DOE/ET/23041-3

Distribution Category UC-63

Preparation and Characterization of Hydrogenated Amorphous Boron Thin Films and Thin Film Solar Cells Produced by Glow Discharge Decomposition Methods

Third Quarterly Progress Report

for period July 1, 1979 - September 30, 1979

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November 1979

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Prepared for the U.S. Department of Energy, Division of Solar Energy

Under Contract DE-AC03-79ET23041

This quarterly report is an account of recent progress in our program to produce hydrogenated amorphous boron thin films, to characterize these films, and to produce and evaluate solar cells from such amorphous boron films.

In exact analogy with the situation previously existing for amorphous silicon, amorphous boron, without hydrogenation, has poor semiconducting properties due to defect states in the band gap. The decomposition of diborane, penataborane, and/or decarborane to produce thin films can reasonably be expected to result in amorphous boron thin films containing substantial quantities of hydrogen. The current program aims directly at the growth and doping of such hydrogenated amorphous boron thin films, the evaluation and optimization of their semiconductor properties, and the fabrication and testing of thin film solar cells from them.

During the past quarterly period we have continued to produce both intrinsic and doped a-boron thin films. Our film characterization efforts have been primarily focused on controlling the optical band gap by annealing the as-deposited films in vacuum at 400°C, and measuring the resulting optical gap as a function of bake-out time. Because the optical band gap of a-boron has been observed to vary from 0.8 eV to over 2.0 eV as a function of hydrogenation, it should be possible, by controlled annealing, to obtain a-boron films with an optimal band gap of 1.45 eV. In addition, work is nearing completion on our cryostat which will be used to measure the electrical gaps of our a-boron films.

Film Fabrication

Amorphous boron films continued to be produced in this quarter, in addition to intrinsic a-boron films, film doped with carbon, phosphorus, and silicon were fabricated. The doping was accomplished by introducing respectively ethylene, phosphine, and silane into our diborane-hydrogen glow discharge.

Optical Measurements

In our studies of the optical gap of a~~n~~morphous boron, we are attempting to produce a film with the optimum gap of 1.45 eV.

Our optical measurements are made with a Beckman DK-2A spectrophotometer as described in the previous quarterly report.

We have used the method of Freeman and Paul (1978) to calculate the absorption coefficients of our films. Then plotting $(\alpha\ h\nu)^{1/2}$ versus $h\nu$ lead to a value of the optical gap, according to the work of Mott and Davis (1970). They found the relationship expressed in Eg. (A):

$$(\alpha h\nu)^{1/2} = \text{const.}(h\nu - \varepsilon_0) \qquad \text{(A)}$$

where α is the absorption coefficient, h is Planch's constant, ν is the photon frequency, and ε_0 is the optical gap.

A representative graph for one of our films is shown in Fig. 1, from which the optical gap is seen to be 2.16 eV by Eq. (A).

The optical band gaps measured to date for a number of our as-deposited amorphous boron films range from 2.05 to 2.22 eV.

Our confidence in the film properties obtained through the technique has increased greatly since we now have access to a Bendix Proficorder profilometer to measure film thickness. Previous thickness measurements had been made using a miraud interferometer microscope attachment. The profilometer data, we believe, is considerably more trustworthy. Film thickness can now be measured routinely to within 10%.

As these gaps for the films as-deposited are considerably higher than that for maximum efficiency under AM1 illumination, we have been annealing the specimens in an attempt to optimize the gap. This treatment consists in putting the boron films, under vacuum, into one our salt pots. These salt pots precisely regulate the temperature at which a film is baked. Previous work with a Brew vacuum furnace showed that the device could not easily be made to regulate at temperatures as low as those at which we desired to conduct the bake-out procedure. Optical band gap changes as a result of these bakings are contained in Table I. By baking at 400°C, we have been able to lower the band gap in stages from 2.19 eV in the as-deposited state to 1.42 eV, which is close to the ideal optical gap of 1.45 eV.

The initial indications are that heat treatment of hydrogenated amorphous boron films does indeed affect the optical band gap. These very encouraging results lead us to believe it may be quite possible to tailor the band gaps of our films.

Future plans are to continue the bake-out tests for films produced under a variety of deposition conditions. We intend to eventually produce films with ideal properties. Furthermore, hydrogen content will be measured for the films at various stages of the bake-out procedure to more completely characterize them. The incorporated hydrogen is believed to be the controlling factor in the variation of the bandgaps in these films.

Electrical Measurements

Further characteristics of boron films will be evaluated in a cryostat which is nearing completion. Then we will be able to measure the resistivity-conductivity of our various boron films at temperatures from 77 K to 300 K.

We expect the conductivity to obey a relation of the form of Eq. (1) (Mott 1970).

$$\sigma = \sigma_0 \exp(-\Delta\varepsilon/kT) \tag{1}$$

where σ_0 is a constant, k is Boltzoman's constant, and $\Delta\varepsilon$ is the energy separation of the bottom of the conduction band. The electrical band gap, in the case of intrinsic materials, is twice the $\Delta\varepsilon$ in Eq. (1). Measurement of the dark electrical conductivity versus temperature will thus reveal the electrical gap.

The encouraging results for the second quarterly report were obtained using a two point resistance measurement. More in harmony with ASTM standard F 43 is our planned four point method.

Measurements of electrical resistance and its variation with temperature will be made, and room-temperature resistivity and electronic band gap computed from the results. A system for making these tests (Figs. 2 and 3) using a two probe, contact dependent, and a four probe, contact independent, method is undergoing testing and a calibration at present. Comparison of the results of the two methods of measurement will be used to infer the ohmic or rectifying properties of the contacts. A thin film specimen with vacuum evaporated contacts in the geometry used is shown diagrammatically in Fig. 4. All measurements are made in an evacuated dewar to obviate the adsorption of water vapor and oxygen by the sample surface. The tests will cover a temperature range of -75°C to 150°C by initially chilling the cryostat with liquid N_2 and subsequently heating the sample holder with resistive elements mounted therein.

References

E.A. Davis and N.F. Mott, Phil. Mag., 22, 903, (1970).

E.C. Freeman and W. Paul, Phys. Rev. B., 18, 4288 (1978).

N.F. Mott, Phil. Mag., 22, 7 (1970).

TABLE I Optical Band Gap as a Function of Nake-Out Time at 400°C

Time (hrs)	Optical Band Gap (eV)
As-Deposited	2.19
0.5	2.07
1.0	1.05
4.0	1.73
8.0	1.68
16.0	1.61
32.0	1.42

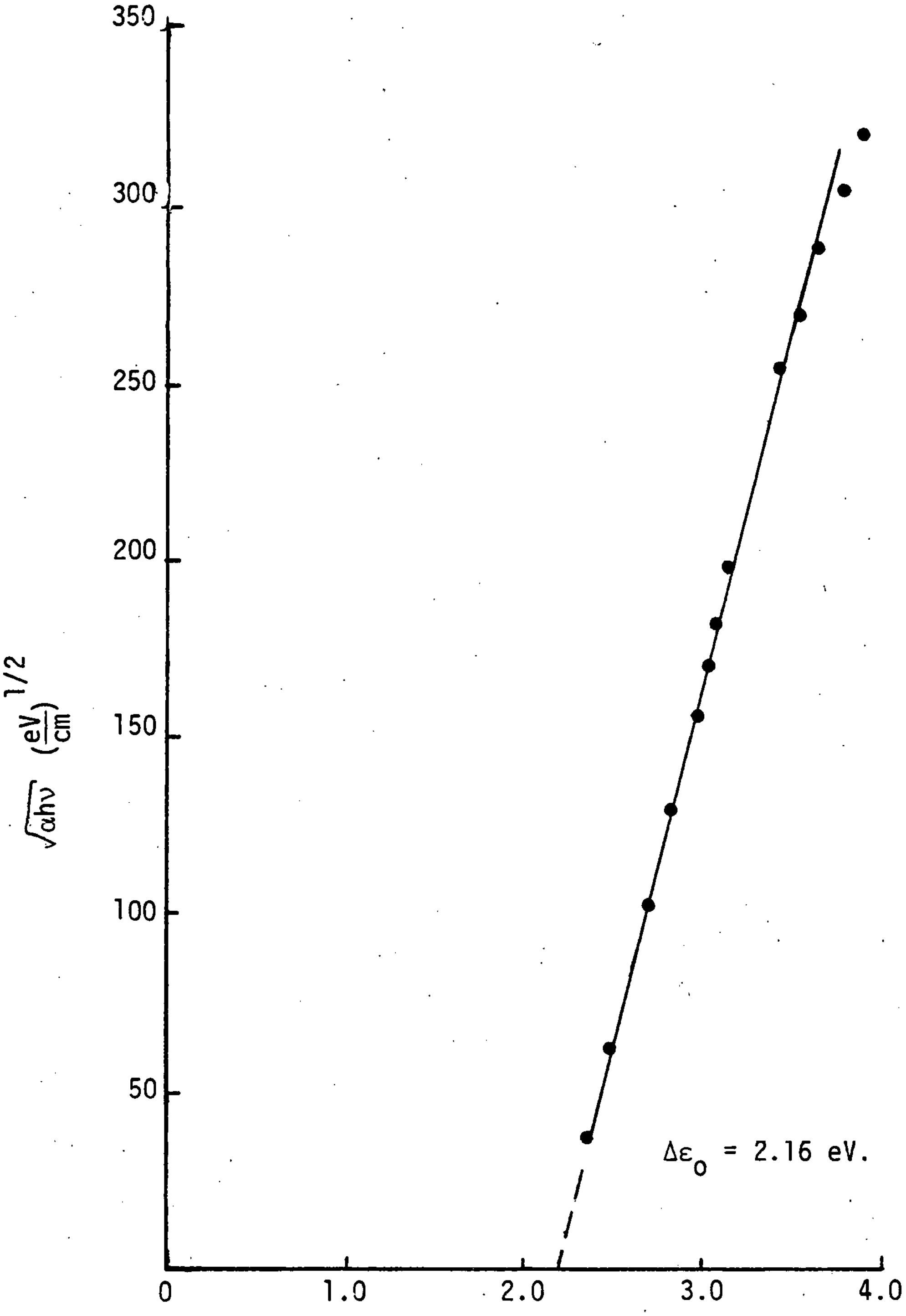

Figure 1. $\sqrt{\alpha h\nu}$ vs. $h\nu$ for a typical as-deposited a-boron film.

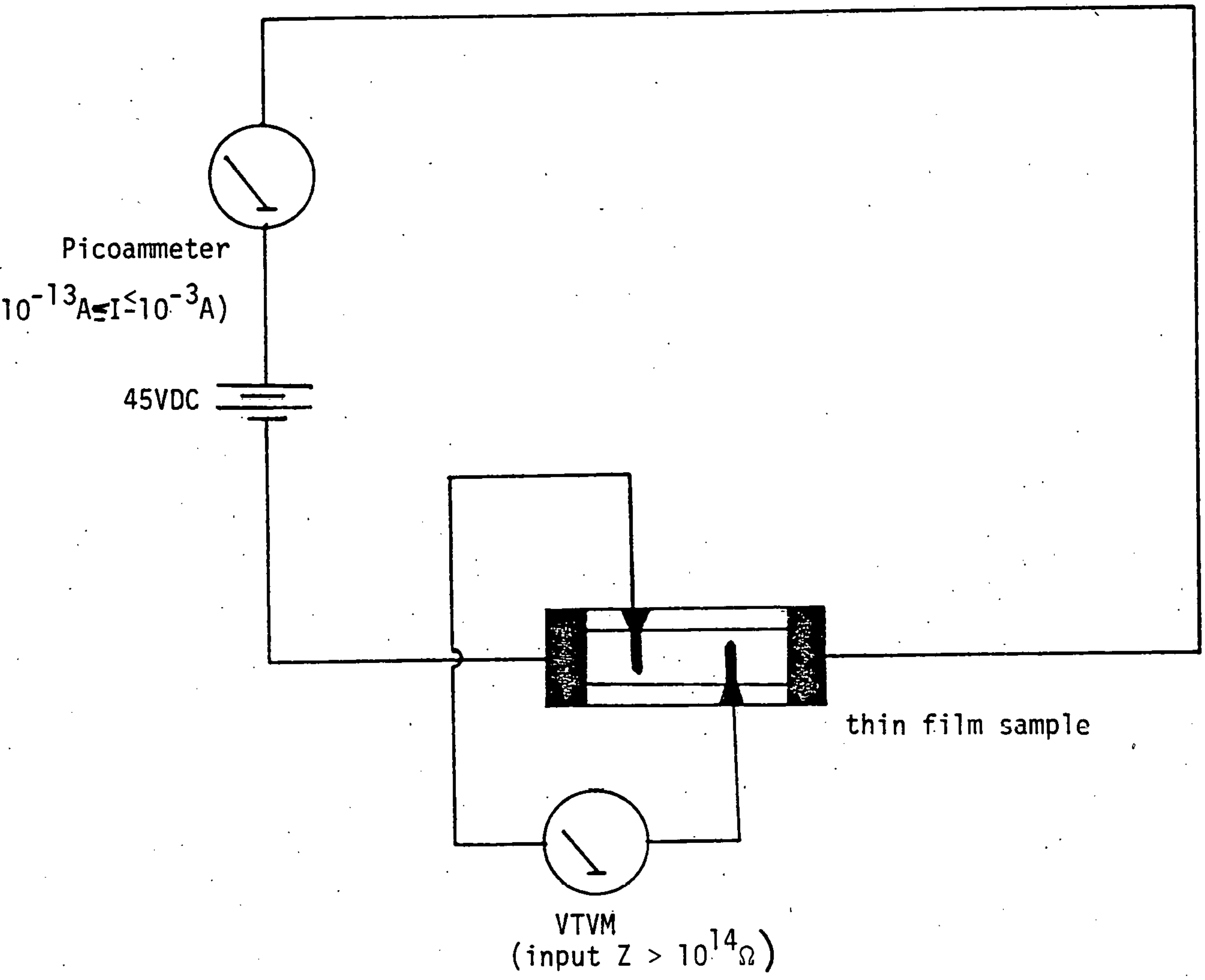

Figure 2. Resistance Measurement Circuit

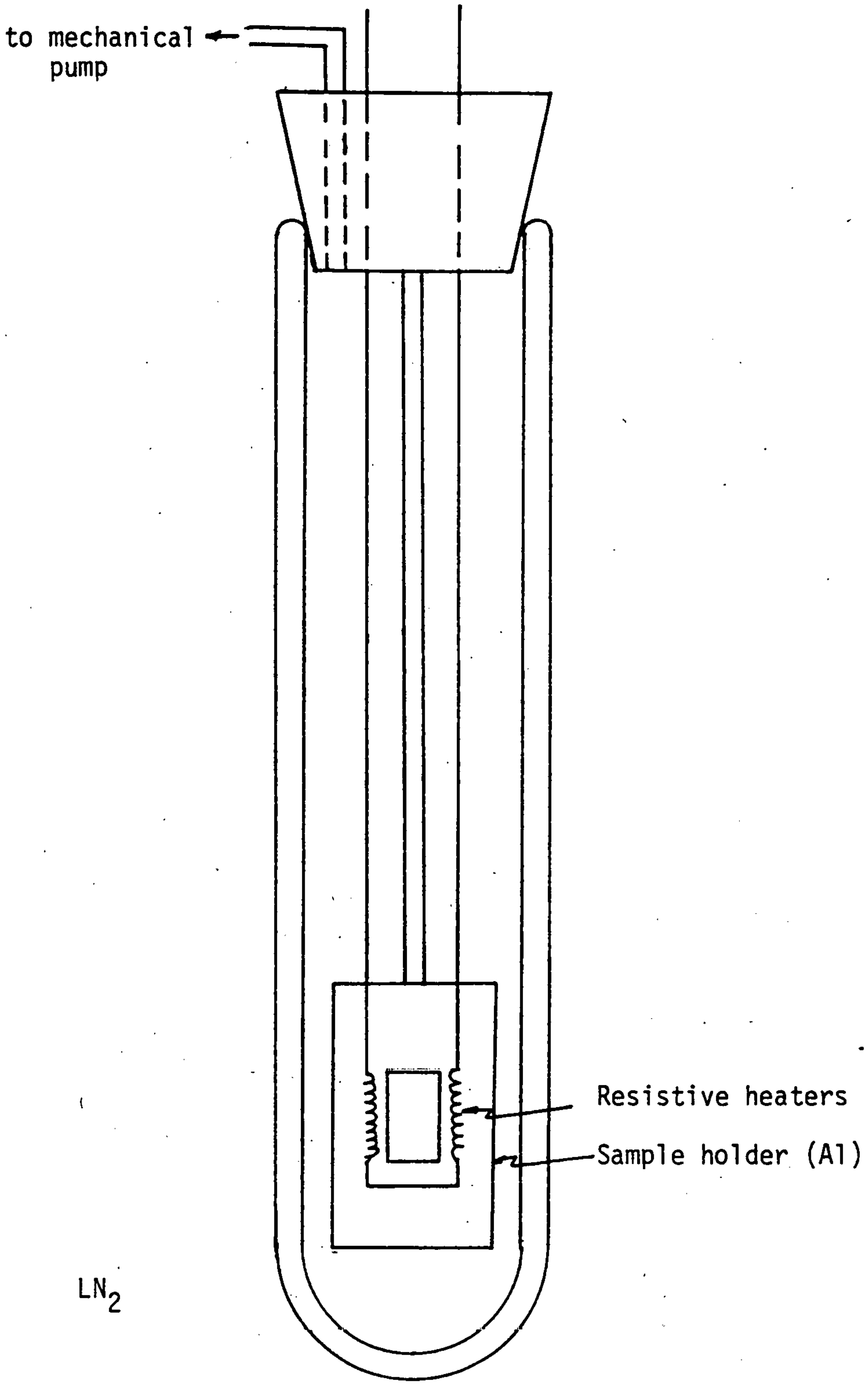

Figure 3. Schematic drawing of specimen test dewar

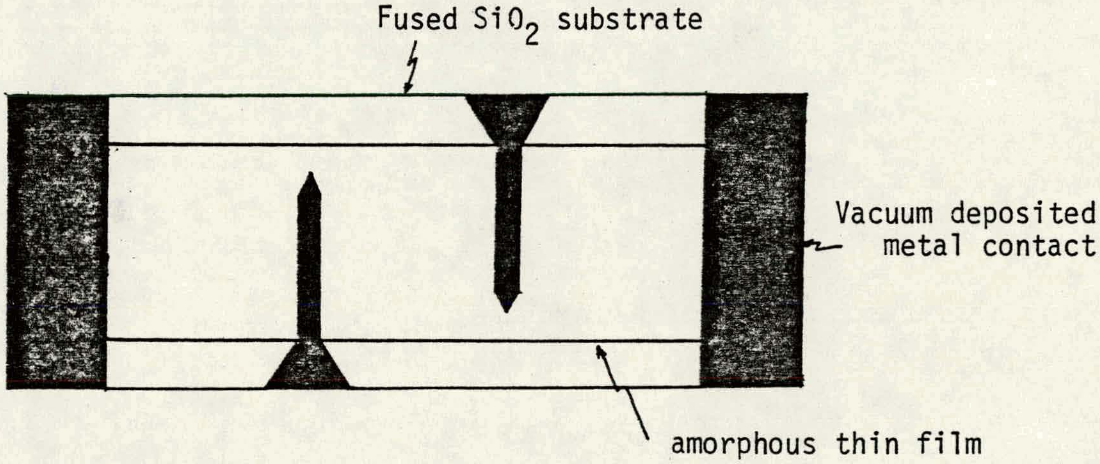

Figure 4. Schematic drawing of thin film specimen.