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

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
JULY 1, 1979 - SEPTEMBER 30, 1979

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

October 1979

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HARVARD UNIVERSITY
DIVISION OF APPLIED SCIENCES
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ABSTRACT

Apparatus has been designed and assembled to perform field effect measurements using two different sample configurations. Preliminary measurements indicate that the field effect response is smaller than expected in view of the results quoted by other workers on silane-derived a-Si:H and the overall similarity in other opto-electronic properties. Some inconsistency has been observed between nominally identical samples, which may be related either to uncontrolled variables of our deposition process or to some unknown impurities present. Computer programs have been developed to analyze the raw data and derive a density of states versus energy. Using the data obtained so far, we have studied the effect of the assumed potential distribution inside the semiconductor and of the choice of the flat band voltage V_{FB} on the derived density of states.

The equipment for the measurement of the time of flight drift mobility has been ordered but has not yet arrived. The design and execution of the experiment will, therefore, be discussed in detail in the next quarterly report.

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.

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INTRODUCTION

There is now a growing body of evidence which suggests that the fundamental properties of a-Si:H prepared by glow discharge in silane or by reactive sputtering in a hydrogen atmosphere are identical. The mechanisms of radiative and non-radiative recombination, the nature of carrier transport in localized gap states and in the bands, the optical properties and the infrared vibrational spectra show very great similarity. Differences do remain, however, and many of them can be traced to the detailed distribution and nature of the states in the gap (GDOS), which is determined by a number of factors, including the physical nature of the structural defects, the hydrogen content and the hydrogen bonding configuration.

Qualitative information about the GDOS can be obtained from studies of the behavior of the electronic and optical properties of the material as a function of the deposition parameters,⁽¹⁻⁶⁾ but there is an obvious and long-standing need for a more direct and quantitative measurement. Several techniques have been tried, including (a) analysis of low temperature dc hopping conductivity, (b) analysis of ac hopping conductivity, (c) tunneling through an oxide layer into the semiconductor, (d) capacitance voltage measurements on Schottky diode structures and (e) field effect. Of these, an interpretation of the first three in terms of a density of states requires a theoretical understanding of the underlying physical phenomenon which we do not have at present, while (d) is limited by being an ac technique and therefore may sample only the small fraction of the total state density which responds to the measuring frequency. The field effect, too, is not entirely satisfactory, but the problems do not lie in our understanding of the physics but rather in the interpretation of the result in terms of bulk states or surface states.

It is our intention, therefore, to develop the experimental capability to perform field effect measurements on rf sputtered a-Si:H. This material has been very well characterized using a large number of other measurements and therefore serves as a useful vehicle to test the validity of the field effect data and to demonstrate in a systematic way precisely what effect hydrogen has on the state density. In this, the first quarterly report, we discuss the design of the experiment and present some very preliminary data.

EXPERIMENTAL

The field effect measurements are made using two geometries, each of which has its advantages and disadvantages. In principle, the experiment consists of applying a field across an insulating material in contact with the sample, thereby inducing charge in the sample surface and monitoring the effect of this excess charge on the sheet conductance between two electrodes on the sample. Experimentally, one of the major difficulties is the choice of insulating material, and that choice then determines the measurement geometry. The insulator has to withstand fields of up to 10^6 V/cm while passing leakage currents of less than about 10^{-12} amps; it has to be in intimate contact with the sample and it must contain no ionic impurities which might drift under the applied field.

We have chosen to try two methods which have proven successful for other workers: (7,8)

(1) using a thin wafer of quartz as substrate for the film and then applying the field across the quartz. With this technique the substrate must be thick enough to withstand handling during the deposition process, which places a lower limit of about 100 μ m on the thickness. This means that some 10 KV is required to achieve fields of 10^6 V/cm.

(2) using a thermally grown oxide on a heavily doped c-Si chip as substrate for the film, with the c-Si serving as the gate contact and the oxide as the insulator. Here the oxide layer is typically 1000 Å thick, and so 10^6 V/cm requires only 10 volts.

These two techniques place different requirements on the sample holder, and so two holders have been built, one for the thicker quartz insulator shown in Figure 1, the other for the thin oxide shown in Figure 2. In the first configuration, the sample rests on top of a brass sphere, through which the high voltage is applied to the back surface of the quartz substrate. The leads to the source-drain contacts are brought in from the top to eliminate any possibility of a discharge which might destroy the electronic equipment used to monitor the source-drain current. A cylindrical heater, which surrounds the sample at a radius of 1 inch, can take the sample up to about 150°C. This is necessary for two reasons: (a) to reduce noise problems associated

Figure 1. Sample holder for thick quartz insulator/substrate configuration.

Figure 2. Sample holder for thin thermal oxide on c-Si configuration.

with measuring the room temperature source-drain current which is $\sim 10^{-12}$ - 10^{-11} amps, and (b) to remove any surface water vapor or to anneal out the metastable changes observed by Staebler and Wronski.⁽⁹⁾ A thermocouple on the substrate surface monitors the sample temperature, and all the measurements are performed in a vacuum of 5×10^{-6} Torr.

In Figure 2 the sample sits on a heated copper block isolated from ground by a Teflon support. The crystalline Si substrate is held in place by a drop of silver paste, and the gate voltage is applied directly to the copper holder.

Figure 3 shows in schematic form the external circuit for making the measurements. The source-drain voltage V_{S-D} is obtained from a resistance controlled and digitally monitored dc power supply with a switch to allow rapid grounding of the source contact as a check for leakage current through the insulator. The source-drain current I_{S-D} is measured using a Keithley 602 electrometer to which a chart recorder is attached to monitor I_{S-D} as a function of time. To supply the gate voltage, we use either a modified Hipotronics high voltage supply for the quartz insulator or a programmable 0-50 V dc supply in the case of the thin oxide insulator. A number of simple protection devices have been included in the circuit to prevent serious damage to power supplies and meters caused by discharging inside the vacuum chamber.

Figure 3. Block schematic of external circuitry.

RESULTS

We have deposited samples using both geometries. To date, the leakage currents through the thin oxide layer have been too high to permit observation of any field effect. However, this may be improved with proper handling techniques which avoid static charge build-up. A field effect has been observed with the thicker insulator/substrate technique, using as substrates quartz and borosilicate glass, both of which withstand the applied field with negligible leakage current. The glass, however, presents a problem in that it contains mobile ions which drift in the applied field and enhance the observed field effect in the sample. This is observed experimentally as a very severe hysteresis in the field effect I_{S-D} vs V_g characteristic. If, for example, V_g is reduced to zero after being held at 7 KV for several hours, the source-drain current will be several orders of magnitude higher than it was before any gate voltage was applied. The sample can then be restored to its original condition by application of large negative V_g and the cycle repeated. In the presence of such hysteresis no meaningful information about the density of states can be derived.

Figure 4 shows curves of I_{S-D} vs V_g for two samples deposited on quartz substrates under nominally identical conditions (substrate temperature = 200°C, hydrogen partial pressure = 2 mTorr, argon partial pressure = 5 mTorr, rf power = 200 Watts). The data have been normalized by plotting the ratio $[I_{S-D}/I_{S-D}(V_g=0)]$, and show that despite the similarity in the deposition parameters, the field effect response of the two samples is very different. The larger the response, i.e. the larger is $[I_{S-D}/I_{S-D}(V_g=0)]$, the lower is the derived state density. Other samples have been prepared under very similar conditions in which virtually no field effect has been observed. We therefore have to be very cautious in proceeding to derive a bulk state density from these data. A completely null result implies a state density in excess of $5 \times 10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$ and, given the electronic properties of our material, particularly the high photoconductivity and the photoluminescence intensity, it is very hard to believe that this represents a true bulk state density in these films.

We also note that while the data for sample 102 were perfectly reproducible with little or no hysteresis, this was not true of sample 116. The

Figure 4. Normalized field effect characteristics for two identically prepared samples.

dashed line and open square on this curve represent I_{S-D} when V_g was reduced from 7 KV to 0. I_{S-D} did not return to its original value. This effect is similar to that observed earlier with the glass, although much smaller in magnitude, and may imply the existence of some mobile ions in our quartz substrates.

These potential problems are now being studied in detail. On the one hand we are looking into the purity of our quartz substrates and looking for alternative suppliers. On the other we are changing procedures to try to eliminate interface states which might exist between the substrate and the sample. Such states, if present in sufficient density, might completely screen the bulk of the sample from the applied gate voltage.

There are also questions which have to be asked about the consistency and reproducibility of our material. The electronic properties of samples 102 and 116 differ significantly, particularly properties such as photoconductivity and photoluminescence, which are sensitive to the distribution of gap states. This appears to be a universal problem with all workers preparing a-Si:H and may be related to deposition parameters which are at present unidentified and outside our control. In our case, we suspect that oxygen contamination, which we know is present in some films, might be very important in altering the localized state density in the gap.⁽³⁾ An impurity concentration of only 100 ppm is equivalent to an atom density of $\sim 10^{18} \text{ cm}^{-3}$, and this could have a profound influence on the state density, which is of approximately the same order of magnitude, while not being detectable at all in measurements of the infrared absorption. We therefore propose to arrange to have our films examined by ion microprobe.

ANALYSIS OF DATA

Although we have serious reservations about the validity of the data in Figure 4, it is nevertheless instructive to follow through with the analysis to get a feeling for the kind of information we can obtain from it and to try out our computer analysis technique. We will therefore ignore the problems discussed in the previous section and assume that the data are genuinely representative of the bulk state density. The analysis is, at this stage, in a fairly primitive form but could be made considerably more rigorous. We will show that the principal limitation to the accuracy of the magnitude of the derived state density comes not from the technique used to analyze the data but from the choice of a quantity called the flat band voltage which is method independent.

Our analysis is based on the method of Barbe⁽¹⁰⁾ in which the potential distribution inside the semiconductor is assumed to decay exponentially from the interface. We assume zero temperature statistics, choose an arbitrary flat band voltage (V_{FB}), and then analyze all the data for which $V_g > V_{FB}$ in terms of a surface accumulation layer for electrons and the data for which $V_g < V_{FB}$ in terms of a depletion layer. The dark conduction is assumed to be by conduction band electrons only, at the temperature of the measurements, and the motion of holes, even at high negative gate voltage, is ignored. This assumption is confirmed by separate conductivity and thermoelectric power measurements and by the absence of any rise in I_{S-D} at high negative V_g .

Figure 5 shows a plot of the density of states versus energy derived in this way for the two sets of data shown in Figure 4. In each case the Fermi level is at the extreme left of the plot, and we approach the conduction band toward the right. The Fermi levels for the two samples are in different positions in the gap, so we do not intend, at this point, to make any direct comparison between the two curves nor draw any detailed conclusions about the state distribution. Our purpose is rather to give the order of magnitude of $N(E)$ and the energy range ΔE over which the bands can be bent at the surface (the energy range over which $N(E)$ can be determined). These quantities are obviously related, since we can put only a limited amount of charge into the surface region.

Figure 5. Density of states plotted from the Fermi level toward the conduction band using the data of Figure 4 and the analysis of Barbe [10]. The dashed curve shows the resulting density of states if the analysis of Spear and co-workers [7] is applied to the data for sample 102.

In sample 102, $N(E) \sim 1.5 \times 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$ and $\Delta E = 0.23 \text{ eV}$; whereas for sample 116, $N(E) \sim 2.5 \times 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$ and $\Delta E = 0.15 \text{ eV}$. We stress again that these numbers may have little validity in view of the uncertainties concerning interface states.

The dashed lines show the density of states obtained using the raw data for sample 102 analyzed by the method of Spear and co-workers⁽⁷⁾ in which it is assumed that the potential distribution inside the semiconductor is quadratic - the classical Schottky barrier. Otherwise, the analysis proceeds in essentially the same way. We see that the assumption of a Schottky barrier appears to give $N(E)$ about a factor of 3 lower, but the shape is little changed.

The results shown in Figure 5 were obtained using $V_{FB} = 0$ for convenience. We now look at the effect of choosing different V_{FB} in Figure 6 using the data of sample 102. The flat band voltage is the gate voltage which has to be applied such that the bands inside the semiconductor are perfectly flat at the interface. In general, interfacial states will give rise to some band bending in the absence of a gate voltage. In Figure 6 we show $N(E)$ for five different choices of V_{FB} as labelled. $N(E_F)$ obviously varies considerably from one curve to another, and there is no obvious discontinuity at E_F which might suggest that any of these values of V_{FB} is a particularly bad choice. Away from the Fermi level, toward the conduction band, the discrepancy is less severe.

Figure 6. Dependence of the density of states deduced from the data of Figure 4 on the choice of flat band voltage V_{FB} .

CONCLUSIONS AND OUTLINE OF FUTURE WORK

It is clear that, while we have been able to detect a field effect, there are many reasons to believe that the data obtained so far do not reflect the true bulk state density of the material. This problem can be tackled experimentally in a number of ways. In the following we list some of these receiving active consideration.

- (1) We are actively engaged in finding other supplies of quartz substrates with lower impurity content.
- (2) We are varying our substrate cleaning procedures and bombardment treatment before deposition.
- (3) We are investigating the possibility of having a glow discharge sample, made by another group and known to have a low state density, deposited on one of our substrates.
- (4) We will continue to investigate the alternative method of using a thin SiO_2 layer on c-Si.
- (5) We are exploring the possibility of using other insulators.

The other difficulty of the irreproducibility of our material is being pursued as part of our overall investigation into the properties of these alloys. We also have plans to make $C(V)$ measurements to assist in the interpretation of the field effect data.

On the analysis side, we are developing a more rigorous treatment of the problem while keeping in mind that it seems that a major source of error lies in the choice of V_{FB} , about which very little can be done without other measurements.

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