Photoionisation cross-sections of interface states in the metal insulator semiconductor structure.

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PHOTIONISATION CROSS-SECTIONS
OF
INTERFACE STATES
IN
THE METAL INSULATOR SEMICONDUCTOR STRUCTURE

by
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# TABLE OF CONTENTS

Certificate of Approval i
Acknowledgements iii
Table of Contents iv
List of Tables vi
List of Figures vii
Notations x

Abstract 1
1. Introduction 2
2. Theory 4
2.1 Occupancy functions and Photocurrents 4
2.2 Dark Capacitance Transients 12
3. Experimental Procedures 14
   3.1.1 Optical Set-up 14
   3.1.2 Calibration and initial set-up 15
   3.1.3 Photocurrent measurements 17
3.2 C-V, G-V frequency dispersion measurements 18
3.3 Barrier Height measurement 19
3.4 Dark Capacitance Transient measurement 20
4. Observations, Analyses and Discussions 21
4.1 Capacitance Dispersion 23
4.2 Steady Photocurrent 25
4.3 Transient Photocurrent 26
4.4 Analysis of the pair generation current 29
4.5 Calculation of the pair generation current 30
5. Conclusions 32
Appendix 33
References 43
Tables 48
Figures 44
Vita 71
<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Methods of Measuring Schottky Barrier Heights extended to MIS diodes.</td>
<td>42</td>
</tr>
<tr>
<td>2.</td>
<td>Measurements on Silicon transparency</td>
<td>43</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

1. Experimental device structure and primary measurements.
2. Energy Band diagram of a MOS tunnel diode.
3. Optical emission and pair generation processes.
5. The Optical setup.
6. Normalised optical intensity vs. wavelength.
7. Effect of stray light on the dark capacitance transient at low temperatures.
8. Schematic of the photocurrent transient experiment.
10. Optical setup and circuit diagram for barrier height measurements.
11. Photocurrent vs. time for different gate bias.
12. Normalised photocurrent peak vs. gate voltage.
15. Capacitance vs. voltage with frequency as the parameter.
16. Steady state photocurrent vs. bias with optical energy as the parameter.
17. Transient photocurrent.
18. Components of the photocurrent transient.
19. Charge released from the interface.
20. $I_{\text{peak}}$ from the interface states.
21. Interface state density vs. trap energy.
22. Dark capacitance transient (log timescale).
23. Dark capacitance transient (linear time scale).
24. Photo-ionisation cross-sections vs. trap energy with photon energy as parameter.
25. Pair generation parameter vs. trap energy.
26. Optical time constant ($\tau$) vs. trap energy.
27. Sum of optical cross-sections vs. trap energy, photon energy as the parameter.
28. Time Constant diagram at 77°K.
29. Time Constant diagram at 300°K.
30. Saturation Photocurrent vs. $h\nu$.
31. Saturation photocurrent vs. temperature at different $h\nu$.
32. Photographs of the devices used in the experiments.
33. Cross-sectional view of a tunnel device.
NOTATIONS

\[a = \frac{(f_m - f)}{T} \quad \text{hole emission by tunnelling to the metal}\]

\[b = \tilde{n}(1-f) \quad \text{electron capture from the conduction band}\]

\[c = (e_n^t + e_n^o)f \quad \text{electron emission to the conduction band}\]

\[d = \tilde{p}f \quad \text{hole capture from the valence band}\]

\[e = (e_p^t + e_p^o)(1-f) \quad \text{hole emission to the valence band}\]

\[C_{HF} \quad \text{high frequency capacitance}\]

\[C_{LF} \quad \text{low frequency capacitance}\]

\[C_{ox} = \frac{\varepsilon_{ox} A}{t_{ox}} \quad \text{oxide capacitance}\]

\[C_{S} = \frac{\varepsilon_s A}{W} \quad \text{depletion layer capacitance}\]

\[d \quad \text{thickness of effective tunneling barrier (Å)}\]

\[D \quad \text{decaying component of AC photocurrent}\]

\[e_n^t = \nu_n e^{(E_t - E_c)/kT} \quad \text{thermal electron emission rate/active trap}\]

\[e_n^o = \phi(t) \sigma_n^o \quad \text{optical electron emission rate/active trap}\]

\[e_p^t = \nu_p e^{(E_v - E_t)/kT} \quad \text{thermal hole emission rate/active trap}\]

\[e_p^o = \phi(t) \sigma_p^o \quad \text{optical hole emission rate/active trap}\]

\[E_c \quad \text{silicon conduction band (eV)}\]

\[E_g \quad \text{silicon band gap (eV)}\]
\[ E_L = E_c - kT \ln n_L \] upper limit of optically controlled region (eV)
\[ E'_L = E_v + kT \ln p_L \] lower limit of optically controlled region (eV)
\[ E_o = \frac{(E_c + E_v)}{2} \] energy where \( e_n^t = e_p^t \)
\[ E_{tn} = E_c - kT \ln n_d \] electron trap Fermi level
\[ E_{tp} = E_v + kT \ln p_d \] hole trap Fermi level
\[ E_v \] silicon valence band (eV)
\[ E = \frac{E_c - kT \ln n}{\omega} \] trap energy where \( e_n^t = \omega \)
\[ E_T \] trap energy (eV)
\[ f \] occupancy function
\[ f_L = \frac{\sigma_n^o \sigma_p^o}{\sigma_p^o + \sigma_n^o} \] trap occupancy function in optically controlled region
\[ f_n \] trap occupancy function in thermal electron emission region
\[ f_m \] occupancy function in metal
\[ f_p \] trap occupancy function in thermal hole emission region
\[ f_T \] trap occupancy function in tunneling controlled region
\[ f_u \] trap occupancy for unmodulated illumination
\[ f_o \] initial trap occupancy
\[ F_s \] semiconductor Fermi level
\[ h\nu \] photon energy (eV)
\[ i_n, i_p \] electron and hole emission currents/trap
\[ i_s \] external short circuit emission current/trap
\[ i_s^{AC} \] AC component of \( i_s \)
\[ \varepsilon_{\text{ox}} \] \quad \text{oxide permittivity}

\[ \varepsilon_s \] \quad \text{semiconductor permittivity}

\[ I_{\text{dec}} \] \quad \text{decaying component of external AC photocurrent}

\[ I_{\text{sat}} \] \quad \text{time-independent component of external AC photocurrent}

\[ I \] \quad \text{maximum value of decaying component}

\[ k \] \quad \text{Boltzmann constant}

\[ M \] \quad \text{modulation factor}

\[ n \] \quad \text{electron density (cm}^3\text{)}

\[ \bar{n} = v_{\text{th}} \sigma_{\text{n}}^n \] \quad \text{electron capture rate/active trap}

\[ v_n = \sigma_n^v v_{\text{th}} N_c \] \quad \text{electron escape frequency}

\[ v_p = \sigma_p^v v_{\text{th}} N_v \] \quad \text{hole escape frequency}

\[ N_D \] \quad \text{donor density (cm}^3\text{)}

\[ D_{\text{it}} \] \quad \text{interface state density (cm}^{-2}\text{eV}^{-1}\text{)}

\[ p \] \quad \text{hole density (cm}^3\text{)}

\[ \bar{p} = v_{\text{th}} \sigma_{\text{p}}^p \] \quad \text{hole capture rate/active trap}

\[ p_s \] \quad \text{hole density at surface (cm}^{-2}\text{)}

\[ q \] \quad \text{magnitude of electron charge (coul)}

\[ Q_{\text{rel}} \] \quad \text{charge released by optical emission}

\[ \psi \] \quad \text{semiconductor potential measured with respect to bulk region}

\[ \sigma_n \] \quad \text{electron photoionization cross section}

\[ \sigma_p \] \quad \text{hole photoionization cross section}

\[ \sigma_{\text{t}}^n, \sigma_{\text{t}}^p \] \quad \text{electron and hole thermal cross sections}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$</td>
<td>time constant</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$t_d$</td>
<td>delay time before starting illumination</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$v_{th}$</td>
<td>thermal velocity (cm/sec)</td>
</tr>
<tr>
<td>$V_f$</td>
<td>final bias voltage</td>
</tr>
<tr>
<td>$V_i$</td>
<td>initial bias voltage</td>
</tr>
<tr>
<td>$V_B, V_G$</td>
<td>bias voltage</td>
</tr>
<tr>
<td>$V_o$</td>
<td>intercept of $1/C^2-V$ plot</td>
</tr>
<tr>
<td>$\omega$</td>
<td>chopping frequency</td>
</tr>
</tbody>
</table>
ABSTRACT

We have studied the photo-ionisation cross-sections of electron and holes at the interface states in the Cr-oxide-silicon structure by measuring the photocurrent transients in both n and p devices. Measurements are reported at different temperatures and incident photon energies. Analysis of data gives the interface state density and the photoionisation cross-sections.

The cross-sections increase monotonically with trap energy in the bandgap, towards the bandedges. A monotonic increase is also observed with increasing photon energy.

We have also measured the dark capacitance transients and the small signal capacitance as a function of gate bias and frequency to determine the interface state density.

All experiments give a U shaped interface state density distribution over the Si bandgap. The interface state density and the cross-sections obtained from the experiments are used to compute the steady-state saturation current as a function of temperature and photon energy. The results show a good agreement between the measured and the calculated values.
1. INTRODUCTION

Extensive research has been directed in the past towards an understanding of the nature and behavior of interface states at the Si-SiO₂. Several techniques and test vehicles for probing these states were developed. But these techniques are primarily limited to electrical measurements on either very thin or very thick oxide MOS structures. Little attention has been paid to the class of devices with oxide thickness in the range 20-50 Å. Gray was the first researcher to report the advantages of using a MOS tunnel diode for measuring the properties of interface states. Subsequently, Kar and Dahlke extracted the interface state parameters using the conductance method.

The first observation of interface state photoemission was by Kamieniecki. More recently Pierret and Roesner and Greve and Dahlke investigated the optical response of these states to different excitations.

The Greve-Dahlke technique involves filling the interface states with majority carriers and then observing the thermal and optical emission of these carriers into the semiconductor bands.

Unfortunately, due to lack of a complete optical characterisation of the interface states, these studies widely differ in their conclusions regarding the density of states and
their optical photo-ionisation cross-sections. Kamieniecki found there are optically active states with a maximum near the midgap and decreasing density towards the band edges, while Greve's results on the density of states have a monotonically increasing trend towards the band edges.

In this work we report for the first time a complete characterisation of interface states. Measurements are made over a wide range of temperatures, oxide thickness, and incident photon energies. Both n and p type MOS devices are examined in detail. Optical emission and pair generation are studied to obtain the density of states, the photo-ionisation cross-sections of captured electrons and holes, and the optical and thermal relaxation time-constants. We present in Chapter II a brief theory of interface occupancy functions and the principles behind the optoelectronic experiments. In Chapter III we describe the details of experiments and their instrumentation. Chapter IV is devoted to observations, interpretation and data analysis. Finally, in Chapter V the major results of this work are summarised.
2. THEORY

In this chapter we present the theory used in analysing the photobemission experiments. The experiment central to the study is illustrated in Fig. 1. The basic test structure is a MOS tunnel diode with oxide thickness between 20 and 50 Å. Transient capacitance and current are recorded as functions of bias, temperature, photon energy and photon flux.

2.1 Occupancy function and Photocurrent.

An accumulating bias applied to the device fills all the interface states. When the bias is switched into deep depletion carriers are emitted into the semiconductor bands either thermally or optically (depending on the dominant process), until a steady state is reached.

The occupancy of the interface states at any given time \( t \) is determined by the following five fundamental emission and capture processes (Fig.2):

- tunneling of carriers into the metal—(a)
- emission of electrons(thermal and optical)—(b)
- emission of holes(thermal and optical)—(c)
- capture of electrons—(d)
- capture of holes—(e)
The rate equation governing the occupancy under the most general conditions has been solved by Greve. His analysis leads to the following expression for the time varying occupancy:

\[ f(t) = f_u + (f_o - f_u(t))e^{-t/\tau} + \frac{i\omega\tau}{1 + j\omega\tau} (f_u - f_L) \frac{e^{i\omega t}}{j\omega \tau L} + (f_o - f_L) \frac{e^{(j\omega - \frac{1}{2})t}}{j\omega \tau L} \]  \hspace{1cm} (1)

- \( f_u \) = final occupancy
- \( f_o \) = initial occupancy
- \( \tau \) = total relaxation time
- \( \omega \) = chopping frequency
- \( f_L \) = light occupancy

The occupancy function has three components:

1. unmodulated decaying (first term)
2. modulated steady (second term)
3. modulated decaying (third term)

For time \( t \ll \tau \), the occupancy oscillates with the chopping frequency around the initial occupancy \( f_o \). With increasing time, the oscillations continue but the average of \( f(t) \) over a few cycles relaxes exponentially from \( f_o \) with a relaxation time \( \tau \). For \( t \gg \tau \), this average reaches the saturation value \( f_u \). This process is shown in Fig.3.
Thus, for smaller times net emission takes place and for times larger than the relaxation time, pair generation occurs. Both of these processes give rise to an external photocurrent. Fig. 4 is an equivalent circuit for an n type device under the experimental conditions. The electron current ($\bar{I}_n$) due to net emission of electrons from the semiconductor is injected into the semiconductor capacitance ($C_s$), while the hole current ($\bar{I}_p$) is injected into the insulator capacitance ($C_{ox}$). The externally measured current ($\bar{I}_s$) is given by:

$$\bar{I}_{\text{measured}} = \bar{I}_S = \frac{C_{ox}}{C_{ox} + C_s} \bar{I}_n + \frac{C_s}{C_{ox} + C_s} \bar{I}_p \approx \bar{I}_n \quad (2a)$$

Since $C_{ox}$ is large compared to the semiconductor depletion layer capacitance the first term in the above expression is dominant. Similarly, for a p-type device

$$\bar{I}_{\text{measured}} = \bar{I}_S = \bar{I}_p \quad (2b)$$

The external photocurrent in both cases is primarily the majority carrier current. Let us calculate this current for a p-type device. In deep depletion, the capture rate of electrons is zero. The current is the net difference of the hole capture rate ($\rho_f$) and the hole emission rate

$$e^{\frac{t}{\tau_p + (1 - f)\rho_f^\circ}}$$
where,

\( e_p^t = \) hole thermal emission rate per active trap
\( e_p^o = \) hole optical emission rate per active trap
\( p = \) hole thermal capture rate/active trap

Substituting for \( f(t) \) in equation 1 we can solve for the external photocurrent. The analysis is done in ref.7 and the final solution is

\[
I_p = q[(\bar{p} - f) - (e_p^t + e_p^o)(1 - f)]
\]

\[
= q[(\bar{p} - \frac{f_u}{\tau}) - (\frac{f^o - f_u}{\tau})e^{-t/\tau} + M_o e^{j\omega t}]
\]

\[
M = [f_u(1-f_L) - \frac{(f_u-f_L)\tau/\tau'}{1 + j\omega \tau}][\sigma^o + \sigma_p^o]
\]

\[
= (f_o-f_u)[1 - f_L - \frac{1}{j\omega \tau'}(\sigma^o + \sigma_p^o)e^{-t/\tau}
\]

where,

\( f_u = \) steady state occupancy
\( f_L = \) light controlled occupancy
\( \phi_o = \) incident photon flux

\( \tau = \) trap total time constant
\( \sigma^o = \) photoionisation cross-section of holes
\( \sigma^o = \) photoionisation cross-section of electrons

\( M = \) modulation factor

This complicated equation needs some explanation. The first term is time independent and represents a direct current due to pair generation process.
The second is the current due to decaying net emission from the traps. Finally, the last sinusoidal term represents the modulated electron current due to chopped illumination. The external photocurrent is therefore,

\[ j \omega t \]

\[ i_s = q \phi e \cdot M \]

The modulation factor M has two components. Its time independent component is caused by processes which result in no net change of occupancy (Figs. 3a, 3b). In Fig. 3a electrons are available for recapture, and we observe a current due to enhanced emission when light is on, followed by recapture when the light is off. Fig. 3b shows pair generation by alternate emission of electrons and holes. The decaying component is due to the relaxation of trap occupancy from initial state \( f_0 \) to a final state \( f_u \). This process is presented in Fig. 3c.

For a continuous distribution of states, \( D(E_\tau) \) the photocurrent is obtained by integrating the contributions from all traps

\[ I_{\text{photo (total)}} = q \phi_0 \int_{E_v}^{E_c} M \cdot dE_\tau \]

(4)

The decaying component of the photocurrent and the charge released are easily calculated as
\[ I_{\text{dec}}(t) = q A \phi_0 \int_{E_L}^{E_{L\text{c}}} D_{\text{it}}(f_o - f_L) \sigma_o^o e^{-\phi_o (\sigma_o^o + \sigma_p^o) t} \, dE_t \]  

(5)

and

\[ Q_{\text{rel}}(t) = q A \int_{E_L}^{E_{L\text{c}}} D_{\text{it}}(f_o - f_L) \frac{\sigma_p^o}{\sigma_p^o + \sigma_n^o} \, dE_t \]  

(6)

In these equations the integration limits are defined by

\[ 1/\tau_L = e_n^F(E_L) \]

\[ 1/\tau_L = e_p^F(E_L) \]

The steady state photocurrent is

\[ I_{\text{sat}}(F_S) = q A \phi_0 \int_{E_V}^{F_S} D_{\text{it}} \sigma_p^o \, dE_t. \]  

(7)

Differentiating eqns.(5),(6),(7) with respect to temperature, interface state density and photoionisation cross-sections are calculated by the following set of expressions:

\[ D_{\text{it}} \big|_{E_t}^{E_t} = -\frac{1}{K \ln \nu_p t_d} \frac{dQ_{\text{rel}}/qA}{dT} \]  

(8)

\[ E_t^{p} = E_v + K T \ln \nu_p t_d \]

\[ D_{\text{it}} \sigma_p^o \big|_{E_t}^{E_t} = -(\frac{1}{q A \phi_0}) \frac{dI_{\text{peak}}}{dT} \bigg|_{t=t_d} x \frac{1}{K \ln \nu_p t_d} \]
\[
\begin{align*}
D_{it}^o|_{E_{tn}} &= - \left( \frac{1}{qA_\phi} \right) \frac{dI_{\text{peak}}}{dT} \bigg|_{t=td} \\
D_{it}|_{E_{tn}} &= - \frac{1}{K\ln\nu n t_d} \frac{dQ_{\text{rel}}/qA}{dT} \\
E_{tn} &= E_c - K\ln\nu n t_d \\
\end{align*}
\]

Here, \( \nu_{n,p} \) is the attempt-to-escape frequency of electrons (holes) and \( t_d \), the time when light is switched on.

Equations (8) and (9) are central to all photocurrent measurements and analyses. Similar relationships hold for n-type devices.

Knowing the optical cross-sections and density of states as functions of trap and photon energies, the saturated value of the photocurrent is evaluated for different temperatures, photon fluxes and photon energies.

We can obtain the optical pair generation current by integrating the simplified form of the modulated factor, over different regions in the energy bandgap. Reference 7 describes the exact solutions applicable for different bias conditions. Since, in this work, the saturation current in deep depletion bias regime is of primary importance, results for this particular case are derived below.
At low temperatures, near midgap the optical timeconstant is the dominant relaxation mechanism and the steady state occupancy is given by the light controlled occupancy,

\[ f_L = \frac{\sigma_n^o}{\sigma_n^o + \sigma_p^o} \]

For \( t \gg \tau \), the modulation factor has a simplified form:

\[ M = \sigma_p^o f_L \]

Integrating over the energy range we get,

\[ I_{\text{sat}} = qA_0 \int_{E_V}^{E_C} (M) D_i \frac{\sigma_p^o \sigma_n^o}{\sigma_n^o + \sigma_p^o} \, dE_t \]

The above expression for \( I_{\text{sat}} \) shows that when \( \sigma_n^o \) or \( \sigma_p^o \) is zero the photocurrent is zero. This condition is always true for photon energy \( h\nu \) less than \( E_g/2 \). This provides a simple check against gross errors during measurements. Photocurrents obtained for \( h\nu < E_g/2 \) is spurious and not caused by interface state photo-emission.
2.2 Dark Capacitance Transients

A change in the occupancy of the interface states causes a change in the device capacitance (C),

\[ \Delta C \propto 1 - e^{-t/\tau} \]  \hspace{1cm} (11)

The capacitance change during emission is entirely due to the change in the interface state charge (neglecting any contribution from bulk states) because there is no inversion layer at the surface. The exact relationship has been derived by Zerost\textsuperscript{3}. Applying that result to interface states gives the interface state density

\[ D_{it} \bigg|_{E_{tn}} = \frac{\epsilon S N_D C_{ox}}{kT} \frac{1}{C^2} \frac{\Delta C}{\Delta \ln t} \]  \hspace{1cm} (12)

The slope of the change in capacitance plotted on a logarithmic scale (in the initial portion of the transient) yields the interface state density. The transient at different temperatures gives the density of states at different energy levels.

Summarising, the initial portion of the photocurrent transient (emission rate) yields information on the photoionisation cross-sections and the density of interface states. We can also use the saturation current to extract the same parameters. Initial portion
of the dark capacitance transient is also suitable for extracting $D_{it}$ as a function of trap energy.
3. EXPERIMENTAL PROCEDURES

In this chapter the experiments to characterise the interface and their instrumentation are discussed in detail. Routine measurements are briefly described and details can be found in ref.12.

3.1 Electro-Optical Measurements

3.1.1 Optical Set-up

A sketch of the optical system used is shown in Fig. 5. The light source, a 45 watt tungsten halogen lamp is imaged on the input slit of a Bosch and Lomb monochromator by a lens placed behind the lamp. The monochromator has a spectral range of 1.4\( \mu \) to 3.2\( \mu \) and a bandpass of 0.075\( \mu \). A silicon interference filter interposed in between the monochromator exit slit and the cryostat window eliminates light of energy greater than bandgap energy. The light is chopped mechanically by a PAR 125A chopper at 340 Hz and focussed on the sample by a fused silica lens.

The device is mounted on a copper block in the cryostat. A copper wire wound on the copper block heats the device and liquid nitrogen pumped through a dewar cools it. A thermocouple monitors the temperature and outputs a voltage proportional to it. The thermocouple and the heater, connected in a PI feedback loop maintain a constant temperature. The overall temperature stability

14
obtained by the arrangement was ± 0.2°C, sufficient for the measurements performed here.

3.1.2 Calibration and initial setup

This phase of the optical experiments involves ensuring that

- the optical intensity reaching the sample is maximised.
- any amount of stray light of energy greater than bandgap energy does not fall on the device (especially the second harmonics passed by the monochromator).
- any stray light does not reach the sample.
- signal/noise ratio is maximised by avoiding ground loops and cross-coupling of the signals.

Calculation of the photoresponse per incident photon requires measurement of the light intensity incident on the device. These measurements were performed using a pyroelectric detector mounted on a micro-manipulator. The short circuit ac current was measured and the photon flux calculated from the incident light intensity (I), using the following conversion formula

\[ \phi = 5.04 \times I \text{ (watts/cm-sec)} \times \lambda \text{ (micron)} \times 10 \]

Fig. 6 is a plot of the normalised intensity incident on the back surface of the device as a function of wavelength. The sharp cutoff around \( \lambda = 1.4 \mu \) is caused by the interference filter. The
second curve in the same figure is the normalised transmitted intensity through a 5-9 Ω cm resistivity wafer. The light transmitted through the bulk silicon material in the experimental device is reduced by the same amount.

The intensity reaching the device depends upon the position of the optical components. These must be properly positioned with respect to the light source.

The output of the monochromator contains second and third order harmonics, which can only be eliminated by using a Si + interference filter combination. A silicon filter alone was not sufficient for this purpose.

Stray light (room light in particular) causes undesirable effects on the response of the devices, especially at low temperatures. It was eliminated by covering the cryostat and the optical set-up with a light sheilding box. The effect of stray room light on the dark capacitance transient is shown in Fig. 7.

The temperature control has a finite regulating range and consequently the liquid nitrogen flow rate must be adjusted to obtain a wide range of temperatures. The required flow rates were:

- 5-7 litres/min for temperatures less than 100°K
- 4 litres/min for temperatures between 110°K to 160°K
2 litres/min for temperatures greater than 160°K

3.1.3 Photocurrent measurements

The basic idea of the photocurrent measurements is to fill the interface states by applying an accumulating bias and then empty them optically after the device is switched into deep depletion. Steady state is obtained after times $t \gg r_L$. Both transient and saturation currents are recorded. The final bias value determines the steady state current and is also recorded as a function of final voltages.

The circuit of Fig.8 is used to measure the photocurrent transient. The boxed area consists of an IEEE-488 controlled HP-85 based, network (details in Fig.9). The HP-85 sends an output pulse through the D/A which is applied to the device. The device is kept in the cryostat at a specific temperature. The ac photocurrent obtained in response to chopped illumination is send to a current sensitive pre-amplifier, with a low impedance input. The output voltage (proportional to the current) is detected by a PAR 121 lock-in amplifier. The DC output voltage of the lock-in amplifier is then fed to the A/D thus completing the cycle.

For steady state photocurrent measurements, a ramp generator applies a slow voltage ramp instead of the pulse to the gate input.
Throughout the measurement the HP-85 monitors each and every phase of the experiment and generates appropriate signals and finally stores the data in the mass storage unit.

3.2 C-V, G-V frequency dispersion measurements

The set-up of figure 9 is used for room temperature small signal capacitance and conductance measurements at different gate bias and ac frequencies. The function generator output (15 mv peak to peak sinusoidal signal) goes to the summing network and the lock-in amplifier reference input. The summing network, consisting of an op-amp circuit, sums the dc bias and the ac signal. This composite signal is then applied to a device kept in a probe station. The LO(gate) terminal of the device is connected to the preamplifier which amplifies the input current. The amplified signal is resolved by a lock-in amplifier into in-phase and quadrature components with respect to the reference input. The lock-in amplifier also provides output signals proportional to the conductance and the capacitance of the device, which are digitised by the A/D and stored on the floppy discs in the mass storage unit.
3.3 Barrier height Measurement

Currents flowing in the external circuit of the MOS capacitor are exponentially related to the barrier height. Hence, the determination of barrier height is essential to the interpretation of these observations. The methods used for measuring barrier heights of Schottky barriers are usually extended to MIS diodes. Some of the methods and their limitations when applied to tunnel diodes are given in Table 1.

A new photo-excitation technique reported by Yun, is simple, accurate, and easy to implement. This technique was utilised to measure the flatband voltage and thereby the barrier height. Infrared light pulses generate excess carriers in the semiconductor space charge region. As a result, current pulses are induced in the external circuit. The current is zero when the applied voltage is equal to the flatband voltage.

The assembly is shown in Fig.10. Since the light energy required in this experiment is greater than the bandgap energy of silicon, filters are not required. Rest of the apparatus is the same as in previous optical experiments.

A peak detector detects the peak of the output current from the preamplifier. This peak is then plotted as a function of time (Fig. 11) as the voltage is swept from accumulation to inversion at a
steady ramp rate. The voltage at which the peak value goes to zero is the flatband voltage (fig. 12).

3.4 Dark Capacitance Transient Measurement

Again we fill the states by applying an accumulating bias and then switching to a deep depletion bias. As the interface states relax towards equilibrium the capacitance of the device changes, and is measured as a function of time.

A "BOONTON 72B" meter measures the capacitance change between its HI and LO terminals. Bias pulses are applied at the external bias terminals of the meter. The analog output of the meter is connected to a 7854 Tektronix Oscilloscope which acquires the fast voltage transient, averages and finally stores it in temporary memory locations. These locations are read serially in "non-real time" through the HPIB interface.
4. OBSERVATIONS, ANALYSIS AND DISCUSSIONS

The data reported in this chapter were obtained from two devices—P37 and N1230. Device N1230 was made on an n-type substrate with an oxide thickness of 1230 Å while device P37 was made on a p-type substrate and has an oxide thickness of 37 Å. Figure 13 shows the I-V characteristic of device P37, taken at room temperature. With the semiconductor biased positively with respect to the metal, the current increases approximately exponentially up to about 0.3 volts. In the reverse direction the current is low and is almost constant over the entire bias range ($V \gg kT/q$). The current in these two regions is similar to the current of a reverse biased p-n junction and limited by the generation-recombination mechanisms in the semiconductor. Above 0.3 volts, the current increases slowly due to an increase in the positive charge in the surface states as the Fermi level sweeps through depletion. The current is now limited by tunneling through the oxide. The series resistance also contributes to the lowering of the slope of the curve. Thus the results fit the qualitative theory developed by Schewshun.

The current density was found to be uniform over several devices of different areas and located in different regions of the wafer. This shows uniformity of the oxide layer over the entire wafer and the absence of pinholes. The saturation obtained in reverse direction is also indicative of a "non-leaky" oxide. The
shape of the I-V curve also shows a high interface state density.  

Devices exhibiting large dc currents are unsuitable for photoexperiments because these large band to band current make detection of the small photocurrent impossible. Large dc currents also increase the shot noise in these devices.

The 1 MHz Mott-Schottky plot of device P37 is shown in Fig.14. The linear behavior in reverse bias indicates a gradual widening of the depletion layer width with reverse voltage. The intercept obtained from this curve is 0.65 volts, which is same as obtained from Yun's method (Fig. 12). The device is at the boundary of depletion-week inversion at zero bias and continues to remain in this state over the entire reverse bias. An analytic expression for the capacitance of tunnel diodes is derived in reference 6. From the expression for $1/C^2$ we see that the intercept is

$$\psi_{\text{inv}} = \frac{2kT}{q} \cdot \ln(N_A/n_i)$$

The measurement of 1 MHz capacitance at different temperatures, produced intercepts on the M-S plot which fit equation (14). The measured doping density from the slope of the $1/C^2$ vs. V curve is consistent with the specified wafer resistivity of 5-9 $\Omega$ cm.

In accumulation degenerate fermi-dirac statistics applies, and
the semiconductor capacitance increases rapidly compared to $e^{Q/\kappa T}$ as a result the capacitance does not saturate in accumulation. In tunnel devices (less than 35 Å thick) the capacitance decreased with an increase in forward voltage. Due to the large currents flowing at these bias points, the capacitance meter was unbalanced, and the output therefore, not proportional to the quadrature component.

4.1 Capacitance dispersion

Figure 15 represents the capacitance-voltage curves at different frequencies. These curves show maximum dispersion around the depletion-weak inversion bias region primarily caused by the high density of states. The hump obtained in the C-V curve increases with decreasing ac frequency. Kar\textsuperscript{15} observed similar effects in a Mg-SiO\textsubscript{2}-p-Si device due to high density of states. The device shows "depletion mode" characteristics at all frequencies.

Interface state density from these curves has been obtained by using the high/low frequency capacitance method. The device capacitance is measured as a function of gate bias at two different frequencies:

1. low enough for immediate response of the interface states to the changing ac signal

2. high enough so that interface states donot respond to the ac signal.
The interface states will contribute to the capacitance of the device, only in the low frequency measurement.

\[
C = \left( \frac{1}{C_{it}} - \frac{1}{C_{ox}} \right)^{-1} \left( \frac{1}{C_{HF}} - \frac{1}{C_{LF}} \right)^{-1}
\] (15)

\(C_{it}\) = interface state capacitance.
\(C_{ox}\) = oxide capacitance.
\(C_{LF}\) = low frequency capacitance (100Hz).
\(C_{HF}\) = high frequency capacitance (1 MHz).

The advantage of this method is that it requires no theoretical C-V curve. A slight complication in applying the capacitance dispersion approach to calculate interface state density is the possibility of errors in accumulation and inversion. Near inversion the high frequency C-V curve does not incorporate the minority carrier response, while near accumulation a "true" high frequency curve is not obtained due to the decreased carrier response time and the high dc currents flowing through the device.

Furthermore, to relate the state density, \(D_{it}\) to energy \(E_t\) in the bandgap, the surface potential \(\psi_s\) has to be determined accurately. The following formulae were used to obtain \(\psi_s\) vs. \(E_t\) from \(\psi_s\) vs. \(V_G\) curve.\(^1\)

\[
\psi_s = \psi_{so} + \int (1 - \frac{C_{LF}}{C_{ox}}) \, dV_G
\] (16)
Any error in the integration constant leads to a translation of the $D_{lt}$ curve in energy.

4.2 Steady Photocurrent

The device is illuminated with optical energy less than $E_g$. A ramp voltage with a ramp rate less than the optical relaxation rate $(1/r)$ is used as the bias source. Typical results are shown in Fig. 16. These curves are representative of all n-type devices and similar to those obtained by Greve. The photocurrent is zero in accumulation and then rises to a maximum $I_{peak}$ and decreases to a constant value in deep depletion. $I_{peak}$ decreases monotonically with increasing temperature for constant $h\nu$ and decreasing $h\nu$ for constant $T$.

In p-type tunnel devices, the surface is in weak inversion at zero bias. To sweep from zero bias towards accumulation, a large applied voltage is needed, causing an enormous band to band tunnel current to flow through the device. The band to band current masks the small pair generation current from the interface states. For reverse bias the steady photocurrent is constant with bias and shows temperature and $h\nu$ variations like their n-type counterparts.

For thick oxide devices, the capture rate of minority carriers
is not negligible and analysis becomes complicated. In view of these facts the calculation of interface state density using steady state photocurrents was abandoned.

4.3 Transient Photocurrent

In this section the time dependent photocurrents are discussed. Fig. 17 shows data obtained on device P37. Initially, the device was biased in accumulation and then switched into deep depletion. Light was switched on after a typical optical relaxation time $\tau_L$ (~13 sec for the intensity used). The resulting transient was recorded for more than 200 seconds. Fig. 18 shows the main components of the photocurrent transient. As derived earlier in Chapter 2, the photocurrent reaches a maximum value immediately after switching on the light, and then decays to its saturation value $I_{sat}$.

The peak component ($I_{peak}$) and the saturation value ($I_{sat}$) both yield information on the interface state density and the optical cross-sections. The transient part was analysed to obtain $D_{it}$, $\sigma_n^0$, and $\sigma_p^0$. These values and their analytical expressions (derived earlier in Chapter II) were used to calculate the saturation current at different temperatures and for different optical energies. The usefulness of such parameters in modeling the tunnel oxide devices is apparent from the excellent fit obtained between the calculated and the experimental values.
$Q_{\text{rel}}$ and $I_{\text{peak}}$ are shown as function of time and optical energy in Figs. 19, 20. These curves are similar to results reported by Greve. The trap parameters were evaluated using equations 8 and 9.

An error is involved in the differentiation of the current and charge with respect to temperature. To smooth data points, a nine point smoothing algorithm was used. Non linear least square method was used to fit a curve through these data points. Differentiation with respect to temperature was done numerically.

Another source of error in the evaluation of charge released, is the final value of time used in integration. This error is large at low photon energies ($h \nu - E_g/2$) where $\tau_L$ is of the order of 100 seconds and a long time is required to completely empty the states. This error in $I_{\text{peak}}$ due to the finite response time of the input filters of the lock-in amplifier was theoretically corrected according to ref. 12.

The interface state density obtained devices P37 and NL230 is plotted against trap energy in Fig. 21. This figure also shows the density obtained from dark capacitance transients (Fig. 22, 23) and the small signal capacitance dispersion (with frequency) experiments. Optical cross-sections obtained from the two devices are plotted in Fig. 24 and are the major results of this study.
The interface state density is minimum near midgap and rises monotonically towards the band edges. The optical cross-sections behave in a similar manner, but vanish for trap energies greater than the optical energy $\hbar \nu$ away from both sides of the bandgap.

States near the band edges cannot be probed by these experiments. Expectation is that the density will be high in these regions, as they are essentially the band tails of conduction and valence bands.

Finally, it should be noted that the experimental result of monotonically increasing cross-sections with trap energies and $\hbar \nu$ is dissimilar to the photoemission model of Lucovsky for discrete bulk states.

4.4 analysis of the pair generation current

The photocurrent saturates when the emission process stops and the trap occupancy reaches the steady state level. Alternate emission of electrons and holes is required for the pair generation process. Hence, states near midgap are efficient pair generation centres. If the light energy is less than half of the bandgap energy, pair generation will not take place. Figure 25 shows the pair generation parameter $\left(\sigma_n^0 \sigma_p^0 / \sigma_n^0 + \sigma_p^0\right)$ plotted as a function of trap energy with photon energy as the parameter. This ratio has a maximum value near midgap. The states within the boundaries of each curve
contribute to the pair generating current. It is obvious, the maximum contribution to pair generation is from the states near midgap.

The optical timeconstant \( \tau_L (1/\phi_n \sigma_{on}^n \sigma_{on}^p) \) is presented as function of trap energy with \( h \) as the parameter in Fig. 26. These curves show that the time constant remains constant over a major part of the bandgap for \( h \nu > E_g/2 \). A slight increase in \( \tau_L \) with decreasing \( h \nu \) is due to two effects:

- the dependence of the sum\( (\sigma^o_n + \sigma^o_{on}) \) on the optical energy (Fig. 27)
- decreasing photon flux at lower energies.

The latter is limited by the monochromator, light source and the filter used in the experiment.

Fig. 26 brings out the fundamental dependence of the optical time constant on trap energy and incident photon energy and flux. An increase in the photon flux decreases the time constant and vice versa. This implies that states can be emptied faster by increasing the photon flux.
4.5 Calculation of the Pair generating current

Knowing the time constant we plot the time constant diagram\(^{17}\) of the system at 77\(^0\)K in Fig.28. Bold lines mark the dominant time constant. In general, near the band edges the dominant time constant is thermal (even at 77\(^0\)K) and over rest of the bandgap optical (\(\tau_L\)). As the temperature increases thermal time constant becomes dominant all over the bandgap and so the photocurrent goes to zero (Fig. 29). In our experimental devices, the oxide was thick enough for the interface states to equilibriate with the semiconductor. Hence, the tunneling time constant is (large and) not plotted in the figures.

Knowledge of the optical time constant and the optical cross-sections enable us to calculate the steady state pair generation current

\[
I_{sat} = qA_f \int_{E_v}^{E_c} E \frac{\sigma_n^0 \sigma_p^0}{\sigma_n^0 + \sigma_p^0} \, dE_t.
\]  

(17)

Results of numerical computation are plotted in figs. 30 and 31. Also shown are experimentally measured data points. The theory is thus able to predict the right values of pair generation current within error tolerance. As the theory predicts, the photocurrent values increase with light energy \(h\nu\). The strong temperature dependence is not so clear. Probably, the minority concentration at
the surface can not be neglected, as has been assumed in the simplified theory. The minority carrier response time has different effects on the steady photocurrent, at different temperatures. A more general treatment is essential for a complete solution of the problem.
5. CONCLUSIONS

We have measured electron and hole photo-ionisation cross-sections and interface states in MOS capacitors. A good agreement has been found between the optical and non-optical measurements of the density of states. All measurements give a U shaped profile for the interface state density. The optical cross-sections increase monotonically with trap energy and photon energy towards the band edges.

We have calculated the optical relaxation time ($\tau$) and the optical pair-generation current ($I_{\text{sat}}$), at different temperatures and photon energies. The calculated values fit the experimental data, providing a verification of the pair generation theory.

Possible applications of the theory and the experimentally obtained parameters include, characterisation of traps in a composite insulator structure (e.g., HfO$_2$), study of inversion layer build up in MIS devices, and the study of electrolyte-insulator-semiconductor system.
The growth of a uniform, pinhole free oxide layer is essential for studying the optoelectronic properties of thin oxide devices. Thus, to ensure reproducibility and reliability of the results, one of the goals was to control the quality of tunnel devices. This quality was judged by tunneling (current density) and capacitance (measurement of fixed oxide charge, interface states and mobile ion charge) standards. Both n and p type MOS capacitors were fabricated. The variable processing parameters were:

1. Oxidation time.
2. Oxidation temperature.
3. Substrate resistivity.
4. Residual deep level traps and bulk defects.

The devices used for final measurements were carefully chosen, based on the device design considerations explained below.

Fig. 32 shows the basic device pattern consisting of three capacitors of different areas. The size was chosen so that the capacitance and conductance signals were large enough to be detected, and gross defects and non-uniformities avoided. Fig. 33 is a cross-sectional view of the tunnel device showing the guard rings and the bonding pad.
The bonding pad is over the field oxide and adds a parasitic capacitance component to the interface state capacitance. This capacitance has to be minimised by increasing the field oxide thickness. (the field oxide thickness was kept at 5000 Å).

In tunnel devices back contact ohmic resistance is important and has to be kept low. Possible ways of decreasing the contact resistance are:

1. sintering after metallisation
2. diffusion of impurities at the back
3. use of epitaxial wafers

The first two are high temperature processes and can not be used for tunnel device fabrication. The third leads to additional complications in the optical experiments. The epi-layer absorbs a major portion of the incident light (even though less than $E_g$ in energy) causing a reduction in the photocurrent.  

A quantitative study was undertaken to determine the percentage of the incident energy absorbed by the free carriers in the epi-layer. The light intensity was measured using a pyroelectric detector. Table 2 lists the measured shortcircuit current values, before and after different silicon wafers were inserted in between the source and the detector. The table shows that the epitaxial wafers have a high absorption coefficient and are not suitable for...
optical experiments.

Finally, p-type substrates of resistivity 5-9Ω cm and n-type substrates of resistivity 0.5-1.1Ω cm were used to make devices for optical measurements. Epitaxial wafers were used for dc characterisation and dark experiments.

Wafer cleaning was performed in two different sequences:

- tichloroethylene-acetone-methanol
- H₂SO₄-HNO₃.

The latter method requires less time and was preferred in subsequent device processing.

The density of bulk states has to be minimised to isolate and study the effect of these on the observed capacitance transients. Cleanliness during processing and additional gettering steps can be introduced to reduce bulk defect density. We used both internal and external gettering in our processing. Contrary to recent reports 9,10 we observed that the minority carrier lifetime deteriorated with an increase in the number of processing steps. The ungettered wafers had the largest value for the minority carrier lifetime, and therefore the minimum concentration of bulk defects. The reason for such observations was not pursued further, and the gettering step eliminated in the following processing batches.
Oxides were grown in dry oxygen in the temperature range 700-1100°C. The lower oxide temperature gave higher interface state densities. This result is in agreement with the Grove-Deal triangle. A larger density of interface states is required to increase the capacitance and conductance signals from the interface states, hence oxide was grown at 700°C. Oxide thickness was controlled by the oxidation time.
Flow Chart 1: PROCESSING SEQUENCE

Starting material
n/p silicon (100)
5-9Ωcm, epi/non-epi

Surface cleaning

Intrinsic Gettering

Extrinsic Gettering

Tunnel oxide
20-50 Å

Thick oxide
100-1200 Å

METALLIZATION

Annealing
in N₂ at
400°C
45 min.

No
Annealing
Processing Steps

1. Cleaning - (a) (1) Trich boil, 5 min
   (2) Acetone boil, 5 min
   (3) Methanol boil, 5 min
   (4) DI water rinse

or (b) (1) Dip in NH\textsubscript{4}OH:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O (1:1:5) hot
   (2) Dip in H\textsubscript{2}SO\textsubscript{4}:H\textsubscript{2}O\textsubscript{2} (6:1) hot
   (3) DI water rinse

(5) Etch in 10% HF room temperature.
(6) D.I. water rinse
(7) Blow dry with N\textsubscript{2} gas

2. Gettering (a) Intrinsic
   (1) Anneal in dry N\textsubscript{2} at 1100\textdegree C (4 hrs)
   (2) Anneal at 700\textdegree C (4 hrs)
   (3) Anneal at 1100\textdegree C (16 hrs)

(b) Extrinsic (phosphorous gettering)
   (1) Steam oxidation at 1100\textdegree C (45 min.)
   (2) Phosphorous diffusion at the back surface - 900\textdegree C (40 min)
   (3) Apply PR at the back
   (4) Bake at 100\textdegree C (20 min)
   (5) Etch oxide - Buffer HF
   (6) Acetone boil - 5 min
(7) Silicon etch HNO₃ + HF (4:1)
    1/2 min

(8) Rinse in DI water

3. Field Oxidation
   Steam oxidation 1100°C (45 min)

4. Photo 1
   (1) Spin PR
   (2) Prebake 100°C (30 min)
   (3) Expose (18 sec) and develop
   (4) Post bake 120°C (20 min)
   (5) Etch in buffered HF until hydrophobic
       in holes
   (6) Acetone boil
   (7) Rinse in DI water
   (8) Blow dry with N₂ gas

5. Tunnel oxidation
   (1) Cleaning (repeat step 1)
   (2) Dry oxidation 700°C (20 min)

6. Metallization
   (1) Clean chromium charge in trich-acetone-
       methanol; DI rinse
   (2) Evacuate vacuum system to 1-5x10⁻⁷ torr
   (3) Heat until evaporation occurs with
       shutter closed
   (4) Open shutter and evaporate

7. Photo 2
   (1) Repeat step 4 (1-4) with the metal mask.
   (2) Etch chromium (480 ml H₂O: 24 ml glacial
       acetic acid: 91 gm cerič ammonium nitrate)
(3) Rinse in DI water
(4) Blow dry with N$_2$ gas

8. Back contact metallization
   (1) Spin PR on front
   (2) Prebake 100°C (30 min)
   (3) Etch in HF until hydrophobic at the back
   (4) Acetone boil (5 min)
   (5) Rinse with methanol
   (6) DI water rinse
   (7) Evaporate Al back contact

9. Post-metal anneal
   Anneal in N$_2$ at 800°C (40 min)
REFERENCES


14. Minority carrier Mis tunnel diodes and their application to electron and photovoltaic energy conversion devices I,


TABLE 1
Methods of Measuring Schottky Barrier Height
Extended to MIS Diodes

<table>
<thead>
<tr>
<th>Method</th>
<th>Limitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Mott-Schottky plot (intercept)</td>
<td>Presence of oxide layer, and a slight inversion layer at the interface reduces accuracy.</td>
</tr>
<tr>
<td>2. I-V characteristics (extrapolated saturation valve)</td>
<td>Tunnelling through the oxide reduces the current significantly, and since the value of $t_{ox}$ and $\chi_s$ are not known precisely gross inaccuracies result.</td>
</tr>
<tr>
<td>3. Richardson plot ($I/T^2$ vs. $1/nT$)</td>
<td>Applicable in cases where the mionic emission is the mechanism of current transport.</td>
</tr>
<tr>
<td>4. Photoexcitation of majority carriers into the semiconductor</td>
<td>Inaccurate results, due to complication from barrier height lowering and photon assisted tunnelling.</td>
</tr>
</tbody>
</table>
### TABLE 2

Measurements on Sample Transparency

Source: Tungsten Halogen lamp

Detector: Pyroelectric, with no aperture + (Si-interference filter)

Wavelength: 1.634 μm

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{det}$ (pA rms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With wafer inserted</td>
</tr>
<tr>
<td>$n/n^+(100)$</td>
<td>23</td>
</tr>
<tr>
<td>epi-10μm, 7-10Ωcm</td>
<td></td>
</tr>
<tr>
<td>$n(100)$</td>
<td>28</td>
</tr>
<tr>
<td>0.55-1.1Ωcm</td>
<td></td>
</tr>
<tr>
<td>$p(100)$</td>
<td>17.5</td>
</tr>
<tr>
<td>7-14Ωcm</td>
<td></td>
</tr>
<tr>
<td>$p/p^+(100)$</td>
<td>0.085-0.095</td>
</tr>
<tr>
<td>epi: 11μm 4Ωcm</td>
<td></td>
</tr>
<tr>
<td>pt: 0.005-0.01Ωcm</td>
<td></td>
</tr>
<tr>
<td>$n/n^+(100)$</td>
<td>0.1</td>
</tr>
<tr>
<td>epi 1Ωcm</td>
<td></td>
</tr>
<tr>
<td>$p(100)$</td>
<td>31</td>
</tr>
<tr>
<td>5.5-9.3Ωcm</td>
<td></td>
</tr>
<tr>
<td>$p(100)$</td>
<td>21.5</td>
</tr>
<tr>
<td>2-3Ωcm</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. Experimental device structure and primary measurements.

Fig. 2. Energy Band-diagram of a MOS tunnel diode.
Fig. 3. Optical emission and pair generation processes.

Fig. 4. Current components of the external photocurrent.
Fig. 5. The Optical Set-up.
Fig. 6. Normalised optical intensity vs. wavelength.
Fig. 6. Normalised optical intensity vs. wavelength.
Fig. 7. Effect of stray light on the dark capacitance transient at low temperatures.
at low temperatures.

Fig. 7. Effect of stray light on the dark capacitance transient
Fig. 8. Schematic of the photocurrent transient experiment.

Fig. 9. Schematic of the C-V, G-V dispersion experiment.
Fig. 10. Optical setup and circuit diagram for barrier height
Fig. 11. Photocurrent vs. time for different gate bias.

Fig. 12. Normalised photocurrent peak vs. gate voltage.
Fig. 12. Normalised photocurrent peak vs. gate voltage.

Fig. 11. Photocurrent vs. time for different gate bias.
Fig. 13. Current -Voltage characteristics of device P37.
Fig. 13. Current-voltage characteristics of device P37.
Fig. 14. Mott-Schottky plot of device P37.
Figure 1.4. Mott-Schottky plot of device P37.

\[ \log (V) \text{ vs. } \log \left( \frac{A}{C} \frac{2}{n^2 F^{-2}} \right) \]
Fig. 15. Capacitance vs. Voltage with frequency as the parameter.
Figure 15. Capacitance vs. Voltage with Frequency as the Parameter.

Diagram showing capacitance (C) versus voltage (V) with frequency as a parameter.
Fig. 16. Steady state photocurrent vs. bias with optical energy as parameter.
Fig. 16. Steady state photocurrent vs. bias with optical energy as parameter.
Fig. 17. Transient Photocurrent.
FIG. 17. TRANSIENT PHOTOCURRENT.

PLOT TRANSIENT PHOTOCURRENT.
Fig. 17: Transient Photocurrent.

[Graph showing transient photocurrent over time]
Fig. 18. Components of the photocurrent transient.
Fig. 18. Components of the photocurrent transient.
Fig. 18. Components of the photocurrent transient.

[Vp]
Fig. 19. Charge released from the interface states.
Fig. 19. Charge released from the interface states.
Fig. 20. Peak of the photocurrent transient at different temperatures and photon energies.
Fig. 20. Peak of the photocurrent transients at different temperatures.

TEMP (K)

PEAK CURRENT (A)
Fig. 21. Interface state density vs. trap energy.
Fig. 2.1. Interface state density vs. trap energy.

--- Dark Cap Trace
--- Cap Disip.
--- Photo Current
Fig. 22. Dark Capacitance transient plotted on a logarithmic time scale
Fig. 22. Dark capacitance transient plotted on a logarithmic time scale.
Fig. 22. Dark Capacitance transient plotted on a logarithmic time scale.
Fig. 23 Dark Capacitance transient plotted on a linear time scale.
Fig. 23 Dark capacitance transient plotted on a linear time scale.
Fig. 23: Dark capacitance transient plotted on a linear time scale.
Fig. 24. Photo-ionisation cross-sections vs. trap energy with photon energy as the parameter.
Fig. 24. Photo-competition cross-sections vs. trap energy with photon energy as the parameter.
Fig. 25. Pair generation parameter vs trap energy.
Fig. 25. Particle generation parameter vs trap energy.

TRAP ENERGY (eV)

SIGMA - N/PSET

N*P/(N+P)*1E-18

0.99 eV
0.97 eV
0.95 eV
0.93 eV
0.91 eV
Fig. 26. Optical time constant vs. trap energy.
Fig. 26. Optical time constant vs. trap energy.
Fig. 27. Sum of the optical cross sections vs. trap energy, with photon energy as the parameter.
Figure 27. Sum of the optical cross sections vs. trap energy with photon energy as the parameter.
Fig. 28. Time constant diagram at 77°K.

Fig. 29. Time constant diagram at 300°K.
Fig. 29. Time constant diagram at 300°K.

Fig. 28. Time constant diagram at 77°K.
Fig. 30. Saturation photocurrent vs. optical energy.
Fig. 30. Saturation photocurrent vs. optical energy.
Fig. 31. Saturation photocurrent vs. temperature at different optical energies.
Fig. 31. Saturation photocurrent vs. temperature at different optical energies.
Fig. 32. Photograph of the devices used in the experiments.

Fig. 33. Cross-sectional view of a tunnel device.
VITA

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