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

MASTER

Final Technical Report for Period July 1, 1979—June 30, 1980

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September 1980

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

FINAL TECHNICAL REPORT
FOR PERIOD JULY 1, 1979 - JUNE 30, 1980

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SEPTEMBER 1980

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Terry Corporation, as a subcontractor to NREC, has also made significant contributions to the program, lending the benefits of its long experience as a steam turbine manufacturer.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
ABSTRACT	1
DESCRIPTION OF PROJECT	1
INTRODUCTION	2
SUMMARY OF RESULTS AND CONCLUSIONS	3
APPENDIX 1 "Interpretation of the Conductance and Capacitance Frequency Dependence of Hydrogenated Amorphous Silicon Schottky Barrier Diodes"	11
APPENDIX 2 "Bulk and Surface States Analysis in a-Si:H by Schottky and MIS Tunnel Diodes Capacitance and Conductance Measurements" . . .	46a
APPENDIX 3 "The Influence of Structural Inhomogeneity on the Conduction Band Transport in a-Si:H Alloys"	105
APPENDIX 4 "An Improved Field Effect Analysis for the Determination of Pseudogap State Density in Amorphous Semiconductors" (abstract) . .	109

LIST OF FIGURES

Figure 1. Preliminary field effect data on a-Si:H deposited directly onto a sputtered layer of SiO_x	5
Figure 2. Schematic of experimental apparatus used for time-of-flight experiments	7
Figure 3. Experimental photocurrent transients for two sputtered films	8
Figure 4. Temperature dependence of the mobility for Si S-144	9

ABSTRACT

This research had two objectives. First, to determine whether field effect could be observed in samples of sputtered hydrogenated amorphous silicon, and, if it could, to compare the pseudogap density of states determined therefrom with estimates made by other methods of investigation. Second, to determine the drift mobility of excess carriers in these materials, and to interpret its magnitude and temperature dependence in terms of current theories of transport in disordered semiconductors. The field effect has been observed, but the conditions required are such as to imply that deductions of the state density from it may not accurately represent the bulk density of states. In the course of this work a simpler method of reducing field effect data has been developed. The drift mobility has also been measured, but these experiments have not yet assembled sufficient statistics for final conclusions to be drawn from them.

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 r.f. 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.

INTRODUCTION

In the first Progress Report we discussed the fact that a-Si:H prepared by glow discharge decomposition of SiH_4 and by sputtering in an Ar- H_2 atmosphere had very similar properties, which suggested closely similar structure, chemistry and electronic band structure. We made a case for measurement of the gap density of states (GDOS) in sputtered material which was otherwise well characterized, and proposed the development of the field effect method to do so.

During the term of this project the following specific tasks have been addressed:

(1) Development of an apparatus to perform field effect measurements.

Several geometries earlier shown to be successful for experiments on glow discharge a-Si:H were tried, such as application of a field across a thin wafer of quartz used as substrate, or across an oxide thermally grown on a heavily doped chip of crystalline Si. These were described in the first Progress Report. Later a technique was developed which used a thin Teflon insulator placed on top of an already-prepared sample. This was described in the second Progress Report. Toward the end of the contract period, experiments were started to deposit an insulating layer of SiO_x on an SiO_2 substrate just prior to deposition of the a-Si:H semiconductor. Despite several difficulties in interpretation of the results of these experiments, it was evident that the techniques developed were, in themselves, successful. Thus, field effect responses were found in glow discharge samples produced both by us and by Mobil Tyco, and also in samples produced and previously measured by Professor Fritzsche's group in Chicago. In the latter case, our results agreed with those of the Chicago group, and this therefore gives us confidence in the validity of our different results for sputtered samples.

(2) Investigation of time-dependent and hysteresis effects in the measured field-effect responses.

These were observed in several of the geometries tried. When some samples of quartz or glass were used as substrates, time-dependent effects were seen which could be attributed to the presence of mobile ions in the insulator. These were discussed in our first Progress Report. When the Teflon insulator technique was used, time-dependent effects were also observed which might have been due, in part, to effects in the Teflon but which could plausibly be attributed to the presence of water vapor on the (top) surface of the sample. A description of these results was included in the second Progress Report.

(3) Investigation of the effects of unwanted contaminant in the sample on the field-effect response.

It is now known that a-Si:H, prepared by either glow-discharge decomposition or by reactive sputtering, contains substantial levels of undesired impurities such as O, C and N. We therefore carried out examinations, by secondary ion mass spectrometry on selected samples, of the profile versus depth of such impurities. These confirmed their presence at levels up to 10^{20} cm^{-3} . Moreover, there was often a significant increase in level near the film-interface boundary, which is the region probed by the field effect. These results were described in the second Progress Report, and the steps taken to reduce the level of impurities were outlined in the third Report. We shall report in

the next Section our conclusions regarding the effect of this impurity density profile on observation of the field effect.

- (4) Investigation of the GDOS by capacitance-frequency measurements on samples produced under identical conditions for field effect studies.

These have not been reported in full detail in earlier Reports, but the conclusions from them will be discussed below.

- (5) Development of improved, simple, techniques for reduction of field effect data to give the GDOS.

These were described in the third Progress Report.

- (6) Development of techniques to determine the drift mobility of excess carriers.

Although equipment was being assembled during the year to carry out these experiments, actual measurements at Harvard were confined to the final quarters. In the meantime, collaborative experiments were carried out with Professor John Brebner of the University of Montreal on our a-Si:H, and experience gained in these was applied to the eventual successful development of our own experimental apparatus and technique.

Subsequent sections of this Final Report will outline the principal conclusions of this study, referring where possible to earlier Progress Reports, published papers or papers submitted for publication. Detailed discussion will be reserved for those aspects of fourth quarter activity not included in the fore-mentioned categories.

SUMMARY OF RESULTS AND CONCLUSIONS

The following conclusions have been drawn from these studies, and our related ones on other properties.

Our measurements on co-deposited samples of conductivity, photoconductivity, photoluminescence and optical absorption have suggested that a-Si:H prepared by reactive sputtering in H_2 should have a GDOS comparable to that in glow-discharge produced material. Extensive measurements using the capacitance-frequency technique by P. Viktorovitch of our group confirmed that the state density near the Fermi level could be as low as $10^{15} \text{ cm}^{-3} \text{ eV}^{-1}$. Our own initial inability to observe a strong field effect response in sputtered material (duplicated by a similar inability of any group elsewhere) could then be most plausibly explained by a high defect density near the film-substrate interface, presumably connected with the sputtering method. Contaminant effects were ruled out, as these were present in glow-discharge films also. Preliminary experiments have suggested that a technique designed to alter the film structure, and therefore the defect density, near the substrate-film interface has been successful. In the following paragraphs we shall elaborate on these summary remarks.

Dr. Viktorovitch's work has been described in two papers: (1) "Interpretation of the conductance and capacitance frequency dependence of hydrogenated amorphous Si Schottky barrier diodes" (in collaboration with G. Moddel) and (2) "Bulk and surface states analysis in a-Si:H by Schottky and MIS tunnel diodes capacitance and conductance measurements". These have been accepted for publication, and are included in this Report as Appendices 1 and 2. The conclusions of the first of these papers are signi-

ficant for practitioners of the method of capacitance versus voltage which is often applied to obtain the GDOS. In the present context the paper establishes that the bulk state densities of our sputtered films near the Fermi level lie between 10^{15} and 10^{17} $\text{cm}^{-3} \text{ eV}^{-1}$. The second paper distinguishes the capabilities of capacitance-frequency and capacitance-voltage measurements for the determination of bulk and surface state densities.

The conclusion that impurities, although present in densities of a fraction of 1 atomic percent, could not be the real cause of the difficulties in observing large field effects in sputtered material was established by the facts that reduction in their density was ineffective, and that similar impurity concentrations in g.d. material did not prevent the observation of field effect. Detailed discussions of (1) different techniques of cleaning the surfaces of substrates (2) acid etching the substrate (3) plasma etching the substrate just prior to deposition (4) various methods to reduce the contamination by O from residual water vapor were given in Progress Reports Nos. 2 and 3. While SIMS analysis showed that these procedures did affect the profile of contaminants near the substrate-film interfaces, there was no correlation with any improvement in field-effect response. It therefore appeared that defects or a film structure near the film-substrate interface indigenous to the sputtering method might be the cause of the difficulties.

The effects of film heterogeneity on transport have been analyzed in work by Anderson and Paul, and a report accepted for the 1980 International Conference on the Physics of Semiconductors in Kyoto, Japan. That report, included here as Appendix 3, suggested that inhomogeneity in the bulk of the film could be responsible for several long-standing anomalies in measurements of conductivity and thermopower as a function of temperature. The possibility that the initial growth of the film on its substrate might produce a higher-than-average density of defects, and that this effect might be more noticeable in sputtered than in g.d.-produced films was therefore considered. It resulted in a different method of attack on the problem which was initiated at the end of the period of the present contract.

The new method is based on the guess that a film of a-Si:H with few defects may grow best if it is grown onto a newly-deposited insulating substrate. Thus, a film of insulating SiO_x is grown onto a quartz substrate to a thickness of several hundred Å, and then, without shutting off the plasma, a-Si:H is grown on top of the SiO_x . The first experiments of this type are illustrated in Figure 1. The field effect response is spectacularly greater than any hitherto observed in sputtered material - yet the other bulk properties of the films produced in these runs are not too different from earlier measurements. We conclude that only the defect density, and related GDOS, near the film-substrate interface has been changed to values closer to those in the film bulk.

Clearly these experiments should be pursued under a new grant before they can be declared conclusive, but there does not appear to be much doubt about them at the time of writing. The deduced GDOS is closer to that found from the $C(\omega)$ measurements. However, the following questions are also evident: (1) to what extent can the new GDOS be regarded as truly representative of the bulk? Will it not usually be the case that field effect experiments, which probe to a depth of 100 Å or so from the film-substrate interface, yield a GDOS representative of a surface layer only? (2) although g.d.-produced material has always given a strong field effect, might it not be the case that

Figure 1. Preliminary field effect data on a-Si:H deposited directly onto a sputtered layer of SiO_x .

there, too, the deduced GDOS, representative of a surface layer, is higher than that in the bulk material? The fact that both $C(\omega)$ and DLTS measurements on glow discharge material have been interpreted to suggest lower DOS than the field effect lends force to these questions. The quality of the first 100 Å of amorphous material has been shown by our experiments to be of crucial importance for the observation of field effect. The general viability of the method for sputtered material is therefore questionable, unless special precautions in the deposition procedure, akin to ours, are taken. It remains to be seen whether the (gentler) process of glow-discharge deposition happens to avoid creating an uncharacteristically-high defect density in the initial 100 Å of deposited material.

During the period of this contract, we have developed a simplified method of analysis of field effect data which was fully described in Progress Report No. 2, and which will be published in the Philosophical Magazine. For the sake of completeness, an abstract of the paper is included as Appendix 4.

Time and effort considerations have constrained our studies of the drift mobility of excess carriers in a-Si:H. A schematic of the apparatus now used is shown in Figure 2.

The initial electron-hole charge distribution is generated near the top electrode with an 8 nsecond flash of light from a Molelectron dye laser pumped by a nitrogen laser. It has been found important to operate the nitrogen laser inside a shielded enclosure to reduce electromagnetic interference from the gas discharge. The nitrogen laser is triggered by a pulse generator, which also generates a variable pulse timed to bias the sample before the laser pulse arrives. The transient photocurrent is recorded by either direct single shot monitoring on a Tektronix storage oscilloscope with one laser pulse or in a repetitive pulse mode (~10 Hz) when a boxcar integrator is employed. The latter instrument considerably extends the range of measurements at low temperatures. No significant difference is detected in the single shot and repetitive mode so that the slow relaxation effects observed in some disordered material are not of significance in these films. However, measurements do reveal that these are likely to be of increasing importance at low temperatures, and a frequency divider and counter is being constructed so that these effects (if existing) can be studied. Measurements are performed in a variable temperature cryostat fitted with a platinum resistor to control the temperature which is measured with a thermocouple positioned close to the sample.

To date only a few samples have been investigated. Figure 3a shows a dispersive transient obtained at room temperature and is typical of the highly dispersive transients seen in high resistance amorphous materials. Figure 3b shows a transient obtained from a sample which has high luminescence efficiency. This transient shows considerably less dispersion and the fall-off is more characteristic of gaussian broadening. Space-charge effects have been observed on the current transient at high injection levels as an initial spike followed by a "cusp". These effects are being investigated.

For the sample shown in Figure 3b, it has been possible to obtain values of mobility as a linear relationship is found between the reciprocal transit time and the applied voltage. Preliminary values of mobility versus temperature over the "nondispersive" regime are shown in Figure 4. An activation energy of 0.174 is obtained at high temperatures, typical of the values found in glow-discharge amorphous silicon (P. G. Le Comber, A. Madan and W. E. Spear,

Figure 2. Schematic of experimental apparatus used for time-of-flight experiments (dotted lines refer to future developments).

(a)

Figure 3. Experimental photocurrent transients for two sputtered films.

(b)

Figure 4. Temperature dependence of the mobility for Si S-144.

J. Non-Cryst. Solids 11, 219, 1972). The room temperature value of the mobility of $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ is considerably higher than that previously reported for sputtered films and is comparable to the values observed in glow-discharge material.

Future studies will involve analysis of highly dispersive transients shown in Figure 3a. It is hoped that parallel characterization of samples by other techniques in the laboratory will throw light on the reasons for the different current shapes in samples prepared under different conditions.

APPENDIX 1

Interpretation of the Conductance and Capacitance Frequency

Dependence of Hydrogenated Amorphous Silicon Schottky

Barrier Diodes

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We present a general model of the frequency dependence of conductance and capacitance in a-Si:H Schottky diodes. In order to circumvent several questionable assumptions required in the analysis of capacitance voltage characteristics, the frequency dependence of sputtered a-Si:H devices is measured with no applied dc voltage. We obtain independent, consistent values of the depletion width and of the density of states at the Fermi level and below from both conductance and capacitance at both low and high modulation frequencies. We show that the linear frequency dependence of conductance cannot be attributed to hopping conductance, but rather to the interaction of gap states with free carriers. Our study shows that the interaction kinetics of the states around the Fermi level with the conduction band carriers is so fast that the response of the diode is limited by the band transport of these carriers, which rapidly thermalize and distribute themselves through the continuum of states from the conduction band to the Fermi level.

1. INTRODUCTION

The determination of the density of states (D.O.S.) distribution $N(E)$ in the gap of hydrogenated amorphous silicon (a-Si:H) is very useful in developing an understanding of the physical properties of the material and, in particular, of the role of hydrogen. Differential capacitance-voltage measurements on Schottky diodes appear to be a promising technique for the determination of $N(E)$.¹⁻⁵ Nevertheless, the reduction of the experimental data is based upon several assumptions⁵ listed below, whose validity is difficult to establish.

(i) The Schottky barrier resistance must be larger than the bulk resistance (which includes that of the back contact). This is certainly not the case when the forward bias exceeds the flat band voltage.

(ii) Analysis of the data is based upon the thermionic approximation, which is equivalent to assuming a flat electron quasi-Fermi level throughout the depletion width. Such an hypothesis is difficult to confirm, as one does not have a precise knowledge of the electron mobility in the band nor of its collection velocity by the metal; also, the range of energy levels from which the carriers are collected by the metal is unknown. Therefore, it is uncertain whether the thermionic or the diffusion theory is more likely to hold in a-Si:H. The temperature dependence of the current-voltage characteristics of the Schottky diode does not show which of the two theories is appropriate.⁶

(iii) Occupancy of the gap states must be controlled by the electron quasi-Fermi level. This, too, is not the case far from equilibrium, in particular under large forward or reverse bias.

(iv) Finally, determination of $N(E)$ from $C(V)$ characteristics assumes that all the involved states are able to follow the modulation of the barrier. However, as the frequency is lowered, the capacitance has been observed to increase without saturation at room temperature. Hence, one cannot be sure that the applied frequency is low enough.^{1,2,5}

The purpose of this paper is to explore the frequency dependence of both the conductance and the capacitance of Schottky devices in order to deduce the depletion width and the D.O.S. in the region of the Fermi level and below. If the frequency dependence is measured and analyzed with no externally applied dc voltage, as is the case for most of this work, the first two assumptions are valid, the third is more likely to be so and the fourth is circumvented:

(i) From current voltage characteristics it is indeed clear that the Schottky barrier resistance is larger than the bulk resistance for zero external applied voltage, the transport across the junction being controlled by the barrier for biases ranging from reverse to small forward voltages (less than the flat band voltage).

(ii) The second assumption is automatically correct, as the electron quasi-Fermi level is simply the equilibrium Fermi level which is flat throughout the material.

(iii) The third assumption can only be approximate when current, either ac or dc, is flowing, because then the electron quasi-Fermi level is shifted away from the equilibrium Fermi level position. However, the average occupation of the energy gap states should be much closer to that determined by the equilibrium Fermi level than when a dc bias is applied.

(iv) We shall show that, by analyzing in detail the frequency dependence of both conductance and capacitance, it is not necessary to reach

the ultimate zero frequency limit of the admittance of the device to obtain quantitative information about $N(E)$.

The analysis presented in this paper may be used to interpret earlier capacitance and conductance measurements performed on metal-insulator a-Si:H devices.^{7,8} We use data obtained with Pt Schottky barriers on rf sputtered a-Si:H to demonstrate the usefulness of the analysis in deducing the width of the depletion region below the metal into the semiconductor and the density of states near the equilibrium Fermi level and below. The sample we have chosen is a convenient one to demonstrate the full power of the technique, although it has a substantially higher state density than our "cleanest" films.

2. EXPERIMENTAL RESULTS

2.1 Experimental Details

Schottky barriers were formed with Nichrome/a-Si/a-Si:H/Pt sandwiches. The 100 nm sputtered unhydrogenated a-Si layer creates an ohmic contact to a 1 μ m a-Si:H film. The a-Si:H was sputtered onto a substrate maintained at 250°C in an atmosphere of argon and hydrogen with respective partial pressures of 5 and 0.6 mTorr. Sputtering details appear elsewhere.⁹ The a-Si:H surface was etched immediately prior to the evaporation of the Pt contact from a resistance source.

Measurements of capacitance $C(\omega, V)$ and conductance $G(\omega, V)$ as a function of frequency were made using the in-phase and quadrature components from a PAR HR8 lock-in amplifier. Modulation voltage remained below 12 mV rms. An operational amplifier adder, to combine ac and dc components, facilitated measurements of $C(\omega, V)$ and $G(\omega, V)$ under bias. During the measurements the sample remained at room temperature in air.

2.2 Results

Figure 1 shows $C(\omega, V)$ curves for various frequencies (2 Hz $< f <$ 15 kHz). They are quite similar to characteristics obtained previously.^{2,5} A description and explanation of the main features of the curves are presented elsewhere.^{4,5} We shall not review these discussions here because the present paper focuses mainly on the frequency dependence of the capacitance and the conductance for $V = 0$. Two specific features deserve reference: the 40 Hz curve which exhibits a minimum at about 0.35 V and the shoulder in the 15 Hz curve which is followed by a steep increase in the capacitance. These phenomena have already been reported,^{2,5} but not explained. We noticed that upon annealing the sample for an

hour at 200°C in forming gas, the higher voltage features disappear: the decrease in the capacitance beyond the maximum is no longer followed by an increase (see dashed curve, Figure 1). Also, from an analysis of the $I(V)$ curves of the device under illumination, which we omit here for brevity, we have determined that annealing reduces a barrier at the back contact of the device. We deduce then that the observed features occurring before annealing are due to a back contact capacitance contribution which becomes significant when the top contact is forward biased.

Figure 2 shows the $G(\omega, V)$ characteristics of the device. They also are quite similar to data previously obtained.⁵ For bias ranging from -1 V to +1 V, the conductance is an increasing function of the frequency. The frequency dependence of the conductance for $V = 0$ will be analyzed in detail in the next section. For a Pt contact on an etched a-Si:H film, we generally find a Schottky barrier height ϕ_B of 1 eV, as determined from the temperature dependence of the extrapolated value of the forward biased current to zero voltage. The sample under consideration was measured to have a free electron transport thermal activation energy E_G of 0.63 eV, under forward bias of 1 V. This is very close to the 0.65 eV activation energy of the conductance measured in a sandwich structure made at the same time as the Schottky diode, using unhydrogenated amorphous silicon ohmic layers for both top and back contacts. These activated regimes were observed over four orders of magnitude of conductivity from room temperature up to 120°C. Conduction close to the Fermi level is therefore negligible in this range of temperatures. The measured value of the conductivity pre-exponential factor is about

500 $\Omega^{-1} \text{ cm}^{-1}$ (450 $\Omega^{-1} \text{ cm}^{-1}$ with the sandwich structure, 650 $\Omega^{-1} \text{ cm}^{-1}$ with the Schottky diode). The flat band voltage or built-in potential V_{bi} is roughly $\phi_B - E_G = 0.4 \text{ eV}$. This value is consistent with the observed transition voltage between the exponential and linear regimes in the forward current-voltage characteristics of the device.¹⁰

3. EQUIVALENT CIRCUIT ANALYSIS

The general ac equivalent circuit describing the frequency dependence of the diode and the corresponding band structure is shown in Figure 3.⁵ All values are expressed per unit area. The depletion region is divided into sections parallel to the metal-semiconductor interface at depth x_i of thickness $x_{i-1} - x_i$. C_i is the capacitance associated with the states around the Fermi level at depth x_i . It is a dynamic capacitance, describing the variation of the charge of the states due to a modulation of the local potential, i.e., of the position of the Fermi level. R_i is a kinetic resistance associated with the states to model their time of emptying and filling with electrons. C_0 and R_0 are associated with the states near the Fermi level at the depletion/neutral bulk boundary ($x = W$, the width of the depletion layer). The elements R_i and C_i ($0 \leq i \leq n$) cannot be ignored as was done elsewhere;³ indeed, ignoring them implies that there is no variation of charge in the material, except in free carrier density, which is negligible for intrinsic a-Si:H, between the top and the back contact with the external voltage modulation. If this were so, the measured capacitance would be the geometric inter-electrode capacitance, independent of voltage and frequency. C_i' is the dielectric capacitance of the i^{th} section:

$$C_i' = \frac{\epsilon}{x_{i-1} - x_i} \quad \text{and} \quad \left(\sum_{i=1}^n \frac{1}{C_i'} \right)^{-1} = \frac{\epsilon}{W},$$

where ϵ is the dielectric constant. R_i' is the resistance of the i^{th} section. C_{ss} and R_{ss} are the capacitance and corresponding kinetic resistance associated with surface states. R_c is the dynamic contact resistance between metal and semiconductor which may be derived from the

thermionic emission model.¹¹ R_B and C_B are respectively the resistance and the dielectric capacitance of the neutral bulk $C_B = \epsilon/(t-W)$, where t is the sample thickness. A similar equivalent circuit has been proposed by Beguwala and Crowell to describe the kinetics of deep-lying states in crystalline silicon,¹² but it takes into account neither the resistive components of the depletion layer (R_1') and of the neutral bulk (R_B) nor the neutral bulk capacitance (C_B), which cannot be neglected in highly resistive a-Si:H thin films, as is shown in section 3.1.4 and section 3.2.

Although it may seem an oversimplification to represent states distributed in energy by discrete circuit elements, we shall demonstrate that such a representation is useful not only for a qualitative understanding but also for a quantitative analysis of the frequency dependence of the device. In general these circuit components will depend on bias, but in the rest of the paper we will restrict the analysis to zero applied voltage.

As we shall show, the equivalent circuit of Figure 3 can be simplified by choosing frequency ranges in which many of the circuit elements may be neglected. We shall assume in the following that the series resistances R_1' are very small compared with the resistances R_1 which describe the kinetics of filling and emptying of the localized states at the Fermi level E_F . This assumption is commonly made in the analysis of $C(V)$ data,^{1,2,5} but it will be discussed later in the paper (see section 3.1.4).

With the assumption that the occupancy of these localized states at E_F is dominated by the kinetics of capture and release directly with the conduction band, we may use the results of a detailed balance calculation¹³

to write an expression for the thermal release time τ_i , where $\tau_i = R_i C_i$:

$$\tau_i = \frac{\exp\left[\frac{E_c(x_i) - E_F}{kT}\right]}{\sigma_i v_{th} kT N(E_c)} \quad (1)$$

where σ_i is the capture cross section of the states, v_{th} the free electron thermal velocity and $N(E_c)$ the density of states in the conduction band. The following analysis is based on this assumption, which will be discussed in section 3.1.4.

3.1 Low Frequency Range

Because of the upward band bending near the semiconductor/metal interface, the separation in energy between the Fermi level and the conduction band increases as the distance to the interface decreases. As the frequency is reduced, states progressively deeper in the gap can respond to the modulation; therefore, the filling and emptying of the states can occur at the Fermi level which is closer to the semiconductor/metal interface.

As the hopping conduction is negligible compared to the transport in the conduction band at room temperature (see section 2.2), the modulation of the occupancy of the states is achieved by supplying or draining electrons via the conduction band. For a given frequency ω , there exists x_i such that for $x > x_i$ ($\omega\tau \ll 1$) most of the states at the Fermi level are able to follow the modulation; for $x < x_i$ ($\omega\tau \gg 1$) very few can, and for $x = x_i$ we have $\omega\tau_i = 1$. As the frequency is decreased, x_i is swept through the depletion region from the neutral bulk boundary at $x_i = W$ to the semiconductor/metal interface at $x_i = 0$. The frequencies for which x_i falls in the depletion region define the low frequency range.

3.1.1 Low Frequency Equivalent Circuit

As shown in Figure 4, the i^{th} loop can be represented by a parallel equivalent circuit with

$$C_{ip} = \frac{C_i}{1 + \tau_i^2 \omega^2} \quad (2)$$

$$G_{ip} = \frac{C_i \omega^2 \tau_i}{1 + \tau_i^2 \omega^2} \quad (3)$$

and $\tau_i = R_i C_i$. If we assume that any variation in C_i with x_i is slow, which is equivalent to supposing that the states swept by the Fermi level in the depletion region do not exhibit a sharp change in density with energy, G_i depends on x_i mainly through τ_i , which varies quickly as a function of x_i . For a given ω , as τ_i varies, G_i exhibits a maximum for $\omega \tau_i = 1$. In other words, for a given ω the main contribution to the measured conductance comes from the states around x_i such that $\omega \tau_i = 1$. The involved states are located within a section δx_i around x_i , in which the local potential varies by a quantity of order kT/q ,¹⁴ where q is the electron charge. It is straightforward to calculate δx_i in the case where the D.O.S. does not vary with energy, which we assume in the following analysis. It will be shown in section 3.1.4 that this assumption is consistent with the experimental data, at least for states lying below the neutral bulk Fermi level down to the mid-gap. Thus

$$\delta x_i = \frac{kT}{q |E_D(x_i)|} \quad (4)$$

where $E_D(x_i)$ is the electric field at x_i . For a uniform energy distribution of states in the energy range swept by the Fermi level, the field

is an exponential function of x_1 :

$$E_D(x_1) = E_D(0) \exp\left(-\frac{x_1}{L_0}\right) ; \quad (5)$$

$$\text{and } E_D(0) = \frac{V_{bi}}{L_0}$$

where V_{bi} is the built-in potential of the diode and L_0 , the Debye length associated with the states, is given by

$$L_0 = \left(\frac{\epsilon}{qN_0}\right)^{1/2} , \quad (6)$$

N_0 ($\text{eV}^{-1} \text{ cm}^{-3}$) being the density of states.^{4,5} Therefore,¹⁵

$$\delta x_1 = \frac{kT}{q|V_{bi}|} L_0 \exp \frac{x_1}{L_0} \quad (7)$$

The density of involved states around x_1 , expressed per eV and per cm^2 is

$$N_1 = \delta x_1 N_0$$

and the corresponding capacitance is

$$C_1 = qN_1 = \frac{kT}{|V_{bi}|} L_0 N_0 \exp \frac{x_1}{L_0} \quad (8)$$

The depletion region boundary at $x = W$ is defined as being where the local potential is kT/q from that of the neutral bulk. From equation (5) we have⁴

$$W = L_0 \ln \frac{q|V_{bi}|}{kT} \quad (9)$$

and from (6), (8) and (9)

$$C_1 = \frac{\epsilon}{L_0} \exp \frac{x_1 - W}{L_0} \quad (10)$$

For $\omega\tau_1 = 1$, according to (2) and (3)

$$C_{ip} = \frac{C_1}{2} = \frac{\epsilon}{2L_0} \exp\left(\frac{x_1 - W}{L_0}\right) \quad (11)$$

$$G_{ip} = \frac{C_1 \omega}{2} \quad (12)$$

In order to calculate the actual admittance measured across the terminals of the device, it is now necessary to consider the remaining capacitive components in the equivalent circuit. The device may be divided into two regions, one for $0 < x < x_1$ and the other for $x_1 \leq x \leq t$. The former contributes a simple dielectric capacitance ϵ/x_1 , as the occupancy of its states is not modulated for $\omega = 1/\tau_1$. In the latter region, if all the states could respond, we would expect a capacitance contribution from this region, for a uniform energy distribution of states⁵ (neglecting C_B , which will be justified later; see section 3.1.2 footnote 18)

$$C_{<1} = \frac{\epsilon}{L_0} ;$$

but because the resonant 1th segment has been accounted for separately above, we must exclude its contribution, leaving

$$C_{<1} - C_1 = \frac{\epsilon}{L_0} \left(1 - \exp \frac{x_1 - W}{L_0}\right) . \quad (13)$$

Finally, adding the parallel components C_{ip} and G_{ip} , the equivalent circuit for $\omega = 1/\tau_1$ can be redrawn as shown in Figure 5.¹⁶

3.1.2 Low Frequency Conductance

The measured low frequency conductance across the terminals is then

$$G(\omega, 0) = \omega \epsilon \frac{2 \frac{L_0}{x_1} \exp \frac{x_1 - W}{L_0}}{\exp \frac{2(x_1 - W)}{L_0} + \left[2 \frac{L_0}{x_1} + 2 - \exp \frac{x_1 - W}{L_0} \right]^2} \quad (14)$$

$$\equiv \omega F(x_1)$$

The two extreme values of G correspond to $x_1 = W$ and $x_1 = 0$. At the highest frequency of the low frequency range, $x_1 = W$ and the states near Fermi Level at the neutral bulk boundary begin to follow the modulation. For $x_1 = 0$, all the states in the depletion region can follow the modulation. We calculate $F(x_1)$ in these two cases, keeping in mind from equation (3) that $\exp(-\frac{W}{L_0}) = q \frac{|V_{b1}|}{kT} = 16$ in our experimental situation.

$$x_1 = 0 \quad F(0) = \frac{1}{32} \frac{\epsilon}{L_0} \quad (14a)$$

$$x_1 = W \quad F(W) = \frac{1}{15} \frac{\epsilon}{L_0} \quad (14b)$$

Hence, $F(x_1)$ varies by approximately a factor of 2, which means that G/ω varies by a factor of 2 when, as can be observed from equation (1), the frequency varies by a factor of $\exp \frac{q|V_{b1}|}{kT} \approx 10^7$. The frequency dependence of the measured conductance is then like ω in the low frequency regime.¹⁷ Figure 6 shows the experimental $G(\omega)/\omega$ plotted for $V = 0$, and we verify that G/ω is roughly constant for frequencies below 40 Hz. It will be shown in the next section that the highest frequency of the low frequency range, corresponding to $x_1 = W$, is about 40 Hz. Using equation (14b) with experimental data obtained at 40 Hz, we find $L_0 = 4 \times 10^{-2} \mu\text{m}$. From relation (9) the depletion width is then $L_0 \ln \frac{q|V_{b1}|}{kT} = 0.12 \mu\text{m}$.¹⁸

3.1.3 Low Frequency Capacitance

The low frequency capacitance could be directly deduced from the equivalent circuit of Figure 4. A more physically transparent and straightforward calculation can be made upon considering that for a

given frequency ω there exists an x_1 such that for $x > x_1$ most of the states respond to the modulation and for $x < x_1$, very few of the states do. We ignore the fact that the intermediate states around x_1 respond only partially to the modulation, which was taken into account in the equivalent circuit of Figure 5. It can be shown that this approximation results in, at most, a 6% error in the calculated value, and this only at the highest frequency of the range, which is the worst case. The measured capacitance is then the dielectric capacitance ϵ/x_1 in series with $C_{<1} = \epsilon/L_0$:

$$C = \frac{\epsilon}{x_1 + L_0} \quad (15)$$

The frequency dependence of C is due to the variation with frequency of x_1 . If ω_0 is the highest frequency of the low frequency range, corresponding to the states around $x = W$, we have, according to (1)

$$\frac{\omega_0}{\omega} = \exp \left[\frac{q|V(x_1)|}{kT} - 1 \right]$$

with $V(x_1) = V_{bi} \exp \left(-\frac{x_1}{L_0} \right)$ (see equation (5))

hence

$$\frac{x_1}{L_0} = \ln \frac{V_{bi}}{V(x_1)} = \ln \left[\frac{\frac{q|V_{bi}|}{kT}}{1 + \ln \frac{\omega_0}{\omega}} \right]$$

Finally

$$C(\omega) = \frac{\epsilon}{L_0} \frac{1}{1 + \ln \left[\frac{\frac{q|V_{bi}|}{kT}}{1 + \ln \frac{\omega_0}{\omega}} \right]} \quad (16)$$

If we again take $V_{bi} = 400$ mV and if we choose $L_o = 4.4 \times 10^{-2}$ μm and $\omega_o = 40$ Hz, the experimental data for $\omega = 2$ Hz, 15 Hz and 40 Hz fit with the theoretical calculation, according to equation (16), within 5% (see Figure 7). The precision in the determination of L_o is very good, as it is only a weak function of $|V_{bi}|$ and ω_o ; indeed, a logarithmic function reduces the effect of variations in V_{bi} once and in ω_o twice. It can be asserted safely that L_o falls between 4×10^{-2} and 5×10^{-2} μm . However, the precision in the determination of ω_o is not as good. The turnover frequency ω_o depends strongly on the choice of L_o and even more on the choice of V_{bi} . For example, ω_o varies from 20 to 50 Hz when L_o is varied from 4×10^{-2} to 5×10^{-2} μm for $|V_{bi}| = 400$ mV, the fit remaining within 15% of the experimental data. If we take $|V_{bi}| = 350$ mV, the average value of ω_o is shifted from 40 Hz to 110 Hz. It turns out that the value of $\omega_o = 40$ Hz, deduced from the best fit between theory and experimental $C(\omega)$ data, corresponds exactly to the turnover frequency between the low and high frequency ranges, as deduced from conductance measurements (see Figure 6). We shall choose this value in the following discussion.

3.1.4 Discussion of Low Frequency Results

No saturation in the measured capacitance is to be expected until the frequency modulation is lower than

$$\omega = \omega_o \exp \left[1 - \frac{q|V_{bi}|}{kT} \right] \approx 10^{-5} \text{ Hz}$$

This result is consistent with experimental data published elsewhere² which show no saturation in $C(\omega)$ for a frequency of 10^{-3} Hz at room

temperature. In our experimental case the states investigated are located in energy within $kT (1 + \ln \frac{\omega_0}{\omega_\ell})$ below the bulk Fermi level. For $\omega_\ell = 2$ Hz, the lowest experimental frequency modulation, that is 100 mV. The D.O.S. deduced from the values of L_0 is $4.1 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ for $L_0 = 4.0 \times 10^{-2} \text{ }\mu\text{m}$ derived from conductance measurements in the low frequency range using equation (14), and $3.4 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ for $L_0 = 4.4 \times 10^{-2} \text{ }\mu\text{m}$ derived from capacitance measurements using equation (16). Although the results of the frequency dependences are consistent with an approximately constant D.O.S. between the midgap and the bulk Fermi level (the surface Fermi level being located just below the midgap), it is possible that the D.O.S. increases slightly with energy. Since the experimental results depend only on the D.O.S. within 0.1 eV below E_F and on the depletion width, the deduced D.O.S. in this range of energy is not affected if the D.O.S. deeper in the gap is significantly lower. Indeed, the depletion width is determined by the D.O.S. mainly at the Fermi level even if the density is significantly lower at the midgap. Such a decrease towards the midgap is consistent with the $C(V)$ curves for $V > .35$ V, from which we may infer that the density of states exhibits a steep increase above the bulk Fermi level, whose position seems to be pinned by this "wall" of states.

From the value of ω_0 and equation (1), we can calculate the capture cross section of the states around the Fermi level in the bulk. We find

$$\sigma = 4 \times 10^{-13} \text{ cm}^2$$

with

$$E_c - E_F = .64 \text{ eV (in the bulk)}$$

and the assumed values of

$$N(E_c) = 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$$

$$v_{th} = 10^7 \text{ cm s}^{-1}$$

This value of σ is very large in comparison with the values usually reported for deep-lying states in crystalline silicon.¹⁹

We shall assume for the moment that the deduced σ is correct and use it to calculate the collection velocity of the involved gap states. For example, at $x_1 = W$ (i.e., $i = 0$) the collection velocity of these states, which are within kT of E_F , is

$$\begin{aligned} v_c &\approx v_{th} \sigma N_o kT (\delta x_1)_{x_1 = W} \\ &= v_{th} \sigma N_o L_o kT \approx 10^5 \text{ cms}^{-1} \end{aligned}$$

We now evaluate the diffusion velocity v_d of the free electrons at E_c for $x_1 = W$:

$$\begin{aligned} v_d &= \mu_o E_D(W) \\ &= \mu_o \frac{kT}{qL_o} \end{aligned}$$

where $E_D(W) = \frac{kT}{qL_o}$ is the electric field at the neutral bulk boundary (see equations (5) and (9)). The electron mobility

$$\mu_o = \frac{\sigma_o}{qkT N(E_c)}, \text{ is about } 10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1},$$

where σ_o is the pre-exponential factor of the activated conductivity of the amorphous material. We find $v_d \approx 5 \times 10^5 \text{ cm s}^{-1}$ which is of the same order as v_c . If the collection velocity were the controlling factor for the occupancy of the gap states in the space charge region, then v_c could be determined from the experimentally derived capture cross section as shown above. However, because the independently derived diffusion velocity v_d is of the same order of magnitude as v_c , it is unlikely

that v_c is the controlling factor. Also, the high frequency behavior (section 3.2) is consistent with such a diffusion controlled occupancy. Therefore, the occupancy of the states around $x = W$, as well as in the entire space charge region, is not controlled by their interaction kinetics with extended states electrons but simply by the transport of these extended state electrons.²⁰ Thus, the response is limited not by the thermalization of electrons into the gap in energy space but by their relaxation into the diode in real space. In other words, the resistance R_1 , rather than R_1' , is to be neglected in the equivalent circuit of Figure 3. This conclusion is completely opposite to the assumption made earlier in the paper in deriving the low frequency behavior of the device (see section 3). Nevertheless, the resistance between x_1 and the bulk is an exponential function of $V(x_1)$, as was the case for the thermal release time τ_1 of the states (see section 3). Consequently, the previous analysis remains applicable; it was based on the exponential dependence of τ_1 on $V(x_1)$ and works equally well if the exponential dependence is due to R_1' . Thus, the quantitative results obtained, except for the value of σ , remain valid.

Because modulation of the gap state occupancy is limited by the transport in the band rather than by the collection velocity, the calculated value of σ is a lower limit. If thermal equilibrium were established directly between states near E_F and electrons at E_c , the estimated value of σ ($\sigma > 4 \times 10^{-13} \text{ cm}^2$) would be genuine. However, it is more likely that the actual σ is smaller and that equilibrium is established via intermediate states. Curves of $\log$ (conductivity) versus $1/T$ exhibit a continuous transition from a well-defined activated region around and above room temperature, corresponding to conduction at E_c , to a region which may be attributed

to hopping conduction at E_F , with no evidence for an intermediate activation energy.²¹ Thus there is no dominant conduction path below E_c . We may infer that there is no peak in the D.O.S. which could be a single dominant intermediate step between E_c and the states near E_F . Therefore, it appears that all the states from E_c to just below midgap participate in the rapid establishment of thermal equilibrium. The states in the upper half of the gap may then be viewed as an extension of the conduction band, through which electrons thermalize to equilibrium.

3.2 High Frequency Range

In the high frequency range the behavior of the diode may be modeled by the simple equivalent circuit shown in Figure 8. All the loops in Figure 3 associated with the states in the depletion region are neglected, since they cannot respond to the fast modulation. Also, R_o is neglected with respect to R_B .²² C_B cannot be neglected in the high frequency range. $C_D = \epsilon/W$ is the depletion capacitance, and $C_B = \epsilon/(t-W)$, where t is the sample thickness. From equation (10), $C_o = \epsilon/L_o$. The frequency dependent capacitance and conductance are then

$$C(\omega) = \frac{C_D(C_o + C_B)}{C_o + C_B + C_D} \times \frac{1 + R_B^2 \omega^2 \frac{C_o C_B}{C_o + C_B} \times \frac{C_o(C_B + C_D)}{C_o + C_B + C_D}}{1 + R_B^2 \omega^2 \left[\frac{C_o(C_B + C_D)}{C_o + C_B + C_D} \right]^2} \quad (17)$$

$$G(\omega) = \frac{R_B \left(\frac{C_o C_D}{C_o + C_B + C_D} \right)^2 \omega^2}{1 + R_B^2 \omega^2 \left[\frac{C_o(C_B + C_D)}{C_o + C_B + C_D} \right]^2} \quad (18)$$

According to equation (18), G/ω exhibits a maximum for

$$\omega_m = \frac{C_o + C_B + C_D}{R_B C_o (C_B + C_D)} \quad (19)$$

and it is straightforward to show that

$$C(\omega_m) = \frac{1}{2} \left[\frac{C_D (C_o + C_B)}{C_D + C_o + C_B} + C_t \right] \quad (20)$$

$$\frac{G(\omega_m)}{\omega_m} = \frac{1}{2} \left[\frac{C_D (C_o + C_B)}{C_D + C_o + C_B} - C_t \right] \quad (21)$$

where $C_t = \epsilon/t$ is the interelectrode geometric capacitance. In our case C_t is about 11 nF/cm^2 , as deduced from a measurement of the capacitance at 15 kHz (which is consistent with a sample thickness t of about $1 \text{ }\mu\text{m}$).

Figure 6 shows that the experimental $G(\omega)/\omega$ curve exhibits a maximum for

$\omega_m \approx 250 \text{ Hz}$.²³ From $G(\omega_m)/\omega_m$ we deduce, using equation (21),

$C_o = 210 \text{ nF/cm}^2$, which corresponds to $L_o = 5.1 \times 10^{-2} \text{ }\mu\text{m}$. From $C(\omega_m)$

we find, using equation (20), $L_o = 4.8 \times 10^{-2} \text{ }\mu\text{m}$. The corresponding

values of the D.O.S. from equation (6) are respectively $2.6 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$

and $2.9 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$. It appears then that capacitance and conductance

data in the high frequency range are quite consistent with each other

and with the low frequency capacitance and conductance data (see Table I).

Finally, from equation (19) with $L_0 \approx 5 \times 10^{-2} \mu\text{m}$, we have $R_B \approx 10 \text{ k}\Omega/\text{cm}^2$. This value is in good agreement (within 10%) with the value of R_B measured directly under high forward bias (1 V). This result justifies neglecting R_0 in the equivalent circuit (Figure 8) and confirms the conclusion deduced from the low frequency data, that the kinetics of the gap states occupancy is controlled by the band transport rather than interaction with free electrons.

CONCLUSIONS

We have presented a general model of the frequency dependence of both conductance and capacitance in a-Si:H Schottky diodes. An analysis at zero bias allows us to circumvent several questionable assumptions required in the study of capacitance voltage characteristics. We have found that quantitative information about the gap state density can be obtained from the frequency dependence and that it is not necessary to make measurements at the low frequency limit (approximately 10^{-5} Hz). The linear frequency dependence of conductance cannot be attributed to hopping conduction, but rather to the interaction of gap states with the free carriers.

In the sample we consider, comparison of theory with experimental data is consistent for both conductance and capacitance in both low and high frequency ranges with an approximately constant density of states between midgap and the bulk Fermi level (located approximately 0.3 eV above the midgap) of average value $3 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$, which corresponds to a depletion width of about 0.14 μm . Although there is evidence that the density of states increases slightly from midgap to the Fermi level, we can safely assert that, at least within the investigated energy range of 0.1 eV just below the bulk Fermi level, the density of states is between $2 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ and $4 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ ($4 \times 10^{-2} \mu\text{m} < L_0 < 5 \times 10^{-2} \mu\text{m}$).

The present analysis is applicable to data published by a number of laboratories.^{1,2,3} To date we have applied it successfully to various rf sputtered a-Si:H films, whose density of states ranges to two orders of magnitude below that deduced here.

Our study shows that the interaction kinetics of the involved states around the Fermi level with the conduction band carriers is so fast that the frequency dependence of the diode is controlled instead by the transport of these carriers. It is likely that the electrons thermalize through the continuum of states from the conduction band to the Fermi level in rapidly establishing an equilibrium.

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16. In our analysis we neglect the contribution of R_c and of the surface states which may dominate for $x_1 \rightarrow 0$. In fact, the lowest frequency of our experiments is 2 Hz, and, as will be shown in the next section, the characteristic frequency of the states near the surface is about 10^{-5} Hz; therefore, at least in the range of our experimental frequencies, surface states contribute to neither the measured conductance nor capacitance. Furthermore, at 2 Hz the measured conductance is one order of magnitude larger than the static conductance derived from the dc $I(V)$ characteristic. Thus, it is valid to neglect R_c in the equivalent circuit for frequencies larger than 2 Hz.
17. This frequency dependence cannot be attributed to hopping conduction, as was erroneously done previously.⁵
18. We may now justify neglecting the bulk capacitance in the low frequency range. The thickness of the neutral bulk is $t - W \approx .9 \mu\text{m}$, compared to $L_0 = 0.04 \mu\text{m}$. $C_B(\epsilon/t-W)$ is in parallel with $C_0(\epsilon/L_0)$, or at least with $C_0/2$ for $x_1 = W$, and is 20 times smaller than C_0 .

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23. The appearance of a peak in the $G(\omega)/\omega$ curve can be considered as evidence that the space charge region extends over a fraction of the sample thickness. If the space charge region occupied the whole sample thickness, C_B would approach infinity and $G(\omega_m)/\omega_m$ would approach zero.

Table I

Density of states from capacitance and conductance data in high and low frequency ranges.

	Low Frequency Range	High Frequency Range
Capacitance measurement	D.O.S. = $3.4 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$	D.O.S. = $2.9 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$
Conductance measurement	D.O.S. = $4.1 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$	D.O.S. = $2.6 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$

FIGURE CAPTIONS

- Figure 1. Capacitance-voltage characteristics of Pt/a-Si:H Schottky diode for several values of ω . Also shown (at 40 Hz) after film was annealed in forming gas at 200°C for one hour.
- Figure 2. Conductance-voltage characteristics of Pt/a-Si:H Schottky diode for several values of ω .
- Figure 3. General equivalent circuit for the Schottky diode. Interaction between the states at the Fermi level and the conduction band is illustrated by the arrows in the partial energy band schematic representation below the circuit diagram.
- Figure 4. Parallel representation of the i^{th} loop of the general equivalent circuit.
- Figure 5. Equivalent circuit in the low frequency regime when $\omega = \frac{1}{R_1 C_1}$
- Figure 6. Conductance $G(\omega, V = 0)$ divided by frequency ω , as a function of ω .
- Figure 7. Capacitance $C(\omega, V = 0)$ as a function of frequency ω : comparison between experiment and theory.
- Figure 8. Equivalent circuit for the Schottky diode in the high frequency range.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

APPENDIX 2

BULK AND SURFACE STATES ANALYSIS IN a-Si:H by SCHOTTKY AND MIS TUNNEL DIODES CAPACITANCE AND CONDUCTANCE MEASUREMENTS

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Abstract

An experimental and theoretical study of both the capacitance and the conductance of Schottky and MIS tunnel diodes made on undoped a-Si:H, versus frequency, temperature and voltage is presented in this paper. It is based on a general model using an equivalent electrical circuit of the devices, which permits an unambiguous distinction to be made between the contributions of bulk and surface states, to determine their respective densities and to analyze their kinetic properties.

It is shown that the bulk density of states (D.O.S.) can be determined from capacitance and conductance measurements versus temperature and frequency on both Schottky and MIS devices, provided the modulation frequency is high enough to prevent any contribution from surface states. It is demonstrated that capacitance-voltage characteristics of Schottky diodes cannot provide reliable information about either bulk or surface states as the diffusion theory and not the thermionic theory is appropriate to describe the transport of electrons across the junction.

It is shown theoretically and experimentally that a MIS device is required to measure surface states, the insulator preventing the screening of their contribution by the metal. The measured surface D.O.S., derived by three different and independent methods, is very high ($5 \times 10^{12} - 2 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$) and essentially the same for all the investigated samples whose bulk D.O.S. around the Fermi level ranges between 5×10^{15} and $4 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$.

From conductance measurements, it is shown that the kinetics of the occupancy of both bulk and surface states is controlled by free electron transport in the conduction band and not by the states' interaction kinetics

with these electrons. The very high derived lower limit of the effective capture cross-section σ_n of electrons by states around the Fermi level E_F ($\sigma_n > 5 \times 10^{-13} \text{ cm}^2$) implies either that the interaction between states around E_F and free electrons takes place via intermediate states or that the actual distance between the bulk Fermi level and the conduction level is smaller than the activation energy E_σ of the conductivity.

1. INTRODUCTION

The determination of both the bulk and surface density of states (D.O.S.) distribution in the gap of hydrogenated amorphous silicon (a-Si:H) is considered to be a necessity in gaining an understanding of the physical properties of the material as well as developing its device applications.

Surface D.O.S. determination has been extensively and successfully carried out on crystalline silicon, using various techniques, such as field effect, capacitance voltage and conductance voltage measurements versus frequency of metal-insulator semiconductor (MIS) structures with a thick ($> 400 \text{ \AA}$) insulating layer or a thin one ($< 100 \text{ \AA}$: MIS tunnel diode). The main reason for this success is that the bulk of crystalline silicon is generally much "cleaner" than its surface, which allows an unambiguous determination of surface states. Deep bulk traps have also been successfully characterized using Deep Level Transient Spectroscopy (DLTS), a high frequency (MHz range) junction capacitance technique which makes it possible to discriminate between surface states and bulk states.

One of the main problems in a-Si:H D.O.S. measurements is making a clear distinction between bulk and surface states. Field effect measurements which have been used for the determination of bulk D.O.S.^{1,2,3} may reflect both surface and bulk distributions of states. This is also one among other weaknesses of the Schottky diode or MIS structure $C(V)$ technique.^{4,5} Yet, interesting studies of the Schottky diode capacitance versus temperature⁶ and frequency^{7,8} were made recently, in an attempt to derive the bulk D.O.S., although they were based on an equivalent circuit for the device, which is of limited validity. Surface state related structures were observed by Balberg⁹ using the tunnel junction conductance technique

on a-Si:H. The D.L.T.S. (capacitance transient) technique was used recently too,¹⁰ in order to determine the nature and the density distribution of deep traps in a-Si:H. Quantitative information about the D.O.S. distribution can be derived from the latter technique, provided the conductivity of the material is greatly enhanced by doping. Therefore, the results obtained should not be directly extended to intrinsic material as the D.O.S. distribution, at least in the bulk, is believed to be significantly modified by doping.¹¹⁻¹⁴

In a recent paper,¹⁵ we presented a general model of the frequency dependence of both the capacitance and the conductance of a-Si:H Schottky diodes. Using this model, we were able to derive the energy distribution and kinetics of bulk states located between the bulk Fermi level and the midgap.

In this work we present an extensive experimental and theoretical study of both the capacitance and the conductance of Schottky and MIS tunnel diodes made on undoped a-Si:H, versus frequency, temperature and voltage. It is shown that a judicious choice of temperature and frequency ranges allows a clear distinction to be made between bulk and surface states and to measure their respective densities. This unambiguous distinction follows from a comparison of the results obtained on both kinds of devices made on the same material. In addition, a detailed analysis of the kinetics of the states occupancy is presented.

The next section contains the basic theoretical concepts which are used throughout this paper. The equivalent electrical circuit and some of the bulk state related properties of the device, already presented in previous publications,^{5,15} are briefly reviewed. The contribution of surface states is analyzed in detail, and the importance of the choice of the frequency and

and temperature ranges, as well as of the type of device (Schottky or MIS tunnel diode) is discussed. The analysis presented in this paper may be used to interpret earlier capacitance and conductance measurements performed on metal-thick insulator-a-Si:H devices.^{16,17}

2. THEORETICAL ANALYSIS

2.1 Equivalent Electrical Circuit

The general ac equivalent electrical circuit describing the frequency dependence of the MIS tunnel diode and the corresponding band structure is shown in Figure 1. We presented a similar circuit previously,^{5,15} describing the behavior of the Schottky diode. The only difference is the presence of the finite capacitance C_I of the insulating layer in the case of the MIS diode (C_I is infinite for a Schottky diode). Also, the dynamic contact resistance R_c between the metal and the semiconductor is larger for the MIS device. Therefore, the theoretical analysis presented in Section 2 can be applied for both kinds of devices; the relevant consequences resulting from the above mentioned differences will be pointed out. We will restrict ourselves to a description and brief review of the main properties of the circuit, presented previously.¹⁵

All values in the circuit are expressed per unit area. The depletion region is divided into sections parallel to the metal-semiconductor interface at depth x_i and of thicknesses $x_{i-1} - x_i$. C_i is the capacitance associated with the states around the Fermi level at depth x_i . It is a dynamic capacitance, describing the variation of the charge of the states due to a modulation of the local potential, i.e., of the position of the Fermi level.¹⁸ R_i is a kinetic resistance associated with the states to model their time of emptying and filling with electrons. C_0 and R_0 are associated with the states near the Fermi level at the depletion region/neutral bulk boundary ($x_i = W =$ the width of the depletion layer). C'_i is the dielectric capacitance of the i -th section:

$$C'_i = \frac{\epsilon}{x_{i-1} - x_i}$$

and

$$\left(\sum_{i=1}^n \frac{1}{C'_i} \right)^{-1} = \frac{\epsilon}{W}$$

where ϵ is the semiconductor dielectric constant. R'_i is the resistance of the i -th section. C_{ss} is the capacitance associated with surface states. R_{ss} and R_{sm} are the corresponding kinetic resistances describing the interaction of the surface states with semiconductor electrons and metal electrons, respectively. R_B and C_B are respectively the resistance and the dielectric capacitance of the neutral bulk. $C_B = \epsilon/(t-w)$, where t is the sample thickness.

We have shown¹⁵ that the interaction kinetics of the bulk states around the Fermi level with the conduction band carriers is so fast that the response of the diode is limited by the band transport of these carriers. In other words, the resistance R_i can be neglected with respect to resistances R'_i in the equivalent circuit whose simplified version is shown in Figure 2. The approximation of zero temperature statistics will be applied throughout the theoretical analysis in the following sections.

2.2 Capacitance

2.2.1 Bulk States

The modulation of the occupancy of the bulk gap states contributes to the measured capacitance across the terminal of the device. In the absence of gap states, or if no modulation were taking place, the measured capacitance would be the geometric interelectrode capacitance (made of the semiconductor

dielectric capacitance ϵ/t in series with the insulator capacitance ϵ/t_I , where ϵ_I is the dielectric constant and t_I the thickness of the insulating layer). The modulation of the occupancy of the states is possible only to the extent that the conduction band is able to supply or to drain the carriers at the modulating rate. This ability depends, of course, on the position in space of the involved states, i.e. whether they are located in a region which is highly depleted of free carriers (i.e., close to the surface in depletion regime). For a given frequency and a given temperature there exists x_i (see Figure 1) such that for $x > x_i$, essentially all the states at the Fermi level are able to follow the modulation, for $x < x_i$, essentially none of them can and for $x = x_i$ states can only partially follow it. As the frequency is decreased or the temperature is increased, allowing the Fermi level states to be provided with sufficient free carriers, x_i is swept through the semiconductor toward the semiconductor/metal interface at $x_i = 0$. The frequency dependence of the capacitance, resulting from modulation of the occupancy of bulk states can be derived from the equivalent circuit and is written as follows, for the case of a uniformly distributed D.O.S. between the bulk and surface Fermi level positions with frequencies and temperatures for which $0 \leq x_i \leq w$:¹⁵

$$C_b(\omega) = \frac{\epsilon}{L_0} \frac{1}{1 + \ln \left[\frac{q|V_{bi}|/kT}{1 + \ln \frac{\omega_0}{\omega}} \right]} \quad (1)$$

In the absence of surface states contribution, the *measured* capacitance C_m is written

$$C_m = \frac{C_b(\omega) C_I}{C_b(\omega) + C_I}$$

the insulator capacitance C_I being in series with $C_b(\omega)$. The effect of surface states will be discussed in Section 2.2.2. If $C_I \gg C_b(\omega)$, $C_m \approx C_b(\omega)$.

The validity of equation (1) is generally limited to the case of zero dc applied voltage across the device.¹⁵ V_{bi} is the built-in potential of the diode, L_0 is the Debye length associated with bulk states:¹⁵

$$L_0 = \left(\frac{\epsilon}{qN_0} \right)^{\frac{1}{2}} \quad (2)$$

N_0 ($\text{eV}^{-1} \text{cm}^{-3}$) being the density of states. ω_0 is the frequency corresponding to $x_i = W$, i.e. the upper limit of the frequency modulation range leading to a change in the occupancy of the states in the depletion range. ω_0 is proportional to $\exp(E_F - E_C)/kT$, where E_F and E_C are the bulk Fermi level and conduction band edge. The low frequency limit or the saturation frequency is reached at the frequency¹⁵

$$\omega = \omega_s = \omega_0 \exp \left[1 - q \frac{|V_{bi}|}{kT} \right] \quad (3)$$

when $x_i = 0$ and $C_b(\omega_s) = \epsilon/L_0$: all the bulk states are then able to follow the modulation. ω_s , which is proportional to $\exp(-\phi_B/kT)$, where ϕ_B is the barrier height of the device (see equation (3) and Figure 1) sharply increases with temperature.

When the saturation frequency is approached the contribution of the bulk states located close to the metal/semiconductor interface is measured, provided the contact resistance R_c is larger than the depletion resistance $R_d = \sum_i R_i$. If it is not so, R_c tends to shunt the capacitance of the states located in the surface region and the measured capacitance contribution from bulk states is lower than ϵ/L_0 . This behavior is to be expected in the case of a Schottky diode when the transport of electrons across the junction is controlled by the depletion region rather than by their collection by the metal, i.e., when this transport is described by the diffusion theory instead of the thermionic theory.¹⁹ The insertion of

an insulating layer between the metal and the semiconductor increases R_c and prevents the screening by the metal of the contribution of the surface region bulk states to the measured capacitance.

2.2.2 Surface States

Modulation of the occupancy of surface states becomes possible when x_i approaches the surface, i.e., when, either by raising the temperature or lowering the ac modulation frequency, the saturation frequency is approached. They contribute fully to the capacitance provided R_c and R_{sm} are larger than $R_{ss} + R_d$, i.e., they are not screened by the metal.²⁰ Therefore, the presence of an insulating layer between the metal and the semiconductor tends to reveal the presence of surface states in capacitance measurements. When the modulation frequency is lower than the saturation frequency and if the previous conditions are fulfilled, their contribution to the capacitance is qN_{ss} ,²¹ where N_{ss} ($\text{cm}^{-2}\text{eV}^{-1}$) is the surface state density. The total semiconductor capacitance is then:

$$C = qN_{ss} + \frac{C}{L_0} \quad (4)$$

and the *measured* capacitance C_m is written

$$C_m = \frac{CC_I}{C + C_I} \quad (5)$$

the insulator capacitance C_I being in series with C . At frequencies

greater than or equal to the saturation frequency, the surface state capacitance is frequency dependent. If the rate of change in their occupancy is controlled by their interaction kinetics with free surface electrons, i.e., if $R_{ss} > R_d$ (as is usually the case in crystalline silicon²¹), $C_{ps}(\omega)$, the capacitance component of the parallel circuit equivalent to C_{ss} in series with R_{ss} (C_{ss} and R_{ss} both depending on frequency) is written as follows (for a continuum of states in the energy range²¹)

$$C_{ps}(\omega) = qN_{ss} \frac{\arctan \omega \tau_s}{\omega \tau_s} \quad (6)$$

with

$$\tau_s = \frac{1}{C_n n_s} \quad (7)$$

$C_n = \sigma_n v_{th}$, where σ_n is the capture cross section of free surface electrons (of density n_s (cm^{-3})) by surface states around the Fermi level and v_{th} the free electron thermal velocity. $C_{ps}(\omega)$ approaches qN_{ss} when $\omega < 1/\tau_s$. On the other hand, if modulation of the occupancy of surface states is controlled by transport of electrons in the depletion region, as is the case for bulk states, $C_{ps}(\omega)$ is simply the capacitance component of the parallel circuit equivalent to C_{ss} ($= qN_{ss}$) in series with R_d :

$$C_{ps}(\omega) = \frac{C_{ss}}{1 + (R_d C_{ss} \omega)^2} \quad (8)$$

C_{ss} is independent of frequency in this case.

2.3 Conductance

2.3.1 Bulk States

The static conductance G_{sta} of the device, measured at frequencies lower than the saturation frequency is the lowest measurable conductance:

$$G_{sta} = \frac{1}{R_c + R_d} \quad (9)$$

When the frequency is raised, the most resistive sections of the depletion region resistance, i.e., the sections located the closest to the interface, tend to be shunted by the capacitance of the corresponding bulk states and the measured conductance increases. For example, at a given frequency, the sections numbered $j > i$ are shunted as soon as

$$\frac{1}{C_i \omega} < \sum_{j=i+1}^n R'_j$$

This is another way to define x_i , the boundary between those states at the Fermi level whose occupancy follows the modulation and those that do not.

We have shown that, in the range of frequency and temperature corresponding to $0 < x_i < W$, the frequency dependence of the conductance, resulting from the above-described bulk states capacitance effect, can be calculated using the equivalent circuit and is written as follows, for the case of a D.O.S. which does not vary with energy.¹⁵

$$G_b(\omega) = \omega \epsilon \frac{\frac{2L_0}{x_i^2} \exp \frac{x_i - W}{L_0}}{\exp \frac{2(x_i - W)}{L_0} + \left[\frac{2L_0}{x_i} + 2 - \exp \left(\frac{x_i - W}{L_0} \right) \right]^2} \quad (10)$$

$G_b(\omega)$ corresponds to the measured conductance under two conditions, (i) surface state contribution is negligible and (ii) $C_I > G_b(\omega)/\omega$. As we shall see in the experimental section (Section 4.2), condition (i) is fulfilled in the

ranges of temperature and frequency where surface states cannot follow the modulation, and condition (ii) applies for very thin insulators. When, by varying frequency or temperature, x_i is swept through the entire depletion region, the variation of $G_b(\omega)/\omega$ is very slight.¹⁵ In other words $G_b(\omega)/\omega$ is almost independent of frequency and temperature. Equation (10) gives the measured conductance provided

(a) The static conductance is negligible, i.e., $(R_c + R_d)^{-1} \ll G_b(\omega)$; this is the case when x_i is not too close to the interface or when $R_c \gg R_d$. In the ideal case of an infinite contact resistance R_c , $G_b(\omega)/\omega$ tends to zero as the frequency is reduced below the saturation frequency, ω_s , which can be achieved either by lowering the modulation frequency or by raising the temperature.

(b) The surface states contribution is negligible. We treat the effect of surface states in the next section.

2.3.2 Surface States

The surface states contribution to the measured conductance arises when the frequency approaches the saturation frequency. It can be measured provided they are not screened by the metal, i.e., R_c and R_{sm} are larger than $R_{ss} + R_d$.

Again, as for the capacitance (see Section 2.2.2), according to whether the rate of change of occupancy of the surface states is controlled by the surface states' kinetic interaction with free surface electrons or by the transport of these electrons in the depletion region, the surface states' contribution to the barrier conductance is given by²¹

$$G_{ps}(\omega) = \frac{qN_{ss}}{2\tau_s} \ln(1 + \omega^2 \tau_s^2) \quad (11)$$

where $G_{ps}(\omega)$ is the conductance component of the parallel circuit equivalent to C_{ss} in series with R_{ss} (C_{ss} and R_{ss} depending both on frequency),

or by

$$G_{ps}(\omega) = \frac{R_d C_{ss}^2 \omega^2}{1 + (R_d C_{ss} \omega)^2} \quad (12)$$

respectively. In the latter case $G_{ps}(\omega)$ is simply the conductance component of the parallel circuit equivalent to C_{ss} ($= qN_{ss}$) in series with R_d . C_{ss} is independent of frequency in this case.

In both cases $G_{ps}(\omega)/\omega$ plotted versus ω exhibits a maximum for ω equal to $1.98/\tau_s$,²¹ and $1/R_d C_{ss}$, respectively. If ω is kept constant, $G_{ps}(\omega)$ plotted versus τ_s or $R_d C_{ss}$ exhibits a maximum when $\tau_s = 1.98/\omega$ or $R_d C_{ss} = 1/\omega$, respectively. Varying τ_s or $R_d C_{ss}$ occurs when varying the temperature (τ_s and R_d are decreasing functions of the temperature) or applying a dc voltage across the device; indeed, an applied reversed dc bias, for example, leads to an increase of τ_s and R_d by lowering the density of free electrons. In other words, the plot of $G_{ps}(\omega)$ versus temperature or bias, for a given frequency, exhibits a maximum.

We must conclude that surface states, in contrast to bulk states, lead to observable structure in the measured conductance G_m plotted versus temperature or applied dc bias as well as in $G_m(\omega)/\omega$ plotted versus frequency, even though they are uniformly distributed in energy. The exact expression of G_m will be derived in the experimental section (Section 4.2.2). Bulk states can lead to observable structure only if there is structure in their distribution in energy.

Summarizing Section 2, conductance and capacitance measurements on both Schottky and MIS diodes can provide reliable information about the density of gap states in the bulk provided that the modulation frequency is high enough and the temperature is low enough to avoid any observable contribution from surface states. Below the saturation frequency this contribution will be partially screened in Schottky diodes, and fully observable only in MIS devices. Therefore an unambiguous study of surface states is likely to be achieved only with the MIS structure.

3. EXPERIMENTAL DETAILS

Schottky barriers were formed by the evaporation of Pt contacts from a resistance source on to sputtered a-Si:H films. The a-Si:H was sputtered on to a temperature-controlled substrate platform in an atmosphere of argon and hydrogen. Sputtering details appear elsewhere.²³ The ohmic back contact was made with Nichrome, sometimes enhanced with an additional unhydrogenated 100 nm a-Si layer sputtered on top of it. The a-Si:H surface was etched in buffered H.F and rinsed in methanol immediately prior to the evaporation of the Pt contact for Schottky devices. No etching was done for MIS tunnel diodes; the insulating layer between the semiconductor and the Pt was thermally grown, prior to the metal evaporation, by heating the sample in air for 3 hours at 300°C. As we shall see, no appreciable change in the bulk D.O.S. of the materials studied in this paper is induced following the thermal treatment.

Measurements of capacitance and conductance were made using the inphase and quadrature components from a PAR 126 lock-in amplifier. Modulation voltage remained below 12 mV rms. During the measurements the samples were kept under vacuum in a cryostat.

The results reported in this paper concern three different materials prepared under different conditions. The three types of films were chosen to span the range of bulk state densities we typically find in our sputtered material. Nevertheless the reader should not conclude that there is a direct relation between the preparation conditions summarized in Table I and the D.O.S. listed later in this paper (see Table III). Other parameters, like impurity content, are relevant to the magnitude of the D.O.S. A paper on this topic is under preparation and will be published shortly. The samples will be referred to by their number (#1, 2 and 3). We measured the electrical characteristics (transport, capacitance, conductance) of each film with both Schottky and MIS contacts.

4. EXPERIMENTAL RESULTS

4.1 Schottky Diode

The barrier height ϕ_B of the Schottky diode, the free electron transport thermal activation energy E_O of the neutral bulk and the built-in potential V_{bi} of the devices were determined as described in reference 15. Table II displays the results.

4.1.1 Capacitance

Figure 3 shows (circles) the temperature dependence of the three Schottky diodes capacitance measured at 2Hz between room temperature and 160 C. In the three cases the capacitance C_m exhibits a regular increase with temperature until a plateau is reached. This increase results from the ability of progressively more states located around the Fermi level, i.e. located deeper in the gap or closer to the interface, to follow the 2Hz modulation. At room temperature essentially none of the states in devices #2 and 3 is able to follow the modulation, because of the large resistivity of the material (large E_O); ω_O is less than 2Hz (see Section 2.2.1) and the measured capacitance is the interelectrode capacitance. At the other extreme, because of its low E_O , the measured capacitance of sample #1 at room temperature involves the contribution of bulk states in the depletion region and ω_O is larger than 2Hz.

The plateau is reached at temperatures for which the saturation frequency becomes larger than 2Hz. All the Fermi level states then follow the modulation. Nevertheless, as it was shown in the theoretical section (§2.2), the measured capacitance does not necessarily reflect the contribution of all the states, because, in the case of a Schottky diode, the

metal is likely to partly screen surface states and bulk states located close to the surface. If such a screening did not take place, we should not observe any frequency dependence of the plateau capacitance; we observe just the opposite. Figure 4 shows $C_m(T)$ curves of sample #3 at 2Hz and 15 Hz. Besides the expected shift to higher temperature of the characteristics at a higher frequency, we note a reduction of the plateau capacitance. This behavior indicates that the contact resistance is lower than or at most of the same order as the depletion resistance, i.e., the screening effect of the metal is observable. This effect probably accounts for the slight decrease in the capacitance of device #2 above 110°C in Figure 3. Therefore, the plateau capacitance which underestimates the overall contribution of bulk and surface states, is not, *a priori*, a reliable parameter for the determination of bulk states or of surface states. It is then advisable to "stay away" from the surface to avoid both the mixing of bulk and surface states and the screening effect of the metal. This can be achieved by lowering the temperature or raising the modulation frequency, and the *bulk* state density is derived from a fitting to the temperature dependence or the frequency dependence of the device capacitance. It has been shown that the D.O.S. distribution between the bulk and surface Fermi level can be considered as approximately constant.^{6,15} We will assume this is true in our samples; the good agreement between experimental results and the theoretical analysis based on this assumption will confirm *a posteriori* its validity. Therefore the expression (1) of the bulk state capacitance can be used for modeling its frequency and temperature behavior. However, the frequency dependence modeling requires the determination of two unknown parameters, L_0 and ω_0 , and the adjustment of V_{bi} which is determined approximately from transport measurements (see the beginning of Section 4.1).

The temperature dependence fitting, on the other hand, requires the adjustment of an additional parameter, E_0 , ω_0 being a function of temperature and proportional to $\exp(-E_0/kT)$. Therefore, the frequency dependence modeling yields a more precise estimate of L_0 , i.e., of the bulk D.O.S. The precision of the determination has been discussed previously.¹⁵

Figure 5 shows the experimental frequency dependence of Schottky device #3 measured at 130°C and the corresponding theoretical curve obtained by choosing the following values of the parameters: $|V_{bi}| = 210$ mV,

$\omega_0 = 150$ Hz and $\epsilon/L_0 = 27$ n F cm⁻², which corresponds to a bulk D.O.S.

$N_0 = 5.7 \times 10^{15}$ cm⁻³ eV⁻¹ as deduced from equation (2) and taking

$\epsilon = 8.1 \times 10^{-13}$ F cm⁻¹ as derived from the measured interelectrode capacitance

and thickness of the sample. The plateau capacitance C_0 is smaller than the above estimated value of ϵ/L_0 ; in other words, if there are any surface

states, they are substantially screened by the metal which also partially

screens bulk states close to the surface. From the plateau capacitance C_0

and neglecting surface states, we estimate a bulk D.O.S. of 3.3×10^{15} cm⁻³ eV⁻¹.

The estimated D.O.S. (between the bulk and surface Fermi levels) from the plateau capacitance and from the frequency dependence of the capacitance

are given in the two first columns of Table III for the three samples. In

all three cases the plateau capacitance leads to a slight underestimation of the D.O.S. and no surface state contribution is observed. However, the

Schottky diode plateau capacitance, i.e., the saturation frequency capacitance provides a reasonably accurate estimate of the bulk D.O.S. The

assumption of a relatively constant D.O.S. between the bulk and surface

Fermi level positions in the three samples is verified *a posteriori* from a fitting of the capacitance frequency dependence based on this assumption.

This is further confirmed by the lack of sharp variation in the temperature dependence of the capacitance; the range of temperature where the capacitance *gradually* increases is consistent with the built-in potential V_{bi} of the

device. Indeed, as expected from equation (3) (with $\omega_0 \sim \exp(E_F - E_C)/kT$), the larger V_{bi} , the wider this range is.

4.1.2 Conductance

Figures 6 and 7 show the conductance G_m temperature dependence of Schottky diodes #1 and 2 measured at 2Hz. On the same figures (dashed lines, circles) the temperature dependence of the static conductance G_{st} is plotted, derived from the slope at zero bias of the dc current-voltage characteristics of the devices. In addition, on Figure 7 is drawn the temperature dependence of the neutral bulk conductance G_{nb} of the sample (dashed line, triangles), derived from the slope of the $I(V)$ characteristic of the diode in the linear region (under 1V forward bias). Let us first examine sample #2.

At room temperature none of the states is able to follow the modulation at 2Hz. Therefore the depletion resistance is entirely shunted by the bulk state capacitance in the depletion region so that the measured conductance is simply the neutral bulk conductance up to about 40°C and exhibits exactly the same temperature dependence as the neutral bulk conductance. Above 40°C, the measured conductance levels off which indicates that bulk states in the depletion region near the neutral bulk boundary ($x=W$) begin to follow the modulation. The measured conductance is then slightly dependent on temperature as expected from equation (10), applicable in the range of temperature corresponding to the sweeping by x_i of the depletion width. When x_i reaches the surface, i.e., when the saturation frequency becomes larger than 2Hz, the measured conductance is simply the static conductance. The neutral bulk and static conductance characteristics are asymptotic curves for the measured conductance temperature characteristic. In case of sample #1, states in the depletion region already respond at room temperature and the measured conductance lies in the plateau region which is better defined than for sample #2, the built-in potential being larger. Therefore,

the asymptotic curves are farther apart. In fact, at room temperature the neutral bulk conductance is more than two orders of magnitude larger than the measured conductance at 2Hz, which is itself larger than the static conductance by at least two orders of magnitude. Coming back to sample #2 and comparing $C_m(T)$ and $G_m(T)$ curves (Figures 3 and 7), it is clear that the capacitance begins to increase when $G_m(T)$ reaches the plateau and that the $C_m(T)$ saturates when $G_m(T)$ begins to rise sharply. In the range of temperature corresponding to the plateau of $G_m(T)$, the depletion region bulk states respond progressively to the 2Hz modulation. This behavior appears even more clearly in sample #3, whose $C_m(T)$ and $G_m(T)$ curves at 15 Hz are shown in Figure 8. Again, the static conductance (circles) and the neutral bulk conductance (triangles) are plotted (dashed lines). The latter, derived as described above under 1V forward bias is slightly larger than expected from $G_m(T)$ curve at 15 Hz for temperatures less than 70°C (before the plateau). It is likely that a slight injection of free carriers increases the bulk conductance in forward bias.

In Figure 9 $G_m(\omega)/\omega$ is plotted versus ω at 130°C for sample #3. Its shape is very similar to the $G_m(T)$ curve; it exhibits a plateau as expected from relation (10) in the intermediate range of frequencies corresponding to the response of the depletion region bulk states. At low and high frequencies, it asymptotes to the curves G_{st}/ω and G_{nb}/ω (dashed lines), respectively.

The assumption of a roughly constant D.O.S. between the bulk and surface Fermi level is confirmed by the lack of any structure in the plateau region for both $G_m(T)$ and $G_m(\omega)/\omega$ curves. Using relation (10) and the measured conductance in the plateau region, the density of bulk states can be derived.¹⁵ The results are given in the third column of Table III, p.18.

The conductance derived bulk state density is systematically larger than the capacitance derived density. But the obtained results are consistent for each sample within a factor of three, although the range of measured densities of bulk states spreads over almost two orders of magnitude. The fact that the lowest estimate is derived from the plateau capacitance has to be accounted for by the screening effect of the metal.

We have shown in a previous publication¹⁵ that the kinetics of the occupancy of bulk states is not limited by states' collection or emission of free electrons but rather by the transport of these electrons in the depletion region, which entitles us to use the simplified version of the equivalent electrical circuit in Figure 2. Similarly, the flow of carriers across the junction is not limited by their collection by the metal but by their transport in the depletion region, which is equivalent to saying that the contact conductance $G_c (= 1/R_c)$ is larger than the depletion conductance $G_d (= 1/R_d)$. Indeed, Figures 6, 7 and 9 show that the measured conductance asymptotes to the static conductance in the high temperature range by increasing continuously. If G_c were smaller than G_d , the measured conductance G_m should decrease to G_c , as G_m is roughly equal to G_d when the temperature corresponding to the saturation frequency is reached. (Let us recall that, in the plateau region of the conductance, G_m is roughly equal to the conductance of the part of the depletion region in which states follow the modulation). This result confirms our interpretation of the behavior of the plateau capacitance at high temperature and the screening effect of the metal (see Section 4.1.1). It is direct evidence that the transport in Schottky diodes on a-Si:H is described by diffusion theory rather than by thermionic theory. It is therefore not possible to derive the D.O.S. distribution in a-Si:H from capacitance-voltage characteristics

of Schottky diodes, as this derivation requires the transport to be described by thermionic theory, i.e., the quasi-Fermi level of electrons to remain flat throughout the depletion region under the applied dc bias.¹⁹

4.2 MIS Tunnel Diode

4.2.1 Capacitance

Also shown in Figure 3 (triangles) is the temperature dependence of the capacitance of the three MIS diodes measured at 2Hz. In the three cases the capacitance is very close to the corresponding Schottky diode capacitance (circles), up to a certain temperature beyond which it increases sharply before reaching a new plateau at higher temperature. In strong contrast to Schottky diodes, the plateau capacitances of the three MIS devices are very close to one another.

The observed additional capacitance may be attributed either to the contribution of bulk states located around the Fermi level and close to the surface or to surface states. In both cases the presence of the insulating layer enhances their contribution, as was shown in Section 2.2.

The first possibility can be easily ruled out. First, it is unlikely that for the three samples, whose D.O.S. around the bulk Fermi level are very different in the major part of the depletion region, the D.O.S. around the Fermi level close to the surface turns out to be nearly the same (approximately the same plateau capacitance). Second, these bulk states might be expected to be located below the minimum D.O.S. in a region where the D.O.S. rapidly increases toward the valence band as revealed by the sharp increase of the capacitance with temperature. If this were so, the measured capacitance should decrease under an externally applied dc forward bias, as the surface electron quasi-Fermi level of the semiconductor is shifted

away from the valence band, i.e., from the region of high bulk D.O.S. We observe just the opposite, as shown in Figure 10, where capacitance-voltage characteristics of sample #2 are plotted for various temperatures and frequencies. The capacitance always increases versus applied voltage until it saturates for $V > 0.5$ V. Therefore in this range of temperatures, the measured capacitance results mainly from interface states, whose density increases when approaching the conduction band.

It can be observed in Figure 10 that the variation from one curve to another in the measured capacitance is less than 10% at forward biases, for the curves at 132°C, 2Hz and 4Hz and at 154°C, 15Hz. This indicates that the measured capacitance in these ranges of temperatures, frequencies and dc voltages is the saturation frequency capacitance. As will be shown in the next Section (4.2.2), this is confirmed by conductance measurements. As the surface states contribution is dominant (particularly in Samples #2 and #3), the measured capacitance C_m is approximately the surface states capacitance C_{ss} in series with the insulating layer capacitance C_I :

$$C_m = C_{m0} = \frac{C_{ss} C_I}{C_{ss} + C_I} \quad (13)$$

with $C_{ss} = qN_{ss}$.

The saturation observed in $C_m(V)$ characteristics in forward bias corresponds to the insulator capacitance C_I , as $C_{m0} = C_I$ for $C_{ss} \gg C_I$. $C_I \approx 425$ nF cm^{-2} , which leads to an insulator thickness $t_I = 80 \text{ \AA}$, choosing a dielectric constant $\epsilon_I = 4\epsilon_0$ (where ϵ_0 is the vacuum dielectric constant), equal to the dielectric constant for silicon dioxide (SiO_2). This evaluation of t_I is very approximate as the dielectric constant of the thin insulating layer, whose stoichiometry and composition are certainly different from SiO_2 , is not known precisely.

From the value of C_m at $V=0$, one can derive the density of surface states located around the surface Fermi level at equilibrium. We find, using equations (13) and (4)

$$C_{ss} = 1300 \text{ nF cm}^{-2} \quad \text{and} \quad N_{ss} = 8 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1},$$

which is a very large surface state density. It should be possible in theory to derive the D.O.S. distribution above the equilibrium surface Fermi level from $C_m(V)$ characteristic since, as will be shown in the next Section (4.2.2), the thermionic theory is likely to describe the transport of carriers in our MIS tunnel diodes, unlike in the Schottky devices (see Section 4.1.2), i.e., the quasi-Fermi level remains flat throughout the depletion region. However, in forward bias, C_m approaches C_I with increasing bias, and because the surface state capacitance is proportional to $1/(C_m - C_I)$, this leads to an increasing error in the determination of N_{ss} . It is also difficult to determine the precise energy levels of the corresponding states, as one cannot accurately determine the surface Fermi level position, because its relation to the external bias is unclear, due to the screening effect of surface states. In fact, a variation dV of the external bias results in a shift of the surface Fermi level.

$$dE_F = \frac{C_I - C_m}{C_I} dV \quad (14)$$

which cannot be determined precisely for the same above mentioned reasons.

Nevertheless, the equilibrium surface Fermi level is located at approximately the same energy position in the MIS diode and the corresponding Schottky diode made on the same material. Indeed, the temperature

dependence of the capacitance for both devices are very similar, when the surface states' contribution is negligible in the MIS diode. This means that the field distribution in the space charge region and hence the barrier height ϕ_B are very similar in both devices. Furthermore, we deduce that the surface D.O.S. steeply increases with energy above the equilibrium Fermi level, located at $\phi_B \approx 1$ eV below the conduction band edge. For example, at $V = 0.15$ V, which corresponds to a surface Fermi level shift of about $V/5 = 30$ mV (see Equation (14)), the surface D.O.S. is about $1.5 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$; the D.O.S. has almost doubled upon rising 30 mV above the equilibrium surface Fermi level. The $C(V)$ characteristics exhibit a shoulder whose extension to reverse bias decreases if the frequency is increased or the temperature lowered. It reveals a definite leveling off from the sharp reduction in the surface D.O.S. when moving away from the conduction band, below the equilibrium Fermi level E_F . This leveling off is actually stronger than it looks from $C(V)$ curves in the shoulder region, as part of the decrease in the capacitance for decreasing bias is due to the fact that surface states become increasingly unable to follow the modulation. This effect is enhanced in far reverse bias and leads to a sharp drop in the measured capacitance.

4.2.2 Conductance

Figure 11 shows the temperature dependence of the conductance of MIS diode #2 at 2Hz. On the same figure is plotted the $C_m(T)$ curve of the MIS diode (dotted line) and the $G_m(T)$ curve (dashed line) of the corresponding Schottky diode, at the same frequency. Below 90°C, the $G_m(T)$ curves of both devices are very similar. Beyond 90°C, the MIS

$G_m(T)$ characteristic exhibits a peak at 107°C. As was shown in Section 2.3.2 the observed peak is due to surface states. The fact that the conductance of the MIS diode on the low temperature side edge of the peak is very close to the corresponding Schottky diode conductance at the same temperature, demonstrates that the rate of change of the surface states occupancy is not controlled by their kinetic interaction with free surface electrons but instead by the transport of these electrons in the depletion region, i.e. R_{ss} is negligible with respect to R_d . Indeed, in the above mentioned temperature range, the equivalent electrical circuit of the MIS diode is shown in Figure 12. The bulk capacitance contribution is neglected. If we assume that the contact resistance R_c is much larger than R_d and R_{ss} (which will be justified later in this section), the measured conductance is written

$$G_m = \frac{(R_{ss} + R_d) C_{m0}^2 \omega^2}{1 + (R_{ss} + R_d)^2 C_{m0}^2 \omega^2} \quad (15)$$

where

$$C_{m0} = \frac{C_{ss} C_I}{C_{ss} + C_I} \quad \text{with} \quad C_{ss} = qN_{ss}$$

independent of frequency (see Sections 2.2.2 and 2.3.2).

On the low temperature side edge of the conductance peak, $\omega(R_d + R_{ss})C_{m0} \gg 1$ and $G_m \approx 1/(R_d + R_{ss})$. Therefore, if, as observed experimentally, $G_m \approx 1/R_d$, R_{ss} is negligible with respect to R_d . (Remember that in the case of a Schottky diode, the measured conductance is the static conductance i.e., the depletion region conductance, since all the bulk states respond to the modulation, i.e. x_i is at the surface.)

According to (15) the peak in the conductance of the MIS diode versus temperature takes place when (as $R_{ss} \ll R_d$)

$$R_d = \frac{1}{C_{m0} \omega} \quad (16)$$

hence

$$G_{\text{peak}} = \frac{G_d}{2} = \frac{C_{m0} \omega}{2} \quad (17)$$

Furthermore, the measured capacitance is, according to the equivalent circuit of Figure 12,

$$C_m = \frac{C_{m0}}{1 + (R_d C_{m0} \omega)^2} = \frac{C_{m0}}{2} \quad (18)$$

Finally at the temperature of the peak,

$$C_{\text{peak}} = \frac{G_{\text{peak}}}{\omega} = \frac{G_d}{2\omega} = \frac{1}{2} \frac{C_{ss} C_I}{C_{ss} + C_I} \quad (19)$$

Figure 11 shows that the equations (19) are indeed verified within experimental error and in view of the approximations made (R_c and bulk states contributions neglected). Therefore the derivations of the surface D.O.S. around the equilibrium Fermi level from conductance and capacitance measurements are in excellent agreement. When the temperature is raised beyond the peak temperature, G_m decreases until it reaches the static conductance $1/(R_c + R_d) \approx 1/R_c$ (see Figures 11 and 12). The contact resistance is, therefore, much larger than the depletion resistance and controls the transport across the junction. In other words, the thermionic theory applies for the MIS device unlike the Schottky diode. In the previous analysis the contribution of R_{sm} has been neglected. Its contribution may be significant to the static contact resistance which is actually

$$R = \frac{R_C R_{sm}}{R_C + R_{sm}} \quad (\approx R_C \quad \text{if} \quad R_{sm} \gg R_C)$$

However, this does not invalidate the results of the foregoing argument because R is substantially larger than R_d and *a fortiori* than R_{ss} .

The fact that the occupancy of surface states is controlled by electron transport in the depletion region implies that the kinetic interaction between these states and free surface electrons at the conduction band edge, i.e., ϕ_B above the surface Fermi level, is very fast. From conductance data one can derive a lower limit for the capture cross-section σ_n of surface states; at the temperature of the peak we have

$$R_d C_{m0} = \frac{1}{\omega} > R_{ss} C_{m0}$$

Furthermore,

$$\tau_s \approx R_{ss} C_{ss}$$

therefore,

$$\tau_s < \frac{1}{\omega} \frac{C_{ss} + C_I}{C_I};$$

we have also

$$\tau_s = \frac{1}{\sigma_n v_{th} n_s}$$

where

$$n_s = kTN(E_c) \exp\left(-\frac{\phi_B}{kT}\right)$$

is the free electron density at the surface. $N(E_c)$ is the density of bulk states at the conduction band edge.

Finally

$$\sigma_n > \frac{C_I \omega}{C_{ss} + C_I} / (n_s v_{th})$$

If we take the following parameters,

$$T = 107 \text{ C (peak temperature),}$$

$$\omega = 4\pi \text{rads}^{-1} \quad (\text{the } G_m(T) \text{ characteristic was plotted at 2Hz, see Figure 11),}$$

$$kTN(E_c) = 10^{19} \text{ cm}^{-3} \quad (\text{see Ref. 1) ,}$$

$$\phi_B = 1 \text{ eV}$$

$$\frac{C_I}{C_{ss} + C_I} = 0.25$$

we find $\sigma_n > 5 \times 10^{-13} \text{ cm}^2$, which is a very large lower limit, compared to usual surface state capture cross-sections measured in crystalline silicon.²¹ It is, in fact, the same lower limit that we have estimated previously for bulk states.¹⁵ In other words, kinetic properties of bulk and surface states appear to be similar.

As shown in Section 2.3.2 and according to equation (15), $G_m(\omega)/\omega$ plotted as a function of ω for a given temperature also exhibits a peak at $\omega = 1/R_d C_{m0}$. Figure 13 shows $G_m(\omega)/\omega$ versus ω for MIS device #2 plotted at 131 C; on the same figure the $C_m(\omega)$ curve is plotted (dotted line). A well-defined peak is observed at about 50 Hz. Its magnitude and the corresponding measured capacitance are both equal to $C_{m0}/2$ in agreement with equation (19) (within experimental error). Figure 14 shows G_m/ω versus applied voltage, plotted at various temperatures and frequencies.

As expected (see Section 2.3.2) these characteristics exhibit well-defined features due to surface states located around the surface quasi-Fermi level (E_{Fn}) of the semiconductor electrons. The peak is shifted to larger reverse bias, either when the temperature is raised for a given frequency, or when the frequency is lowered for a given temperature. Surface states around E_{Fn} can follow the modulation for biases larger than the peak voltage V_{peak} , but cannot respond for V smaller than V_{peak} ; at V_{peak} , E_{Fn} lies at an energy where states can only partly respond to the modulation. It is noteworthy that at 132°C, 2Hz and 4Hz and at 154°C, 15 Hz, the peaks appear only in reverse bias. Therefore, in forward bias, all the states follow the modulation, which confirms that the capacitance measured in this range of temperature, frequency and voltage is in fact the saturation frequency capacitance (see Section 4.2.1). From the magnitude of the peaks one can estimate the corresponding surface state capacitance using equations (15) and (19). This estimate becomes less reliable at lower frequencies because the static conductance contribution increases for larger reverse biases²⁴ and also becomes relatively more important in the ratio G_m/ω . Such is the case of the characteristic plotted at 2Hz and 132°C.

Also in Figure 14 the $C_m(V)$ characteristic at 4Hz and 132°C is plotted (dotted line). We note that, in agreement with equation (13),

$$\frac{G_m(V_{peak})}{\omega} = C_m(V_{peak}) = \frac{1}{2} \frac{C_I C_{ss}}{C_I + C_{ss}} \approx 150 \text{ nF/cm}^2$$

Therefore $C_{ss} = 1.020 \text{ nF/cm}^2$ and $N_{ss} = 6.2 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$, which is the density of surface states located around E_{Fn} , which has been shifted down from the equilibrium surface Fermi level under the reverse bias V_{peak} (4Hz, 132°C).

The actual position of E_{Fn} can be derived easily from equation (14), as the surface D.O.S. does not vary steeply below the equilibrium surface Fermi level E_F (the measured surface D.O.S. around the equilibrium Fermi level E_F is $8 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$, see Section 4.2.1):

$$E_{Fn} - E_F \approx \frac{\langle C_{m0} \rangle - C_I}{C_I} \cdot V_{\text{peak}} \approx \frac{C_I}{\langle C_{ss} \rangle + C_I} \cdot V_{\text{peak}} \quad (20)$$

where $\langle C_{m0} \rangle$ and $\langle C_{ss} \rangle$ are the average values of C_{m0} and C_{ss} for biases between 0 and reverse voltage V_{peak} ; we find

$$E_{Fn} - E_F \approx \frac{V_{\text{peak}}}{4} \quad (21)$$

Actually this relation applies not only for the peak at 4 Hz and 132°C, but also for the other ones whose magnitudes are very close and hence, whose corresponding D.O.S. are very similar. Therefore, from the observed peaks ranging between 0 and 0.5V, we can verify that the surface D.O.S. is roughly constant within $0.5/4 \approx 0.12\text{V}$ below the surface equilibrium Fermi level and is about $6 - 8 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$.

The surface D.O.S. has been derived independently from both capacitance and conductance measurements. It is also possible to derive the surface D.O.S. simply from the frequency dependence of the peak voltage position at a given temperature, if the D.O.S. does not depend strongly on energy. Indeed, a shift δE_F of the surface Fermi level results in a variation of the depletion resistance by a factor $\exp(-\delta E_F/kT)$, which leads to a variation of the peak frequency by a factor $\exp(\delta E_F/kT)$. Therefore, for two given frequencies, δE_F can be calculated and the peak voltage shift δV_{peak} measured; from (20)

$$\delta E_F = \frac{C_I}{\langle C_{ss} \rangle + C_I} \delta v_{\text{peak}} \quad (22)$$

and one can derive the average surface D.O.S. within the energy range δE_F swept by the Fermi level. For example, between 4Hz and 15Hz, the peak voltage is shifted by $\delta v_{\text{peak}} = 0.18\text{V}$ at 132 C (See Figure 14) and $\delta E_F = kT \ln(15/4) = 0.046\text{V} = \delta v_{\text{peak}}/3.9$. Using (22) we find practically the same surface D.O.S. as the one derived directly from $G_m(V_{\text{peak}})$ and $C_m(V_{\text{peak}})$.

In forward bias the surface Fermi level cannot be moved significantly because of the steep increase in the surface D.O.S. In other words, most of the applied voltage is dropped across the insulator, preventing the observation of peaks in $G_m(V)$ characteristics.

5. DISCUSSION AND CONCLUSION

A general model for the temperature, frequency and voltage dependence of capacitance and conductance of both Schottky and MIS diodes on a-Si:H has been presented in this paper. This model is based on an equivalent electrical circuit of the device, whose applicability has been proven through its ability to support a comprehensive and self-consistent interpretation of our experimental results. It permits an unambiguous distinction to be made between the contributions of bulk and surface states, to determine their respective densities and to analyze their kinetic properties.

It has been shown that the bulk D.O.S. can be determined from capacitance and conductance measurements versus temperature and frequency on both Schottky and MIS devices provided the modulation frequency is larger than the saturation frequency (below which all the states respond to the modulation), which prevents any contribution from surface states. The bulk D.O.S., ranging between $5 \times 10^{15} \text{ cm}^{-3} \text{ eV}^{-1}$ and $3 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ for the samples investigated, does not exhibit strong variations with energy between the neutral bulk Fermi level position (0.65 - 0.9 eV below the conduction band edge) and the surface Fermi level position (1 - 1.1 eV below the conduction band edge) which is to be expected if the minimum in the bulk D.O.S. is located around 0.9 eV below the conduction level. It was demonstrated theoretically and experimentally that capacitance-voltage characteristics of Schottky diode cannot be used to derive the bulk D.O.S. distribution in a-Si:H, even below the saturation frequency, for two reasons: (a) the diffusion theory and not the thermionic theory is appropriate to describe the transport of electrons across the junction, i.e., the electron quasi-Fermi level E_{Fn} does not remain flat under an externally applied voltage, (b) the surface states may contribute to the measured capacitance.

In fact, reason (a) implies that the surface state contribution is at least partially screened by the metal in the Schottky diode as is the case for the contribution from bulk states located close to the interface. It has been shown that the full effect of both these contributions can be observed provided an insulating layer is inserted between the metal and a-Si:H. However, it is difficult to determine whether the experimentally observed surface states in MIS devices existed before the formation by oxidation of the insulator and are simply revealed by its presence in admittance measurements, or whether they are created during the oxidation process. Three independent and consistent determinations of the surface D.O.S. have been derived from the measurement of the conductance peak magnitude, the capacitance and the shift of the conductance peak with frequency in MIS diodes. The measured surface D.O.S. is very high and essentially the same for all the investigated samples, despite the strong differences observed in the bulk D.O.S. It is about $6-8 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$, is roughly uniform in energy within at least 0.12 eV below the surface equilibrium Fermi level and rises steeply above it, exceeding $1.5 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$ within 0.03 eV.

From conductance measurements, it was shown that the kinetics of the occupancy of surface states is controlled by free electron transport in the conduction band and not by the surface states' interaction kinetics with these electrons. In other words, the interaction kinetics of the involved surface states around the Fermi level with conduction band carriers are very fast and imply an effective capture cross-section of free carriers by these states larger than 10^{-13} cm^2 , just as for bulk states. It is therefore likely that the interaction is not direct but takes place via the intermediate continuum of states between the conduction band edge and the

Fermi level. An alternative explanation for such a large effective capture cross-section is that the conductivity activation energy E_G in the neutral bulk or the Schottky diode barrier height ϕ_B at the surface is not the actual distance between the conducting path for electrons or conduction band edge and the Fermi level. The actual distance between the electron conducting path and the bulk (surface) Fermi level might be less than $E_G(\phi_B)$ if, for example, the mobility is activated or if the real conduction band edge/Fermi level distance decreases with temperature.²⁵ If this were so, a reasonable free electron capture cross-section σ_n might be compatible with the kinetics of states controlled by free electron transport. (The lower limit of σ_n being reduced by a factor $\exp(\delta E_G/kT)$, where δE_G is the difference between the apparent conduction band edge derived from E_G or ϕ_B , and the real one.) This would imply, too, a lower actual mobility of carriers (by the same factor) than the one derived ($10^2 - 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) directly from the pre-exponential factor σ_0 ($10^3 - 10^4 \text{ } \Omega^{-1} \text{ cm}^{-1}$)²⁶ of the conductivity, assuming that E_G is the real distance between the conduction band edge and the Fermi level, and would be compatible with the direct evidence given in this paper that the transport across the Schottky junction is controlled by the diffusion of electrons across the depletion region and not by their collection by the metal, i.e., the diffusion theory and not the thermionic theory is appropriate to describe this transport.

Although one does not know whether the observed surface states are due to the thermal oxidation, the large measured density may indicate that no significant field effect is likely to be observed on sputtered a-Si:H in contrast with glow discharge a-Si:H.²⁷

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27. We are presently carrying out similar surface state investigations on glow-discharged a-Si:H using MIS tunnel diodes. Preliminary results give evidence of a significantly smaller density of surface states than on sputtered material.

FIGURE CAPTIONS

- Figure 1. General equivalent electrical Circuit for the MIS device. In the case of Schottky diodes C_I is infinite. Interaction between the states at the Fermi level and the conduction band is illustrated by the arrows in the partial energy band schematic representation below the circuit diagram.
- Figure 2. Simplified version of the electrical equivalent circuit. The kinetic resistances R_i are neglected.
- Figure 3. Capacitance-temperature characteristics of Schottky (circles) and MIS (triangles) diodes plotted at 2Hz.
- Figure 4. Capacitance-temperature characteristics of Schottky diode #3 plotted at 2Hz and 15Hz. Note the shift to higher temperature and the lower saturation capacitance at higher frequency.
- Figure 5. Capacitance of Schottky diode #3 as a function of frequency (at $T=131^\circ\text{C}$): Comparison between experiment and theory.
- Figure 6. Conductance G_m temperature dependence (full line) of Schottky diode #1 at 2Hz. Also plotted is (dashed line, circles) the static conductance G_{st} temperature dependence.
- Figure 7. Conductance G_m temperature dependence (full line) of Schottky diode #2 at 2Hz. Also plotted are the static G_{st} (dashed line, circles) and neutral bulk G_{nb} (dashed line, triangles) conductance temperature dependences.

Figure 8. Conductance G_m and capacitance C_m temperature dependences (full line) of Schottky diode #3 at 15Hz. Also plotted are the static G_{st} (dashed line, circles) and neutral bulk G_{nb} (dashed line, triangles) conductance temperature dependences.

Figure 9. G_m/ω of Schottky diode #3 versus frequency at 130°C. Also plotted are the static (dashed line, circles) and neutral bulk (dashed line, triangles) conductances divided by ω , versus frequency.

Figure 10. Capacitance-voltage characteristics of MIS diode #2 for various temperatures and frequencies.

Frequency (Hz)	15	40	15	4	2
Temperature (°C)	154	132	132	132	132
Symbol	+	□	o	x	Δ

Figure 11. G_m/ω of MIS tunnel diode #2 plotted at 2Hz versus temperature (full line). Also plotted are the MIS diode capacitance at 2Hz (dotted line) and G_m/ω of the corresponding Schottky diode #2 (dashed line).

Figure 12. Simplified equivalent circuit of the MIS diode: the bulk state contribution and R_{ss} are neglected.

Figure 13. G_m/ω and C_m of MIS diode #2 plotted at 131 C versus frequency.

Figure 14. G_m/ω -voltage characteristics of MIS diode #2 for various temperatures and frequencies (full line). Also plotted (dotted line) the capacitance-voltage characteristic at 4Hz and 132°C.

Frequency (Hz)	15	40	15	4	2
Temperature (°C)	154	132	132	132	132
Symbol	+	□	o	x	Δ

Table I. Preparation Conditions of the samples.

Table II. Electrical parameters of the devices.

TABLE I

Film	Argon Pressure	Hydrogen Pressure	Substrate Temperature	Thickness
1	5 mT	.6 mT	250°C	1 μm
2	5 mT	.4 mT	355°C	1.75 μm
3	5 mT	1.6 mT	275°C	2.95 μm

TABLE II

Schottky Diode	ϕ_B (eV)	E_G (eV)	V_{bi} (V)
1	$1.00 \pm .05$	.63	$.37 \pm .05$
2	$1.02 \pm .05$	.87	$.15 \pm .05$
3	$1.12 \pm .05$	.91	$.21 \pm .05$

TABLE III

Sample	Bulk D.O.S. ($\text{cm}^{-3} \text{eV}^{-1}$) N_0 between the bulk and surface Fermi levels from:		
	Plateau Capacitance	Capacitance Frequency Dependence	Plateau Conductance
1	1.4×10^{17}	3.4×10^{17}	4.1×10^{17}
2	3.0×10^{16}	4.0×10^{16}	10^{17}
3	3.3×10^{15}	5.7×10^{15}	9.0×10^{15}

Figure 1.

Figure 2.

Figure 3.

Figure 4

Figure 5.

Figure 6

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

Figure 14.

APPENDIX 3

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THE INFLUENCE OF STRUCTURAL INHOMOGENEITY ON THE CONDUCTION BAND TRANSPORT IN a-Si:H ALLOYS

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We present new data on conductivity and thermopower for rf sputtered a-Si:H having low gap state density and low H-content. The band transport is characterized by $E_s = E_g$, $\sigma_0 \sim 5 \times 10^3 \Omega^{-1} \text{cm}^{-1}$, $S_0 = -kA/|e| = 0 \text{ mV/K}$ and no high temperature kinks. Data showing $E_s < E_g$, $S_0 \sim -0.5 \text{ mV/K}$ and kinks in both σ and S are interpreted in terms of a two-phase model of a-Si:H islands with a H-rich connective tissue. The implications of the large value of σ_0 in both types of sample are also considered.

I. Introduction

Transport measurements on a-Si:H, howsoever prepared, have always been interpreted assuming the material is structurally homogeneous although disordered. This has occurred despite evidence of structural inhomogeneity in early studies of evaporated unhydrogenated material, and despite common knowledge that many films nucleated and grew in a manner leading to gross and easily observable inhomogeneities. Recently, Knights and Lujan [1] have pointed out that many films produced by glow discharge possess microstructure on a scale of about 100 Å which is even observable as columns stretching over 1 micron from substrate interface to the free surface. They have also attempted to identify the chemical and structural differences between the columnar material and the intercolumnar tissue, and to correlate these with differences in measured properties. However, the full implications of heterogeneity for the interpretation of transport data have not been explored.

There is an impressive agreement of published experimental results on transport in a-Si:H films prepared under a wide variety of conditions, suggesting that several observations which, at first sight, seem not to accord with current theory are not artifacts of the preparation method or the measurement procedure. Attempts to explain these observations have met with only limited success under rather strained assumptions and only when a subset of the totality of results is considered.

In Section II we survey the principal experimental results which appear to be general, and present pertinent new data. In Section III we suggest that most films studied are structurally inhomogeneous and examine to what extent a model based on film heterogeneity can account for apparent anomalies.

II. Theory of Diffusive Transport and the Experimental Results

We confine our attention to temperatures T where the experimental

conductivity σ and thermopower S may be described by

$$\sigma = \sigma_0 \exp[-E_0/kT] \quad \text{and} \quad S = [E_s/eT] + S_0. \quad (1)$$

The transport is assumed to occur in a conduction band of delocalized states of density N , independent of energy above E_c . If we suppose that the Fermi level E_f displaces linearly with T as $E_c - E_f = (E_c - E_f)_0 + \gamma T$, and that the mobility μ and thermopower S are given by formulae for diffusive transport derived in the random phase approximation [2], then the theoretical σ and S may be written as

$$\sigma = ne\mu = ne(a/kT) = eNa \exp(-\gamma/k) \exp[-(E_c - E_f)_0/kT], \quad (2)$$

$$S = (k/e) [(E_c - E_f)/kT] + A = [(E_c - E_f)_0/eT] + (Ak/e). \quad (3)$$

Here a is a T -independent constant, $A \approx 1$, and we identify E_0 and E_s with $(E_c - E_f)_0$, σ_0 with $eNa \exp(-\gamma/k)$ and S_0 with (Ak/e) . For $N = 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$, $T = 300 \text{ K}$, and plausible choices of other parameters, we calculate $\mu \approx 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $S_0 \approx 0.1 \text{ (mV-K}^{-1})$ and $\sigma_0 \approx 40 \text{ exp}(-\gamma/k) \text{ (ohm-cm)}^{-1}$.

Figure (1) shows our typical data for σ and S for undoped a-Si:H of high H-content ($>10 \text{ at.}\%$), prepared at low substrate temperatures T_s (200°C), and partial pressures p_H greater than 1 mTorr (Samples Type α). We exclude consideration for the moment of the data below $10^3/T = 2.2$ ($T \geq 440 \text{ K}$) and all data on doped material. Extrapolation of the data to $1/T = 0$ gives $\sigma_0 = 5.6 \times 10^3 \text{ (ohm-cm)}^{-1}$ and $S_0 = -0.59 \text{ mV-K}^{-1}$. These values of σ_0 and S_0 characterize our samples thus-prepared and, significantly, are also typical of those for glow-discharge produced material.

Figure 1 σ and S data for Sample Type α (large c_H) and Type β (small c_H). In the expanded high T region of the inset, the data for Type α show a clear kink not present for those of Type β .

The disagreements between theory and experiment may now be identified. (1) Since $\sigma_0(\text{exp}) = 6 \times 10^3 (\text{ohm-cm})^{-1} = 40 \exp(-\gamma/k)$, a high value of $\gamma = -4.3 \times 10^{-4} \text{ eV } ^\circ\text{K}^{-1}$ is required to reconcile theory with experiment. While there are insufficient data to discount this value, it appears implausible that it should be consistently high in many sample preparations. (2) Figure (1) and other reports in the literature yield $E_0 - E_s$ finite, between 0.1 and 0.2 eV. (3) Figures (1) and (2) illustrate clearly a decrease in the slopes of σ vs $1/T$ and S vs $1/T$ for $10^3/T \leq 2.2 \text{ K}^{-1}$. Similar data have been reported earlier on sputtered a-Ge:H and SiH_4 -derived a-Si:H [3]. These kinks, always observed for Samples Type α , the high values of σ_0 and S_0 , and the finite $E_0 - E_s$ are therefore real properties of many samples, independent of measurement system, electrode geometry or material, method of preparation or laboratory of origin.

The detailed deposition parameters, as much as the final H-content, determine the transport in all a-Si:H. We now discuss a new regime of our preparation not previously reported. Type β films have low H-content (3-10 at.%), and are prepared at low p_H and high T_s ($\geq 300^\circ\text{C}$). All Type β samples, with typical results illustrated in Fig. (1), have σ_0 consistently near $5 \times 10^3 (\text{ohm-cm})^{-1}$, $S_0 \approx 0 \text{ mV } ^\circ\text{K}^{-1}$, and $E_s = E_0$ within experimental error. The simplest interpretation is that the transport is single-band, with no activation energy for mobility, and $A \approx 1$ as predicted by all simple transport mechanisms. Because of the similarities in σ_0 and E_0 for Sample Type β and Sample Type α below the kink, we identify the transport in Type α for $10^3/T \geq 2.2$ as band transport also.

III. Discussion of Structural Inhomogeneity

We now focus on the likelihood that many a-Si:H films are structurally inhomogeneous on a scale of $\sim 100 \text{ \AA}$. When T_s is high ($\sim 350^\circ\text{C}$) and p_H is low ($< 1 \text{ mTorr}$), isolated H atoms are postulated to compensate dangling Si bonds and reduce the incidence of long Si-Si bonds. These compensating effects dominate the potential for the increased defect production when the network is forced to grow around the growth termination at a Si-H site. Thus, the film nucleates and grows in islands which successfully knit together with a minimum volume of defected connective tissue. However, when p_H is increased beyond 1 mTorr at any T , the increased creation of network defects near Si-H sites and the increased concentration of multiply bonded SiH_x complexes makes it difficult for growing nuclei to coalesce. The result is essentially a second phase of highly defected, probably H-rich connective tissue with, importantly, a different band structure and conductivity. This model clearly resembles Knights' work [1] on the growth morphology of silane-derived a-Si:H prepared at different T_s . Although we have no evidence from S.E.M. measurements on Type α and β films of columnar growth, we believe the existence of two interlinked phases to be very likely, and have analyzed the changes in transport with p_H on this basis [4]. Here we focus discussion on the anomalies already described.

We refer for convenience to the island material as phase 1 and the connective tissue as phase 2. It seems reasonable that the transport in both is activated, with a different activation energy; guided by experiment, we suppose phase 2 to have the lower activation energy, but that $|\sigma_1| \approx |\sigma_2|$ near $(10^3/T) = 2.2$. For a heterogeneous mixture of the two phases, with neither forming a continuous channel between the electrodes, the conductance will be governed by the phase of lower conductivity, and measured σ vs $1/T$ with downward kinks like those of Fig. (1) will eventuate. Of course, the relative volumes of

the two phases matter, but the rapid variations of σ_1 and σ_2 with T probably ensure that the kinks in σ vs $1/T$ will all occur near the same T . Although we expect this model for σ to be borne out by percolation calculations, it is not clear what the behavior of S will be. We suppose that the far smaller range in magnitude of S with $1/T$ means that both phases contribute to $S(\text{measured})$, and that this both reduces the apparent slope E_g and increases the extrapolated $|S_0|$.

We conclude that the data for $10^3/T > 2.2$ in Figs. (1) and (2) represent transport in the conduction band of a-Si. The linear $\log \sigma$ vs $1/T$ over six orders of magnitude, the equality of E_g and E_s and the magnitude of σ_0 of $5 \times 10^3 (\text{ohm-cm})^{-1}$ all suggest band transport with no mobility activation energy at a sharp density of states edge and no contribution from tail-state hopping. The deduced value of mobility (order of $10^2 \text{cm}^2 \text{V}^{-1} \text{S}^{-1}$) is high even when a plausible value for γ is chosen, and is more appropriate for quasi-free particle motion with occasional scattering than for transport at a mobility edge. Additional experimental and theoretical work is required to reconcile this conclusion with the absence of a Hall effect in undoped homogeneous samples at high T [4].

In summary, many of the apparent anomalies in the transport data for tetrahedral amorphous solids may be accounted for by considering the effects of film inhomogeneity. Clearly a more quantitative test of our model is necessary, and an attempt to correlate directly the observation of kinks in the transport with the existence of microstructure is now underway.

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AN IMPROVED FIELD EFFECT ANALYSIS FOR THE
DETERMINATION OF PSEUDOGAP STATE DENSITY
IN AMORPHOUS SEMICONDUCTORS

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ABSTRACT

A method is described for determining the gap state density $N(\epsilon)$ of an amorphous semiconductor from field effect data, in which no assumptions are made about the form of the band bending in the semiconductor. The problem is reduced to three successive integrations over an assumed $N(\epsilon)$ by change of variable from depth x to voltage V , and the best fit to the experimental data is obtained by iteration of the assumed state density. The method is shown to be no less rigorous and considerably more economical than the recent analysis of Goodman, Fritzsche and Ozaki (1980). In addition, we demonstrate an experimental means of determining flat-band conditions to an accuracy of $1/2 kT$ of band bending, by finding the value of V_g for which $(kT/e)d \log I_{SD}/dV_g$ is independent of temperature.