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MASTER

AMORPHOUS Si SOLAR CELLS

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Third Quarterly Report

1 July, 1979 - 30 September, 1979

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Table of Contents

	Page
Summary	1
I. Introduction	3
II. Material Growth	4
III. Material Characterization	6
IV. Device Formation	8
V. Device Design and Analysis	9
VI. Plans for Fourth Quarter	11
VII. References	12

Appendices:

- A. "Thermopower and Conductivity Measurements and Analysis", Paul H. Nielsen

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Summary

This report describes the work at the University of Delaware and the University of Chicago during the third quarter of DOE contract 03-79-ET-23034. The accomplishments during the third quarter are:

1. Material Growth

- . A new technique, using controlled DC voltages in addition to RF voltage, was developed to deposit a-Si:H and a-Si:F,H,O films. This technique allows the growth of films with uniform morphology and yet avoids ion-induced damage. Reproducible films with high photoluminescence efficiency, indicative of low defect densities, have been grown.
- . Fluorinated films have been doped n and p type. Fluorinated n-type films have been made degenerate.

2. Material Characterization

- . A new measurement technique, thermo-electric power (TEP) has been used to measure the movement of Fermi level in n and p-doped materials. Simultaneous measurements of TEP and conductivity have revealed that the Fermi level in n-type a-Si:F,H can be moved quite easily by doping, and that it probably moves into the conduction band at ~75 ppm AsH₃ doping. This result is very significant, since it is the first time that a-Si has been made degenerate, indicating that fluorination probably results in passivating the gap states in the top half of the gap.

- . The conductivity of n-type fluorinated a-Si is very high. We have achieved $\sigma = 20 (\Omega\text{-cm})^{-1}$, approximately 10^3 times higher than the best hydrogenated a-Si. However, p-type fluorinated films are not significantly different from p-hydrogenated a-Si.
- . Bandgap measurements on B-doped a-Si have revealed that B doping, even at low B levels (~2000 ppm) leads to the formation of B:Si alloy with resultant bandgap shrinkage. This result can explain the poor performance of a-Si p-i-n junction devices with B doped p layers.

3. Device Manufacture

- . $p^+ i n^+$ junctions have been made in hydrogenated a-Si. The junctions show good I(V) characteristics, and follow $I = I_0[\exp(qV/1.8 kT) - 1]$ behavior.
- . The junctions are photovoltaic, and we have obtained $V_{oc} = 755 \text{ mV}$ in a $p^+ i n^+$ junction device

4. Device Design and Analysis

- . A heterojunction model has been developed which partially explains the poor collection efficiency of p-i-n junctions made with B-doped p layers. A design has been evolved which may eliminate this problem. The design consists of using a wider gap a-Si to make the p-layer so that shrinkage due to B-doping would result in a pseudo-homo-junction instead of a low-gap heterojunction.

I. Introduction

During the third quarter, we have continued our work on growth and characterization of materials and design and analysis of devices. We have also started work on device manufacture, and have successfully made p-i-n junctions and measured their diode and photovoltaic properties. This report describes our work during the third quarter (July 1--September 30, 1979) of the contract.

II. Material Growth

1. Controlled-voltage growth

We have modified our cathodic growth system, described in the first quarterly report, to allow film deposition at controlled negative voltages.

The reasons for using controlled negative voltages are:

- (a) Negative voltages induce uniform, non-columnar growth.^[1]
- (b) A high negative voltage induces excessive ion-damage.^[2]

In order to reduce the deleterious effects of (b), we have modified the apparatus so that the negative voltage seen by the film is controlled. The apparatus is simple and is shown in Fig. 1. We can now control voltages from 0 to -1000V. Typically, we find that -40 to -60V produces uniform films with high photoluminescence efficiency. A comparison of the relative photoluminescence efficiency of a-Si produced by controlled voltage and one produced by our previous cathodic deposition is shown in Fig. 2. (The slight shift in energy is due to a slight shift in bandgap which is also a result of the modification of the deposition method.) For comparison, we also show a RCA sample. It is obvious that controlled-voltage deposition has produced a film with ~35% higher photoluminescence efficiency indicating a lower density of non-radiative defects.

2. Doping of a-Si:F,H and a-Si:H

Fluorinated films have been produced by using (H_2+SiF_4) mixtures. They have been doped both p and n type by using ($B_2H_6+H_2$) for p-type dopant and (AsH_3+H_2) for n-type dopant. It is found that n-type a-Si:F,H films have a very high conductivity, but the p-type films are very similar to p-type hydrogenated a-Si films.

Fig.1

Controlled Voltage Growth

IEC79210

Figure 2

Comparison of Delaware vs. RCA Samples

One interesting result of p-doping of a-Si:H films is that the bandgap shrinks upon B-doping. (Fig.3) This is a clear indication of the formation of Si:B alloy^[3], probably due to the very strong Si:B bond. The formation of this alloy, even for very low B₂H₆ concentrations (2000 ppm) and the shrinkage in gap, indicate that an a-Si,B:H/a-Si:H heterojunction is formed when B is used to form the p-layer of a supposedly a-Si homojunction. This fact can be used to partially explain the poor photovoltaic behavior of a-Si p-i-n junctions. (See Section V below.)

In view of the problems associated with B-doping to make p-layer, we shall investigate Al and Ga doping to make p-layers.

Figure 3

Influence of B doping on
Absorption of a-Si

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III. Material Characterization

1. Doping Properties

Doping of a-Si is obviously important for making devices. Usually, only the conductivity of doped films is measured and activation energy for conductivity (σ) is reported. [4] However, measurement of σ vs. $(1/kT)$ alone cannot reveal independent information about the Fermi level position, since mobility as well as carrier concentration are temperature activated. [5] Therefore, it is necessary to use an independent method for measuring Fermi level position. This can be done by simultaneously measuring σ and thermo-electric (TEP) measurements as a function of temperature. [5,6]

We have set-up and utilized an apparatus for simultaneously measuring σ and TEP. The details of the apparatus and the preliminary analysis are in Appendix A. Among the important results obtained by this analysis technique are:

- (a) Both TEP and σ reveal a change in conduction mechanism at $\sim 125^\circ\text{C}$.
The reasons for this change are not clear.
- (b) Fluorinated a-Si films can be made highly conducting by doping with AsH_3 . The Fermi level appears to be degenerate in n-a-Si:H,F made with about 75 ppm AsH_3 in the gas mixture. This is a remarkable result which indicates that the density of defects in the top half of a-Si:F,H is very low, allowing easy movement of Fermi level. The degeneracy should help in making ohmic contacts to a-Si devices. The conductivity is in the range of $\sim 20(\Omega\text{-cm})^{-1}$, about 10^3 higher than best hydrogenated films.
- (c) p-type a-Si:F,H does not appear to be very different from p-type a-Si:H. The reasons for this are not clear, but may be due to Si:B bonding, or due to H and F splitting Si:Si bonds at the top

of the valence band and introducing new defect states while moving the valence band edge down in energy. This is possible because both Si:H and Si:F bonds are stronger than Si:Si bonds, and H and F may induce breaking of the weakest Si:Si states, namely the anti-bonding orbitals at the top of the valence band. The possibility of O, which is present as an impurity in SiF₄ (~0.3% air), causing excess states near the valence band cannot be ruled out either. Clearly, more work is needed on understanding doping of p-type a-Si films.

2. Understanding Photo-Induced Change

Photo-induced changes in dark conductivity of a-Si:H films are well known. [7] We have started experiments to see if surface states are responsible for photo-induced changes. Preliminary results indicate that surface states indeed play a role in changing the dark conductivity of a Si films which have been subjected to illumination for a prolonged time. More work on this subject will be done during the fourth quarter.

Figure 4

a-Si p+ / n+ Junction

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IV. Device Formation

We have made p^+-i-n^+ junctions in a-Si:H by successively depositing As-doped, undoped, and B-doped a-Si:H films on a 7059 glass coated with 1000 Å of molybdenum. A typical device structure is shown in Fig. 4. These diodes were grown primarily to test diode characteristics and not for solar cells.

A typical diode $I(V)$ curve is shown in Fig. 5. The diodes follow exponential $I(V)$ curves with a diode factor of 1.8. The open-circuit voltage of this diode was measured by subjecting the diode to quartz-iodine lamp illumination of 90 mW/cm^2 . An open-circuit voltage of $\sim 755 \text{ mV}$, corrected for $J_{sc} = 10 \text{ mA/cm}^2$, was obtained. This is quite encouraging, since the diode was not designed as a solar cell. (It had a poorly transparent moly layer as top contact, had no AR coating, and had a very thick p^+ layer). We expect to achieve $V_{oc} > 800 \text{ mV}$ in the next quarter with better designs of diodes.

Figure 5

p+ / n+ Diode No. 79-132

a-Si:H

V. Device Design and Analysis

1. Effect of Bandgap Shrinkage of B-doped p Layers

From Section II.2, we know that B doping leads to a shrinkage of the bandgap of p layers. As a result, the band structure of a p-i-n cell may look as in Fig. 6. Instead of a homojunction, we may have a heterojunction between a-Si:B:H and a-Si:H. There also may be a spike in the conduction band at the junction interface (Fig. 6).

The consequences of a spike and the bandgap shrinkage are quite serious. The bandgap shrinkage leads to excess photon absorption in the p layer (see Fig. 3). Since the p layer has a poor lifetime, a significant number of photogenerated electrons recombine in the p layer before reaching the junction. Consequently, the excess photon absorption in p-layer would lead to lower currents in p-i-n cells than if the bandgap did not shrink. The spike can also reduce the currents by impeding the flow of electrons across the junction. [8]

Thus, this preliminary model explains the poor currents obtained in p-i-n cells with B-doped p-layers. [9] We shall quantify this model in the next quarter.

2. Design for Higher Efficiency

The above model also points a way to increasing the efficiency of p-i-n cells. One method of overcoming the shrinkage in the heterojunction formation is to make the p-layer of a larger bandgap than the i-layer. We have demonstrated previously (see second quarter report) that fluorination increases the bandgap. Thus, a possible structure may consist of i and n^+ layers being made from a-Si:H, but p^+ layer is made from a-Si:F,H,O. Then, the shrinkage of the higher gap junction

Figure 6

Effect of B-induced Bandgap Narrowing on a-Si p-n junctions

IEC79212

(a-Si:F,H,O) by B may still leave the bandgap of p^+ higher than the gap of base layer. (Fig. 7) Thus, the spike may disappear, and there will not be any excess photon absorption in the p^+ layer.

An alternative would be to make the p^+ layer at a higher pressure and lower temperature, thereby increasing the bandgap. [10]

In practice, perhaps both these approaches need to be followed. We shall pursue this device structure further.

VI. Plans For Fourth Quarter

1. Material Growth: Study growth of fluorinated films and continue experiments with p doping.
2. Material Characterization: Complete the studies on movement of the Fermi level with doping. Continue the work on surface state effects on conductivity.
3. Device Formation. Make diodes with better quality factors (~ 1.5). Make diodes with $V_{oc} > 800\text{mV}$. Make (higher gap p^+)-(lower gap i)-(lower gap n^+) diodes.
4. Device Analysis. Quantify effects of B doping and bandgap shrinkage. Analyze spectral response of diodes.

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THERMOPOWER AND CONDUCTIVITY
MEASUREMENT AND ANALYSIS

Paul H. Nielsen

October 15, 1979

Introduction

Thermoelectric power measurements are a very useful technique for determining the position of the Fermi level relative to conduction and valence bands, and the average energy of conducting electrons or holes. [1-5]. A simultaneous measurement of thermoelectric power S , Peltier coefficient Π , and conductivity σ as a function of temperature reveals important information about conduction mechanisms and Fermi level positions, information that cannot be obtained from a measurement of σ alone. Thermoelectric power is particularly important in amorphous semiconductors, because the mobility is temperature activated [4].

We have studied thermoelectric power and conductivity as a function of temperature for both hydrogenated and fluorinated a-Si films. In this report, we describe our apparatus and results, and discuss the results in terms of a comprehensive but simple theory of thermopower measurements [1,4]. We show that Fermi level moves with doping, both n and p-type. A startling result is that n-type fluorinated a-Si has a small negative thermopower, with a positive slope in $1/kT$, which in the simple theory implies that the material is degenerate, i.e. the Fermi level is above the conduction band edge. Whether or not a more detailed analysis confirms this conclusion from the simple theory, the small thermopower is itself a very interesting result, since it indicates that the top-half of the gap in a-Si:F,H must be relatively free of defect states, in contrast to a-Si:H, in which the Fermi level cannot be brought closer to the conduction band than

~ 200-300 meV, by high arsenic doping. A low density of defects and a high Fermi level position imply good currents, high voltage and low contact resistance, obviously useful properties for solar cells.

Apparatus and Measurement Techniques

The first configuration we used for making thermopower, conductivity, and some limited photoconductivity measurements is shown in Fig. 1(a). The parts shown in the figure were all contained in an ion pumped vacuum chamber with a typical pressure of 10^{-6} torr during the measurements.

This system was used in the following manner to obtain most of the results discussed later: first, the sample (on glass) was mounted against the heated substrate block using silicone vacuum grease loaded with ZnO powder to improve its thermal conductivity, and wires were attached to four strips of vacuum evaporated Mg using a high temperature indium-containing solder. A mica insulator was stuck to the sample close to the metal strip used as the thermopower cold junction, with thermally conductive silicone grease. A type K thermocouple (0.003" wires) was pressed against the mica and thermally joined with more silicone grease to permit measurement of the sample (cold junction) temperature. The hot junction and electrical contact was made by contacting the end of a 1K resistor lead against the sample. The configuration of the resistor with thermocouple and leads is indicated in Fig. 1(b). Leads are attached to minimize extraneous voltages from developing due to thermal gradients and current flow in the resistor.

Once mounted, the sample was placed in the chamber and the chamber was evacuated. Conductivity measurements were made as the sample was heated, in the dark, to 180 to 200°C (depending on the sample), and the measurements were continued as the sample was maintained at a constant high temperature for about

one hour to anneal out any trapped charge which might cause a temporary change in conductivity. Then thermopower measurements were made, alternating with four terminal conductivity measurements, at a number of stabilized temperatures.

To measure the thermopower a Keithley 616 electrometer was used to measure the thermal voltage difference $V_s(T)$ between the grounded hot junction produced by the hot resistor lead, and the cold junction formed by one of the evaporated metal strips. The wires connecting the meter to the sample were all copper, and so the sample thermal voltage is referenced to copper. An amplifier using a LM308A integrated circuit was used to amplify the voltage difference between the type K thermocouple attached to the sample surface and the second identical thermocouple soldered to the hot junction resistor lead. The output of this amplifier, and the output of the 616 electrometer were used to drive the X and Y axes of a recorder. The ratio of the sample thermopower to that of the type K thermocouple was obtained by varying the power in the resistor and making a scan of $V_s(T)$ vs ΔT over a range of about $\pm 5^\circ\text{C}$. Generally the temperature of the hot junction was increased and then reduced back to its original value to make sure that the results were reliable. Suitable computer programs were written and used to calculate T , $1/T$, thermopower S , and Peltier coefficient Π from the measured output of the sample temperature thermocouple and the slope of the plot of sample vs thermocouple thermopowers. The present results for S and Π neglect the absolute thermopower of the copper reference materials [6], but as it is only about $2\mu\text{V/K}$, or less, this represents an error of much less than 1%.

Because there was no overall thermal radiation shield in this apparatus, there was about 3 to 4°C temperature difference registered on the ΔT thermocouple pair when the sample thermal voltage $V_s(T)$ was zero, at a temperature of

180-200°C. This temperature difference decreased as the sample temperature was reduced closer to room temperature. However, the existence of this offset necessitated the determination of the thermopower by plotting ΔT vs $V_s(T)$ as previously described, rather than just measuring ΔT and $V_s(T)$ at one value of ΔT .

Although this apparatus gave results for thermoelectric power that generally appeared precise to within a few percent, there was some question as to whether the hot junction contact was really at the measured temperature; the nonuniformity in sample temperature was certain to lead to errors in the measurement of conductivity vs temperature [$\sigma(T)$]; and the measurement procedure was slow because of the necessity to stabilize the substrate temperature before scanning the $V_s(T)$ vs ΔT curves. Therefore, a second apparatus was developed which is shown in Fig. 2.

It was hoped that by making the temperature measurements at the points where the thermal voltage contacts were located, by providing an overall thermal shield and heater assembly, and by providing a smaller sample temperature gradient in the vicinity of the contacts several benefits would accrue:

- (1) because ΔT would be zero when $V_s(T)$ was zero it would be possible to vary the sample temperature continuously and make single point measurement of thermopower with reasonable accuracy;
- (2) elimination of strong thermal gradients would permit more accurate measurement of $\sigma(T)$ and $S(T)$;
- (3) the improved heater to thermal press contact would result in more rapid response to changes in input power, with consequent better thermal response time;
- (4) the addition of a cooling loop would facilitate more rapid sample cooling.

A calculation of the steady state temperature distribution across the sample, at several distances above the aluminum sample holder is shown in Figure 3. It is evident that at a distance of 3 mm or more from the centerline between the hot and cold sides of the sample holder the gradient of temperature is negligible. Measurement of thermopower using contact points separated from the temperature measurement point confirmed the low gradient and gave us increased confidence in the accuracy of thermopower and conductivity results. (See points marked "■" in Fig. 4) The improved thermal characteristics of the apparatus have also been confirmed.

By passing LN_2 through the cooling loop the sample can be cooled to 25°C from 200°C in about one hour instead of the previous 6 to 10 hrs. After improving the initially poor contact between the glass insulated heating tape heater and the copper shield by impregnating the heating tape with an alumina/silicone grease thermally conductive compound, the time for the sample temperature to stabilize to within $1/4^\circ\text{C}$ is less than 6 min from the time at which the temperature controller comes into the proportional range. It takes about 1 hour to heat the sample from 25°C to 200°C and obtain a stable temperature.

Unfortunately, point (1) is still not achieved. The ΔT offset at $V_s(T) = 0$ has been reduced from as much as 5°C at 200°C to about $3/4^\circ\text{C}$, but this still would produce a 10% error at a ΔT of 7.5°C . The reasons for the offset are still under study, and we hope to reduce it further, but at the present is still appears necessary to scan ΔT after stabilizing the sample temperature.

The thermopower results obtained on sample 79063 with the previous apparatus and the present apparatus are compared in Fig. 4, which also indicates the precision that is attainable. The sample conductivity changed somewhat between the measurements so it is not possible to exclude a change in thermopower also, but it appears that the accuracy of the previous arrangement for thermopower measurements was comparable to that of the present arrangement.

Theory of thermopower and conductivity analysis

There have been a number of articles during the past ten years which examine the significance of thermoelectric power measurement in amorphous semiconductors. The most notable are given as Ref. 1-5. A careful reading of Friedman, Dohler and Persans shows that while considerable information about Fermi level shifts and density of states variation with energy in the band gaps of a-Si can be obtained if various assumptions about the temperature dependence of mobility are made, there is no strong justification for such assumptions. Indeed, Friedman has made use of the best measurements that exist for the temperature and energy dependence of the mobility and for the density of states in the band gap, and is thereby able to obtain good agreement with measured thermopower values in the same samples. In contrast, Dohler and Persans have made specific (but contradictory) assumptions about the temperature dependence of mobility in order to deduce information about the density of states which in Friedman's analysis was provided by other experiments.

It therefore appears to me to be preferable to make use of the basic integral equations for $\sigma(T)$ and $S(T)$ presented by Fritzche [1], which are

$$\sigma(T) = e \int_{-\infty}^{\infty} N(E) \mu(E,T) f(E) (1-f(E)) dE \quad (1)$$

and

$$\Pi(T) = \int_{-\infty}^{\infty} \sigma(E,T) (E-E_F) dE / \int_{-\infty}^{\infty} \sigma(E,T) dE \quad (2)$$

The simple interpretation of (2) is that $\Pi(T)$ measures the average energy carried by charge carriers in the material.

If the mobility is activated with a single activation energy E_μ , $f(E)$ may be approximated by $\exp(-\frac{E-E_F}{kT})$, and $N(E)$ is constant above E_c and zero below it, and if E_F is constant, it follows that:

$$\sigma(T) = ekT N\mu_0 \exp(-E_\mu/kT) \exp(-(E_c-E_F)/kT) \quad (3)$$

and

$$\Pi(T) = eST = -(E_c-E_F + kT) \quad (4)$$

Hence,

$$S = -\left(\frac{E_c-E_F}{eT} + \frac{k}{e} \right) \quad (5)$$

Even if the Fermi level shifts with temperature the form (5) is maintained, but with an additional constant term (4). Thus, the slope of $S(T)$ vs T gives the E_c-E_F value, while the slope of $\ln \sigma$ gives the sum of mobility activation energy and E_c-E_F , for this simple model.

The form of (2) and (3) is such that in the general case it is not possible to go from $\sigma(T)$ and $\Pi(T)$ back to $N(E)$, $\mu(E,T)$ and $E_T(T)$. Indeed, it is obvious that there is less information in $\sigma(T)$ and $\Pi(T)$ than in the various factors that determine them. But even in this general case $\Pi(T)$ gives the average energy carried by the charge carrier in the material and so has a significant value

in an investigation of the properties of doped a-Si films. The conductivity activation energy will not necessarily be a simple sum of terms giving E_{μ} , $E_c - E_{F0}$ and the variation of E_F with temperature. But this provides a useful starting point for further analysis.

Analysis of our data has been done so far using the simple activated mobility expression (5) with the additions discussed by Beyer, et al (3). Additional analysis using the temperature dependence of the Peltier coefficient will be presented for these and other samples in the next report.

Results and preliminary analysis

Conductivity and thermopower curves for a series of boron doped p-type samples are shown in Fig. 5. Table I provides the preparation conditions for this series of samples and the least squares curve fits to the conductivity and thermopower. The samples are successfully doped p-type, with an energy $E_V - E_F$ which decreases from about 1eV to 0.29 eV as the doping level increases. The conductivity activation energy does not decrease as much as $E_V - E_F$ from the thermopower results, which suggests that the boron dopant is introducing additional traps or some other impediment to the carrier transport. This is evident also in the 300K conductivity, which changes by 100X on increasing the doping from 1000 to 2000 ppm, but by only 10X upon a further increase to 4000 ppm.

An undoped (n-type) sample and a number of arsenic-doped samples made with the same deposition conditions are compared in Fig. 6, and in Table II. The undoped material, although n-type, has the constant activation energy and variation of $S(T)$ with temperature that was characteristic of the boron doped samples. The activation energy of conductivity of 0.73 eV and the slope of the $S(T)$ curve indicate that the Fermi level is about 0.65 eV below the conduction band mobility edge. This value is in close agreement with the 0.62 - 0.64 eV reported by Jones, et al [7] for the least doped of their phosphorous doped samples. Upon increasing the As level (as volume parts AsH_3) to 100 ppm, the conductivity at 300K increases by 10^4 , and the thermopower temperature dependence and magnitude both decrease considerably. At the same time, a well defined change in the slope of $S(T)$ appears at 400K, and a change

in slope of $\sigma(T)$ also appears at this temperature. This abrupt change in slope contrasts with the more gradual changes reported in previous work [4,6] and with other samples of ours, for example see Fig. 4. If changes in slope are due only to a change in Fermi level with temperature, the difference $\ln \sigma - eS/k$ should have a single slope and intercept at all temperatures [4]. In fact Table II shows that this is not the case for these samples, and so the cause of the slope change must be elsewhere. Although the lower temperature slope of $S(T)$ suggests that $E_c - E_F$ is about 0.15 eV, the large constant term in $S(T)$, the magnitude of the Peltier energy at 300K 0.38 eV for the doped samples, and the activation energy of the conductivity all indicate that the average energy of the conduction electrons is more like 0.3 to 0.4 eV.

This series of samples shows no significant variation in properties over the dopant range of 100 to 500 ppm, a result similar to that reported by Jones, et al [7]. This indicates a low density of states for the first 0.3 to 0.4 eV above the Fermi level of the undoped material, and a rapidly rising density of states closer to the conduction band edge. We plan a series of samples at lower dopant levels to determine the amount of dopant required to shift the Fermi level into the region of high density of states, and thereby permit an estimate of the density of states in the band gap of our material.

We have measured one AsH_3 doped sample (75 ppm AsH_3) prepared by the decomposition of SiF_4 rather than SiH_4 . Although the results remain to be duplicated on other similarly prepared samples, they seem to be of sufficient

interest to describe in some detail. Figure 7 shows the conductivity and thermopower, and Fig. 8 the Peltier energy for this sample. The conductivity is much higher than in any SiH_4 prepared samples and the activation energy is an order of magnitude lower, being only 0.03 eV. There was only a small change during storage of this sample between May and September. The thermopower is also about an order of magnitude less than in SiH_4 samples, and in contrast to those samples is negative, but with a positive slope of 0.047 V. Within the context of the simple analysis of Eq. 1-5, the negative thermopower implies an n-type sample but the positive slope implies E_c is less than E_F , or in other words, that the material is degenerate. However, the simple analysis presented is not valid in detail for kT so close to $E_c - E_F$, and a more complete analysis must be made.

The Peltier energy and the slope of $\sigma(T)$ are shown in Fig. 8 for this sample. The average energy of a charge carrier is only 0.05 to 0.08 eV near room temperature. This indicates that the 75 ppm dopant level has been much more effective in shifting the Fermi energy to the conduction band than are similar dopant levels of AsH_3 in SiH_4 films. Clearly measurements need to be made on samples prepared without any dopant, and with much reduced levels. The small slope of $\sigma(T)$ and small $\Pi(T)$ show that the high conductivity of this sample is not due to an increase in mobility alone, although such an increase cannot be excluded, but primarily to a phenomenal decrease in the density of states close to the band edge, with perhaps also an increase in the actual fraction of the incorporated As atoms that act as donors in the materials.

Summary

To briefly summarize: A properly operating apparatus for the measurement of thermopower and conductivity as a function of temperature in a vacuum of about 10^{-6} torr or better has been built, tested on a variety of samples, and used to measure many different series. We have determined that our preparation conditions are adequate to prepare n and p type samples with properties similar but not identical to those described by others.

We have prepared and measured a film prepared by the decomposition of SiF_4 which shows evidence of degeneracy, as well as other properties significantly different from SiH_4 films. The degeneracy may be desirable for the preparation of good contacts. The apparent low density of states in the gap, if confirmed in further experiments, indicates the possibility of obtaining larger open circuit voltages by shifting E_F closer to the band edges.

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Table I: Properties of boron doped cathodic samples prepared with a substrate temperature of 350°C, a total reactor power of 20W, and a total pressure of 0.25 torr composed of 10% SiH₄ in He plus 1% B₂H₆ in H₂ to give the specified dopant level in VPPM.

Sample	doping	$\ln \sigma$	es/k	$\sigma(300) (\Omega\text{cm})^{-1}$
105	600 ppm	$-\frac{0.807}{kT} + 9.00$	$+\frac{1.234}{kT} + 14.5$	2.6×10^{-10}
106	1000 ppm	$-\frac{0.730}{kT} + 8.47$	$+\frac{0.710}{kT} + 1.87$	2.6×10^{-9}
107	2000 ppm	$-\frac{0.555}{kT} + 6.39$	$+\frac{0.507}{kT} + 1.52$	2.8×10^{-7}
109	4000 ppm	$-\frac{0.530}{kT} + 7.66$	$+\frac{0.290}{kT} + 4.87$	2.6×10^{-6}

Table II: Properties of arsenic doped cathodic samples prepared with a substrate temperature of 350°C, a total reactor power of 10W, and a total pressure of 1 torr composed of SiH₄ ($\approx 5/22$ torr), 1000 ppm AsH₃ in H₂ to give the specified dopant level in VPPM, and H₂ to make up the balance.

Sample	dopant	$\ln \sigma$	eS/k	$\ln \sigma - eS/k$	$\sigma(300)$
118	none	$-\frac{0.731}{kT} + 10.07$	$-\frac{0.638}{kT} - 0.94$	$-\frac{0.093}{kT} + 11.01$	1.2×10^{-8}
120 T>125°C	100 ppm	$-\frac{0.409}{kT} + 6.81$	$-\frac{0.440}{kT} - .38$	$+\frac{0.031}{kT} + 7.19$	
120 T<125°C	100 ppm	$-\frac{0.337}{kT} + 4.67$	$-\frac{0.144}{kT} - 8.82$	$-\frac{0.193}{kT} + 13.49$	2.33×10^{-4}
125 T>125°C	200 ppm	$-\frac{0.405}{kT} + 6.27$	$-\frac{0.380}{kT} - 1.74$	$-\frac{0.025}{kT} + 8.01$	
125 T<125°C	200 ppm	$-\frac{0.295}{kT} + 3.03$	$-\frac{0.118}{kT} - 9.49$	$-\frac{0.177}{kT} + 12.52$	2.3×10^{-4}
119 T>125°C	500 ppm	$-\frac{0.433}{kT} + 8.47$	$-\frac{0.400}{kT} - .95$	$-\frac{0.033}{kT} + 9.42$	
119 T<125°C	500 ppm	$-\frac{0.296}{kT} + 4.52$	$-\frac{0.110}{kT} - 9.41$	$-\frac{0.186}{kT} + 13.93$	9.3×10^{-4}

(Sample is 2.54 cm square)

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(Sample is 2.54 cm square)

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Fig 4

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Fig 6

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