizing redox couple, the bands bend "up", i.e., holes arrive at the solution interface and electrons travel through the external circuit to the counterelectrode. An oxidizing photoanode and reducing counterelectrode result. If a p-type semiconductor is immersed in a reducing redox solution the bands bend "down" and electrons travel to the solution interface while holes travel to the counterelectrode. The surface of the illuminated semiconductor now acts as a photocathode, reducing the redox couple, while the counterelectrode acts as an anode. In well-behaved regenerative semiconductor–liquid junction solar cells, the anode and cathode reactions are equal and opposite. There is no net chemical change in the cells: Only electrical power is produced.

Cells with either photoanodes or photocathodes can also be operated, in the absence of a redox couple, to oxidize or to reduce a substrate instead of producing power. Thus protons can be reduced at photocathodes to produce hydrogen, and hydroxide anions can be oxidized at photoanodes to produce oxygen. When an external potential is required to supplement the photopotential to cause electrolysis, the process is termed photoassisted electrolysis.

Early Results: Overcoming Photocorrosion and Forming Thin-Film, Polycrystalline Cells by Anodization

In his first paper on regenerative systems, Gerischer studied the n-CdS/$K_4Fe(CN)_6$–$K_3Fe(CN)_6$–KOH/Pt solar cell. He observed photocorrosion by holes oxidizing the semiconductor to Cd^{2+} ions and elemental sulfur, an insulator which covered the surface of the photoanode and stopped it from functioning.[5] It was obvious to me, as it was to E. A. Chandross in our laboratory and to others, that this layer can be dissolved in a sulfide solution and that a sulfide solution would suppress the dissolution of Cd^{2+}. More importantly, however, Barry Miller argued that the hole transport kinetics to surface-adsorbed sulfide ions would be favored over that to crystal bound species. The ~1-V difference between the $Fe(CN_6^{4-}/Fe(CN)_6^{3-}$ and the S^{2-}/S_2^{2-} redox potentials would buy kinetic stability; i.e., all the holes would be captured by the oxidizable ion well before these could oxidize the semiconductor.

To prove that one can achieve stability to photocorrosion and also to establish our premise that the new cells can be made with very small grained, polycrystalline semiconductors, we chose to form our n-CdS/Na_2S-Na_2S_2-NaOH/C cell simply by anodizing a sheet of cadmium metal in the redox couple solution. We observed, in our first experiment, the expected improvement in stability as well as substantial photovoltages and photocurrents.[15] Because CdS has a bandgap of 2.4 eV, larger than the 1.0–1.6 eV optimum for solar conversion, we repeated the experiment with a bismuth metal electrode, forming 1.3-eV bandgap n-Bi_2S_3.[15,16] Independently, two other groups also stabilized cadmium sulfide and selenide photoanodes against photocorrosion by using the S^{2-}/S_2^{2-} couple.[17,18] None of us was, however, the first to conceive such stabilization. It was G. C. Barker, an esteemed contributor to modern electroanalytical chemistry, who first suggested the idea of stabilizing the n-CdS photoanode by a sulfide solution.[19]

Bands, Bonds, Recombination, and Pinning at Photoelectrodes: The First Efficient Single-Crystal and Ceramic Semiconductor Liquid Junction Cells

Our results on cells made with semiconductors formed by anodizing metals convinced us that kinetic solutions to photocorrosion problems can be found. The question that we faced in the spring of 1976 was whether the stabilized cells could be efficient. We knew that there is no point in testing photoanodes for efficiency until we addressed the issue of surface and near-surface states, in which the photogenerated electrons and holes are trapped and recombine. In extreme cases, such recombination results in losses of photocurrent or quantum efficiency. Otherwise losses in photovoltage and power at the maximum power point result.

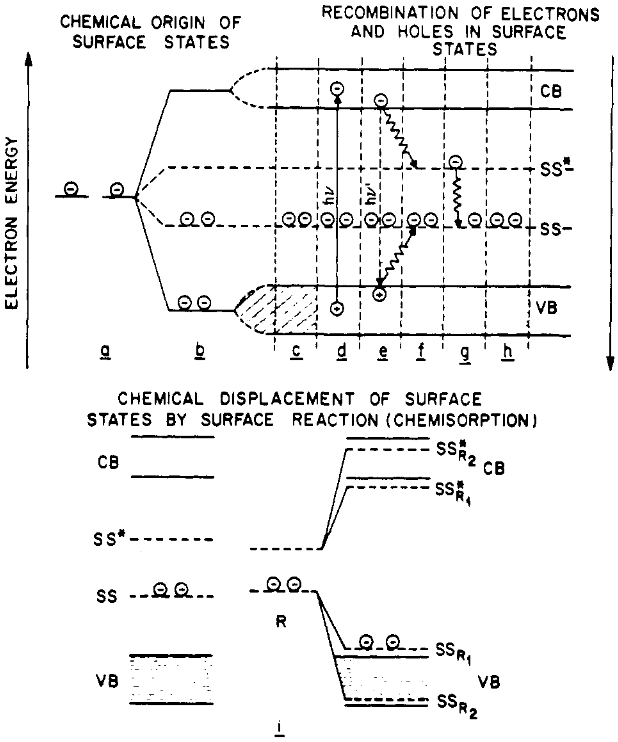

Figure 4. Bands in covalently bound semiconductors are formed when atoms (a) combine to form bonding and antibonding orbitals (b), which coalesce upon evolution of a lattice to form, respectively, valence (VB) and conduction (CB) bands (c). Weaker bonding at a surface or at a grain boundary leads to less splitting between the bonding and antibonding orbitals (b, c) and introduces surface states (SS, SS*) between VB and CB. Electrons and holes produced by absorption of light (d) may radiatively recombine (e) or recombine in a nonradiative process involving SS* and SS (f–h). Nonradiative recombination leads to losses in current efficiency near the maximum power point (low "fill factor") and in open circuit voltage ("pinning"). We discovered that these losses can be reduced by chemical reaction of the surface or grain boundary with a strongly bound reagent R (i). The reaction eliminates the weaker bonds and thus moves the surface and grain boundary states toward the bands, away from the center of the bandgap. "Deep" states, near the center of the bandgap, are most efficient, and "shallow" states, near VB or CB (SS_{R_1}, $SS^*_{R_1}$), are least efficient electron–hole recombination centers. When moved into CB or VB the surface states (SS_{R_2}, $SS^*_{R_2}$) no longer trap electrons or holes and do not cause recombination.

To explain the role of surface states and recombination losses, let us start with concepts of bonding in a lattice. As shown schematically in Figure 4a–c, a valence band forms in a semiconductor when molecular bonding orbitals merge upon the creation of a periodic lattice of identical bonds. A conduction band forms when antibonding orbitals merge. Since the distance between the highest bonding and lowest antibonding orbital measures the energy required to undo the binding of the most weakly bound electron, there is a qualitative correlation between the strength of the weakest bond and the band gap (unless the transitions involve nonbonding electrons). At a semiconductor surface, at a lattice dislocation, at a single-crystal defect, as well as at the grain boundaries of polycrystalline semiconductor, bonding is weaker and states between the valence and conduction bands are introduced. These states trap and recombine photogenerated electrons and holes (Figure 4f–h). Thus, for example, cleavage of diamond under vacuum results in the formation of higher energy carbon atoms at the surface. These are less strongly bound than those in the bulk and may trap electrons to form carbanions or trap holes to form carbonium ions. The two are annihilated by surface recombination.

In a semiconductor crystal, photogenerated electrons or holes decay either by radiative recombination, lead-

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ing to luminescence at wavelengths corresponding to the band gap, $h\nu'$ (Figure 4e), or by nonradiative recombination in surface states, grain boundaries, defects, or other sites associated with weaker chemical bonding (Figure 4f–h). Recombination is evidenced by a decrease in the intensity and lifetime of the bandgap luminescence, $h\nu'$ (Figure 4e). In a semiconducting photoelectrode, recombination is evidenced by a loss in quantum efficiency for oxidation or reduction. The loss is associated with an increase in the recombination current flowing in a direction opposite to the photocurrent. Since the open circuit voltage is the potential at which the rate of photogeneration of electrons or holes equals the rate of their recombination, i.e., when the opposing currents balance, recombination results in lower open circuit voltage. The electron–hole recombination rate, S_R, is

$$S_R = \sum_i \sum_j \sigma_{ij} N_e^i N_h^j$$

where N_e^i is the electron population in the ith state, N_h^i is the hole population in the jth state, and σ_{ij} is the cross section for their recombination. The recombination current is an exponential function of the electrode potential, i.e., the Fermi level of the semiconductor, since the populations N_e^i and N_h^i depend (by Fermi statistics) on the energy difference between the Fermi level and the trapping state. The potential at which the recombination current reaches the solar photogeneration current defines a limit to the achievable open circuit voltage. When this limit is reached, the open circuit voltage no longer depends on the redox potential of the solution and is said to be "pinned" by the (surface, lattice defect, or grain boundary) state causing the recombination. When the recombination current is substantial near the maximum power point, a loss in fill factor (vide supra) is observed. In some cases recombination persists even at the solution potential, i.e., when the electrodes are shorted, and a loss in short-circuit current is seen.

The first probe introduced to observe and eliminate surface and near-surface defects states was two-beam photocurrent (and photovoltage) spectroscopy.[20,21] With an intenses laser beam populating the traps and a second variable wavelength beam measuring the incremental photocurrent (or photovoltage), we could observe trapping and recombination and also identify some of the causes. This allowed us to develop chemical etching methods which eliminated near-surface defects and opened the way to the first efficient semiconductor liquid junction solar cells.[20,21]

The initial phase of our work centered on the n-CdSe/Na_2S–Na_2S_2–NaOH/C cell, the subject of earlier studies at MIT and at the Weizmann Institute.[17,18] By removing trapping states we achieved 7.5% solar-to-electrical conversion efficiency.[21] To prove that there is little loss in efficiency when polycrystalline materials are used, Murray Robbins prepared ceramic n–CdSe by hot pressing CdSe powder, made by precipation from solution. By late 1976 we reached 5.3% solar-to-electrical conversion in a cell made with the resulting ceramic material.[22] This represented an unprecedented retention of 75% of the single-crystal efficiency of a solar cell made with small grained (10–20 μm) crystallites. The experiment established that it is possible to approach single crystal efficiencies with polycrystalline materials and confirmed our premise of the feasibility of using these simple, inexpensive materials in semiconductor liquid junction solar cells. Beyond demonstrating the premise of retention of the efficiency, our work on polycrystalline n-CdSe also demonstrated another principle of interest to the science of solar cells. In the Cd vapor annealing step we heavily doped the edges of the grains, creating n^+ zones.[22] The n^+/n junctions at the grain boundaries deflected the holes away from the boundaries, preventing their trapping and recombination.

Problems of Ion Exchange: Stabilizing the n-CdSe/Na_2S-Na_2S_2-NaOH/C Cell

Having confirmed that reasonably efficient polycrystalline CdSe based cells could be made, we concentrated our second objective, that of identifying causes for instability and degradation.

We[23] and others[24-26] found that rapid ion exchange in the n–CdSe/Na_2S–Na_2S_2–NaOH/C cell creates a n–CdS_xSe_{1-x} surface layer, which introduces a barrier for the transport of holes to the interface.[23] The layer is created in a process similar to that of photocorrosion, except that the Cd^{2+} ions reprecipitate on the surface as CdS:

$$\begin{array}{ll} \mathrm{CdSe} + 2h^+ \rightarrow \mathrm{Cd}^{2+} + \mathrm{Se}^0 & \\ \mathrm{Se}^0 + \mathrm{S}^{2-} \rightarrow \mathrm{SeS}^{2-} & \text{photocorrosion} \\ \mathrm{Cd}^{2+} + \mathrm{S}^{2-} \rightarrow \mathrm{CdS} & \text{reprecipitation} \end{array}$$

Photocorrosion takes place only when the kinetics of hole transport to the S^{2-} ions in solution are inadequate to cope with all the photogenerated holes. Thus ion exchange damages performance only at or above rates of photogeneration of holes corresponding to normal solar irradiance. We solved the ion-exchange problem by dissolving small amounts of elemental selenium in the sulfide solution. In the presence of the SeS_2^{2-} ion the $CdSe_xS_{1-x}$ surface retains a sufficient selenide concentration to avoid the barrier problem. The stabilization experiments led to the first efficient (i.e., 7%) cell that operated for months without change in its electrical characteristics.[23]

The n-GaAs/K_2Se-K_2Se_2-KOH/C Cell

GaAs is one of the few available, well-characterized semiconductors. Its absorption rises to 10^5 cm^{-1} near the 1.3-eV bandgap, which is optimal for solar conversion. K. C. Chang, Miller, and I undertook the study of n–GaAs based semiconductor liquid junction solar cells in the spring of 1976. We searched, as we did in our initial work on CdS, for a redox couple that would be fast and adequately reducing, to assure that the rate

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of oxidation of the couple will greatly exceed the rate of photocorrosion. We found[27] that while n-GaAs anodes photocorrode in basic S^{2-}/S_2^{2-} solutions, they do not photocorrode in Se^{2-}/Se_2^{2-} at high concentrations of selenide. The selenide captures holes by the desired reaction

$$2Se^{2-} + 2h^+ \rightarrow Se_2^{2-}$$

The MIT group carried out concurrent studies on n-GaAs photoanodes. Although they also observed oxidation of Se^{2-}, they did not realize[28] that photocorrosion can be prevented by using a high enough selenide ion concentration to discharge the holes and thus prevent photocorrosion. The ratio of the corrosion current to the total current declines with the inverse of the third power of $[Se^{2-}]$. At 2 M K_2Se the rate of photocorrosion under 100 mW/cm^2 sunlight is a few micrometers per year.[27]

Chemical Modification of Surface and Grain Boundary States in Photoanodes: 12% Efficient Single-Crystal and 7.8% Efficient n-GaAs Thin-Film Cells

Early in 1977, while experimenting with n-GaAs/K_2Se-K_2Se_2-KOH/C cells, we observed variations in fill factors, and corresponding variations in efficiency between 7 and 10%. From work in the 1960s it was evident that impurities, in submonolayer quantities, introduce surface states and change the electrical properties of semiconductor–electrolyte junctions.[29,30] Thus the observed variations in efficiency were not unexpected, and in 1977 we undertook a study of the effect of adsorbed ions on the performance of the n-GaAs/K_2Se-K_2Se_2-KOH/C cell. We found that cations could be divided into three groups. Some, like Ca^{2+}, Sr^{2+}, and Ba^{2+}, were not adsorbed and had little effect on cell characteristics; weakly chemisorbed ions, such as Bi^{3+}, caused deterioration in cell performance; and very strongly chemisorbed ions, like Ru^{3+} and Pb^{2+} improved the performance.[31] By chemisorbing Ru^{3+} and etching a textured structure into the surface of the n-GaAs crystals (to reduce light reflection losses), we increased the solar-to-electrical conversions efficiency of the n-GaAs cell to 12% (Figure 6).[32,33]

To explain the effect of strongly chemisorbed ions such as Ru^{3+}, we proposed a model[34-36] according to which chemisorption shifts the position of the surface states closer to, or even into, the near band of the semiconductor, as shown in Figure 4i. This reduces the rate of recombination because σ_{ij}, the cross section for electron hole recombination, is decreased when the largest energy gap to be crossed nonradiatively increases. Such a decrease is expected from perturbation theory, and a correlation between σ_{ij} and the largest gap has been borne out in studies by Lax on Si and Ge.[37-39] The relevant physical picture, common to radiationless transitions in these as well as in other types of systems, is simple: The more energy that one must dissipate in a single step of a radiationless process, the more collisions or phonons are needed for the transition to take place, and the less likely the transition becomes.

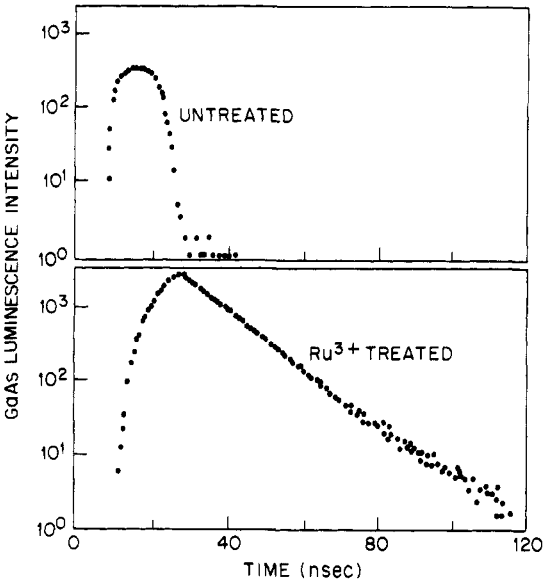

Figure 5. The rate of nonradiative recombination of electrons and holes at the surface of an n-GaAs crystal is reduced 30-fold upon chemisorption of one-third of a monolayer of Ru^{3+} ions. The figure shows the rise and decay times of the bandgap luminescence for the same crystal before and after dipping into a Ru^{3+} solution. The decay time measures the lifetime of the holes generated by a 20-ns pulse of light.

The idea of shifting the surface states by chemical reaction of the surface in order to reduce recombination was revolutionary. It had been assumed that impurities on a surface only add damaging surface states and aggravate recombination problems. The object was to keep surfaces clean. We proposed, however, that the cause of surface and grain boundary recombination is in the weaker chemical bonding (Figure 4a–h) and that the solution to the problem is in strengthening the weak chemical bonds.[36]

We proved[40] that ruthenium acts primarily by reducing the surface recombination velocity rather than by catalyzing electrode reactions in the following series of experiments. We first measured, by Rutherford backscattering, the depth and surface density of the adsorbed ruthenium atoms. The ruthenium was found to be exclusively on the surface, forming on the (100) face one-third of a monolayer. Next, we measured the luminescence intensity and luminescence decay time due to radiative recombination of electrons in the conduction band with holes in the valence band. We found that upon chemisorption of Ru^{3+} both the intensity and the decay time increase (Figure 5) and that the surface recombination velocity decreases from 10^6 to 3×10^4 cm/s. Since the sample was in air, not in contact with

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an electrolyte, this proved that the improvement upon Ru^{3+} chemisorption was not associated with any electrochemical reaction and could not be due to electrocatalysis. It could only be explained by the chemical redistribution of surface states.

Reduction of Recombination at n-GaAs Grain Boundaries by Chemisorbed Ions: Efficient Chemically Deposited Photoanodes

The minimization of recombination of electrons and holes at grain boundaries necessitates, to make the most efficient solar cells, the use of high-quality single crystals. Were it possible to solve this recombination problem, the cost of materials for photoelectrochemical cells would be lowered by factors between 10 and 100. By building on our model for reducing trapping and recombination in surface states by strongly chemisorbed ions, we were able to increase the efficiency of the n-GaAs/K_2Se-K_2Se_2-KOH/C solar cell made with thin, polycrystalline chemically vapor deposited films of n-GaAs on graphite.

The concept behind the efficient polycrystalline cells follows from the reduction of the surface recombination velocity by strongly chemisorbed ions. The boundary between two crystallites is a region in which some of the chemical bonds are weaker than in the bulk. Thus, the principles that we established in our analysis of the problem of surface states could be applied also to grain boundaries, and we were able to predict that diffusion of strongly chemisorbed species into grain boundaries will dramatically improve the efficiency of polycrystalline semiconductor based solar cells.

Since diffusion of ions in grain boundaries is much more rapid than in the bulk, soaking of the polycrystalline films in aqueous solutions of cations proved adequate for reacting the grain boundaries in the top 10^3-Å light absorbing region. By diffusing Ru^{3+} into boundaries of a polycrystalline, chemically vapor deposited film of n-GaAs on graphite, we *quadrupled* the solar to electrical conversion efficiency (Figure 6).[41] Subsequent experiments on a superior GaAs film led to 7.3% efficient cells[42] and by co-adsorbing Ru^{3+} and Pb^{2+} we reached, for an average grain size of 9 μm, a 7.8% solar to electrical conversion efficiency, retaining two-thirds of the single crystal cell efficiency.[43] These experiments showed for the first time that it is possible to improve the performance of a polycrystalline semiconductor based solar cell by a simple chemical treatment.

Photocathodes: Removing the Obstacle of Pinning and Achievement of 11.5% Efficient Solar to Electrical Conversion Efficiency

Our success in solving the problems of surface and grain boundary states in n-GaAs prompted us to address the issue of efficient photocathodes. Photocathodes have an important advantage over photoanodes. While photoanodes corrode under intense illumination (when hole transport kinetics to the redox couple cannot cope with all the photogeneated carriers), photocathodes are protected against oxidative corrosion by the photogenerated electrons arriving at the interface. The effect of light is thus equivalent to cathodic protection of the semiconductor. While reductive corrosion is possible, it is far less likely because reduction products, such as hydrides, are less easily formed than oxidation products.

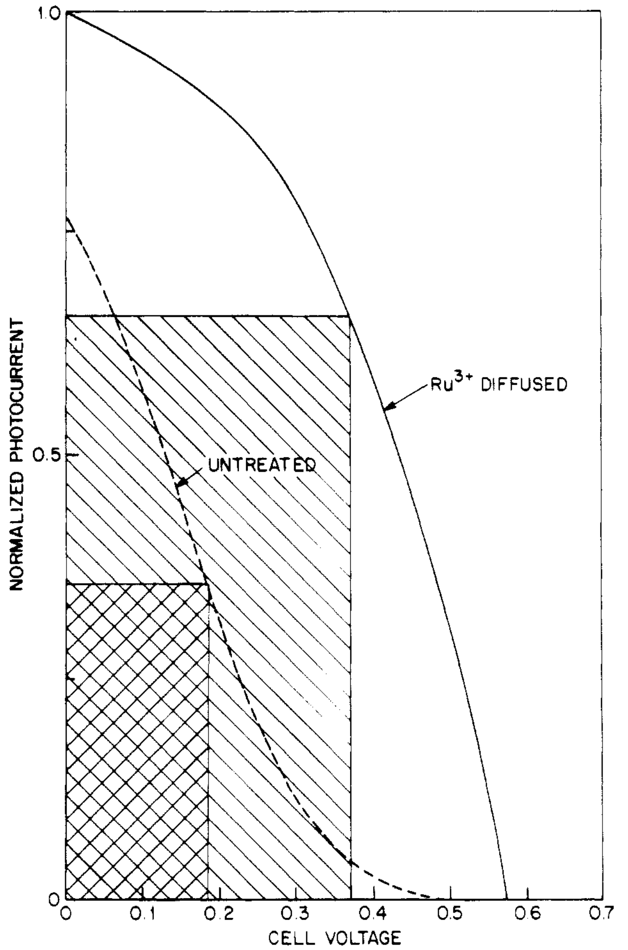

Figure 6. Top: First observation of an increase in the efficiency of a polycrystalline solar cell by a chemical treatment of grain boundaries. The efficiency of the cell n-GaAs/K_2Se-K_2Se_2-KOH/C (shaded area) quadruples when Ru^{3+} is chemisorbed at the grain boundaries. A film of n-GaAs on graphite, formed by reacting $Ga(CH_3)_3$ with AsH_3, was used.

Although the study of p-GaP photocathodes dates back to 1969,[44] the efficiency of the best of these had been only 3% or less. It has been suggested[45-47] that the problem is in pinning by surface states. If pinned, the photovoltage achievable in a junction between a p-type semiconductor and a redox couple is no longer defined by the difference between the Fermi level and the redox potential but by the difference between the bulk and the surface Fermi levels of the semiconductor.

With the strong chemisorption model in mind, we looked for indications of extensive redistribution of surface states and reduction in surface recombination velocities upon chemisorption of oxygen.[36] We found evidence for these in the case of InP in the work of Casey and Buehler[48] and of Spicer and his col-

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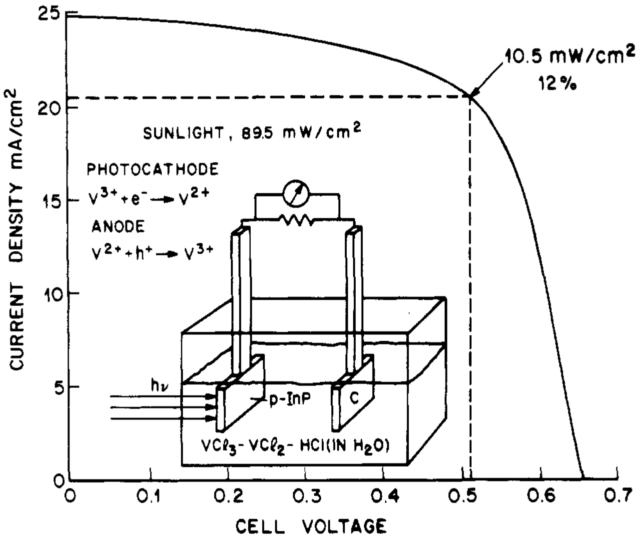

Figure 7. Current voltage characteristics of the p–InP/VCl_3–VCl_2–HCl/C cell. The cell is the first efficient photocathode based cell. It converts 11.5% of the incident sunlight into electrical power. The photocathode is stabilized against oxidative corrosion by the light-generated electrons arriving at the semiconductor liquid interface. An oxide monolayer or submonolayer on the surface of the photocathode prevents electron–hole recombination.

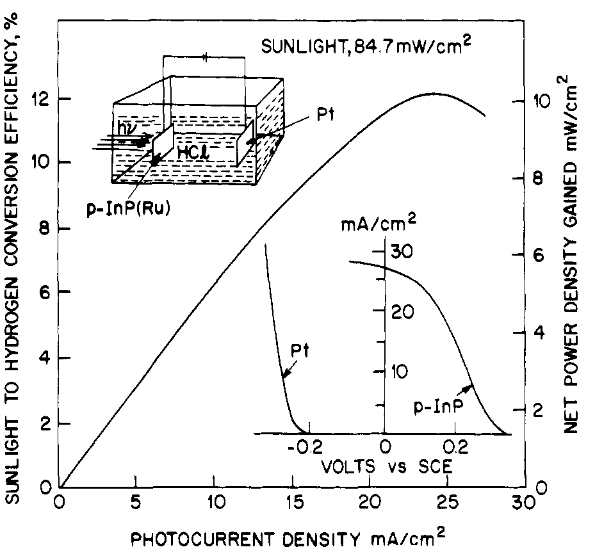

Figure 8. 12% of the incident solar energy is converted to hydrogen and oxygen by photoassisted electrolysis of water in cell p–InP(Ru)/HCl–KCl/Pt. The cell represents the most efficient system for the direct conversion of sunlight into a storable fuel. The current voltage characteristics of a platinum and a p–InP photocathode at 84.7 mW/cm² sunlight are compard in the insert. With the p–InP photocathode, hydrogen evolution starts at +0.36 V vs. the saturated calomel electrode or 0.64 V vs. oxygen. Platinum requires −0.23 or 1.23 V vs. oxygen.

leagues.[49,50] Indeed, our experiments showed that the open circuit voltage of the cells p–InP|V^{n+}—$V^{(n+1)+}$—H^+|C[51] and p–Si|V^{n+}—$V^{(n+1)+}$—H^+|C[52] do vary with solution redox potential, as expected, over a >0.5-V range and that over this range surface states do not pin the photovoltage. We reached 9.3% solar to electrical conversion efficiency using either air exposed or anodized p–InP photocathodes in the p–InP/VCl_3–VCl_2–HCl/C cell.[51] Upon improving cleaning and oxidation of the surface the efficiency of the cell increased to 11.5% (Figure 7).[53] As predicted, the cells were quite stable. The simple electrode reactions, $V^{3+} + e^- \rightarrow V^{2+}$ at the photocathode and $V^{2+} \rightarrow V^{3+} + e^-$ at the carbon anode, are fast at the concentrations employed. The first efficient semiconductor liquid junction cell that was no longer subject to oxidative corrosion upon illumination, however intense, was achieved.

Hydrogen: 12% Efficient Sunlight-Assisted Electrolysis of Water

The efficient p–InP photocathode opened an avenue to the long-sought objective of efficient photoassisted electrolysis of water. Much of the worldwide effort had centered on photoanodes. These were inefficient because stability at the potentials required to generate oxygen could be achieved only either in large bandgap materials, absorbing only a small fraction of the sunlight, or in materials with an inadequate hole diffusion length/light absorption length ratio, where the quantum efficiencies were low. While photocathodes such as p–Si[54] and p–GaP[55–59] and p–GaAs[60] have been used for generation of hydrogen, their conversion efficiencies were 3% or less.

With pinning no longer a critical problem, we chose p–InP photocathodes for generating hydrogen. The 1.35-eV bandgap of InP is ideal for solar conversion. InP is also a direct bandgap semiconductor, with an absorbance of $\sim 10^5$ cm^{-1} in the visible and in the near-infrared. Surface-oxidized p–InP is a poor electrocatalyst for hydrogen evolution. We found, however, that the hydrogen generation efficiency can be increased by four orders of magnitude by electrodepositing less than 100 Å of Rh, Ru, or Pt and then etching away most of the metal, so that microscopic islands of the catalyst are left. Protons adsorbed on these metal islands react with photogenerated electrons from the semiconductor to form hydrogen. In the cell p–InP(Ru)/1 M HCl–1 M KCl/Pt_2, the threshold voltage for electrolysis of water is reduced from 1.23 to 0.64 V when the photocathode is illuminated by 84.7 m W/cm² sunlight. At this level of illumination the cell yields a current density of 24 mA/cm² at a voltage saving of 0.43 V with respect to a platinum cathode (Figure 8); 10.2 mW/cm² of the incident 84.7 mW/cm² sunlight is thus used in the production of hydrogen.[61] The resulting engineering efficiency of 12% is the highest ever for any scheme that uses sunlight to generate a fuel. Green plants are

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able to convert 1–3% of the incident sunlight to combustible fuels.

Concluding Remarks

Photoelectrochemical solar cells based on semiconductor liquid junctions have been developed over the past 6 years into efficient converters of sunlight into electrical energy or hydrogen. Solar conversion efficiency has increased from less than 1% to 12% and operational life from hours to months.[23,33,51] The new cells retain about 70% of their single-crystal efficiency when made with chemically formed, polycrystalline materials, far more than other types of solar cells.[15,22,41–43]

Gains in performance paralleled the understanding of the chemistry of surfaces and grain boundaries in semiconductors. Through such understanding it became possible to chemically manipulate the position of surface and grain boundary states and thus to reduce losses due to electron–hole recombination.[34–36,40] Chemisorption of Ru^{3+} ions on n–GaAs photoanodes increased the efficiency of the single-crystal n–GaAs/K_2Se–K_2Se_2–KOH/C cell to 12%,[31–33] and diffusion of Ru^{3+} and Pb^{2+} into grain boundaries of polycrystalline n–GaAs films on graphite quadrupled the efficiency.[41–43] Surface oxidation of p–InP led to the first efficient photocathode, which, in contrast to photoanodes, is not prone to oxidative photocorrosion at high light intensities.[51,53] Light tends to cathodically protect the semiconductor surface. With the p–InP photocathode, 11.5% solar to electrical conversion efficiency has been achieved in the p–InP/VCl_3–VCl_2–HCl/C cell.[53] By photoassisted electrolysis of water, 12% solar to hydrogen conversion efficiency has been reached in the p–InP(Ru)/HCl–KCl/Pt cell.[61] The latter represents the most efficient system for conversion of sunlight into energy stored in a fuel.

The contributions of my colleagues with whom I had the privilege to work are evident from the references. E. A. Chandross, B. Miller, and F. H. Winslow improved the manuscript.