A number of photoelectrochemical (PEC) cells employing semiconductor electrodes for the conversion of radiant to electrical energy (liquid junction photovoltaic cells) have been described (1-17). Most have employed n-type semiconductors and have been used for the instantaneous production of electricity without chemical storage. The possibility of a photochargeable electrode stability were encountered. Investigations of chemical storage. The possibility of a photochargeable electrode stability were encountered. Investigations of chemical storage. The possibility of a photochargeable solution have been discussed, however (8-9, 15-17). Studies of aqueous systems with p-GaAs and p-GaP have been reported (15-16, 18), but the observed efficiencies of these were usually quite small and in many cases problems with electrode stability were encountered. Investigations of p-GaAs electrodes in acetonitrile solutions suggest good stability under strict water-free conditions (19).

We report here investigations of the p-GaAs electrode immersed in aqueous solutions containing 1,1'-dihexyl-4,4'-bipyridyl (heptyl viologen, HV$_2^+$) bromide. The reduction of HV$_2^+$ bromide on metal electrodes yields a precipitate of the violet radical cation of electrochemical displays (20-22). The formation of such a precipitate by photoreduction at a p-type semiconductor would allow low capacity energy storage via a solid material, just as occurs in secondary batteries. We will show that such a photoelectrochemical low capacity storage cells based on this reaction and utilizing simultaneous addressing with light and electrical signals are also proposed.

ABSTRACT

The photoreduction of aqueous solutions of 1,1'-dihexyl-4,4'-bipyridyl (heptyl viologen, HV$_2^+$) bromide on p-GaAs was investigated. Under irradiation with light of wavelengths below 885 nm, the photoreduction of HV$_2^+$ to form a precipitate of violet HV$_{2+}$ bromide on p-GaAs at potentials $\sim$400 mV more positive than the reversible potential of the HV$_2^+$-HVBr couple on Pt. Oxidation of HV$_{2+}$ back to soluble HV$_2^+$ occurs in the dark at more negative potentials. Photoelectrochemical low capacity storage cells based on this reaction with Cu, Ni, or H$_2$Nb$_2$O$_7$ counter electrodes were constructed. In such cells, under illumination, the p-GaAs electrode behaves as the cathode, a photovoltage develops, and current flows in the external circuit, while HVBr precipitates on the electrode surface, and the counterelectrode is oxidized. In the dark, the current flows in the opposite direction, the p-GaAs is the anode, and reduction occurs at the counterelectrode. Such a cell also produces an alternating electrical output under periodic illumination. Photoelectrochemical cells based on this reaction and utilizing simultaneous addressing with light and electrical signals are also proposed.

$\text{HV}_2^+ + \text{Br}^- + \epsilon \rightarrow \text{HV}^+ + \text{Br}^- \quad [1]$
addressed by light and an electrical signal is described here.

**Experimental**

The single crystal p-GaAs was obtained from Atomergic Chemicals (Long Island, New York) with acceptor concentration $3 \times 10^{18}$ cm$^{-3}$ (Zn-doped) and was mounted as an electrode as previously described (13). The surface (face 111) was first polished with 0.5 µm alumina powder and then etched for 10-15 sec in a solution which contained $H_2SO_4: H_2O: 30\% H_2O_2$ in concentration ratio 3:1:1. In some experiments single crystal p-GaP was also employed. The surface of this crystal was etched in 11M HCl for 10 sec before use.

As light sources either a 450W xenon lamp or a He-Ne laser (1.6 mW power) was used. The potentiostatic measurements were carried out with a Princeton Applied Research (PAR) potentiostat Model 173, with a cell consisting of an aqueous saturated calomel reference electrode (SCE) and a Pt wire as the counter-electrode. The electrochemical cell was provided with Pyrex windows for the passage of light. Nitrogen gas was passed through the solution before the experiments and above the solution during the experiments, since viologen radical cations are very sensitive to oxygen.

In the two electrode PEC cell experiments the voltage of the photocell between the p-GaAs and the oxide counter-electrode was measured on an x-t recorder through a voltage follower. The photocell current was measured on an x-t recorder through a current-to-voltage converter. For short time measurements of the cell short-circuit current, a Nicolet Model 1090A digital oscilloscope was used. The light intensity at the semiconductor surface was varied by means of neutral density filters.

**Results**

*Cyclic voltammetry.*—The i-V curve at a p-GaAs electrode of an unstirred solution of 0.01M $HVBr_2$ and 0.2M KBr at a scan rate of 100 mV/sec is shown in Fig. 1. In the dark (curve a) there was only a small current in the cathodic region with a very small peak on scan reversal. Under illumination of the p-GaAs electrode surface with the full power of the 450W xenon lamp, a larger cathodic current beginning at $-0.1V$ vs. SCE appeared (curve b). Simultaneously with the appearance of this cathodic current, the precipitation of the violet $HVBr$ was observed on the electrode surface. On reversing the scan direction, a sharp anodic current peak occurred, either in the dark or under illumination. During the passage of the anodic current the violet precipitate on the semiconductor surface disappeared. Thus the overall process is that shown in [1], with illumination necessary for the reduction process, as is usual for p-type semiconductors.

These cyclic voltammograms could be repeated many (at least 100) times with only a small change in the peak height of the cathodic photocurrents, demonstrating good chemical reversibility of the deposition and stripping process. Upon illuminating the electrode with the narrow beam of a He-Ne laser, violet spots appeared on the electrode surface at exactly the location and of the size of the laser beam spot. The response time of the process was investigated by potential steps under illumination or by irradiation with chopped light with the electrode held at a constant potential (Fig. 2). A good coloration was observed on the electrode surface within $0.5$ sec after illumination of the electrode. Although the intensity ratio for $HVBr$ deposited on dark p-GaAs is not very high, the deposition was easily discernable and this type of process can be considered for use as an electrochromic display controlled by both light and electrode potential and may also be applicable to photoimaging purposes (24, 25).

![Fig. 1. Cyclic voltammograms recorded with p-GaAs at 100 mV/sec with aqueous solution containing 0.01M $HVBr_2$ and 0.2M KBr: (a) in the dark; (b) under illumination; (c) cyclic voltammogram recorded with the same solution on a Pt disk electrode (100 mV/sec); (d) cyclic voltammogram recorded with p-GaAs in solution containing only 0.2M KBr. Light source, 450W Xe lamp.](image1)

![Fig. 2. Current-time transients in potential step experiments on p-GaAs in solution containing 0.01M $HVBr_2$ and 0.2M KBr: (a) potential stepped between $-0.5$ to $-0.1V$ under constant illumination; (b) the potential held at $-0.35V$ vs. SCE under chopped illumination. Light source, 450W Xe lamp.](image2)
The cyclic voltammograms of the solution of 0.01M HV$_2$+ dibromide and 0.2M KBr at a Pt electrode is shown in Fig. 1c. By comparison of this voltammogram with that obtained with p-GaAs under illumination, one can see that significant photoreduction of HV$_2$+ can occur on p-GaAs at potentials ~400 mV less negative than on Pt. The photocurrent attributable to the reduction of protons on the p-GaAs in a KBr solution not containing HV$_2$+ was very small (Fig. 1d). Photoreduction of HV$_2$+ was also investigated with a p-GaP photocathode. In this case, the underpotential for the reduction process was even larger than in the case of p-GaAs, but the process was not very reversible and the back oxidation occurred only at more positive potentials than on a Pt electrode. Thus, upon scanning a p-GaP electrode over roughly the same potential region (Fig. 3), a gradual accumulation of HVBr occurred on the electrode surface and the cathodic current gradually decreased.

With the low intensity used in the experiments described above, the photoreduction current on p-GaAs was limited by the rate of diffusion of HV$_2$+ to the electrode surface, as demonstrated by the proportionality of the cathodic photocurrent to the square root of scan rate, v (Fig. 4). Moreover, as shown in Fig. 5, while the potential for photocurrent onset and the current at the foot of the wave depended upon the light intensity, at more negative potentials the maximum current was almost independent of intensity and was limited by the rate of diffusion of HV$_2$+ to the electrode surface.

PEC cells.—Since the photoreduction of HV$_2$+ occurs on p-GaAs with an underpotential of about 400 mV while the back-oxidation in the dark on p-GaAs occurs at the same potentials as on Pt, one can envision a sort of solar storage cell composed of a p-GaAs and another chemically reversible electrode (Fig. 6). This counter electrode should have a redox potential between the potential for the photoreduction of HV$_2$+ on p-GaAs and the potential for oxidation of HVBr in the dark (Fig. 6c). In such a cell, when light irradiates the p-GaAs, it is the cathode of the cell and HVBr precipitates (Fig. 6a). The HVBr precipitate on the p-GaAs is stable at open circuit, and can be oxidized in the dark back to the original HV$_2$+ while the counter electrode becomes the cathode of the cell (Fig. 6b). Three counter electrodes with redox potentials suitable for such a photocell, Cu/Cu-oxide, H$_2$Nb$_2$O$_7$/Nb$_2$O$_5$, and Ni/Ni-oxide, were used. The open-circuit voltages and the short-circuit currents of such cells composed of p-GaAs, and the three counter electrodes under periodic illumination are shown in Fig. 7. The relative polarity of the p-GaAs shows the expected changes (Fig. 6) as the semiconductor is subjected to the chopped beam. In the photocharged condition, the HVBr remained on the electrode surface and the open-circuit voltage was stable for at least 2 hr. The maximum open-circuit voltages were found with the Cu counterelectrode with potential excursions of up to 0.4 V observed (Fig. 7A). The short-circuit currents of these cells are shown in Fig. 7B. In the light, current flows in the external circuit during which precipitation of the purple HVBr on the surface of the p-GaAs occurs. The current decays almost to zero in about 10 sec because a thick opaque film of HVBr builds up on the electrode surface and the HV$_2$+ concentration is depleted near the electrode surface. The cell can be regarded as a storage battery. The precipitate of HVBr can be stored on the p-GaAs, and then oxidized in the dark to yield a current in a direction opposite to that observed under illumination. Obviously, the capacity of such a cell is very small; the maximum charge in the form of HVBr which can precipitate on the p-GaAs before the current drops to zero is about 10 mC/cm$^2$. Alternately, the cell can be considered as a type of a-c device under periodic illumination. In this mode the p-GaAs cell performance was very stable with all three cells and no deteriora-
Fig. 6. Schematic description of the HVBr$_2$-based photoelectrochemical cell operating: (a) under illumination (photocharge); (b) in the dark (discharge); (c) relative energy levels and potentials at the counterelectrode, and at the p-GaAs, required for operation of the cell shown in (a) and (b).

Fig. 7. (A) Open-circuit potentials and (B) short-circuit current under chopped illumination for the cells: (a) p-GaAs/HVBr/HVBr$_2$, KBr/Cu; (b) p-GaAs/HVBr/HVBr$_2$, KBr/Nb$_2$O$_5$; (c) p-GaAs/HVBr/HVBr$_2$, KBr/Ni. Light source, 450W Xe lamp.

Fig. 8. Initial short-circuit photocurrents for the three cells described in Fig. 7 as a function of light intensity (He-Ne laser).

Discussion

The behavior of the p-GaAs/solution interface and a rationalization of the observed PEC cell behavior can be presented in terms of the surface controlled model for GaAs proposed elsewhere (26) (Fig. 9). In this model, the Fermi level of the semiconductor is pinned by surface states located about one-third of the way up in the gap (i.e., ~0.4-0.5V above the valence band-edge) (Fig. 9a). The maximum open-circuit photopotential, $V_{on}$, observed under intense illumination would then be ~0.4V, and the open-circuit photovoltage would be the difference between $V_{on}$ and $V_{redox}$ of the counterelectrode reaction (Fig. 9b). In the dark after deposition of HVBr, oxidation of HVBr occurs via the surface states and the p-GaAs essentially behaves as an inert contact to the layer (Fig. 9c). The counterelectrode in a two-electrode PEC cell must have a redox potential between $V_{on}$ and that of the HV$^2+$/HVBr system, so that only couples in a relatively narrow range of potentials are suitable.

Storage cells based on this type of electrode reaction will necessarily have small capacities, unless films which deposit on the electrode surface can be found which are both transparent to the wavelengths absorbed by the semiconductor and are electrical conductors. Moreover, higher concentrations of the soluble form are required to prevent mass transfer limitations to the photocurrent even before film formation causes current decay. Such cells may, however, find application in very low capacity batteries or as a-c devices under periodic illumination.
The application of such a system to produce a display addressable both optically and electrically (a photoelectrochromic display) is perhaps of greater interest (Fig. 10). One can envision the operation of such a device in which a light beam produces a raster on the electrode surface, and the electrode potential is switched to (i) the deposition potential (coloring), (ii) open circuit (hold), or (iii) the stripping potential (erase). The advantage of such a display, compared to the more familiar electrochromic ones, is that only two leads need be provided to the cell rather than the multiple leads and complicated electrical addressing required for a large screen or multi-character display. While the contrast ratio for HVBr on GaAs is not very good, in principle a wide bandgap semiconductor (e.g., > 3 eV), which would appear white and would be addressed with an ultraviolet beam could be employed. For a display involving rapid scanning, a system with a faster response time is also required. Similar concepts involving semiconductors and metal deposits for photomaging have been reported (24, 27).

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REFERENCES

Semiconductor Electrodes

XXIII. The Determination of Flatband Potentials from Differential Stress Measurements with Attached Piezoelectric Detectors

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ABSTRACT

A new method for the determination of the flatband potential, Vfb, of semiconductor electrodes by differential stress measurements of a piezoelectric detector bonded to the semiconductor is reported. Values of Vfb for single crystal n-SrTiO3 and p-GaAs, and polycrystalline n-TiO2 in 1N NaOH and 1N H2SO4 are shown to be in good agreement with previously determined values. Possible application of such measurements to the study of surface changes and breakdown is suggested.

The flatband potential, Vfb, of a semiconductor/electrolyte solution interface is an important parameter in explaining the electrochemical characteristics of the system in the dark and under illumination (1-3). Vfb is a function of both the semiconductor material and the solution composition, and is measured to determine the locations of the semiconductor valence and conduction band edges with respect to solution energy levels. Usually Vfb-values are determined by direct measurements of the space charge differential capacity, Csc (Schottky-Mott plots) or by determinations of the open-circuit photopotential (or the potential for the onset of the photocurrent) under intense irradiation. Even for nonpolarizable electrodes this term may be small and is equal to zero at the flatband potential, 

\[ \delta V_{fb} / \delta E = -q - \delta q / \delta \theta \]  

where \( \delta \) is the ratio of the surface area before and after deformation. For an ideally polarized electrode, the term \( \delta q / \delta \theta \) is zero, since the charge density does not depend upon the deformation of the electrode surface. Even for nonpolarizable electrodes this term may be small and is equal to zero at the flatband potential, because at Vfb there is no charge on the electrode.

For semiconductor electrodes, the excess charge \( q \) is distributed in the space charge region. At potentials negative of the flatband potential, the space charge region has an excess of electrons and the differential stress measurements will be positive. At the flatband potential there is no excess charge and the differential stress is zero. For potentials positive of the flatband potential there is an accumulation of holes in the space charge region and the differential stress will be negative. Thus, as implied by Eq. [1], the differential stress tracks the space charge, and the intercept of the dif-