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(54) SEMICONDUCTOR LIQUID JUNCTION PHOTOCELL

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED of 222 Broadway, New York, New York State, United States of America, a Corporation organized and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates generally to semiconductor liquid junction photocells.

Concern over the possible depletion of fossil fuel energy sources had generated intense interest in recent years in the search for and development of alternative energy sources. Contemplated alternative energy sources include solar energy utilized as electricity either directly through photovoltaic devices or indirectly through thermal devices. The latter has not received as much attention as the former which will, as presently contemplated, use semiconductor devices. These devices are presently relatively expensive power sources compared to fossil fuel, because the devices collect light generally in proportion to the area of the photosensitive junction which must be large to generate useful photocurrents. The cost of manufacturing such devices depends mainly upon the area of the photosensitive junction and is presently too high to permit successful commercial exploitation in other than specialized applications.

Considerable time has therefore been expended in attempting to find ways to reduce the cost of solar energy obtained from semiconductor devices. One approach that has generated much interest and enthusiasm recently is a liquid semiconductor solar cell in which the active part of the cell is a junction formed at a liquid-solid interface. These devices

promise to be less costly to manufacture than are devices in which the junction is formed between two solids as relatively costly epitaxy or diffusion procedures are not required to form the junction, which forms spontaneously in these devices at the semiconductor-liquid interface.

A variety of reasons has prevented these cells from being fully exploited at the present time. One reason is that some semiconductor materials, having bandgaps of a size favourable for efficient conversion of solar energy into electricity and therefore desirable for use as the solid electrode material, are not stable. That is, the efficiency of the cell declines with operating time for any of several reasons. For example, photoexcitation may produce holes at the surface which chemically reacts with the electrolyte. This and other processes corrode and/or passivate the semiconductor surface and cause degradation of cell efficiency as manifested by a decrease in the photocurrent from the cell as the operating time of the cell increases. Other mechanisms such as chemical etching or deposition of impurities on the semiconductor surface may also be active.

GaAs has a bandgap of about 1.4 eV and, since a bandgap of approximately this magnitude theoretically will give the most efficient photovoltaic conversion of solar power into electricity, a cell using this material and producing a stable photocurrent over an extended time period would be extremely desirable from a commercial point of view. Cells using GaAs have, however, appeared especially susceptible to electrode degradation, with attendant decline in photocurrent output, arising from photochemical reactions of the GaAs electrode with the redox electrolyte. Reported liquid-semiconductor junction photocells using GaAs such as the ones

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reported by Gerischer, *Journal Electroanalytical Chemistry and Interfacial Electro Chemistry* 58 263 (1975) and Wrighton *Bulletin of the American Physical Society* 22 60 (1977) had lifetimes too short to permit serious consideration of useful commercial exploitation or were unable to support photocurrents of a useful magnitude.

We have discovered that GaAs may be used as the semiconductor electrode in a liquid-semiconductor junction photocell having an extended period of life.

The invention provides a photocell containing a photovoltaic junction between gallium arsenide and a liquid electrolyte containing a redox couple wherein the redox couple has a potential more negative than -0.5 volt and a concentration greater than 0.1 Molar.

A GaAs photocell made in accordance with the invention has high efficiency, approximately 9% solar to electrical power conversion, with a reasonably constant photocurrent. The lifetime can exceed one year.

A photocell embodying the invention will now be described by way of example and with reference to the accompanying drawings, in which:—

Fig. 1 is a plot of the theoretical energy conversion efficiency for photovoltaic devices using semiconductor materials, taking into account the solar spectrum, as a function of the bandgap of the semiconductor material;

Fig. 2 is a schematic representation of a liquid-semiconductor photocell;

Fig. 3 is a plot of the ratio of the corrosion current to the total current as a function of selenide concentration; and

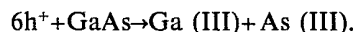
Fig. 4 is a plot of the photocurrent density as a function of time of operation of the photocell.

Fig. 1 is an idealized plot of the efficiency of the conversion of solar energy into electricity as a function of the semiconductor bandgap with the solar spectrum taken into account. The range of efficiencies for each bandgap value results from different atmospheric conditions and assumptions about voltage losses. As can be seen, GaAs with a bandgap of approximately 1.42 eV is close to the most theoretically efficient material.

The cell structure of Fig. 2 comprises a container 20, electrolyte 21, counter electrode 22, which in our devices is carbon, although other inert materials may be used, and the active electrode 23. The electrolyte is usually aqueous although nonaqueous electrolytes such as propylene carbonate and tetrahydrofuran can be used. Electrode 23 is insulated with epoxy 24 except where illuminated and activated glass or plastics

material. The bottom of the cell, opposing electrode 23, is transparent to pass incident light as shown.

Under illumination, in a suitable electrolyte, typically an aqueous electrolyte, holes come to the surface of the n-type GaAs and cause its oxidative dissolution by the reaction



If this is the only reaction, the material photoetches. The photoetching reaction can be suppressed if a competing reaction can be found that will scavenge for holes and compete directly with the photoetching reaction although it may be unable to completely suppress photoetching. It has been found that as the redox potential becomes more negative it scavenges more successfully for holes. However if the redox potential is not more negative than -0.5 volt it is unable to scavenge sufficient holes to suppress the photocorrosion at GaAs to acceptable levels, $\text{Se}^-/\text{Se}_2^-$ and $\text{Te}^-/\text{Te}_2^-$ redox couples or a mixture thereof satisfy this criterion and have been found to suppress photoetching in GaAs cells sufficiently that usable cells can be made. The selenium accepts charge, for example, through the reaction $2\text{Se}^- + 2h^+ \rightarrow \text{Se}_2^-$ at the illuminated electrode. The reaction at the dark electrode is $\text{Se}_2^- + 2e^- \rightarrow 2\text{Se}^-$ and there is no chemical change in the cell. Suitable redox electrolyte concentrations range from a maximum represented by a saturated solution to a minimum of approximately 0.1 M which represents the minimum concentration in an aqueous solution required to consume sufficient holes, when illuminated by sunlight, to prevent unduly rapid photoetching. Other than aqueous electrolytes may be used but since they generally have a lesser electrical conductivity, cell efficiency is reduced. For high concentrations, light absorption in the electrolyte can be compensated by making a thin liquid layer.

Diselenide ion and polyselenide ions may be formed in the solution by passing H_2Se into a basic solution, such as an aqueous solution of KOH, and permitting air to oxidize some of the Se^- to Se_2^- or by directly dissolving Se metal. Other bases such as NaOH and NH_4OH may also be used.

Photocells as just described were made with the active electrode 21 formed from an n-type GaAs single crystal with a thickness of 600 microns and $\text{Se}^-/\text{Se}_2^-$ redox electrolytes. Cells were made with different selenide concentrations all having a $\text{Se}^-/\text{Se}_2^-$ ratio of approximately eight and the weight loss from the GaAs electrode was measured. Illumination was provided by a quartz-halogen lamp operating at a level

corresponding roughly to 3AM2 (three air mass two) suns. AM2 corresponds approximately to noon time sunlight in middle latitudes. The applied potential of the GaAs electrode was controlled at -0.4V versus saturated calomel or 0.56V positive of the solution Fermi level. This level is 1V more oxidizing than that measured at maximum power and the rate of photocorrosion under these conditions ought to be substantially higher than that of a cell operating at maximum efficiency, although the actual interfacial potential is not known. Fig. 3 is a plot of the ratio of the corrosion current to the total current as a function of selenide concentration. The curve represents the expression

$$\frac{i_c}{i_T} = (1 + 3500C_{Se}^3)^{-1}$$

where C_{Se} is the total molar concentration of selenium in the solutions. The measured weight loss of the electrode was converted to corrosion current through the dissolution stoichiometry of six electrons per GaAs molecule as confirmed by the etch rate for zero selenide concentration. The ordinate represents the fraction of photocurrent not going to the desired regenerative solar cell path and thus causing etching. As can be seen, high selenide concentrations lead to a relatively small corrosion current although the corrosion current is never completely suppressed.

The current voltage characteristics of a typical cell with an n-type GaAs electrode and an aqueous electrolyte containing KOH and a nominal 1 molar total selenium concentration and operated under sunlight are as follows. The short circuit current at an irradiance of 69 mw/cm² is 16.5 ma/cm² which corresponds to a quantum efficiency of approximately 65 percent for a solar AM2 spectrum. Maximum power is delivered at 0.45V and 13.5 ma/cm² which yields a fill factor of approximately 57 percent and an efficiency of approximately 8.8%. The crystal for this cell was doped with Sn and had a free electron concentration of approximately 2×10^{17} /cm³. Other materials that give n-type behaviour, e.g., Si and Te, might also be used as the particular dopant used does not appear crucial. The upper limit dopant is desirably less than 5×10^{18} /cm³. Above this value, the space charge layer is too thin to permit essentially all light to be absorbed within the space charge layer and the resulting recombination of carriers reduces cell efficiency.

A plot of the photocurrent from this cell versus time during an extended run under a quartz-halogen lamp having an intensity equivalent to 3AM2 suns is shown in Fig. 4. The photocurrent is essentially constant over a period that exceeds 400 hours. i_c/i_T , for the approximately 1 molar total selenium concentration used, is approximately 0.001 giving an average corrosion penetration less than 12 microns over the 400 hour period. The stable output is attributed not only to suppression of the photoetching reaction but also to the continued integrity of the semiconductor surface during cell operation. The limited and controlled removal of semiconductor material, while establishing an ultimate lifetime for the cell, offsets deposition of impurities whether from the electrolyte or a chemical reaction between the GaAs and the electrolyte, on or near the semiconductor surface and thus maintains its integrity and quality.

Although the cells described use a single crystal GaAs electrode, the principles that permit a stable photocurrent to be obtained from a cell using a single crystal GaAs electrode are also applicable to cells using polycrystalline GaAs electrodes.

Although the cells have been described with respect to their utility as solar cells, they are of obvious utility for converting energy from light sources other than the sun and are therefore more properly called photocells rather than solar cells.

Attention is drawn to our copending application No. 6146/78. (Serial No. 1,572,773).

WHAT WE CLAIM IS:—

1. A photocell containing a photovoltaic junction between gallium arsenide and a liquid electrolyte containing a redox couple wherein the redox couple has a potential more negative than -0.5 volt and a concentration greater than 0.1 Molar.
2. A photocell as claimed in claim 1, wherein the electrolyte is a solution containing anions of either selenium or tellurium or a mixture thereof.
3. A photocell as claimed in claim 1, wherein the electrolyte is propylene carbonate or tetrahydrofuran.
4. A photocell as claimed in any one of claims 1, 2, or 3, wherein the GaAs electrode comprises a single GaAs crystal.
5. A photocell as claimed in claim 4, wherein the GaAs is n-type and doped with either Sn, or Si or Te.
6. A photocell as claimed in claim 5,

wherein the dopant concentration is less than $5 \times 10^{18}/\text{cm}^3$.

7. A photocell substantially as hereinbefore described with reference to
5 and illustrated in Figs. 1-4 of the accompanying drawings.

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