

ter. After passage of more current, the crystal became more metallic with resulting decreases in photoresponse. Similar results were obtained for spontaneous intercalation of Li in HfS_2 crystals in propylene carbonate electrolytes.

STUDY OF AMORPHOUS HYDROGENERATED BORON THIN FILMS

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The objective is to characterize hydrogenated amorphous boron as a novel material to be employed in photoelectrochemical cells for the conversion and storage of solar energy.

The optimum optical band gap of a semiconductor electrode for the maximum theoretical photovoltaic conversion efficiency of the solar spectrum in a photoelectrochemical cell is approximately 1.45 eV. Therefore, amorphous hydrogenated boron, whose optical band gap can be consistently controlled at approximately 1.5 eV, becomes an attractive active electrode material. Amorphous boron, without hydrogenation, has been known to have poor semiconducting properties. However, in analogy with the situation existing for amorphous hydrogenated silicon, the presence of boron-hydrogen bonding is believed to have significantly improved its semiconducting characteristics. In view of these advantages, Giner Inc., carried out an evaluation of the performance of this material as a photoelectrode in a photoelectrochemical cell. As far as is known, no previous attempt of this type has ever been made.

In this study, the electrochemical and photoelectrochemical characteristics of amorphous hydrogenated boron in both aqueous and nonaqueous redox electrolytes were investigated. A systematic screening of redox couples, mostly in acetonitrile, covered a redox potential range from 1.08 to -1.00 on the standard calomel electrode (SCE) scale. Furthermore, the long-term stability of this material was determined.

The results indicate that amorphous hydrogenated boron currently produced by the radio frequency (RF) glow discharge of diborane appears to be chemically stable in several redox electrolytes. As to its suitability as a photoelectrochemical cell electrode material, the current n-type a-B:H was found to produce a photovoltage of several millivolts, and p-type material did not exhibit any photovoltage response at all, despite the wide redox potential range covered in the work. The semiconducting properties of a-B:H will have to be significantly improved in order to produce a more useful photoelectrical effect. Specifically, boron films with higher carrier mobility, as well as better photoconductivity, must be obtained to be used as an

attractive photoelectrochemical cell electrode material. This may be accomplished through the modification of the film growth parameters (*e.g.*, temperature, dopant, etc.) or by the introduction of another element to form a boron-based compound (*e.g.*, boron arsenide). More study is needed to gain further understanding of the semiconducting properties of a-B:H.

The program completed in 1982 involved the preparation and characterization of both n- and p-type hydrogenated amorphous boron (a-B:H) thin films on conductive substrates (*e.g.*, Mo-, Ta-, or SnO₂-coated glass) to be evaluated as potential photoelectrode materials in the photoelectrochemical conversion of solar radiation into electricity. The a-B:H films were prepared using the RF glow discharge of diborane (B₂H₆). The optical band gap (E_g) of these semiconducting thin films has been maintained, through the control of substrate temperature, in the vicinity of 1.5 ± 0.1 eV for maximum conversion efficiency of the solar spectrum. With regard to dopants for boron, n-type a-B:H films were doped by Si with the addition of silane (SiH₄) to the diborane gas during the glow discharge process, while p-type material was prepared through the diffusion of Mg into the undoped a-B:H film (from the front or back side). The ohmic contact between the substrate and the semiconducting thin film was made using a heavily doped layer (n⁺ or p⁺ doped).

Both the n- and p-type thin films were prepared, and they appeared to be adherent and uniform. The optical band gap of the n-type (Si-doped) a-B:H film is about 1.5 ± 0.1 eV. The film thickness is approximately 5000 Å. The absorptivity of the film is approximately 10⁴ cm⁻¹ at 500 nm. The conductivity is approximately 10⁻¹¹ ohm⁻¹ cm⁻¹ in the dark and approximately 10⁻⁹ ohm⁻¹ cm⁻¹ in AM1 sunlight. It should be noted that this conductivity in the dark is several orders of magnitude lower than that of a typical a-Si:H film, and the photoconductivity under AM1 sunlight is scarcely two orders of magnitude above the dark conductivity. An attempt has been made to increase the concentration of the dopant (SiH₄) in the diborane glow by a factor of about 1000. However, the conductivity of the film was not found to be significantly greater than 10⁻¹¹ ohm⁻¹ cm⁻¹.

The photoelectrochemical characteristics of this Si-doped n-type a-B:H film were studied in eight different redox electrolytes. A wide redox potential range from 1.08 to -1.0 V (versus SCE) was covered. A total of thirteen n-type and eight p-type a-B:H thin film electrodes have been investigated. In most cases, the open circuit potential of the a-B:H electrode in the dark is quite different from the corresponding redox potential measured using a Pt electrode. This effect is most often ascribed to either the inherent slow electron transfer across the semiconductor/electrolyte interface, corrosion, or film formation. It was also concluded that pinholes usually exist on those a-B:H films that quickly reach the equilibrium redox potential.

Measurements of instantaneous photovoltage showed that the majority of the electrodes do not exhibit any voltage response to light with the exception of one sample. In this case, a small photovoltage (approximately 5 mV) has been repeatedly observed for hours. This result was encouraging because

it clearly demonstrates that the a-B:H film, in spite of its low carrier mobility (usually signaled by high resistivity), still exhibits a photoelectrochemical effect. It is then reasonable to expect that such an effect can be enhanced through the improvement of the semiconducting properties of thin n-type Si-doped a-B:H thin films.

It has been established that the chemical stability of the a-B:H film produced by the glow discharge of diborane is stable in both aprotic and alcoholic solvents. It is also more resistant to dissolution in aqueous electrolytes than would be expected based solely on thermodynamic considerations.

In conclusion, it was found that the highly resistive n-type Si-doped a-B:H prepared in this work indeed exhibits a small photoelectrochemical effect. Its semiconducting properties must be further modified to favor a more enhanced photovoltage to be considered as a suitable electrode material for a photoelectrochemical cell.

MOLTEN SALT CELL RESEARCH

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The objective of this project is to conduct the research required to develop cells for an advanced electric-vehicle battery that has very high specific energy and power, long cycle life, and an acceptable cost. The performance and lifetime goals for the cells are a minimum specific energy of 160 W h/kg (3 h discharge rate), volumetric energy density of 400 W h/l, peak specific power of 240 W/kg (20-s pulse at 50 percent discharge), and lifetime of 1000 cycles. Although the present emphasis is on lithium-alloy (e.g., Li-Al, Li-Si, Li-Al-Si) negative electrodes and transition metal disulfide (FeS_2 and NiS_2) positive electrodes, other active materials are also under consideration.

During 1982, this project consisted of four tasks: negative electrode research, positive electrode research, materials research, and electrode and cell modeling. The major accomplishments during this period were as follows:

- A determination of the sequences of phases formed during the discharge of FeS_2 , NiS_2 , and CoS_2 electrodes was completed.
- The electromotive force (emf) for the first discharge reaction of the FeS_2 electrode ($\text{FeS} + \text{Li}_3\text{Fe}_2\text{S}_4$) has been determined as a function of temperature; preliminary emf data have been obtained on the discharge of NiS_2 to NiS.