DETERMINATION OF PSEUDOGAP STATE DENSITY AND CARRIER MOBILITY
IN r.f. SPUTTERED AMORPHOUS SILICON

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
OCTOBER 1, 1979 - DECEMBER 31, 1979

William Paul, Principal Investigator
David A. Anderson, Staff Scientist

January 1980

Work Performed under Contract DE-AC03-79ET23037

HARVARD UNIVERSITY
DIVISION OF APPLIED SCIENCES
CAMBRIDGE, MASSACHUSETTS 02138

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

DETERMINATION OF PSEUDOGAP STATE DENSITY AND CARRIER MOBILITY
IN r.f. SPUTTERED AMORPHOUS SILICON

QUARTERLY TECHNICAL PROGRESS REPORT
FOR PERIOD OCTOBER 1, 1979 - DECEMBER 31, 1979

WILLIAM PAUL
Principal Investigator

DAVID A. ANDERSON
Staff Scientist

JANUARY 1980

HARVARD UNIVERSITY
DIVISION OF APPLIED SCIENCES
CAMBRIDGE, MASSACHUSETTS 02138

PREPARED FOR THE
U.S. DEPARTMENT OF ENERGY
SOLAR ENERGY
UNDER CONTRACT DE-AC03-79ET23037

ABSTRACT

Analysis by Secondary Ion Mass spectrometry has shown levels of about 1000 ppm of O and other chemical species in our a-Si:H, which is about the same as is found in samples from other laboratories where such measurements have been carried out. There is also an increase in the level of contaminant near the substrate-film interface which is judged to be the likely cause of our hitherto low field effect response. Our methods of preparation are being changed in an attempt to eliminate the contaminant. We have also measured the field effect near the top surface of our samples, using a teflon insulator. Analysis of these data, following the procedures adopted by others as reported in the literature, indicates densities of states in the pseudogap as low as several times 10^{16} cm^{-3} . Such densities are comparable with the best that have been published. However, we feel that both the field effect experiment and its analysis (ours and others) are flawed by experimental errors and necessary assumptions. Efforts are being made to reduce these.

DESCRIPTION OF PROJECT

The purpose of this project is (a) to investigate the density of states in the gap of a-Si:H as a function of the rf sputtering deposition parameters by means of field effect experiments and (b) to study the drift mobility of excess carriers in the bands of the material by a time of flight technique.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
ABSTRACT	i
DESCRIPTION OF PROJECT	ii
INTRODUCTION	1
EXPERIMENTAL	1
(1) SIMS Analysis of Impurity Concentrations	1
(2) Tests of Experimental Procedure	5
(3) Use of Teflon as an Insulator	5
SUMMARY OF CONCLUSIONS AND FUTURE PLANS	15
DISTRIBUTION LIST	16

LIST OF FIGURES AND TABLES

Figure 1. SIMS depth profiles	4
Figure 2. Source-drain currents <u>vs</u> time for several gate voltages	7
Figure 3. Source-drain currents <u>vs</u> gate voltage, using Teflon sheet method	9
Figure 4. Source-drain currents <u>vs</u> gate voltage at several sample temperatures	11
Figure 5. Density of states from measurements of Figure 4	12
Figure 6. Effect of choice of flat band voltage on derived densities of states	14
Table I Contaminant levels of O, N, C, Cl and F	3

INTRODUCTION

This quarterly report continues an account of our investigation of the density of states in the pseudogap of a-Si:H alloys through measurement of the field effect. The background to this investigation and the argument for field effect measurements were given in our first quarterly report.

EXPERIMENTAL

SIMS Analysis of Impurity Concentrations

Both the fact that a-Si:H can be substitutionally doped with As, P and B, and analysis of field effect data in the literature, suggest that the state density in the center of the pseudogap is sufficiently low that trace amounts of accidentally incorporated impurity, say 10 ppm, could control the electronic properties. Guided by our early work on the considerable effect on properties of deliberate oxygen additions to a level of about 1%, we have continued to investigate the possible role played by oxygen unintentionally introduced during film deposition. That oxygen is present is clear from IR vibrational spectra for thick films, but its source until recently remained unidentified. We take particular measures in our deposition process to try to eliminate oxygen: our base vacuum before back filling with 99.999% pure argon is better than 5×10^{-7} Torr; we routinely take an RGA trace of the gases present in our base vacuum; and we have recently added purifiers to both argon and hydrogen gas input lines to eliminate oxygen brought in with the sputtering gases - yet oxygen is still present in the films at an estimated level of about 0.1%.

The residual gas analysis shows that by far the major constituent in our base vacuum is water vapor, which appears to be pumped relatively slowly by our turbomolecular pumping system. We have found that we can reduce the water vapor in our base vacuum appreciably, if we take such measures as: reducing the time the system is open to atmosphere between runs, leaking nitrogen rather than air into the vacuum chamber to bring it up to atmospheric pressure, and cleaning the stainless steel shields only when necessary rather than after every run. The adoption of these changes in our procedure has led to an improved base vacuum of $< 3 \times 10^{-7}$ Torr, which is achieved in

a much shorter pumping time. There appears to be a resultant reduction in the oxygen content of our films, inasmuch as we are unable to detect IR vibrational absorption near 1100 cm^{-1} in films approximately 5 microns thick.

To examine this more quantitatively, we have had a number of samples analyzed by Charles Evans Associates using SIMS. They employ a Cs^+ ion source for sensitivity to elements such as oxygen, nitrogen, carbon, fluorine and chlorine in the 10^{17} cm^{-3} range. Table I lists the approximate concentrations of these impurities for two representative rf sputtered a-Si:H samples: the first having a clearly observable Si-O vibration in IR, the second having none. The results, while confirming our conclusions about oxygen from IR work, also show a disturbingly high concentration of all of the above elements even in films we had regarded as relatively pure. At present it is impossible to compare these data with samples made by other techniques in other laboratories, since to our knowledge, there is no published account of the level of these impurities. However, in view of the care we take to reduce the base vacuum and to cleanse our system of all impurities, it is not unlikely that similar or higher impurity concentrations could be found in most of the material being studied.

Another significant finding of more immediate concern to the field effect measurements is shown in Figure 1. Here we show a depth profile, taken all the way through to the sample-substrate interface, of the elements listed in Table I with the addition of hydrogen and silicon. The substrate was a c-Si wafer. On the sample side of the interface the traces all rise appreciably toward the interface from a fairly constant level in the bulk of the film, suggesting some source of contaminant in the system which is present in high concentration when sputtering begins and then decays slowly over about an hour of sputtering to a well-defined asymptote. Similar profiles were seen in all the samples studied, although the interfacial impurity content did vary from sample to sample. It seems very likely that an increased gap density of states, caused by the high impurity density, is the source of the poor field effect response and the inconsistency of response from sample to sample. The geometry which uses the quartz substrate as insulator probes the region of the sample closest to the sample-substrate interface, which it now appears is not representative of the bulk of the sample.

TABLE I

Impurity	Sample Showing Evidence of Si-O in IR	Sample Showing No Evidence of Si-O in IR
O	$4.1 \times 10^{20} \text{ cm}^{-3}$	$1.0 \times 10^{20} \text{ cm}^{-3}$
N	$4.2 \times 10^{19} \text{ cm}^{-3}$	$5.0 \times 10^{19} \text{ cm}^{-3}$
C	$1.9 \times 10^{19} \text{ cm}^{-3}$	$3.4 \times 10^{19} \text{ cm}^{-3}$
Cl	$8 \times 10^{16} \text{ cm}^{-3}$	$1.3 \times 10^{17} \text{ cm}^{-3}$
F	$5 \times 10^{16} \text{ cm}^{-3}$	$5 \times 10^{16} \text{ cm}^{-3}$

The absolute value of these numbers is expected to be correct to within about a factor 2 but the comparison between the samples can be made with much higher precision.

Figure 1. Cs^+ ion SIMS depth profiles of the elements Si, H, O, C, N, Cl and F in a typical r.f. sputtered a-Si:H sample. The ordinate is in arbitrary units and the magnitude of each trace has to be corrected for the sensitivity of the system to each ion.

Removal of this interfacial layer of contamination has therefore been made an item of high priority. We are currently exploring various methods of doing this, which will be discussed in our next report.

Tests of Experimental Procedure

Last quarter we reported inconsistent measurements of our field effect response, whose overall magnitude was much lower than that reported by others. There appeared to be three elements in our measurement technique which might cause trouble: the substrate material and its preparation, the external measurement circuitry, and the sample material.

To examine the first of these, we have tried using different types of quartz, both synthetic and nonsynthetic, and subjecting the surface to various treatments, including acid etching immediately before deposition, cleaning with organic solvents and cleaning with detergent and hot water with only one final alcohol rinse. None of these treatments improved the field effect response. As a further test of the substrate material and also of the measurement circuitry, we have had several samples deposited onto our quartz substrates by the group at Mobil Tyco using the glow discharge dissociation of silane. The deposition conditions were chosen to give only one IR stretch vibration at 2000 cm^{-1} , since it has been claimed that this material has the lowest density of gap states. These samples showed a much larger field effect response than we had seen in sputtered Si but not as large as that quoted in the literature for other glow discharge samples. Nevertheless, this result does focus attention on the sputtered material itself as the origin of the small field effect.

Since other material properties of our samples are strikingly similar to those reported for a-Si:H made from SiH_4 , it is unlikely that the field effect data are representative of the bulk state density. Instead, it appears that the narrow interfacial region between substrate and sample, which is where all the field effect transport occurs, is a region of higher state density than the rest of the sample.

Use of Teflon as an Insulator

In parallel with our efforts to settle the question of contaminants at the sample-substrate interface, and the role they play in the field

effect measurements, we have been experimenting with a new system which uses the region of the sample close to the sample-air interface. Ultimately, this could be a useful method of distinguishing between bulk and surface states, since it is unlikely that identical surface or interface states would be found at the front and the back of the sample.

The technique and apparatus used are identical to those described in the last report for the measurements on quartz substrates. Now, however, instead of using the substrate as insulator, we place a 130 μm thick Teflon sheet between the high voltage terminal and the top surface of the sample. Because the Teflon has a dielectric constant approximately half that of the quartz, and the thickness is approximately the same, the charge induced in the sample surface for a given gate voltage is reduced by a factor of two. This technique has the great advantage that it can be applied to samples on any insulating substrate and specifically to earlier sample depositions upon which much of our interpretation of the role of hydrogen on the electronic and optical properties of our material has been based.

There are, however, some difficulties in the application of the technique which we will illustrate below using a series of measurements made on one sample, chosen because photoconductivity and photoluminescence data suggested that it had a relatively clean gap.

In Figure 2 we show a section of the plot of source-drain current (I_{S-D}) as a function of time through a series of increments and decrements of the gate voltage V_g . Following an increase in V_g , I_{S-D} increases instantaneously and then decays, first very rapidly and then much more slowly. After several minutes it appears to approach a steady-state value. Similarly, as V_g is decremented, I_{S-D} drops very suddenly and then increases, again approaching a steady value after several minutes. We associate the rapid part of the return to the steady state as a capacitive response to the increase or decrease in gate voltage, but the origin of the slower part is unknown. For our purpose, the presence of this time dependence, which can become appreciable, particularly at high gate voltage, makes it very difficult to establish the true I_{S-D} for a particular V_g . Should we, for example, regard this time dependence as a slow response inside the sample and therefore wait until equilibrium is established, or is the instantaneous value of

Figure 2. Output of Keithley electrometer showing the time dependence of I_{S-D} through a series of increases and decreases of the gate voltage V_g , showing the slow approach to an equilibrium value several minutes after the application of each new gate voltage.

I_{S-D} immediately following a change in V_g the more correct? If we choose the former, how do we reconcile the differences in the asymptotes for V_g increasing and V_g decreasing? The answers to these questions must await a more detailed study than we have yet performed, but this subject has not been addressed in any of the published work on field effect in a-Si:H (although privately other workers admit to seeing similar effects) and could have considerable bearing on the validity of the derived density of states. In the following we will assume that the asymptotic values give the magnitude of the genuine effect and will show, only where significant, the difference between data obtained with increasing and decreasing V_g .

Many of the high hydrogen content samples have shown a decrease in the magnitude of the dark conductivity after the sample has been heated in vacuum for the first time beyond 150°C. The decrease has never been more than an order of magnitude, and subsequent heating and cooling in vacuum results in no further change. Re-exposure to air returns the conductivity to its original value. These changes, although smaller in magnitude, are similar to the data of Tanielian et al., who deliberately expose a glow discharge a-Si:H sample surface to a controlled atmosphere of water vapor. Since our new field effect configuration also probes the top surface region of the sample, we might expect to see the effect of water vapor in these measurements, too.

In Figure 3 we illustrate this by showing a number of field effect, I_{S-D} vs V_g , characteristics all obtained at room temperature but after different thermal treatments. Curve (a) shows the data obtained when the sample, after sitting in a box for several months, was mounted on the holder and the system evacuated to $\sim 10^{-5}$ Torr. The increase in I_{S-D} is extremely modest and would suggest a rather high state density. Curve (b) shows a repeat of the measurements after the sample had been heated to 180°C for one hour in vacuum, then cooled and remeasured immediately. Now the field effect response is considerably larger and also, significantly, the dark conductivity has decreased. Curve (c) was taken after the sample had been sitting for several days in a 10^{-5} Torr vacuum at room temperature and shows a considerable reduction in the field effect response. We have repeated this cycle by re-exposing the sample to air and found that the time scale

Figure 3. Room temperature data of I_{S-D} vs V_g obtained using a Teflon sheet as insulator. The three curves were obtained after different heat treatments: (a) measured immediately, (b) after heating to 180°C , cooling to room temperature and measured within a few hours, (c) as (b) but measured after several days at room temperature in a vacuum of 10^{-5} Torr.

for the decrease in the field effect response after heat treatment can be measured in days rather than hours. We therefore believe that, provided all the water vapor on the sample surface has been removed by the 180°C heat treatment, curve (b) represents the true field effect response in this sample.

The presence of residual water vapor on the surface could have two effects on the data, depending upon the nature and the location in energy of the surface states it creates. If these states lie in the region of the Fermi level, then the derived state density will include them and therefore be regarded only as an upper limit to the state density in the bulk. If, on the other hand, the states are filled and lie well below the bulk Fermi level, they could lead to band bending at the interface in the absence of an applied gate voltage, and a sizeable flat band voltage, V_{FB} . The effect of V_{FB} on the derived density of states will be discussed below.

Measurements of the field effect were made at temperatures between 25°C and 110°C. Some of these curves are shown in Figure 4, the measurements being made as the sample was heated. As expected, the magnitude of the response decreases as the measurement temperature increases because of the Boltzmann factor which dominates the expression for I_{S-D} . The density of states derived from the data of Figure 4 is shown in Figure 5, where we see that despite the difference in the magnitude of the field effect response, the data give an almost identical state density on the positive side of the Fermi level (the conduction band side). On the other side, a depletion mode calculation is used to analyze data taken using negative gate voltage. The errors in this calculation are generally greater, since the source-drain current is usually small; changes in it are also small, and it takes longer to ascertain that an asymptote has been reached after V_g has been changed. Given the time-dependent effects seen earlier in the room temperature data and the unlikelihood that the gap density of states changes its shape with temperature, it appears probable that the apparent spreads in the state distributions at different temperatures are not real.

The points on these curves are not data points, but are used as markers to distinguish between the three sets of data. The energy range over which each curve is plotted as a solid line shows the excursion of the Fermi level

Figure 4. I_{S-D} vs V_g measured at different temperatures for the same sample using the Teflon insulator technique.

Figure 5: Density of states distribution obtained from the data of Figure 4. The symbols are not data points; they are used only to identify the curves.

at the surface during the measurements. The dashed portions are extrapolations of the state density generated by the analysis.

These curves have been obtained from the raw data by applying a new method of analysis which is based on the principles of the method used by Goodman and Fritzsche but which has been simplified so that the calculation can be handled by a mini-computer without any loss of rigor. Since this method is still being developed and evaluated, we will postpone a full discussion of it until the next report. The data are presented here only to demonstrate that we can obtain density of states information from field effect measurements using a Teflon insulator.

Although the state density at the Fermi level is higher than that claimed by other workers, the Fermi level is sitting in a rising density of states; and if we assume a flat band voltage of zero (as we have in Figure 5), the minimum state density appears to be about $3 \times 10^{16} \text{ cm}^{-3} \text{ eV}^{-1}$ at a depth of 0.4 eV below the bulk Fermi level. The conductivity activation energy for this sample was measured to be 0.80 eV, which would place the minimum in the state density at between 1.0 and 1.2 eV below the conduction band. Since other measurements on similarly prepared samples suggest exactly the opposite, that there is a maximum in the state density at that energy, we must approach this result with care. However, it is readily apparent that, by varying the assumed V_{FB} , we can reconcile the derived state density with the results of other measurements. Thus, choice of a more positive V_{FB} shifts the minimum in the density of states distribution to lower energy, while, conversely, a more negative V_{FB} shifts the minimum to higher energy. The latter is shown in Figure 6, in which we compare the results of the analysis of the room temperature data of Figure 4 assuming $V_{FB} = -1 \text{ KV}$ and $V_{FB} = 0 \text{ KV}$.

It is probably premature to say too much about where and how deep this minimum is because of the uncertainties in the depletion mode analysis we discussed above. We simply point out that, if we use the same general criteria as others in choosing a flat band voltage, we obtain a minimum state density of between 10^{16} and $10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$, which is comparable with the best values quoted for any a-Si:H based material.

Figure 6. Effect of the choice of V_{FB} on the state distribution derived from the room temperature data of Figure 4.

It should be evident from the above discussion that great care must be exercised in quoting numbers for the density of states derived from field effect data, since these numbers can depend very sensitively upon the parameters used in the analysis. We hope that, by accumulating data using the Teflon technique on a large number of samples which have been thoroughly characterized in other ways, we can correlate the field effect with the other electronic properties and arrive at a self-consistent picture of the state distribution in the gap. We should also be able to correlate variations in the state density with the preparation parameters.

SUMMARY OF CONCLUSIONS AND FUTURE PLANS

From the work done this quarter we believe that the main problem in obtaining consistent field effect results in samples deposited on a quartz insulator is that there is a layer of contaminant at the sample-substrate interface and that states associated with these contaminants are effective in screening the bulk semiconductor from the applied gate field. We are now attempting to eliminate this contaminated layer by giving the deposition system a more effective discharge clean in a nitrogen atmosphere prior to sample deposition. To establish the effectiveness of the treatment requires further expensive and time-consuming SIMS analysis of our films, which we regard as necessary before we resume field effect measurements on material on quartz substrates.

In the meantime, we have demonstrated that useful data can be obtained using a Teflon sheet as insulator. Since this technique requires no new samples to be made and is not affected by contaminant at the substrate, we shall use it to investigate a variety of existing samples. Provided that due care is taken to reduce the influence of adsorbed surface water on the data, we expect to obtain thereby a more detailed survey of the bulk state densities in a variety of films than we have had up to now.