NAME OF AUTHOR/NOM DE L'AUTEUR: Randall Byron North

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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS REÇUE
APPLICATION OF THE TANTALUM OXIDES
TO PHOTOVOLTAIC ENERGY CONVERSION

by

Randall Byron North, B.Sc. Eng.

This thesis is submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of

Master of Engineering

Department of Electronics
Faculty of Engineering
Carleton University
Ottawa, Canada
April, 1980
The undersigned recommend to the Faculty of Graduate Studies and Research the acceptance of the thesis:

"Application of the Tantalum Oxides to Photovoltaic Energy Conversion"

submitted by Randall Byron North in partial fulfillment of the requirements for the degree of Master of Engineering.

April, 1980

Prof. R. E. Thomas
Thesis supervisor and
Acting Chairman,
Department of Electronics
ABSTRACT

This thesis studies the use of the tantalum oxides in inversion layer (IL) solar cells. Three methods for preparing oxides of tantalum were chosen. The first involved the low temperature thermal oxidation of tantalum on silicon. Secondly, tantalum oxide pressed powder was evaporated in a partial oxygen ambient on silicon substrates. Lastly, a solution containing tantalum oxides was spun on prepared silicon slices.

MIS-IL solar cells fabricated using the spin-on solution have demonstrated total area AM1 efficiencies greater than 16%. This efficiency is the highest yet obtained for either the inversion layer or MIS (or combination of the two) solar cells. Also active area AM1 efficiencies greater than 13% have been obtained on WACKER, SILSO polycrystalline material. Because the spin-on solution is highly reactive with the atmosphere, stabilization of cell performance has been a problem. However, the efficiencies obtained demonstrate that the MIS-IL cell has the potential to be a cost effective replacement for the diffused junction on polycrystalline material.
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Most of all, I would like to thank Anna, not only for the typing, but also for being there when I needed her.
# TABLE OF CONTENTS

## ABSTRACT

1

## ACKNOWLEDGEMENTS

11

## TABLE OF CONTENTS

111

## LIST OF FIGURES

v

## LIST OF SYMBOLS AND ABBREVIATIONS

viii

## CHAPTER 1. INTRODUCTION

1

1.1 Historical Background

1

1.2 Goals of this Thesis

2

1.3 Thesis Outline

3

## CHAPTER 2. FUNDAMENTALS OF PHOTOVOLTAIC ENERGY CONVERSION—CONVENTIONAL AND INVERSION LAYER SOLAR CELLS

4

2.1 Introduction

4

2.2 The Sun

4

2.3 Photovoltaics

7

2.4 The Conventional Solar Cell

8

2.5 Losses and Efficiency

12

2.6 The Inversion Layer Solar Cell

13

2.7 The MIS Tunnel Diode

16

2.7.1 The Insulating Layer

17

2.7.2 Results

18

2.8 Summary

20

## CHAPTER 3. PROPERTIES OF THE SILICON-TANTALUM OXIDE INTERFACE

21

3.1 Introduction

21

3.2 Thermally Grown Tantalum Oxide in Silicon

23

3.2.1 Oxidation and Ellipsometry

28

3.2.2 C-V Analysis

31

3.2.3 Electronic Properties of the Interface

37

3.3 Evaporated Pressed Tantalum Oxide Powder

42

3.3.1 Experimental Results

43

3.4 Spin-on Tantalum Oxide

47

3.4.1 C-V Results

49

3.5 Characterization of the Oxides as Antireflective Coatings

50

3.6 SEM Analysis

51
CHAPTER 4. MIS-IL SOLAR CELL CHARACTERIZATION

4.1 Introduction 54
4.2 Fabrication 54
4.3 Photovoltaic Results 58
4.3.1 Measuring Apparatus 58
4.3.2 Single-Crystalline Silicon 61
4.3.3 Polycrystalline Silicon 66
4.4 Modelling 70
4.4.1 Current Efficiency 70
4.4.2 ILSCEL Simulation 74
4.5 Stencil Mask Results 76
4.6 Stability 78

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS 85

5.1 Nature of Oxide Charge 85
5.1.1 Thermally Grown Tantalum Oxide 85
5.1.2 Evaporated Tantalum Oxide Powder 86
5.1.3 Spin-on Tantalum Oxide Solution 87
5.2 Summary 89
5.3 Recommendations For Future Work 90

REFERENCES 92

APPENDICES 98

APPENDIX A "Basic Listing for TRS-80 Solar Cell Tester". 98

APPENDIX B "Analysis of Ellipsometry Measurements". 106

APPENDIX C "Detailed MIS-IL Cell Fabrication Schedule". 112
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>DESCRIPTION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Spectral power density for terrestrial solar energy (AM1) and for solar energy just outside the earth's atmosphere.</td>
<td>6</td>
</tr>
</tbody>
</table>
| 2.2        | (a) Cross-section of conventional solar cell  
(b) One dimensional energy band diagrams for both short and open circuit conditions. | 9    |
| 2.3        | (a) Solar cell equivalent circuit  
(b) Dark and light current voltage curves | 11   |
| 2.4        | (a) Cross section of the inversion layer solar cell  
(b) One dimensional energy band diagram under strong inversion conditions. | 14   |
| 2.5        | (a) Dark log(I)-V curves for single-crystalline, polycrystalline, and ideal silicon MIS diodes.  
(b) Experimental test set-up | 19   |
| 3.1        | (a) Schematic of the evaporator used  
(b) Close-up of the hearth showing the 270° electron beam gun. | 24   |
| 3.2        | (a) Plot of refractive index versus oxidation time at a temperature of 450°C  
(b) Gradient of refractive index through the thermal oxide | 24   |
| 3.3        | (a) MOS capacitance structure  
(b) Charge distribution  
(c) Equivalent capacitance  
(d) Energy band  
(e) Ideal C-V curve for both the low frequency and high frequency bias. Also included is an actual measured curve. | 32   |
| 3.4        | (a) Commonly accepted model for fast surface states. Acceptor states "accept" an electron and become negative. Donor states give up an electron, becoming positive.  
(b) Capacitance versus voltage measurement apparatus. | 36   |
| 3.5        | Ideal and representative C-V curves for a capacitor on an "N" type substrate. Thermal tantalum oxide was used as the dielectric. | 39   |
3.6 Capacitance versus voltage curves for a capacitor on a "P" type substrate. The dielectric used is evaporated tantalum oxide powder. Shown is the ideal curve shifted towards negative bias by the work function difference (\(\phi\)), the measured curve, and the complete model predicted by "CHEVCE".

3.7 (a) Schematic of the apparatus used to measure reflectance.
(b) Measured curves for the three oxides investigated.

4.1 (a) Cross section of the spin-on tantalum oxide MIS-IL solar cell structure.
(b) The effect of the contact grid finger spacing on the output power of an inversion layer solar cell [15].

4.2 Metallization mask for inversion layer solar cells. Grid finger spacing =39 fingers/cm.

4.3 Schematic of the computer controlled solar cell test facility.

4.4 (a) Illuminated I-V curves for evaporated and spin-on tantalum oxide MIS-IL solar cell.
(b) A family of illuminated I-V curves for a typical spin-on solar cell, showing the method for calculating \(R_s\).

4.5 (a) Typical illuminated I-V curve for a spin-on tantalum oxide MIS-IL solar cell fabricated using a 20 cm contact grid.
(b) Explanation for the decreased efficiency observed in this cell.

4.6 Illuminated I-V curve for a MIS-IL tantalum oxide solar cell on a polycrystalline substrate.

4.7 Measured and calculated external current efficiency for various MIS-IL tantalum oxide solar cells.

4.8 Comparison of a measured I-V curve for a tantalum oxide spin-on MIS-IL solar cell with the curve predicted by the computer simulation.

4.9 (a) Illuminated I-V curve for a spin-on tantalum oxide MIS-IL solar cell, showing the degradation with time.
(b) How the active area efficiency changes during this period.
4.10 A tentative explanation for the degradation observed in spin-on tantalum oxide MIS-IL solar cells. The oxide cracking accelerated the oxidation of the film.

A.1 Dark and light current-voltage routine
A.2 Short circuit current and open circuit voltage routine
A.3 Maximum power point routine
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>area</td>
<td>cm²</td>
</tr>
<tr>
<td>ADC</td>
<td>analog-digital converter</td>
<td></td>
</tr>
<tr>
<td>AMO(1,2)</td>
<td>air mass zero(one,two)</td>
<td></td>
</tr>
<tr>
<td>AR</td>
<td>anti-reflective</td>
<td></td>
</tr>
<tr>
<td>BSF</td>
<td>back surface field</td>
<td></td>
</tr>
<tr>
<td>C-V</td>
<td>capacitance-voltage</td>
<td></td>
</tr>
<tr>
<td>C((\lambda))</td>
<td>collection efficiency</td>
<td></td>
</tr>
<tr>
<td>C_{ox}</td>
<td>oxide capacitance</td>
<td>F/cm²</td>
</tr>
<tr>
<td>C_s</td>
<td>semiconductor capacitance</td>
<td>F/cm²</td>
</tr>
<tr>
<td>C_{mos}</td>
<td>total MOS capacitance</td>
<td>F/cm²</td>
</tr>
<tr>
<td>DAC</td>
<td>digital analog converter</td>
<td></td>
</tr>
<tr>
<td>DI</td>
<td>de-ionized</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>electron energy</td>
<td>eV</td>
</tr>
<tr>
<td>E_c</td>
<td>electron energy at conduction band edge</td>
<td>eV</td>
</tr>
<tr>
<td>E_F</td>
<td>electron energy at fermi level</td>
<td>eV</td>
</tr>
<tr>
<td>E_g</td>
<td>width of forbidden gap</td>
<td>eV</td>
</tr>
<tr>
<td>E_{1}</td>
<td>electron energy at intrinsic level</td>
<td>eV</td>
</tr>
<tr>
<td>E_v</td>
<td>electron energy at valence band edge</td>
<td>eV</td>
</tr>
<tr>
<td>EHP</td>
<td>electron hole pair</td>
<td></td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
<td></td>
</tr>
<tr>
<td>g((\lambda))</td>
<td>generation efficiency</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>Planck's constant (6.626 \times 10^{-34})</td>
<td>J-s</td>
</tr>
<tr>
<td>HF</td>
<td>hydrofluoric acid</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>output current density</td>
<td>A/cm²</td>
</tr>
<tr>
<td>I_o</td>
<td>reverse saturation current density</td>
<td>A/cm²</td>
</tr>
</tbody>
</table>
$I_L$ photogenerated current density $A/cm^2$

$I_{sc}$ short circuit current density $A/cm^2$

$IL$ inversion layer

$IR$ infrared

$I-V$ current-voltage

$k$ Boltzmann's constant $1.38 \times 10^{-23}$ $J/K$

$k(\lambda)$ extinction coefficient

$MIS$ metal insulator semiconductor

$MOS$ metal oxide semiconductor

$n$ exponential constant

$n_i$ intrinsic electron concentration $cm^{-3}$

$n_{ox}$ refractive index of oxide/AR coating

$N_a$ acceptor doping density (p-type) $cm^{-3}$

$N_d$ donor doping density (n-type) $cm^{-3}$

$N_0(\lambda)$ photon flux $cm^{-2} \mu m^{-1} \text{sr}^{-1}$

$N_{ss}$ surface state density $cm^{-2} \text{eV}^{-1}$

$P_{max}$ maximum cell output power $W/cm^2$

$P_{in}$ incident power $W/cm^2$

$q$ electronic charge $1.602 \times 10^{-19}$ $C$

$Q_{e}(\lambda)$ external current efficiency

$Q_{FB}$ effective flatband charge density $C/cm^2$

$Q_{ox}$ effective oxide charge density $C/cm^2$

$Q_{ss}$ surface state charge density $C/cm^2$

$Q_d$ depletion charge $C/cm^2$

$Q_n$ inversion charge $C/cm^2$

$Q_G$ gate charge $C/cm^2$

$R(\lambda)$ reflection coefficient
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{IL}$</td>
<td>inversion layer resistance</td>
<td>$\Omega \cdot \text{cm}^2$</td>
</tr>
<tr>
<td>$R_m$</td>
<td>resistance of metal, bulk and contact</td>
<td>$\Omega \cdot \text{cm}^2$</td>
</tr>
<tr>
<td>$R_S$</td>
<td>effective series resistance</td>
<td>$\Omega \cdot \text{cm}^2$</td>
</tr>
<tr>
<td>$r_s$</td>
<td>sheet resistance of inversion layer</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$t_{ox}$</td>
<td>oxide thickness</td>
<td>$\mu$m</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature</td>
<td>K</td>
</tr>
<tr>
<td>$Ta$</td>
<td>tantalum</td>
<td></td>
</tr>
<tr>
<td>$uV$</td>
<td>ultra-violet</td>
<td></td>
</tr>
<tr>
<td>$U_s$</td>
<td>normalized surface potential</td>
<td></td>
</tr>
<tr>
<td>$V$</td>
<td>solar cell output voltage</td>
<td>V</td>
</tr>
<tr>
<td>$V_{FB}$</td>
<td>flatband voltage of MOS capacitor</td>
<td>V</td>
</tr>
<tr>
<td>$V_G$</td>
<td>MOS gate bias voltage</td>
<td>V</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>open circuit voltage</td>
<td>V</td>
</tr>
<tr>
<td>$V_{ox}$</td>
<td>voltage drop across oxide</td>
<td>V</td>
</tr>
<tr>
<td>$X$</td>
<td>distance into silicon from front surface</td>
<td>cm</td>
</tr>
<tr>
<td>$X_d$</td>
<td>depletion width</td>
<td>cm</td>
</tr>
<tr>
<td>$X_j$</td>
<td>junction depth</td>
<td>cm</td>
</tr>
<tr>
<td>$\alpha(\lambda)$</td>
<td>optical absorption coefficient of silicon</td>
<td>$\text{cm}^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_{ox}$</td>
<td>permittivity of oxide</td>
<td>F/cm</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>permittivity of silicon</td>
<td>F/cm</td>
</tr>
<tr>
<td>$n$</td>
<td>power conversion efficiency of solar cell</td>
<td>%</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
<td></td>
</tr>
<tr>
<td>$\phi(x)$</td>
<td>charge density</td>
<td>$\text{C/cm}^3$</td>
</tr>
<tr>
<td>$\tau_n$</td>
<td>electron lifetime</td>
<td>s</td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>hole lifetime</td>
<td>s</td>
</tr>
<tr>
<td>$\phi(x)$</td>
<td>electric potential</td>
<td>V</td>
</tr>
<tr>
<td>$\phi_{ms}$</td>
<td>metal semiconductor work function</td>
<td>eV</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Historical Background

The major industrial nations of the world are at present facing both economic and social crises due to the cost, availability, and pollution effects of fossil fuels. As a consequence, considerable effort is now being devoted to alternative sources of energy. Although the indications are that nuclear energy (fission in the short term, fusion in the long) will eventually provide most of our needs and will become dominant in the twenty-first century; many alternate sources of energy based on the utilization of solar energy either directly or indirectly are at present under consideration. These sources are expected to supply a significant portion of our energy requirements in the next 50 years.

The "solar cell" belongs in this category. Briefly, this device converts electromagnetic radiation into electricity via the photovoltaic effect. This phenomenon relies upon the development of a voltage across the junction of two dissimilar materials such as that which occurs when a P/N, or a metal/semiconductor junction is exposed to light or other radiant energy. First demonstrated in 1877 [1], it was not until 1954 that power efficiencies of up to 6% were achieved with \( 1\frac{1}{4} \) inch diameter P/N solar cells [2]. In 1956, 1cm X 2cm cells having 7% efficiencies were produced and used on the U.S. space satellite, Vanguard. In 1961, simple grid structures were added to the top cell surface, thereby reducing series resistance to give 8%
efficiency. Many innovative improvements, including antireflective coatings, and shallow junctions were added in 1962 for the Telstar communication satellite. Efficiencies remained fairly constant at around 10% until the energy crunch of the seventies necessitated research into terrestrial applications. Significant innovations included: "Back Surface Field" (BSF),[3], "violet cell" [4], and the "non-reflective cell" [5]. Also, because the cost of single crystalline silicon became prohibitive, solar cells on polycrystalline substrates started to receive considerable attention [6].

One new approach, conducive to low-cost production, has been the inversion layer (IL) solar cell [7]. Substantial research has been done at Carleton University on this concept [8,9]. Because simple theory predicted that the IL cell would have inherent advantages over conventional (diffused junction) cells [10], radiation studies were undertaken that indicated that the structure was well suited for space applications [11]. Refinements to the fabrication process have since yielded efficiencies of up to 12% [12]. To eliminate the high temperature oxidation and diffusion steps associated with this cell, Metal Insulation Semiconductor (MIS) diodes were successfully incorporated along with low temperature deposited oxides [13,14].

1.2 Goals of this Thesis

To date, the primary oxide to be investigated at Carleton University for use in IL cells has been silicon dioxide ($\text{SiO}_2$) [15,16]. Elsewhere, excellent results have been achieved using either titanium dioxide ($\text{TiO}_2$) [17], or silicon monoxide ($\text{SiO}$) [18,19,20]. Both of these films are fair antireflective coatings. It has been shown, how-
ever, that significant improvement in the short wavelength response and fill factor (F.F.) of silicon solar cells can be achieved by using, among other things, a tantalum pentoxide antireflection film [21]. This film has considerably less absorption in the ultraviolet end of the spectrum, and as a result, was chosen for use with the "violet cell" [4]. Because an IL cell has a "junction" which is extremely shallow (on the order of 20-25 nm, [22]), it is inherently sensitive to the short wavelengths as well, and it would appear that the use of tantalum pentoxide would be a logical choice. However, any oxide used in IL cells has to be able to induce the necessary junction, and to date very little research has been done on the charge characteristics of tantalum oxide films on silicon [23].

The purpose of this thesis, therefore, is to investigate various methods for preparing tantalum oxide thin films, and to characterize these films with the ultimate objective of using the oxide in the inversion layer silicon solar cell.

1.3 Thesis Outline

This thesis is divided into 5 chapters. The first introduces the topic. Chapter 2 reviews the basics of conventional and inversion layer solar cells, and introduces the MIS diode. Chapter 3 covers the characterization of the silicon-tantalum oxide interface as well as spin-on tantalum oxide. Chapter 4 outlines the photovoltaic results for evaporated and spin-on tantalum oxides. Chapter 5 discusses the nature of the oxide charge, and the nature of the spin-on solution. A summary, and recommendations for future work are also included in this chapter.
CHAPTER 2

FUNDAMENTALS OF PHOTOVOLTAIC ENERGY CONVERSION-
CONVENTIONAL AND INVERSION LAYER SOLAR CELLS

2.1 Introduction

This chapter will outline briefly the basics of solar energy as it applies to photovoltaic cells. To illustrate these concepts, both the conventional (diffused junction) and the IL cell will be described. For further detail on other solar cell structures, and solar energy in general, the reader is referred to two very excellent books [24,25].

2.2 The Sun

Of course, the most important element in any solar power system is the sun itself. This dwarf yellow star located in the gravitational centre of our solar system operates as a gigantic thermonuclear reactor. Although the central core occupies only 3% of the total volume of the sun, it is here that all the energy is produced by fusion:

\[
4 \text{ H}_{nuclei} \xrightarrow{\text{fusion}} \text{He}
\]  

This reaction releases the gamma radiation that has the shortest wavelength of any electromagnetic energy known (\(1 \times 10^{-8}\) nm) [26].
Physicists and engineers find it convenient to consider this radiation as a particle having zero mass, no electric charge, and an indefinitely long lifetime. This particle or "photon" has a quantum amount of energy.

\[ E = hf = h\nu/\lambda \]  \hspace{1cm} (2.2)

Where, \( h \) is Planck's constant (6.626 \( \times \) 10\(^{-27} \) ergs-s), and \( f \) is the frequency of the photon, or the velocity of light (\( \nu \)) divided by the wavelength of the particle (\( \lambda \)). As the photons travel through the 50,000 Km thick outer shell of the sun, they undergo collisions which reduce their energy, thus increasing their characteristic wavelength.

By the time these photons reach the earth, their wavelengths vary from 0.115 \( \mu \text{m} \) (deep ultraviolet (uv)) to 1300 \( \mu \text{m} \) (infrared (IR)). The total power available to satellites outside the earth's atmosphere per unit area (defined as the solar constant) is approximately 1353 W/m\(^2 \) [27]. A plot of the spectral distribution of this power is shown in figure 2.1. As these photons travel through the earth's atmosphere, even more are absorbed, scattered, and reflected, and thus the spectral distribution changes once again. The amount of the atmosphere the light travels through leads to the concept of air mass [28]. Ideally, the air mass is the secant of the sun's angle relative to the zenith, measured at sea level on a clear day. Alternatively, it is the number of standard air-masses that the light travels to reach the observer. Thus, air mass zero (AM0) occurs outside the earth's atmosphere and air mass one (AML) would occur under the aforementioned conditions. The spectral distribution for the AM1 spectrum is also plotted in figure 2.1. Integrating this, the total power is only about 1000 W/m\(^2 \).
Fig. 2.1 Spectral power density for terrestrial solar energy (AM1) and for solar energy just outside the earth's atmosphere (AM0).
This power is what is available for terrestrial photovoltaic energy conversion under ideal conditions. However, such factors as weather, latitude, pollution, and time of year govern just how much solar power is actually available. This obviously must figure prominently into the economic considerations for any solar energy system.

2.3 Photovoltaics

The semiconductor that offers the most promise for cost reduction is silicon. A very abundant element, it has a bandgap energy of 1.1 eV. If silicon is exposed to light, any photon with energy greater than or equal to 1.1 eV will generate one electron-hole pair (EHP). The absorption rate of these photons is governed by Lambert's law [28].

\[ N(\lambda, x) = N_0(\lambda) \exp(-\alpha(\lambda)x) \quad \text{photons/sec-cm}^2 \cdot \text{nm} \quad (2.3) \]

Where \( \alpha(\lambda) \) and \( N_0(\lambda) \) are the absorption coefficient for silicon, and the photon flux, respectively. Since the light has a spectral distribution, they are measured per incident wavelength (\( \lambda \)).

The absorption coefficient has been measured to be a strongly decreasing function of \( \lambda \) [29], and as a result, most of the high energy ultraviolet radiation is absorbed very close to the surface (\( x = 0 \)). On the other hand, many of the infrared photons pass through the cell, not being absorbed at all, since for wavelengths greater than 1100 nm photons have insufficient energy to generate electron-hole pairs. (Some absorption does occur, but this effect is due to lattice vibration or phonon-assisted absorption [30]).
The rate of EHP generation is just the negative differential of equation (2.3):

$$G(\lambda, x) = \frac{-dN_0(\lambda)}{dx} = a(\lambda)N_0(\lambda) \exp[-a(\lambda)x] \text{ photons/s-nm-cm}^2 \quad (2.4)$$

If these EHP's are not separated in some way, they would eventually recombine, (depending upon the bulk lifetime, \(\tau\)) and no useful work could be done. Therefore, as part of their structure, a built-in field must be included to collect these free carriers. Much research has been done on the creation of this electrostatic potential in silicon. Shottky barriers [31], MIS tunnel junctions [32], inversion layers [10] and MIS technology in combination with inversion layers [16] will all provide the necessary field. The precursor to all of these technologies, however, is the P/N junction diode solar cell. Since an understanding of the operation of this cell is necessary to the comprehension of the inversion layer cell, it will be discussed in detail in the next two sections.

2.4 The Conventional Solar Cell

The conventional solar cell is illustrated in figure 2.2(a).

Into a Boron doped (p-type) single crystal substrate is diffused phosphorous to create a shallow (0.2 to 0.5 \(\mu\)m) N type layer. This large area diode will inherently produce the potential necessary for the collection of carriers. These carriers may be drawn off the front surface by means of a fine mesh grid (to minimize shading), and contact to the back surface is made by using a sintered metal, covering the entire back of the wafer. Usually, an antireflection
Fig. 2.2  
(a) Cross section of conventional solar cell.  
(b) One dimensional energy band diagrams for both short circuit and open circuit conditions.
coating is added to reduce the extremely large (>30%) reflection losses of bare silicon [33]. Also, a cover glass is sometimes bonded to the cell to add radiation protection for space applications.

Figure 2.2(b) shows the one dimensional energy band diagram for the cell under both short circuit and open circuit conditions. For the latter case, a voltage will build up across the depletion region as charge separation occurs, forward biasing the diode. At steady state, when the diode injection current (I_D) exactly balances the light produced photocurrent (I_L), the voltage across the junction will be the open circuit voltage (V_{oc}).

Like most electronic phenomena, the solar cell may be modelled by an equivalent circuit (Figure 2.3(a)). I_L is represented by a current source in parallel with an ideal diode. The cell's total series resistive losses are modelled by R_S. (A shunt resistor is sometimes included, but it is usually so large it may be neglected.) Using simple diode theory, a formula for the output current may now be derived:

$$I = I_L - I_0[\exp(q(V+IR_S)/nkT) - 1]$$

(2.5)

Where I_0 is the diode reverse saturation current, kT/q is the normalizing voltage (0.026 V at T = 300°K), and n is the diode ideality factor, which is a measure of the degree to which the diode fits the simple theory (n = 1 for ideal diode). Plotting as in figure 2.3(b), it is easy to see that the output curve is merely the diode dark I-V curve shifted down the current axis by the solar cell short circuit current (I_{sc}, normally equal to I_L).

For any solar cell, the most important parameter is the maximum power which can be obtained (P_{max}). A parameter closely related to
Fig. 2.3  (a) Solar cell equivalent circuit.
(b) Dark and light current voltage curves.
\( P_{\text{max}} \) is the fill factor (FF) which is a measure of the squareness of the illuminated I-V curve:

\[
\text{FF} = \frac{P_{\text{max}}}{V_{\text{oc}} \cdot I_{\text{sc}}} \tag{2.6}
\]

We now have all the parameters needed to define the losses and efficiency of a solar cell.

2.5 Losses and Efficiency

Aside from those already mentioned, many other factors combine to reduce the operating efficiency of silicon solar cells [34]. Since each EHP has approximately 1.1 eV of energy, photons possessing more than this have the excess wasted as heat dissipated in the silicon. Because of this, only half the energy in the solar spectrum is useable [28]. Once generated, some EHP's will be lost to recombination in the bulk, the diffused layer, the front and back surfaces, and/or grain boundaries. The fraction that are actually collected by the built-in electrostatic field is called the collection efficiency, \( C(\lambda) \). The portion of the incident photon flux that actually produces a current flow at short circuit is designated as the external current efficiency, \( Q_{\text{e}}(\lambda) \).

\[
Q_{\text{e}}(\lambda) = (1-R(\lambda)) \cdot (g(\lambda)) \cdot (C(\lambda)) \tag{2.7}
\]

Where \( R(\lambda) \) is the reflectance of the solar cell's surface and \( g(\lambda) \) is essentially the number of photons which generate EHP's. Therefore, the cell's photocurrent is given by:

\[
I_{\text{L}}(\lambda) = qN_0(\lambda) \cdot Q_{\text{e}}(\lambda) \ A/cm^2-nm \tag{2.8}
\]
The total cell output power may be calculated by integrating equation (2.8) across the usable spectrum:

\[ P_{\text{max}} = qV_{\text{OC}} \int_{0}^{\infty} N_0(\lambda) Q_e(\lambda) \lambda \, d\lambda \quad \text{W/cm}^2 \]  

(2.9)

Since this thesis is concerned with terrestrial solar cells, the total input power is 100 mW/cm², as discussed previously for the AM1 spectrum. Therefore, the overall conversion efficiency is given by:

\[ n = \left( \frac{P_{\text{max}}}{100} \right) \times 100\% = \left| \frac{P_{\text{max}}}{100} \right| \]  

(2.10)

Many people have studied the problem of just what is the maximum efficiency of silicon solar cells [35]. Calculated under almost ideal conditions, the AM1 efficiency has been estimated to be on the order of 22%.

2.6 The Inversion Layer (IL) Solar Cell

The conventional diffused junction solar cell is not without problems. Because of the use of single crystalline substrates, and the high temperature fabrication, it is inherently expensive. The diffusion introduces substantial lattice damage, reducing the minority carrier lifetime considerably. Surface recombination is a problem, as there is little or no electric field at the top of the cell. The net result of this is a poor ultraviolet collection efficiency. The inversion layer solar cell (depicted in figure 2.4(a)) eliminates these problems by simply avoiding the diffusion. Instead, charge (\(Q_{0x}\)) in a suitable oxide grown [10], or deposited [16] on the semiconductor surface creates an inversion layer which is then contacted by a diffused [12], or a MIS grid [17]. Because of the obvious superiority of the MIS
Fig. 2.4 (a) Cross Section Of The Inversion Layer Solar Cell.
(b) One Dimensional Energy Band Diagram Under Strong Inversion Conditions.
diode grid, especially for polycrystalline substrates, current IL cells at Carleton University use the MIS method exclusively [37].

The energy band diagram for the active region of this cell in strong inversion is shown in figure 2.4(b). Strong inversion is said to exist when the electron concentration at the surface is equal to the hole concentration in the bulk. The theory of operation of this cell, based on charge neutrality, Poisson's equation and Gauss' Law, is well understood, and only the important results will be discussed [10]. As the electric field is strongest at the interface between the oxide and the silicon, surface recombination is not a problem. With no "dead layer", plus the fact that the inversion layer is very shallow, carriers generated close to the surface are collected very efficiently. Also, the ability to fabricate with completely low temperature processing implies that cheaper substrates, and higher minority lifetimes are possible [36]. High lifetime improves collection from the bulk. All these effects combine to make the IL cell superior at ultraviolet wavelengths, but, since electrons collected by the induced junction must all flow through the inversion layer sheet resistance \( r_s \) to reach the contact, a fine grid must be used to reduce the series resistance, \( R_s \). This resistance has been shown to be equal to [15]:

\[
R_s = R_m + R_{IL} \ \Omega \cdot \text{cm}^2
\]

(2.11)

where \( R_m \) includes the resistance of the metal, front and back contact resistances and interconnect resistance. \( R_{IL} \), the larger of the two, is the inversion layer series resistance, dependant upon grid geometry [15]:

\[
R_{IL} = \frac{r_s}{12} \frac{e}{m} \ \Omega \cdot \text{cm}^2
\]

(2.12)

The number of grid fingers per centimeter is denoted by \( m \). The problem
of grid design will be covered in Chapter 4.

2.7 The MIS Tunnel Diode

One of the most important elements of any solar cell is the method by which the electrostatic field is contacted on the top surface. The Metal-Insulator-Semiconductor (MIS) diode offers P-N like behavior without the aforementioned disadvantages associated with diffusions. All that is necessary to fabricate such a device is to deposit a low work function metal such as aluminum on top of a thin insulating layer over a P-type silicon substrate. Electrons are attracted to the insulator-semiconductor interface producing an inversion layer [38].

Usually current flow in a metal contact on silicon is dominated by majority current flow. However, this results in very low open circuit voltages when these diodes are used in solar cells [39]. Fortunately, if a thin insulator is introduced (<20Å) between the low work function metal and the P-type silicon, the current flow in the diode will be dominated by electrons tunnelling from the metal into the semiconductor conduction band, rather than by thermionic emission of holes (majority carrier flow) from the valence band into the metal [39]. Such a MIS device is therefore termed a minority carrier diode. For sufficiently small forward bias (≈0.35V) the theoretical model also predicts that the quasi-fermi level for electrons at the semiconductor surface will be pinned to the fermi-level in the metal. The current in this regime is sometimes termed "semiconductor limited", because the transport of electrons from the induced junction at the surface into the semiconductor bulk is the process limiting the current flow. Behavior is almost identical to that of an N⁺P diode, as the total current is the sum of the currents due to recombination of the electrons in the
depletion region and that due to electrons diffusing into the quasi-neutral base. As the forward bias increases, the quasi-fermi level becomes unpinned, and the diode current becomes "tunnel limited", as the current flow is limited by tunnelling through the insulator rather than by transport through the semiconductor. Thus, in this mode of operation, the MIS contact may be modelled as an ideal N⁺P diode in series with a resistor. Because of this electronic equivalence, and the simple, low temperature fabrication, the MIS diode is ideally suited for use in inversion layer solar cells.

2.7.1 The Insulating Layer

The requirements for the thin insulating layer are twofold: it should have a low defect density and a low density of surface states at the interface with the semiconductor. Further, the method in which the oxide is grown should result in stable, reproducible layers. Most of the early MIS solar cells used the spontaneously occurring native oxide that grows on freshly etched silicon [14,16]. Greater control of the oxide thickness and other properties has subsequently been achieved by using a deliberate thermal oxidation.

It has been found that the open circuit voltage for MIS diodes on N-type substrates is usually smaller than that obtained in P-type substrates [32]. This has been explained as being due to the incorporation of silicon in unoxidized form in the oxide near the interface. This silicon-rich region would help to invert the surface of P-type silicon, by virtue of the positive charge it contains. This emphasizes the fact that thin oxides are not homogeneous; in fact they have been measured to have a stochiometry of SiO_{1.4} until a thickness of
at least 50 Å is achieved [41]. Thus the films may "age", and with time, the positively charged sites may be neutralized. Therefore, it appears advantageous to oxidize P-silicon in dry oxygen as opposed to wet (where hydroxyl ions would eliminate the charge). Because of this, and lifetime considerations, it was decided to oxidize in dry oxygen at 450 °C [36]. Ellipsometry measurements indicated that a thickness of 20 Å was attained after a ten minute run.

2.7.2 Results

MIS diodes were fabricated on both single and polycrystalline substrates. The large grain* (≥1mm) cast polycrystalline material was chemically polished to remove surface work damage, and MIS diodes were made in the same manner as single crystal devices.

The experimental dark log I-V characteristics for both these types of diodes, along with the ideal diode characteristic are plotted in figure 2.5(a). The measuring apparatus is outlined in figure 2.5(b). Obviously, the diodes are of the minority carrier type, as the inverse slope is around 2 for low bias and 1.1 for high bias [32]; whereas in the case of dominant thermionic emission current, a single exponential curve results with a n-factor between 1 and 2.

There does not seem to be any problems with grain boundary recombination, since it is possible to get a good curve whether the diode was placed in regions of high or low grain density, and the I-V curve is almost identical to that for single crystal silicon. Thus, the MIS diode is demonstrated to be very compatible with polycrystalline substrates, as was suggested earlier.

---

*Wacker-Chemistronic SILSO substrates
(a) Dark log(I)-V curves for single-crystalline, polycrystalline, and ideal silicon MIS diodes.

(b) Experimental test set-up.

Test gear is enclosed in a shielded room.
2.8 Summary

This chapter has served to introduce the basics of photovoltaic energy conversion. The physics of the conventional cell was contrasted with that of the inversion layer cell. Because of the absence of the lattice damage normally caused by diffusions, combined with the shallow induced junction, the IL cell was found to have a superior ultraviolet response. Losses associated with both of these structures were discussed, and formulae for basic cell operation were derived. As the minority carrier MIS diode is an integral component of the MIS-IL solar cell, its theory of operation was briefly described, and some experimental I-V curves were presented.

In the next chapter, various oxides of tantalum on silicon will be analyzed for possible use in MIS-IL silicon solar cells.
CHAPTER 3

PROPERTIES OF THE SILICON-TANTALUM OXIDE INTERFACE

3.1 Introduction

Ever since the reports of Vermilea [42] and Miller [43], concerning the usefulness of thin films of tantalum and tantalum pentoxide for the production of hybrid circuits, considerable effort has been expended on the study of both the production and properties of tantalum oxide films. Since then, oxides of tantalum have found use as capacitor dielectrics, passivating layers for integrated circuits, gate dielectrics for field effect transistors, and even as optical waveguides [44]. Unfortunately, very little work has been carried out using tantalum pentoxide for photovoltaic conversion [45]. This is surprising, considering the fact that the oxide is the best single layer antireflective film on silicon, yielding the largest short circuit current in solar cells with shallow junctions [46]. The MIS-inversion layer cell fits nicely into this category, as mentioned previously. Because the optical properties of any oxide used are extremely important in determining the ultimate efficiency of this cell, it is necessary to discuss what characteristics such a film must have. In addition to the obvious requirements, i.e., as little absorption as possible for wavelengths greater than about 300 nanometers, and a refractive index between 2.0 and 2.5 [33], the oxide should be prepared such that it is in the non-crystalline state.
but with a reasonably high degree of short range order. Solids with this property are termed "vitreous". Non-crystallinity is important since grain boundaries in a polycrystalline film cause light scattering, and hence decrease the transparency. Also, it is a well known fact that dielectric films used in capacitor and semiconductor devices must be non-crystalline to achieve the best possible properties [47]. The stability and reproducibility of various film properties are enhanced in an oxide with short range order [21]; also unsaturated bonds cause light absorption in completely amorphous films. For example, thermal SiO₂ used previously in IL solar cells is vitreous [15], while SiO [18,19,20] is completely amorphous. This underscores the importance of the preparation technique in obtaining well defined, non-crystalline tantalum oxide films.

Many methods have been used in the past to fabricate such films. Evaporation [48] and chemical vapour deposition [49] of the oxide tend to form amorphous layers. Anodic [50] and thermal [51] oxidation of tantalum offers films on silicon with the best optical properties, and evidence suggests that the silicon/oxide interface is of high perfection [48]. Because of the limited facilities and materials available at Carleton University, it was decided to investigate tantalum pentoxide films prepared by the following three methods: evaporation of tantalum pentoxide powder, thermal oxidation of tantalum film on silicon, and the use of a tantalum-alcohololate solution. The purpose of this chapter, therefore, is to characterize the properties of the silicon-oxide interface of the aforementioned films for possible use in the MIS-IL solar cells.
3.2 Thermally grown tantalum oxide on silicon

Tantalum was first discovered in 1802 by a Swedish chemist named Ekeberg. He named the element after the Greek "Tantalos" because he was "tantalized" about the apparent insolubility of the oxide. Because of this problem it was not until 1903 that the first relatively pure ductile metal was produced. Tantalum is a gray, heavy and very hard metal, (density of 16.6 gm/cm\(^3\)), almost completely immune to chemical attack at temperatures below 150°C. Only sulphur trioxide, hydrofluoric acid and other acids containing the fluoride ion manage to etch it. It's melting point (2850°C) is exceeded by only tungsten and rhenium. Near the melting point, tantalum is extremely reactive, and for this reason, it has excellent "gettering" properties. Found naturally as the mineral "columbite-tantalite" \([(Fe,Mn)(Nb,Ta)_2O_6]\), 70% of world consumption is used for electrolytic capacitors and vacuum furnace parts. Also, because tantalum is completely immune to body liquids, and is non-irritating, it has found wide use in surgical instruments.

Two simple methods exist for fabricating thin tantalum films on silicon. Electron beam evaporation is widely used to deposit other elements, but because of the high reactivity of tantalum near it's melting point, the possibility of impurities being incorporated in the film is quite high [52]. Sputtering involves the use of an atmosphere (usually argon) with the distinct possibility of gaseous inclusion [52]. Therefore, because contamination by impurities may be controlled somewhat, while gaseous inclusion cannot, it was decided to prepare the thin films by electron-beam evaporation.

The schematic of the equipment used is shown in figure 3.1. It has been found that when the vapour pressure (Pv) of an element is
Fig. 3.1 (a) Schematic of the evaporator used.
(b) Close-up of the hearth showing the 270° electron beam gun.
raised to approximately $10^{-3}$ Torr in a sealed container, a film will be deposited on a suitably placed substrate. Honig [55] in 1962 measured the vapour pressure of tantalum to be equal to:

$$\log_{10} P_v = 11.1 - (4.7 \times 10^3 / T) \quad (3.1)$$

where $T$ is the absolute temperature and $P_v$ is in Torr, and if $P_v$ equals $10^{-3}$ Torr, the temperature should be slightly past the melting point, or 3060°C. The electron beam supplies the energy necessary to achieve this rise in temperature without introducing contamination by the water cooled crucible.

The power to the electron beam is adjusted by the Airco-Temescal film deposition controller. This microprocessor based controller is capable of storing all the parameters required to deposit up to six independent and totally unrelated films. The thickness and rate of deposition of the film is sensed by the change in frequency of a quartz crystal, caused by the evaporant accumulating on it. This crystal is located just behind the substrate. The power supply used is a direct current, constant voltage source able to deliver up to 10 KV at 0.8 A to the hearth.

Five nines (99.999%) pure tantalum metal was obtained with the assistance of W. Westwood at Bell Northern Research. The sample was given a standard degreasing (trichloroethylene, acetone and alcohol boils) followed by a prolonged cleaning etch in hydrofluoric acid. The evaporator hearth was then sand blasted clean, and the sample was placed in the crucible. To outgas the freshly etched metal, a vacuum was drawn and the metal was melted using the electron beam. A side effect was that any residual gases in the chamber were gettered by the evaporated tantalum.
The power was then turned off, and the system was kept under high vacuum for 24 hours to ensure complete outgassing.

To obtain a controlled deposition of tantalum, it was necessary to obtain the density of the film in order for the controller to calculate the thickness of the evaporated layer accurately. Fortunately, tedious and often times inaccurate weight measurements did not have to be taken, as the deposition controller features a simple method for calculating density. All that is necessary is to deposit a film using an estimated density for the controller, measure the thickness of the film, then adjust the density until the displayed thickness agrees. To accomplish this, glassware cleaned microscope slides were first coated with tantalum, overlapped and coated again in the evaporator so that a step in the tantalum film resulted. The thickness of this step was determined by using sodium interferometry. The correct density was then ascertained using the aforementioned method. The average density obtained after many trials with varying thicknesses was 13.0 g/cm³. This value is less than that for bulk tantalum, indicating that evaporated films are porous. Also, the density agrees exactly with that obtained by Kirkendall [54], who used weight measurements.

Having established most of the deposition parameters, a tantalum film was evaporated onto a "pre-furnace cleaned" silicon wafer. The precautions outlined previously were taken to prevent contamination. It was found that the rate of evaporation affected the uniformity of the film. This is not uncommon, as high rates induce sputtering by positive tantalum ions [55]. The best rate was determined experimentally to be 3 Å/sec. (A complete list of deposition parameters is kept in the manual beside the evaporator.)
As it is a well known fact that the thickness of the oxide in IL cells does not affect the inherent charge [15], it was decided to deposit only 300 Å of tantalum on silicon. This thickness was determined by anticipating the reflectance of the oxidized film to be a minimum at 5400 Å. The index of refraction was assumed to be 2.23 in agreement with thermal Ta₂O₅ films on silicon obtained in the past by Revesz [56]. If n is this index of refraction, and d is the required thickness of the oxide in Angstroms, then:

$$\frac{5400}{4} = nd \quad ; d = 605 \text{ Å}$$

(3.2)

Knowing the necessary thickness of the oxide, it was straightforward to work backward and estimate the thickness of the tantalum to be deposited. From molecular weights, Ta₂O₅ is 441.89/180.94 = 1.221 times heavier than Ta. Using the reported density of 8 gm/cm³ for thermal tantalum pentoxide [51,56], and assuming that growth of the oxide occurs in only one dimension, we get:

$$\frac{\text{Volume of Ta}_2\text{O}_5}{\text{Volume of Ta}} \cdot x_o = \text{Thickness of Ta}_2\text{O}_5$$

(3.3)

Where \(x_o\) is the thickness of the evaporated tantalum. Substituting values:

$$x_o = 605 \text{ Å} \cdot \frac{1}{13} \text{ cm}^3/\text{Å} \cdot \frac{1.221}{8} \text{ cm}^3 = 305 \text{ Å}$$

(3.4)

Tantalum films of this thickness were evaporated onto both "P" and "N" type (100) and (111) etched substrates prior to the following oxidation experiments. The resistivity of the films were measured to be in the range of 180 µΩ·cm which is characteristic of a tetragonal crystal structure known as the beta phase which has a resistivity much higher than the bulk material (20 µΩ·cm) [52].
3.2.1 Oxidation and Ellipsometry

The 300 Å thick tantalum layers on silicon were oxidized in a dry oxygen ambient at 450 °C to get the benefit of the highest possible lifetime out of the starting material [36]. The apparent thickness and refractive index were determined by using an ellipsometer and measuring at ten minute intervals. Because of the high accuracy needed, and the large refractive index of the film at 5461 Å, a program was written to analyze the data [Appendix B]. The oxidation of the thin tantalum film was considered to be complete when the apparent refractive index of the oxide reached its maximum value, (see figure 3.2(a)) and the corresponding time was taken as the oxidation time. As is evident from the graph, the oxidation time at 450°C was prohibitively long. Because of this, a different temperature of 530°C was tried, and this resulted in a very fast (<10 min.) oxidation. The final refractive index is obtained when the tantalum film becomes completely oxidized and transparent. This value, (2.23) can be compared with the refractive index of anodic Ta₂O₅ films (n=2.22) [50], and for the range of values (2.14<n<2.25) reported for the thermal oxidation of sputtered tantalum films on glass or other insulator substrates [58].

No discernible features could be observed with either optical or electron microscopy (section 3.6), suggesting the films are indeed non-crystalline, as predicted by theory. The films also exhibited bright blue interference colours as might be expected from antireflective coatings. No appreciable differences were noticed between "N" and "P" type silicon, or between (100) and (111) orientations. However, the thickness measured appeared to be slightly larger than what might be expected based on the tantalum thickness. This might be due to
Fig. 3.2 (a) Plot of refractive index versus oxidation time at a temperature of 450°C.

(b) Gradient of refractive index through the thermal oxide.
Inaccuracies in the calculations made in the last section, but recently published results suggest that thermal tantalum pentoxide films incorporate a significant amount of silicon in oxidized form in the film [57]. This finding is quite unexpected, since when bare silicon is oxidized at 450°C for ten minutes only about 20 Å of oxide is formed [32]. In an attempt to verify this finding, thick (900 Å) evaporated tantalum films were oxidized on silicon. Using a versatile sodium hydroxide etch [59], which removes Ta₂O₅ at the rate of 1500 Å/min, the substrate was stepwise etched, and the thickness and refractive index was measured after each step. A gradient in the refractive index across the thickness of the film was measured, as might be expected if there were an interaction between the silicon and the oxide. The refractive index increases from the silicon-oxide interface to the outer surface (see figure 3.2(b)). Because of this result, and subsequent data which suggested that all tantalum pentoxide films might not be completely stoichiometric, the film will hereafter be referred to as only "tantalum oxide".

An important consequence of the interaction described here is not that the original silicon-ambient interface is simply replaced by the silicon tantalum interface, but that the interface actually reacts with the silicon crystal. In this respect, the situation is very much like the thermal oxidation of silicon. Also, because the Si-SiO₂ interface is quite perfect [60,54], it can be expected that the Si-Ta₂O₅ interface may be also. This was subsequently verified using capacitance-voltage (C-V) measurements. Before reporting these results, however, the theory behind the C-V curve, along with the measuring procedure will be explained in the following section.
3.2.2 C-V Analysis

One of the most accurate and widely used methods of determining oxide charge and the quality of the oxide silicon interface is through the use of capacitance-voltage (C-V) plots [61]. To perform this measurement, all that is necessary is to define a metal gate on top of the oxide, thus forming a MOS capacitor, and then plotting the capacitance as a function of gate bias. Because MOS physics is well understood [13,61], only the salient theory will be discussed.

Consider the MOS capacitor shown in figure 3.3(a). The oxide is assumed to have a fixed positive (or negative) charge density \( Q_{ox} \), plus a bias dependant charge \( Q_{ss} \) that has its origin in mobile charge and something called surface states to be explained shortly. A large positive voltage \( V_G \) applied to the gate will drive the surface of the P-type silicon into heavy inversion, if the surface is not already inverted, due to \( Q_{ox} \). Under these conditions, the charge distribution for the system is shown in figure 3.3(b). Obviously, the total MOS capacitance \( C_{mos} \) may be modelled as in figure 3.3(c) as two capacitors in series:

\[
C_{mos} = \frac{C_{ox} C_s}{C_{ox} + C_s} \quad \text{F/cm}^2 \quad (3.5)
\]

Where \( C_{ox} \) is just the fixed oxide capacitance determined by the oxide permittivity \( \varepsilon_{ox} \) and the thickness \( t_{ox} \):

\[
C_{ox} = \frac{\varepsilon_{ox}}{t_{ox}} \quad \text{F/cm}^2 \quad (3.6)
\]

\( C_s \) is similarly defined as the semiconductor capacitance due to the depletion width \( x_d \) in the semiconductor, and the permittivity, \( \varepsilon_s \) of the silicon:

\[
C_s = \frac{\varepsilon_s}{x_d} \quad \text{F/cm}^2 \quad (3.7)
\]
Fig. 3.3 (a) MOS capacitance structure, (b) Charge distribution, (c) Equivalent capacitance, (d) Energy band diagram with the potential distribution, (e) Ideal C-V curve for both the low frequency and high frequency bias. Also included is an actual measured curve.
This capacitance would be very large in both accumulation or inversion because of the high charge density [61]. Therefore, under these conditions \( C_{\text{mos}} \) would be equal to \( C_{\text{ox}} \). In view of this, the voltage across the oxide is defined: (figure 3.3(d))

\[
V_{\text{ox}} = - \frac{Q_{ss} + Q_{ox} + Q_{s}}{C_{\text{ox}}} = V_G + \varphi - \varphi_f \text{ Volts (3.8)}
\]

Defining the metal semiconductor work function \( \varphi_{\text{ms}} \) as:

\[
\varphi_{\text{ms}} = \varphi_f + \varphi_e \text{ Volts (3.9)}
\]

And, substituting into (3.8) and solving for the gate voltage, we get:

\[
V_G = \varphi_{\text{ms}} - \frac{Q_{ss} + Q_{ox}}{C_{\text{ox}}} + 2 \varphi_f - \frac{Q_{s}}{C_{\text{ox}}} \text{ Volts (3.10)}
\]

If the flatband voltage, \( \varphi_{\text{FB}} \) is defined as that voltage which when applied to the gate will flatten the energy bands, then it obviously has to be large enough in magnitude to overcome the fields due to the charges \( Q_{ss} \) and \( Q_{ox} \), and also the metal-semiconductor work function, \( \varphi_{\text{ms}} \):

\[
\varphi_{\text{FB}} = \varphi_{\text{ms}} - \frac{Q_{ss} + Q_{ox}}{C_{\text{ox}}} = \varphi_{\text{ms}} - \frac{Q_{\text{FB}}}{C_{\text{ox}}} \text{ Volts (3.11)}
\]

\( Q_{\text{FB}} \) is thus defined as the flatband charge.

The theoretical C-V curve for a MOS capacitor on a P type substrate is plotted in figure 3.3(e), along with an actual measured curve. (For capacitors on N type substrates, the curve would be the mirror image around \( V_G = 0 \).) Consider the ideal curve first. Varying the gate bias takes the capacitor from strong accumulation to deep inversion.
In the preceding development, it was assumed that steady state conditions apply at all values of the surface potential, $U_S$. If this is the case, the resulting C-V curve will be the low frequency one, shown as the dotted line in figure 3.3(e). In practice, however, C-V measurements are made by using an A.C. signal superimposed upon the D.C. gate bias. The inversion charge, $Q_n$, is then not able to follow this high frequency signal, as the electrons are only generated thermally, a very slow procedure. As charge neutrality must be maintained at all times, the result is that the depletion width, $X_d$, is modulated, changing $Q_d$. Because the capacitance seen by the signal is across both the depletion and the oxide regions, the C-V curve remains low in inversion.

The measured plot in figure 3.3(e) differs from the ideal in two important respects. First of all, the effect of the work function $\phi_{ms}$, is to produce a parallel shift of the C-V curve without distortion along the voltage axis by an amount equivalent to the work function difference. If $\phi_{ms} > 0$, the shift is towards positive gate bias, if $\phi_{ms} < 0$, the shift is toward negative gate bias. The second difference to note is that the slope of the real curve is reduced. This effect is due to what are termed fast surface states. These states, which result from traps or defects at the oxide-silicon interface, are termed fast because they are able to charge to follow the applied D.C. bias (ramp). These states fill or empty depending upon the gate bias, introducing positive or negative charge as they do. This causes a stretching out, or softening of the C-V curve, proportional to the number of states, $N_{ss}$ (states per cm$^2$ of surface area per electron volt of bandgap) that are affected. A defect-free superior oxide, then, would have a C-V curve whose slope near flatband would be very high. There are numerous papers
discussing fast surface states, \( N_{ss}^{\text{FAST}} \), and their evaluation \([61, 62]\). The most commonly accepted model \([63]\) is depicted in figure 3.4(a). As can be seen, the occupancy or vacancy of such states depend upon the position of the fermi level at the surface. In reality, \( N_{ss}^{\text{FAST}} \) varies across the bandgap, but since the charge due to this interface state density is typically smaller than \( Q_{FB} \), it is convenient to consider it to be constant. If this is assumed, a method of calculating \( N_{ss} \) from the real curve also becomes apparent. Considering figure 3.3(e) again, the slope of the ideal curve is represented by a voltage \( \Delta V_1 \). This is the voltage between flat band and a constructed point found by extrapolating the straight line segment of the curve until it intersects the minimum capacitance. \( \Delta V_1 \) would thus correspond to a change in surface potential of 2 \( \phi_f \) (i.e., from strong inversion to flat band). A similar exercise yields \( \Delta V_a \) for the actual C-V curve. Thus \( N_{ss}^{\text{FAST}} \) is given by:

\[
N_{ss}^{\text{FAST}} = \frac{C_{ox}}{q\phi_f} (\Delta V_a - \Delta V_1) \quad \text{states/cm}^2\text{ev (3.12)}
\]

The true fixed charge, \( Q_{ox} \), may be calculated by subtracting the positive charge contribution of \( N_{ss} \) at flatband, from \( Q_{FB} \):

\[
Q_{ox} = Q_{FB} - q\left(\frac{KT}{q}\phi_f N_{ss}\right) \quad \text{C/cm}^2 \quad (3.13)
\]

Surface states unable to follow the D.C. bias, termed \( N_{ss}^{\text{SLOW}} \), also exist. Due to mobile ionic charge, charge trapping, or polarization of the oxide, \([62]\), their net effect is to cause a hysteresis in the C-V curve as it is swept from positive to negative and back again. \( N_{ss}^{\text{SLOW}} \) may be estimated by \([14, 15, 62]\):

\[
N_{ss}^{\text{SLOW}} = \frac{C_{ox}}{q(\phi_f)^2} \Delta V_h \quad \text{states/cm}^2\text{ev (3.14)}
\]
Fig. 3.4 (a) Commonly accepted model for fast surface states. Acceptor states 'accept' an electron and become negative. Donor states give up an electron, becoming positive.
(b) Capacitance versus voltage curve measurement apparatus.
Where $\Delta V_n$ is the hysteresis shift in the C-V curve. The apparatus used for measuring high frequency C-V curves is shown in figure 3.4(c).

Because of the tedious calculations needed to analyze practical C-V curves, a fortran program called CEEVEE [15], was written for the Xerox/Honeywell Sigma 9 computer at Carleton University. To generate the C-V curve for any MOS system the user specifies the bulk doping $N_d$, the oxide thickness $t_{ox}$, the flatband charge $Q_{FB}$, the density of surface states $N_{ss}$, and the vacuum work function of the metal ($\Phi_m$). The computer prints out the data needed to draw the C-V curve. This curve is then compared with the actual one, and the values of $Q_{FB}$ and $N_{ss}$ that give the best fit are assumed to be correct. Because of the great number of C-V curves measured in the following sections, it was decided to implement a simpler version of this program based on a paper by Lehovec [63] on a programmable calculator. This program calculates the density of fast surface states by measuring the slope of the C-V curve at flatband. The fixed oxide charge is also estimated. The results, although based on approximate theory, agreed with CEEVEE very closely.

3.2.3 Electronic Properties of the Interface

MOS capacitors were fabricated to evaluate the properties of the thermal tantalum oxide interface using the methods outlined in the last section. To avoid changing any important electrical characteristics of the oxide, a decision was made to evaporate gold as the back contact for the previously oxidized wafers. Because of the low (350°C) sintering temperature required for this metal, it seemed unlikely that any oxide charge would be adversely affected. For reasons to be explained shortly,
the sintering was also done in an oxygen ambient to avoid destroying any oxide charge. The oxide thickness was determined using the ellipsometer, and the front surface was coated with a 10 kÅ thick aluminum layer. Photolithography was used to define a matrix of capacitor dots (Mask # A-0220-C). The areas of these capacitors, which varied from $1 \times 10^{-4}$ to $2.6 \times 10^{-3}$ cm$^2$, were determined by using an IN/$\sqrt{\text{traveling microscope}}$. An alternative method would have been to define the dots by using a metal mask during evaporation; but, the capacitors thus formed would have been very ill defined.

Capacitors were prepared on oxides that had been grown under many different conditions. Different oxidation times and temperatures were used, and some had been heat treated in either nitrogen or oxygen, and some had not. Capacitance-voltage curves, for which the D.C. bias was swept at 0.01 Hz, were then measured in the dark (to avoid any optical biasing). The results for all these measurements were very consistent. First of all, the earliest experiments indicated that the fixed oxide charge was negative. This agreed with the findings of other investigators [23,64], and therefore all subsequent experiments were confined to N type substrates. This was done in the hope that sufficient negative charge could be achieved to warrant fabricating an IIL cell with an inversion layer of holes instead of electrons at the surface. Such a configuration would have been unique, as most oxides exhibit a positive charge instead of negative. Unfortunately, for reasons to be explained, this was not realized.

A representative high frequency C-V curve for a capacitor on "N" substrate is shown in figure 3.5 along with the calculated ideal curve. No important electrical changes were noted when the oxidation
Fig. 3.5 Ideal and representative C-V curves for a capacitor on an 'N' type substrate. Thermal tantalum oxide was used as the dielectric.
temperature was changed from 450°C to 530°C. The characteristics were not even affected when the capacitors were heat treated in oxygen for periods of up to seven hours. No hysteresis occurred during any of the measurements in which the D.C. bias voltage was swept from -10V to +10V and back again. This indicated that the density of slow surface states was not significant. However, when the D.C. bias voltage was increased to 25 volts or greater and left for periods longer than 10 minutes, a very small shift in the curve occurred in some oxides. This effect could be due to a small amount of mobile ionic charge in the oxide.[61]

The effective fixed charge density, \(Q_{ox}/q\) was measured to be consistently in the range of \(-3 \times 10^{11}\) to \(-5 \times 10^{11}\) charges/cm\(^2\). As alluded to before, the only thing to affect this charge was a heat treatment in nitrogen. Any time spent in an N\(_2\) ambient at temperatures above 300°C completely annihilated the oxide charge. This phenomenon has been observed before,[23,64] and was theorized to be due to positive nitrogen ions being incorporated in the oxide, thus neutralizing the negative charge. Another phenomenon that is evident from the graph is that the flatband voltage is slightly positive. Unfortunately, this was not always evident as the effect of the metal work function difference sometimes obscured this fact for oxides with a smaller \(Q_{ox}\). This is because \(\phi_m\) is about -0.3V for N type silicon at the doping levels used (8-10\(^{12}\)-cm), and this tends to shift \(V_{FB}\) toward negative bias, reducing the apparent effect of \(Q_{ox}\).

For example, if gold were used for the top contact instead of aluminum, \(V_{FB}\) would shift towards positive bias by about +0.3 Volts.

The density of surface states was consistently about \(5 \times 10^{10}\) states/cm\(^2\)-ev for (100) substrates and only slightly larger for (111) substrates, due to dangling bonds [15]. This result demonstrates that
the Si-Ta2 interface is surprisingly good, considering the fact that
the oxide film is non SiO2 and no high temperatures were used. The
importance of a growth, as opposed to a deposition process, and the flex-
ibility of the non-crystalline structure in obtaining a nearly perfect
interface has already been pointed out. It is a well known fact that
non SiO2 dielectric films on silicon tend to have a high density of sur-
face states, instabilities, etcetera [47]. It is very probable that the
reason for the relatively low density of surface states in this case is
due to the incorporation of silicon into the oxide film during its growth
[54, 57]. As a result of this interaction, the quality of the interface
is quite good. In fact, the density of surface states measured is
comparsable to that obtained when silicon is thermally oxidized [15], even
though the oxidation of the tantalum was carried out at much lower
temperatures, and no high temperature annealing was applied. Also,
reflectance curves (see section 3.5) indicated that the oxide was nearly
ideal. In contrast to this, a tantalum oxide film deposited by a chemical
vapour deposition technique resulted in an extremely large density of
surface states [49].

By using the capacitance measured in the strong accumulation
region in combination with the thickness (d_ox) and the area of the cap-
acitor (A), an estimate for the relative dielectric constant (\varepsilon_r) may
be obtained:

\[
\varepsilon_r = \frac{C_{ox} + ox}{A_0 \varepsilon_0}
\]  

(3.15)

Where \( \varepsilon_0 \) is the permittivity of free space, \( 8.86 \times 10^{-14} \text{ F/cm} \). Using
the results of approximately 100 measurements from different experiments,
\( \varepsilon_r \) was determined to be 11.14. This increased value of \( \varepsilon_r \) relative to
thermal SiO2 (\( \varepsilon_r = 3.8 \)) diminishes the effect of interface states, for
a Si-SiO₂ interface having the same surface state density as the Si-Ta₂O₅ interface would give rise to a C-V curve significantly less sharp than the curve depicted in figure 3.5.

The results reported here demonstrate that thermally oxidized tantalum is very stable, yielding reproducible negative charge densities sufficient to invert 8-10Ω-cm substrates. The nature of this charge will be discussed in chapter 5. There does not appear to be much prospect of increasing this fixed charge, as heat treatment has little affect. Perhaps if the tantalum was deposited on the silicon under different conditions, the charge might be affected. For example, it might be worthwhile to investigate evaporation in an oxygen ambient, or sputtering of the tantalum onto silicon substrates.

The quality of the Si-Ta₂O₅ interface appears to be comparable to thermal SiO₂ in that a very low surface state density was evident. Unfortunately, computer modelling predicted that if inversion layer cells were to be fabricated using this oxide, at best only 5%-6% efficient cells would be achieved [15]. Therefore, research into this area was discontinued in favor of simpler and more efficient techniques to be described in the following sections.

3.3 Evaporated Pressed Tantalum Oxide Powder

Very little work has been done on preparing tantalum oxide films by the direct evaporation of the oxide. It is usually very difficult to get uniform well controlled films because of reduction and sublimation of the oxide during evaporation. For example, dielectric films were prepared by Carlough et al [48] by electron beam evaporation of Ta₂O₅ powder in pressures between 10⁻⁵ and 10⁻⁸ Torr and at deposition rates between 10 and 300 Å/min. Extreme care had to be taken in choosing the deposition conditions to obtain stoichiometric films, otherwise mixtures of Ta and the
stable suboxides, Ta₂O and TaO₂ were obtained. Oil free, ultra high vacuum systems were used to avoid this oxide reduction by hydrocarbons. Unfortunately, although the oil used in the vacuum system at Carleton University is non-hydrocarbon based, an extremely high vacuum cannot be achieved. As some residual gases in the vacuum chamber are known to cause oxide reduction [65], it was decided to deliberately introduce oxygen gas after the system had pumped down as far as possible. This was intended to make conditions favorable for the formation of stoichiometric Ta₂O₅. This same technique has been used before to form oxides by the reactive evaporation of metals in an O₂ ambient (10⁻⁵ Torr). The oxides thus formed were found to be very stable and stoichiometric.

The second problem encountered is that some dielectrics sublime instead of passing through a liquid phase during evaporation [65]. In this case, if the beam remains in one position very long, it creates a crater, which then collimates the stream of evaporant, causing nonuniform distribution, and minimal bulk evaporation. Fortunately, the electron beam source at Carleton University is equipped with electromagnets which can sweep the beam in both the longitudinal and lateral axes. As a result the electron beam spends equal amounts of time at all points along its traverse. This feature had never operated since the evaporator was purchased, and thus a considerable amount of time and effort was spent in repairing the sweep circuitry.

3.3.1 Experimental Results

Very pure (325 mesh) tantalum oxide pressed powder was obtained* and placed in a non-reactive carbide crucible in the evaporator. A vacuum was drawn, and the system was left to pump down overnight to outgas and achieve as little background pressure as possible. An oxygen pressure of 10⁻⁵ Torr was then introduced through a valve at the top of

*Materials Research Corporation, Orangeburg, N.Y.
the vacuum chamber. During evaporation, the beam was swept as fast as possible to attain a uniform deposition. It was found that high beam powers actually resulted in the oxide being blown out of the crucible, and consequently all subsequent evaporation were carried out at the comparatively slow rate of 2 Å/sec.

To obtain the density of the oxide, test runs of evaporated tantalum oxide powder were deposited on silicon substrates, and the thickness was measured using the ellipsometer. Using the methods outlined in the last section, the correct density was obtained. The value, 7.4 gm/cm² is somewhat smaller than that of pure Ta2O5 (8.2 gm/cm²) indicating that the films were either porous, or non uniform in composition. The chemical composition of the film turned out to be impossible to determine, as the small size of the crucible used (5 cm³) allowed only a maximum of 700 Å of the oxide to be deposited. Although this is sufficient to make good antireflective coating, it is too thin to perform any kind of stoichiometry analysis such as energy dispersive microprobe, or a SEM X-ray probe [66]. Therefore, as the precautions outlined should be sufficient to obtain uniform films, any density discrepancy will be assumed to be due to porosity.

The refractive index at 5461 Å was determined by ellipsometry to be in the range of 2.04-2.07. This compares with 2.1 for sputtered Ta2O5 films [67], and 2.09 for evaporated Ta2O5 [46].

Gold back contacts were evaporated on cleaned "P" and "N" type substrates of both orientations. Sintering was then done at 300°C. For the optical reasons outlined in the last section, 650 Å of tantalum oxide was deposited. Using aluminum as a top contact, MOS capacitors were then defined with photolithography. Summarizing the important results of the C-V measurements that were subsequently made, the oxide charge was found to be positive and quite reproducible. The fixed charge obtained
was in the range of $4 \times 10^{11}$ to $6 \times 10^{11}$ charges/cm$^2$. This result underlines the importance of having a well controlled deposition procedure, as similar experiments done in the past without using the electron beam sweep or the partial O$_2$ ambient achieved little or no oxide charge [68].

A typical C-V curve for the evaporated oxide is shown in figure 3.6, for P type (111) substrates. As might be expected for such a deposited oxide, the density of fast surface states is quite high, being in the range of $1 \times 10^{11}$ to $3 \times 10^{11}$ states/cm$^2$-ev. No differences were noted between (100) and (111) orientations, consistent with this fabrication technique. Also, some hysteresis is evident in the plot, indicating a slow surface state density of $1.05 \times 10^{11}$ states/cm$^2$-ev. This effect could be due to mobile charge impurities in the oxide [61]. In contrast to what was obtained for thermally oxidized tantalum, any heat treatment in O$_2$ at temperatures above 300°C reduced both the surface state density and the positive charge, while treatment in N$_2$ had little or no effect. The nature of this fixed charge will be discussed in Chapter 5.

The modelled curve from CEEVEE is also shown in figure 3.6. The dotted line is the ideal curve shifted to the left by $\varphi_m$, while the effect of surface states and oxide charge combine to model the measured curve very well.

The interfacial quality is obviously not as good as that for thermal tantalum oxide. The reflection curves in section 3.5 tend to back this up. Also, stepwise etching experiments similar to those done in the last section demonstrate that no gradient existed in the refractive index through the oxide, implying that very little interaction, if any, with the silicon is occurring; a finding that is consistent with the simple deposition technique used. The relative dielectric constant ($\varepsilon_r$) was determined to be 7.83, which is less than that for thermal
Fig. 3.6 Capacitance versus voltage curves for a capacitor on a 'P' type substrate. The dielectric used is evaporated tantalum oxide powder. Shown is the ideal curve shifted towards negative bias by the work function difference ($\phi_{ms}$), the measured curve, and the complete model predicted by 'CEEVEE'.
tantalum oxide. Possibly, the porosity of the oxide is the cause for this reduced value.

As before, the fixed oxide charge is still just barely sufficient to invert 8-10 \( \mu \)-cm silicon, and computer modelling again estimated that only 5-6\% efficient solar cells would have been obtained \( [15] \). As discussed previously, the fixed oxide charge was not increased by any heat treatments, thus it was not expected to improve on this predicted efficiency. Perhaps sputtering of the tantalum oxide powder onto silicon substrates would affect the charge. The results of photovoltaic testing are reported in Chapter 4.

3.4 Spin-on Tantalum Oxide

The third and final method that was investigated for preparing tantalum oxide films on silicon was through the pyrolysis of an oxide-alcohol solution known as TANTALUMSILICAPLMT* . This solution was theorized to be a mixture of tantalum and silicon alkoxides in an approximate 80\%-20\% ratio, respectively. The chemical character of this mixture is analyzed in chapter 5. In normal use as an antireflective film, the wafers to be coated are baked at 200\(^\circ\)C for about 30 minutes to drive off any moisture, and then cooled. The solution is then applied from an eye dropper and spun for 15-30 seconds at 3500 R.P.M. to spread a thin uniform layer over the surface. The films are then baked at 100\(^\circ\)C to drive off the alcohol. Films prepared in such a manner usually demonstrated a refractive index of 1.8 and a thickness of 720 \( \AA \). This combination results in a good optical match to the solar spectrum at 5400 \( \AA \). The reflectance for this coating as a function of incident wavelength is

* Emulsitone Corporation, Whippany, N.J.
plotted in the next section.

To begin in characterizing the interface, it was necessary to determine how, if at all, the solution was affected by the heat treatment at 100°C. Empirical evidence suggested that this heat treatment caused pyrolysis of the coating, changing it to a stoichiometric Ta₂C₅ and SiO₂ mixture. (See Chapter 5) In an attempt to indicate that compositional changes do indeed occur, ellipsometry experiments were performed as follows:

TANTALUM SILICAFILM was spun on freshly etched silicon wafers at 3500 R.P.M. The thickness measured was consistently around 850 Å when a fresh bottle of solution was used. However, it was noted that in the course of normal usage, the solution tended to densify by liberating ethyl alcohol to the atmosphere every time the cap was taken off. As a result, the spin speed had to be increased periodically to achieve reproducible results. To prevent this from occurring, small amounts of alcohol were added to the solution occasionally. The refractive index was measured to be equal to 1.6, again a good optical match to 850 Å [33]. It should be noted that a deep null in the ellipsometer's meter was impossible to obtain for the "as-spun" coating until it dried somewhat. This points out the unstructured nature of the solution. Some of these films were then left to dry at room temperature for periods of one month or greater, while others were immediately heat treated at 100°C. The net result of this experiment was that the refractive index of the films left in air slowly increased as they dried, verifying that compositional changes did indeed occur in the films as they aged. The final value reached was 1.8 while the thickness densified to around 730 Å. These
values agreed almost exactly with those oxides that had been heat treated, implying that the chemical composition of the two are identical. Obviously, then, the "as-spun" films are quite different from the heat treated films, and therefore had to be considered separately in the subsequent investigation.

3.4.1 C-V Results

To determine the electrical properties of the interface for both "as-spun" and the baked films, back contacts were evaporated on P and N type silicon wafers. Sintering was then done in N\textsubscript{2} for 10 minutes at 450°C. The solution was then spun on as before, with the exception that some of the films were baked and some were not. Because of the volatility of the unbaked solution, it was decided not to evaporate a metal for the front contact, as this could possibly contaminate or change the characteristics of the film. Instead, C-V measurements were done using a mercury probe. This technique involves using a small drop of mercury as the top capacitor contact. This has the advantage of being quick and simple, however, the capacitors thus formed have very ill defined areas, making it impossible to estimate the relative dielectric constant for the films accurately. C-V measurement indicated that the heat treated films were free of charge, while the "as-spun" films had a surprisingly high oxide charge in the range of $1 \times 10^{12}$ to $3 \times 10^{12}$ charges/cm$^2$. These films, however, exhibited an extremely large amount of hysteresis, as the average slow surface state density was $6 \times 10^{11}$ states/cm$^2$-ev. This result is similar to another tantalum alcoholate film [49]. $N_{SS}^{SLOW}$ is probably due to mobile ions in the not yet densified oxide. The fast surface state density, however, is comparable to that for the evaporated oxides, $5 \times 10^{11}$ states/cm$^2$-ev.
Tremendous potential, therefore, exists for the "as-spun" tantalum oxide solution in MIS-IL cells. Unfortunately, the fixed charge disappears as the oxide densifies and ages. The stability of the film is investigated in more detail in the next chapter.

3.5 Characterization of Oxides as Antireflective Coatings

Because of the inherent sensitivity of the MIS-IL cell to ultraviolet radiation [14], the oxide should absorb and reflect as little as possible at short wavelengths. Theoretically, the reflectance of a thin uniform dielectric layer on a semi-infinite silicon substrate may be calculated by considering the optical impedance mismatch resulting from the change in the refractive index occurring as the light travels from the air, through the oxide, and into the silicon [33]. The resulting power reflection coefficient for normally incident light as a function of (λ) is given by:

\[
R(\lambda) = \frac{R_{ox} + R_{si} \exp(-j2\theta)}{1 + R_{ox} R_{si} \exp(-j2\theta)}^{2}
\]  

(3.16)

\(R_{ox}\) and \(R_{sub}\) are the reflectances for the oxide and the silicon respectively, and \(\theta\) is the phase thickness of the coating:

\[
\theta = \frac{2\pi n_{ox} t_{ox}}{\lambda}; \quad R_{ox} = \frac{1 - n_{ox}}{1 + n_{ox}}; \quad R_{si} = \frac{n_{ox} - n_{si}}{n_{ox} + n_{si}}
\]  

(3.17)

Generally speaking, the indices of refraction \(n_{ox}\) and \(n_{si}\) are complex:

\[
n_{si} = n(\lambda) - jk(\lambda); \quad k(\lambda) = \frac{\lambda a(\lambda)}{4\pi}
\]  

(3.18)

For silicon and most oxides, the extinction coefficient \(k\) is negligible
over most of the visible spectrum, however, at ultraviolet wavelengths, absorption (\(\alpha\)) can be quite significant.

The apparatus used to measure reflectance is depicted in figure 3.7(a) [68]. A set of narrow band optical filters were used to obtain nearly monochromatic light from the wide band xenon source used. This technique for calculating reflectance is described elsewhere [68].

The measured reflectance spectrum for the various oxide surfaces is plotted in figure 3.7(b), along with the characteristics of bare silicon. As expected, the average reflectance for the thermal tantalum oxide (10%) is less than that for either the spin-on (17%) or the evaporated films (15%). A fortran computer program (REFLEX) [15] was used to model these curves. The index of refraction calculated for the oxides (\(n_{ox}\)), indicated that both the spin-on and evaporated tantalum oxides exhibited some absorption at wavelengths below 400 \(\text{nm}\), whereas, the thermally grown oxide was nearly perfect. Absorption and transmission measurements performed by other researchers on thermal and evaporated tantalum oxides agree with this result [46]. The absorption has been theorized to be due to the presence of unsaturated valences or Ta-Ta bonds in the film [56].

These experiments demonstrated that, in accordance with the fundamental considerations outlined at the beginning of this chapter, the grown oxide has the highest degree of short range order, and less unsaturated bonds than either the evaporated oxide or the spin-on film. The most unstructured coating, the spin-on solution, has the worst optical characteristics.

3.6 SEM Analysis

With the assistance of V. Sulway at SEMCO instruments, samples
Fig. 3.7 (a) Schematic of the apparatus used to measure reflectance.

(b) Measured curves for the three oxides investigated.
of each of the oxides (some heat treated, and some not) were studied in the scanning electron microscope (S.E.M.) As expected, all the films were extremely uniform, with no discernable features noticeable at magnifications up to 10,000 times. In the past, both transmission and electron diffraction analysis of tantalum oxides on silicon showed that such films were non-crystalline [54,60]. The only interesting point to be discovered using the SEM was some localized crystallization in the heat treated evaporated oxides. Crystals, up to 0.3 \text{ m} in diameter, were observed in some films that had been heat treated in either nitrogen or oxygen at temperatures up to 530\textdegree C, while all the as-deposited films were uniform. Possibly, contamination introduced during the evaporation caused crystallization during the subsequent heat treatments.

This chapter has demonstrated that all the oxide films investigated are potentially suitable for MIS-IL cells. However, only the spin-on solution promises to yield highly efficient solar cells. The results of photovoltaic testing will be reported next.
CHAPTER 4

MIS-IL SOLAR CELL CHARACTERIZATION

4.1 Introduction

This chapter reports the highest total area AM1 efficiency (16%, using spin-on tantalum oxide) yet achieved for MIS-IL silicon solar cells [37,70]. Because of the low temperature simple fabrication techniques involved, and the physics underlying the induced junction, the MIS-IL cell has for long time been assumed to be superior to the diffused junction on polycrystalline substrates. For the first time, this hypothesis has been verified, with total area AM1 efficiencies of up to 13% obtained on large grained polycrystalline material [69].

Unfortunately, the spin-on tantalum oxide solution (Ta_xO_y) is highly reactive, and the stabilization of these cells has been a problem. Even so, these efficiencies demonstrate conclusively that the MIS-IL structure has the potential to be a cost effective replacement for the diffused junction on polycrystalline material.

4.2 Fabrication

Solar cells were made by following the detailed fabrication schedule outlined in Appendix "C". It is important to note that the highest temperature encountered by the substrate is only 450°C, a value that should enhance the starting lifetime of the material considerably [36]. Also, fabrication takes only 2-3 days, a great improvement over
past processes [12, 14, 16]. A cross section of the completed structure is shown in figure 4.1(a).

Because of the nature of the IL cell, one of the most important aspects to be considered is the design of the contact grid. As mentioned earlier, this grid should cover as little area as possible, while at the same time, minimize the lateral series resistance by providing good contact to the inversion layer. These conflicting requirements are satisfied through the use of an equally spaced grid of "m" narrow conductors. To optimize this trade-off, the grid finger spacing must be chosen carefully, as the resistance of the inversion layer is very high and proportional to $1/m^2$ (equation 2.12). Figure 4.1(b) shows the effect the finger spacing has on the output power of an IL cell [15]. For the range of oxide charges normally encountered, a spacing of 200 to 300 $\mu$m seems to be optimal. Arbitrarily choosing a spacing of 254 $\mu$m, C. E. Norman designed the metallization mask depicted in figure 4.2, for IL cells using thermal $SiO_2$. (Mask # = CM008020A) [22]. A nominal line width of 17 $\mu$m was chosen to allow for misalignment errors, and to provide for reliable metal continuity using the available photolithographic process. The pattern is actually a standard 2 cm x 2 cm cell sectioned diagonally into 1 cm$^2$ quarters. The grid shades only 7.7% of the active area, around which is a wide metal band to prevent carrier collection from outside the cell area.

Because of the many test devices that are positioned around the outside, this mask was also used for the MIS-IL solar cell experiments involving tantalum oxide. The pads around sections A, B, and C are actually MIS diodes, and were used for the measurements reported in Chapter 2. Also, a 2000 square metal resistor, a 250 square diffusion
Fig. 4.1 (a) Cross-section of the spin-on tantalum oxide MIS-IL solar cell structure.
(b) The effect of the contact grid finger spacing on the output power of an inversion layer solar cell[15].
Fig. 4.2 Metallization mask for inversion layer solar cells.

Grid finger spacing = 39 fingers/cm.
resistor, (not applicable to MIS cells) and a 1/10.5 square inversion layer resistor are included.

Obviously, a production cell would have the entire wafer covered by a single grid pattern, with a smaller contact pad. The design of such a 2" diameter grid pattern is undertaken in section 4.3.2

4.3 Photovoltaic Results

4.3.1 Measuring Apparatus

After fabricating the MIS-IL solar cells with the optimal oxide thickness, it was necessary to test their photovoltaic performance. Figure 4.3 shows the schematic of the computer controlled solar cell I-V test facility used. A plot of the illuminated I-V curve is obtained by forcing current through the cell and sensing the resulting voltage. The controlling software is described in Appendix "A".

The ORIEL solar simulator has the ability to approximate both the terrestrial and extra-terrestrial solar spectra. Unfortunately, the late arrival of the necessary filters, and subsequent difficulties with calibration prevented its use. The primary method that has been used in the past by investigators at Carleton University and elsewhere to simulate the solar spectrum has been to increase the intensity of a tungsten lamp until the AM1 short circuit current was obtained in a calibrated reference cell [12-20]. Depending upon how far the cell is situated from the lamp, this intensity may change from measurement to measurement. Because the tungsten lamp behaves as a "blackbody", spectral shifts could then occur. That is, the higher the operating temperature of the filament, the higher will be the percentage of radiation which falls in the visible portion of the electromagnetic spectrum. A true blackbody,
Fig. 4.3 Schematic of the computer controlled solar cell test facility.
or a body which emits the maximum possible amount of energy at every wavelength for a specified temperature, does not exist in nature. However, many surfaces may be assumed to be black for engineering considerations. The terrestrial solar spectrum may be modelled adequately as a blackbody at a temperature of $5762^\circ K$ [71]. A 300 W tungsten lamp approximates this spectrum well [71]. A plot of the AML spectrum, and the calculated spectrum of a blackbody at $5762^\circ K$ (normalized so that the total power is 1000 W/m²) is shown in figure (2.1). Therefore, an improved method of calibration that was used for this thesis was to adjust the distance away from the standard cell, until the AML short circuit current was obtained. This ensures that the spectrum is consistent between measurements, and closely models AML conditions.

Although the metallization pattern shown in figure (4.2) has an edge band to reduce peripheral collection, some collection from outside the cell, via the inversion layer under the band, does occur. Experimentally, this fringing current was found to add almost 10% to the short circuit current for the 1 cm² cells. Therefore, to obtain meaningful measurements, it was necessary to define the active area with a mask. This in turn caused a slight problem because near the open-circuit voltage condition, the shaded peripheral regions became forward biased via the inversion layer. Dark current injection then takes place. According to the simple theory, $V_{oc}$ is given by [24,25]:

$$V_{oc} = \left( kT/q \right) \ln \left( \left( I_{sc}/I_{o} \right) + 1 \right) \text{ Volts} \quad (4.1)$$

When the mask is used, $I_{o}$ increases, and hence $V_{oc}$ decreases. However, as this effect is dependant upon the logarithm of the change, the open circuit voltage is actually affected only marginally. Thus, the mask was used for all normal intensity (AML) measurements.
4.3.2 Singlecrystalline Silicon

Following the procedure explained in the last chapter, tantalum oxide powder was evaporated through the MIS grid structure to form a MIS-IL solar cell. Verifying the computer prediction, only a 0.2% efficient cell could be obtained, as depicted in figure 4.4(a). Using the 1/10.4 square inversion layer resistor (figure 4.2), the sheet resistance of the inversion layer was measured to be 30 KΩ. This corresponds theoretically to a fixed oxide charge of 5 x 10⁻¹¹ charges/cm² [15]. A heat treatment in dry oxygen at 300°C reduced the efficiency to less than 1%, while any heat treatment in N₂ only dropped the efficiency by a maximum of 0.5%.

For the reasons discussed in section 3.3.1, it was expected that no further improvements in efficiency could be achieved. After demonstrating that this result was reproducible, research into this area was discontinued.

As expected from the oxide charge measurements, the "as-spun" tantalum oxide produced exceptional MIS-IL solar cells. Based on an average of 15 to 20 cells, a typical illuminated I-V curve for 1 cm² cell on single crystal silicon is plotted in figure 4.4(a). The efficiency was calculated according to equation (2.10), however the 0.077 cm² area of each cell shaded by the metal grid was not taken into account; hence the term "active area". Total area efficiencies would just be a factor of (1/0.923) or 1.083 smaller than this, yielding an average total area efficiency of 15.0% for all the cells. One cell achieved a total area efficiency of 16.5%. These values are the highest yet achieved for either MIS or IL (or combination of the two) solar cells. The use of spin on TİOₓ [13,17], when used with back surface fields (BSF) achieved efficiencies up to 12% [78]. In the past, 12% efficiencies have also
Fig. 4.4  (a) Illuminated I-V curves for evaporated and spin-on tantalum oxide MIS-IL solar cells.
(b) A family of illuminated I-V curves for a typical spin-on solar cell, showing the method for calculating $R_s$. 
been achieved at Carleton University using thermal SiO₂ [12]. The highest active area AM1 efficiency reported to date has been 18% for an MIS-IL structure using evaporated SiO [20]. However, this result required the use of an extremely fine grid geometry (up to 200 lines/cm), which increases the shading to almost 30%. The total area efficiency is therefore only on the order of 13%, less than that reported here.

Many important solar cell parameters may be deduced by a careful consideration of the illuminated I-V curve in figure 4.4(a). First of all, the fill factor (F.F.) is very high, up to 0.82 for some cells. This implies that not only are the series and shunt resistive effects negligible [23,24], but also that the diode dark saturation current (Iₒ) is very small [73]. This is in agreement with the diode curves reported in Chapter 2. Secondly, the high open circuit voltage (up to 0.57) indicates that not only is Iₒ small (equation (4.1)), but that recombination via any interface states at the surface is not a problem [74]. Lastly, the extremely high values of short circuit current (up to 43mA/cm²) is probably due to the high bulk lifetime of the substrate [36], combined with the excellent antireflective properties of the film.

To verify that the series resistance was negligible, a graphical technique was employed. Figure 4.4(b) shows a family of illuminated I-V curves for a typical spin-on MIS-IL solar cell measured at several different light intensities. It can be readily demonstrated that the negative inverse slope of the line joining the points I = Iₛ - ΔI for any reasonable value of ΔI (i.e. 10mA/cm²) will be equal to Rₛ [75]. The value obtained by this method was 0.75 Ω-cm², a result that is conducive to highly efficient operation.

This series resistance may also be calculated by considering
the inversion layer sheet resistance, \( r_s \). This parameter was measured to be on the order of 10 k\( \Omega \), a value that corresponds to a fixed oxide charge density of \( 3 \times 10^{12} \) charges/cm\(^2\) [15] in agreement with the results of the last chapter for 8 \( \Omega \)-cm substrates. Using equation (2.12) the inversion layer resistance for the 1 \( \text{cm}^2 \) cell is: \( R_{IL} = 0.55 \Omega \cdot \text{cm}^2 \).

Aluminum sheet resistance has been measured to be 0.01\( \Omega \), and combining this with the bulk resistance of 8 \( \Omega \)-cm material, and the estimated MIS contact resistance (0.06 \( \Omega \cdot \text{cm}^2 \)) [15], \( R_m \) can be estimated to be 0.25 \( \Omega \cdot \text{cm}^2 \). Now applying equation 2.11; \( R_s = 0.60 \Omega \cdot \text{cm}^2 \), a result which agrees closely with the measured value.

To be economical, production MIS-IL solar cells would have to be fabricated on two or three inch substrates. The main problem associated with such large wafers in the design of the contact pattern. To date, no researcher has attempted to optimize a MIS-IL grid structure for a 2" substrate. Therefore, using the procedure outlined in reference [68], in which the output power is maximized with respect to the grid finger spacing, mask No. CU02001 was designed. Surprisingly, the design called for 40 lines/cm, the same as the previous mask. Because of the larger bus-bar, metal shading is only slightly higher, at 11.6\%, while the line width is 15 \( \mu \text{m} \). The design was based on an inversion layer sheet resistance of 10 k\( \Omega \), and an AIM output power of 300 mW, or an average of 15\% total area efficiency.

A typical illuminated I-V curve for a spin-on tantalum oxide MIS-IL cell fabricated using this mask is plotted in figure 4.5(a).

Unfortunately, the average total area efficiency was only 12\% or 3\% less than designed. This appeared to be due to the substantially higher series resistance implied by the low fill factor. On the average, this parameter
Fig. 4.5 (a) Typical illuminated I-V curve for a spin-on tantalum oxide MIS-IL solar cell fabricated using a 20 cm² contact grid.

(b) Explanation for the decreased efficiency observed in this cell.
was measured to be $3.5 \text{ cm}^2$. Since the method of forming the MIS contact had not changed, the contact resistance must be the same as before. The metal thickness and the substrate also were unchanged, therefore only a higher inversion layer sheet resistance could account for the increase in series resistance. Based on the resistance value of $3.5 \text{ cm}^2$, the sheet resistance must be $62 \text{ k}\Omega$, implying an oxide charge density of only $4 \times 10^{11} \text{ charges/cm}^2$ [15]. This apparently reduced oxide charge may be explained by the fact that it was very difficult to obtain a uniform layer of tantalum oxide over the entire $2''$ wafer by spinning. Figure 4.5(b) presents a possible explanation. Microscopic inspection revealed that the oxide was thinner on one side of the grid fingers near the edges of the cell. It is likely that slight discontinuities in the inversion layer are contributing to this increase in resistance.

4.3.3 Polycrystalline Silicon

The very high efficiencies reported in the last section are useful, but only from a theoretical point of view, if the cost of production cannot be reduced. For example, the single crystalline substrate used accounts for an estimated 30-40% of the total costs. The compatibility of the MIS-IL structure to low cost non-singlecrystalline silicon has already been discussed.

Generally, polycrystalline silicon is characterized by a conglomerate of individual crystal grains, separated by boundaries. These grain boundaries act as internal surfaces in the material, and the high density of interface states associated with these boundaries will cause them to act as efficient recombination sites for photogenerated
carriers. This effect decreases both the photocurrent and the apparent minority carrier lifetime of the substrate. To produce high efficiency polycrystalline solar cells, recombination must therefore be minimized. Firstly, the grain size should be increased, preferably so that the grains are larger than the minority carrier diffusion length normally found in single crystal silicon. Secondly, the substrates should not be thicker than one grain size, or more desirable, the grains should be oriented so that the grain boundaries run through the complete substrate from front to back. Such a "fibrously oriented" wafer would have the grain boundaries perpendicular to the surface, thus most minority carriers within each grain can cross the junction boundary before recombining. It has been shown [6,25,76] that a solar cell fabricated on such a substrate acts like a parallel combination of individual columnar cells. These small cells behave in the normal manner, with the exception that some minority carriers recombine on the side of each filament. However, if the grain size is large enough, most photogenerated carriers have a high probability of being collected, and the device will behave very much like a single crystal solar cell.

Fibrously oriented substrates have been prepared by casting non-crystalline silicon, followed by a tightly controlled cooling process* [6]. With an average grain size of 1mm, 4 cm^2 diffused junction solar cells have achieved total area efficiencies of up to 16% [76], with 10-12% efficiencies much more common [6]. Also, efficiencies of up to 10.0% have been reported using this substrate in an MIS-IL structure [20, 77]. Although this material is as expensive as single crystal silicon at the present time, high volume production would reduce the price

*WACKER-CHEMTRONIC "SILSO" polycrystalline silicon
considerably.

Fifteen, 5 Ω-cm, "P"-type WACKER polycrystalline substrates were used in MIS-IL experiments with the spin-on tantalum oxide solution. These 2" x 2" square wafers were purchased in an "as-sawn" condition, and subsequently had to be etched to remove work damage. This was accomplished with an anisotropic etch containing 91 parts of 70% nitric acid, 21 parts of 48% hydrofluoric acid, 72.5 parts of acetic acid, and 1 part aniline [78]. A total of 50 μm was removed at 8 μm/min from the front and back of each of the wafers. As a result, the average bulk resistivity increased to 7 Ω-cm. After going through the standard MIS-IL fabrication procedure, (Appendix "C") the cells were tested under AM1 illumination. Plotted in figure 4.6, is the illuminated I-V curve for one of the best 1 cm² cells. On the average, total area efficiency was 11.5%. Surprisingly, the short circuit current is almost as large as that obtained in single crystal cells. Because MIS diode measurements seem to indicate that grain boundary recombination has very little effect, this difference could be attributed to the higher reflectance that this substrate has. A texturizing etch could reduce this reflectance, but this was left for future work. The short circuit current could also be affected by the higher series resistance that was measured. On the average, this parameter was 1.3 n cm². This value also accounts for the slightly decreased fill factor. It is thought that the carriers encountering grain boundaries in the bulk increased the resistance slightly. As before, the open circuit voltage is very high, indicating excellent diode characteristics.

The argument developed in the last section to explain the decreased efficiency of 20 cm² MIS-IL cells seemed to apply to the WACKER substrates also. Average total area efficiency and series resistance
MIS-IL solar Cell Number R4
Polycrystalline WACKER "Silso" Substrate

AM1 Conditions
Temperature = 25°C
Active Area Efficiency = 13.7 %
Total Area Efficiency = 12 %
Fill Factor = 0.71
Open Circuit Voltage = 0.57 Volts
Short Circuit Current = 31.5 mA
Total Cell Area = 1 cm²

Fig. 4.6 Illuminated I-V curve for a MIS-IL tantalum oxide solar cell on a polycrystalline substrate
were only 8.9% and 3.7 cm$^2$ respectively. Obviously, further research is needed to improve the performance of the tantalum oxide coatings on large wafers.

This section has demonstrated that the MIS-IL polycrystalline approach is now a viable competitor to single crystals. Aside from being able to fabricate highly efficient cells, "SILSO" wafers have the potential advantages of: low cost, better mechanical stability (no cleavage), greater power dissipation [76], and high volume production with sheets or ribbons of silicon [6].

4.4 **Modelling**

This section will apply computer simulations to the results of illuminated I-V and current efficiency measurements of spin-on MIS-IL tantalum oxide solar cells. Suggestions for the optimization of this cell structure will also be presented based on computer predictions.

4.4.1 **Current Efficiency**

One of the most revealing insights into how well a solar cell structure collects photogenerated carriers is obtained through the measurement of its external current efficiency ($Q_e(\lambda)$) over the complete solar spectrum. The apparatus used, and the method of measuring $Q_e(\lambda)$ have been adequately described elsewhere [15,68]. Suffice it to say that the current efficiency is measured by comparing the short circuit current of a calibrated inversion layer cell to the test cell when they are both illuminated by the same narrow band source. The results of $Q_e(\lambda)$ measurements for both single and polycrystalline spin-on tantalum oxide solar cells are plotted in figure 4.7. Since the filters used have some out
Fig. 4.7 Measured and calculated external current efficiency for various MIS-IL tantalum oxide solar cells.
of band leakage, the fortran program QFIX [15] was used to correct the measured values. The plotted results are thus accurate to ± 5% [22].

Consider the curve for the single crystalline, spin-on tantalum oxide MIS-IL cell first. It is now evident why the short circuit current was so large. The external current efficiency is very close to unity for most of the usable spectrum. This means that most of the incident photons in this range contribute to current flow at short circuit (see equation 2.8). Plotted in the same diagram is the response for a 13% efficient diffused junction solar cell [68]. As expected for diffused cells, the ultraviolet performance is very poor due to the likely presence of a "dead layer" [25], and subsequent high surface recombination. The MIS-IL cell, on the other hand, has excellent ultraviolet response because of the high electrical field at the surface [12]. At longer wavelengths, the current efficiency is consistently higher than that for the conventional cell, indicating that the lifetime for the spin-on tantalum oxide cell is larger [28], consistent with the low temperature fabrication process used.

An exact determination of the minority carrier lifetime of the cell may be obtained by simulating the measured $Q_e(\lambda)$ curve by using the fortran program QEFF [15]. This program accepts as inputs all the important parameters of the cell being tested, i.e., cell thickness, bulk doping density, ambient temperature, minority carrier lifetime, oxide charge, thickness and refractive index. The theoretical external current efficiency and reflectance as a function of wavelength are among the many outputs. The result of applying QEFF to the single crystalline MIS-IL cell is plotted as the dotted line in figure 4.7. The best fit was obtained for a minority carrier lifetime of 14 µs. Although this value is smaller than expected [36], it is important to remember that the $Q_e(\lambda)$
measurements were taken with a current level in the cell of only a few mA/cm². An increase of lifetime of up to a factor of 5 from a low level to the higher level injection encountered in AM1 conditions has been reported [36]. The lifetime may also be influenced by the ohmic back contact. Because of the nearly infinite back surface recombination velocity, some of the EHP's caused by low energy photons will recombine at the contact. This will tend to decrease the measured current efficiency at longer wavelengths.

As explained in Chapter 2, no EHP's should be generated at wavelengths greater than 1100 nm, but all real cells exhibit some response due to lattice vibration. The computer model simulates this by artificially extending the absorption coefficient of silicon past 1100 nm [15].

In the past, "parasitic absorption" was thought to occur at the interface between titanium or silicon oxides and silicon [13,22]. The measured \( Q_e(\lambda) \) points are consistently above the modelled curve in the ultraviolet region for the spin-on TaO\(_x\) \( y \) cell, indicating that this absorption is not present. Probably the MIS oxide acts as a passivating layer.

The reason for the decreased short circuit current in the WACKER polycrystalline cell is evident in Figure 4.7. The current efficiency is considerably lower, although the short wavelength response is still better than the diffused cell. This agrees with the results of other researchers [77]. The flatness of the curve indicates that the reflectance is very high over most of the spectrum. Clearly, to optimize this structure, a texturizing etch should be employed in future research. Using QEFP, the "effective minority carrier lifetime" was only about 5 ms, a value that would reduce collection from the bulk. This is evident in the infrared response.
4.4.2 "ILSCEL" Simulation

The fortran computer program ILSCEL [15], written by C. E. Norman, is an attempt at a full two-dimensional modelling of inversion layer solar cells. Figure 4.8 compares the theoretical I-V curve predicted by this model along with the measured curve for a spin-on single crystalline MIS-IL solar cell. The short circuit photocurrent was obtained by integrating the $Q_e (\lambda)$ response (figure 4.7) over the complete spectrum. Although there are subtle differences, the two plots are in good agreement, demonstrating the validity of both the parameters used, and the IL theory. The computer also takes into account the effect of bus bar shading, metal resistance, and peripheral collection. A lifetime of 50 µs provided the best fit to the results, justifying the arguments presented in the last section. This demonstrates the advantage of completely low temperature fabrication, as the highest minority carrier lifetime obtained in the past was only about 10 µs for thermal SiO$_2$ IL cells [22]. The very small (<3.0%) differences could be attributed to the uncertainty in determining the exact spectrum used. By modelling the electron and hole distributions, and determining the point where the electron concentration equals the hole concentration, (as a function of bias) the effective junction depth was found to vary between 0.1 and 0.2 µm, less than the "violet cell" [4], and without causing the lattice damage associated with diffusions.

The main advantage of ILSCEL lies in its ability to demonstrate where changes could be made on the MIS-IL structure to increase the efficiency. The potential for improving the open circuit voltage by including a back surface field (BSF) has already been demonstrated [72]. ILSCEL predicts that for charge densities in excess of $10^{12}$ charges/cm$^2$, 

Fig. 4.8 Comparison of a measured I-V curve for a tantalum oxide spin-on MIS-IL solar cell with the curve predicted by the computer simulation.
the optimum doping level would be $5 \Omega \cdot \text{cm}$, with a substrate thickness of 300 $\mu\text{m}$, if the BSF were incorporated [15]. Also, if the lifetime can be kept greater than 30 $\mu\text{s}$ by annealing [36], and the reflectance reduced by texturizing, the open circuit voltage could conceivably be greater than 600 mV and the efficiency increased by as much as 2% [72]. Presumably, the same principles would also apply to polycrystalline cells, although no attempt was made to model the effect of grain boundaries.

Even though the efficiency can be improved by adding the BSF region, in the final analysis, the most important parameter is the cost per peak watt of output power, which might not be minimized. Therefore, experiments are necessary to determine whether such an addition is warranted.

4.5 Stencil Mask Results

Although the MIS-IL process may be suitable for production in its present form, it is useful to consider how costs may be reduced. Two of the most expensive steps in the fabrication procedure are the vacuum metallization and the photolithography. The metallization step might be eliminated if the contact grid could be screen printed on the wafer. Unfortunately, the metal pastes used at the present time are unsuitable for MIS contacts. The photolithographic step might be replaced by the direct evaporation of the metal through a stencil mask. Based on computer predictions using ILSCEL, this change appeared not to be feasible. For example, in $5 \Omega \cdot \text{cm}$ material, with an oxide charge density of $3 \times 10^{12}$ charges/cm$^2$, a grid finger spacing of 30 fingers per centimeter would result in an active area efficiency of only 8%. If 25 fingers per centimeter were used, 5 percent efficient cells
would be obtained. 10 fingers/cm would give 2% cells, and so on. For this reason, it seemed that this approach was unsuitable. However, very recent results for MIS-IL cells using SiO and a grid finger spacing of only 12 fingers/cm have demonstrated total 4 cm² area efficiencies of 13.5% on 0.5 cm single crystal substrates. Encouraged by this success, it was decided to attempt to fabricate a stencil mask for use with the spin-on Ta$_{x}$O$_{y}$ solution. Phosphor-bronze shimstock, 5 mils thick was purchased for this purpose. For purely mechanical reasons, (bending of fingers) a line thickness of 5 mils (127 μm), and a grid finger density of 32 lines/inch (12.6 lines/cm) were chosen. This design has a shading of only 8%. The resulting mask (#CU026010A) was used in the photolithographic step to expose the shimstock. Etching of the metal was then done in a saturated ferric chloride solution. Aluminum metal of 3 μm thickness was evaporated through this stencil mask onto prepared silicon substrates to form the MIS structure. A more optimum doping level of 5 Ω-cm was used to decrease series resistance and thus increase the efficiency. Tantalum oxide was spun on as before.

The results were very disappointing, as none of the cells exhibited any appreciable photovoltaic output. The short circuit currents were below 10 mA/cm² and the fill factors were decreased so much that only 2% total area efficient cells could be obtained. The open circuit voltage was above 0.52 volts however. This implies that the degradation can only be attributed to an excessive increase in series resistance, exactly what the computer model predicted would happen. Similar results were obtained on the WACKER "SILSO" polycrystalline substrates. I am unable to explain why Godfrey et al [20] were able to fabricate such excellent cells, as it appears that a grid finger density of at least 35 fingers/cm is needed for 10-13% AM1 total area efficiency when using an oxide with a charge density in excess of 3 x 10¹² charges/cm².
4.6 Stability

Although the potential of MIS-IL solar cells for achieving high efficiencies has already been demonstrated, commercial cells using the tantalum oxide solution would, of course, have to be stable. Unfortunately, as discussed in Chapter 3, the oxide charge of the "as-spun" solution tends to degrade with time. Not surprisingly, the MIS-IL tantalum oxide cells degraded also. Figure 4.9(a) shows the initial I-V curve of such a cell, along with the curve after 30 days. A plot of how the total area efficiency varied with time is shown in figure 4.9(b). As the cell slowly "died", series resistance, and cracking of the oxide around the grid fingers increased. There also appeared to be a correlation between severity of cracking, series resistance and cell efficiency. Figure 4.10 presents a tentative explanation for this phenomenon. The reader is asked to accept for the time being that free, positive tantalum ions exist in TANTALUMSILICAFILM due to ionic disassociation. This conjecture would also explain the high positive charge densities measured, as tantalum exists in the +5 ionic state [79]. Based on the high electronegativity difference between tantalum and oxygen (2.0) [79], these ions would very much like to oxidize, forming charge neutral Ta₂O₅. The reason they do not do so, is because when the solution is spun onto the wafer, the surface immediately oxidizes, shielding the ions near the interface. Of course, oxygen can still leak through the surface and neutralize these ions, but cracking of the oxide would accelerate this process considerably. The oxide is thought to crack because of the mismatch in the thermal coefficients of expansion between the aluminum and the oxide. As depicted in figure 4.10, the point of most stress occurs where the solution laps up the side of the grid fingers.
Fig. 4.9  
(a) Illuminated I-V curve for a spin-on tantalum oxide MIS-IL solar cell, showing the degradation with time.  
(b) How the active area efficiency changes during this period.
Fig. 4.10 A tentative explanation for the degradation observed in spin-on tantalum oxide MIS-IL solar cells. The oxide cracking accelerates the oxidation of the film.
Any thermal stress, such as that which occurs during photovoltaic testing, will cause cracking. The loss of the inversion layer under the cracked oxide would increase the series resistance and degrade the cell efficiency. In an attempt to verify this theory, a number of experiments were performed.

If the positive tantalum ions do indeed exist, then any heating of the oxide would accelerate the reaction with oxygen. A 15% efficient tantalum oxide MIS-IL cell was fabricated according to appendix "C" and subsequently baked in air at 50°C for 15 minutes. Photovoltaic testing then revealed that the cell became only 7% efficient and some cracking around the grid fingers was evident. The cell was then placed back into the oven, and the bake was continued for another 15 minutes, after which testing revealed that the cell was dead. Heavy cracking occurred around the grid fingers. To ensure that this degradation was due to the loss of ionic charge, and was not totally due to the physical cracking and lifting of the oxide, a 14.5% efficient cell was baked at the same temperature in an oxygen ambient. After a bake time of only 10 minutes, the cell was tested as being only 2% efficient. As expected, the oxygen accelerated the neutralization of the tantalum ions. Simple chemical principles suggested that increasing the bake temperature would also increase the rate of reaction [79]. Any tantalum oxide cell baked at temperatures above 70°C in either O₂ or air for periods greater than 30 minutes degraded completely, verifying this assumption.

In the hope that if the cracking of the oxide could be prevented, the lifetime of the cell would subsequently be increased, thinner oxide layers were spun on the wafers. To obtain uniform thin layers, TANTALUM-SILICAFILM was diluted in ethyl alcohol, and the spin speed was increased.
It appeared that very thin layers (~250 Å) reacted completely with the atmosphere during spinning, as no appreciable photovoltaic output was measured. After experimenting with dilution and spin speeds, the best solution turned out to be a 50% dilution spun on at 5000 R.P.M. The oxide thickness was only 330 Å, and the total area efficiency after spinning was 12%. This decreased value can be attributed to the optical mismatch resulting from using a thin oxide. This cell exhibited no cracking during its entire 40 day lifetime, after which the efficiency was only 5%. As before, baking at 50°C increased the rate of decay, although in this case no cracking was apparent. Since the lifetime of the cell was only increased marginally without the oxide cracking, and the efficiency was greatly reduced by using the thinner oxide, a decision was made to keep the thicker layer and search for a better means of stabilization.

All degraded cells, whether they "died" due to baking or aging in air, could be made to recover by spinning on a second layer of tantalum oxide. It appears that this solution acts as a solvent, "dissolving" any previous tantalum oxide layer. This procedure even worked for the evaporated tantalum oxide cells. Because of the thicker oxide layer obtained after spinning, these cells were 1-2% less efficient. Unfortunately, degradation by air and heat treatment still occurred.

All the preceding evidence suggests that the main problem in stabilizing this MIS-IL cell structure lies in preventing the atmosphere from reacting with the solution. To verify this theory beyond any doubt, high efficiency tantalum oxide cells were placed in the evaporator and a vacuum was drawn. Of course, any solvent in the oxide would be removed in the vacuum. If the fixed charge were due to the solvents, the cells
would test out as being "dead" on removal. If the theory is correct, the tantalum ions would be unchanged, as no atmosphere is available to neutralize them. After remaining under high vacuum for three days, the cells were removed and inspected. Ellipsometry revealed that the oxide layer had densified by $100\%$, probably due to removal of the solvents. No cracking was evident at this time. Photovoltaic testing revealed only a slight (1%) change in efficiency. This can be easily attributed to the thinner oxide. Unfortunately, cracking became very severe, and cells were dead after exposure to air at room temperature for one week.

All the experimental evidence suggests that the theory proposed at the beginning of this section is indeed correct. Therefore, a practical method of stabilization would be to shield the ionic charge from reaction with the atmosphere by surrounding the cell with an inert ambient. This task could be accomplished by using the encapsulation technique in widespread use for diffused junction solar cells [68]. However, since contacting to aluminum is a problem, and only a demonstration of principle is necessary for this thesis, a simpler procedure was chosen. Four spin-on tantalum oxide MIS-IL solar cells were fabricated and tested. Three were placed in supposedly "inert" liquids: one in paraffin oil (structure unknown), another in glycerin ($\text{CH}_2\text{OHCHOHCH}_2\text{OH}$), and the third was immersed in a silicon fluid similar in structure to the pottant used at Carleton University [68]. The fourth cell was placed in a glass bell jar where the atmosphere had been replaced by argon gas.

All the cells were retested after a period of one month. Two had degraded: the solar cell left in paraffin was only 7% efficient, and the cell surrounded by argon gas was less than 2% efficient. The
container used for the latter cell was found to be not completely airtight, and as a result, it is probable that the oxide charge was neutralized. Since the chemical composition of the paraffin oil is unknown, it is impossible to ascertain why the cell efficiency decreased. The most exciting result was that all the other MIS-IL solar cells retained their high efficiency for the full month. These cells were returned to the glycerin and silicone fluid respectively, and were retested 2 months later. At this point, both of the cells were "dead". It is probable that during the process of testing the cells the first time, air was introduced to the oxide, which subsequently neutralized the charge.

These experiments indicate that this direction of research is very promising, as the lifetime of the solar cells has been extended to at least a month and beyond. It is likely that further research will achieve total stabilization, paving the way for commercial applications.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Nature of the Oxide Charge

Theories explaining the origin of the fixed charge measured in the various tantalum oxides investigated during the course of this thesis will be presented. Also, an attempt will be made to explain the chemical composition of TANTALUMSIlicaFILM based on the observed properties of the solution.

5.1.1 Thermally Grown Tantalum Oxide

It was proposed in Chapter 3 that silicon is incorporated in the thermally grown tantalum oxide. In fact, other researchers have shown that silicon is already present in the vacuum deposited tantalum film, and the amount of silicon further increases during oxidation [54]. The refractive index was found to vary through the thickness of the oxide, increasing from the Si-Ta2O5 interface towards the surface. This gradient can only be attributed to a profound change in the molecular polarizability of the oxide [56]. Such a change could occur if a non-negligible impurity concentration was present in the film, or if the composition of the oxide was non-stoichiometric. Because thermally grown tantalum oxide films on silicon have been found to be stoichiometric to a first approximation [57], the latter theory could be ruled out. Since silicon is the most likely impurity, it is important to determine how this element
would affect the molecular structure at the interface, and hence the
fixed charge. Based on Rutherford backscattering analysis, Hirvonen [57],
rules out the possibility that the films are mixtures of stoichiometric
Ta$_2$O$_5$ and SiO$_2$. Another theory is that tantalum silicides (Ta-Si) are
present. However, the reflectance measurements revealed that the film
is non-absorbing over most of the spectrum where silicides absorb [65].
The most viable proposition is that Ta-O-Si bonds exist. Such a
molecular structure would form a dipole with the tantalum end positive,
and the silicon end negative [79]. Since the bulk of the silicon would
be nearest the interface, the result would be a fixed negative charge.
Because all the available silicon would have bonded to the (Ta-O) com-
plexes after oxidation, any subsequent heat treatment in oxygen should
have little effect, a theory which agrees with experimental results.

5.1.2 Evaporated Tantalum Oxide Powder

Even though the precautions outlined in Chapter 3 were
thought sufficient to prevent oxide reduction, it is possible that some
disassociation of the oxide did occur during evaporation due to scattered
electrons or soft X-rays from the electron-beam gun [32]. Tantalum is
known to have a valance of 5, 4, 3, 2, or even 1 [80]. This means that
the following sub-oxides could have been formed: TaO$_2$, Ta$_2$O$_3$, TaO, and
Ta$_2$O. Of these, only the dioxide TaO$_2$ is stable [80]. It is likely
that the source of the positive charge in the oxide is due to either
this molecule and/or free tantalum ions that might exist near the silicon
surface due to heat induced metallic migration during evaporation [32].
Both of these theories would agree with experimental observations. It
was discovered that heat treatment in O$_2$ annihilated the positive charge,
while any heat treatment in N₂ had little or no effect. If free tantalum ions exist, then they could readily oxidize to charge neutral Ta₂O₅. Also, tantalum dioxide burns to tantalum pentoxide when heated in oxygen [80]. Of course, nitrogen would prevent any oxidation. Some capacitors fabricated using the evaporated tantalum oxide powder tested as being "leaky", providing further support for the existence of electrically conductive TaO₂ [80]. Perhaps these particular capacitors had a higher local concentration of the dioxide in their dielectrics.

5.1.3 Spin-on Tantalum Oxide Solution

An explanation for the nature of the charge in the tantalum oxide solution was proposed in the last chapter. In the hopes that this might be clarified further, the chemical composition of TANTALUMSILICA-FILM was investigated. Although the exact formula is proprietary, communication with the makers of the film verifies that the solution is a combination of organometallic compounds of tantalum and silicon in an approximate 4:1 ratio [81]. These compounds are dissolved in ethyl alcohol. This information, although meager, is enough to eliminate most organic solutions. In fact, further research only uncovered two tantalum alcolholates that are soluble in ethanol. These are: Tantalum pentaethyrate, (Ta(OCH₃)₅) [82,83], and tantalum dichloro-diethoxy-acetylacetonate (TaCl₂(OCH₃)₂ C₅H₇O₂) [49].

Consider the tantalum pentaethyrate first. This compound is formed by adding solid tantalum pentachloride (TaCl₅) to ethanol [79]. Part of the chlorine is then displaced as HCl, with the formation of tantalum dichloride triethoxide (TaCl₂(OCH₃)₃). This compound may in turn be reduced further by passing ammonia through the mixture. When
this is done, ammonium chloride is precipitated and the pentaethyrate is formed in solution. This mixture is a colorless, mobile liquid at room temperature, as is TANTALUMSILICAFILM. On exposure to air, the alkoxide will hydrolyze (decompose in presence of water) very readily to Ta$_2$O$_5$ [82]. To determine how sensitive TANTALUMSILICAFILM is to hydrolysis, a high efficiency MA$S$-IL solar cell was fabricated according to appendix "C", tested, placed in water at room temperature for 3 minutes and tested again. The cell was found to have degraded in efficiency by 3%. Subsequent experiments determined that either 30 seconds in boiling water or 4 hours in water at 23°C "killed" the cells. Thus, it appears that TANTALUMSILICAFILM is sensitive to water also.

The second candidate, TaCl$_2$(OC$_2$H$_5$)$_2$C$_5$H$_7$O$_2$, is much more difficult to synthesize [49]. However, it is also soluble in ethanol, is clear, and also hydrolyzes to Ta$_2$O$_5$ at low temperatures. It appears that either one of these alkoxides could form the major constituent of TANTALUMSILICAFILM. Further communication with Emulsitone cleared up this problem, as TANTALUMSILICAFILM yields HCl as a by-product of decomposition [81]. Only the second alkoxide is capable of this.

Tantalum-dichloro-diethoxy-acetylacetonate (TaCl$_2$(OC$_2$H$_5$)$_2$C$_5$H$_7$O$_2$) has a very unstructured chemical composition, thus it is possible that free tantalum ions could exist in solution, giving rise to the positive charge. TANTALUMSILICAFILM also has a silicon alkoxide, probably used to reduce the refractive index of the resulting film below that of pure Ta$_2$O$_5$. It is likely that some silicon ions contribute to the positive charge.
5.2 Summary

Three methods for preparing tantalum oxide films on silicon were investigated. The first method, thermal oxidation of evaporated tantalum films, was found to yield reproducible negative charge densities in the range of $-3 \times 10^{11}$ to $-5 \times 10^{11}$ charges/cm$^2$, thought to be due to the polarization of Ta-O-Si bonds. The tantalum oxide/silicon interface was found to be of high perfection. Unfortunately, the fabrication of MIS-IL solar cells was not attempted because of the low conversion efficiency predicted by ILSCEL.

The second method involved the evaporation of tantalum oxide powder in an O$_2$ ambient. Stable positive charge densities in the range of $+4 \times 10^{11}$ to $+6 \times 10^{11}$ charges/cm$^2$ were measured. Either the existence of free tantalum ions or tantalum dioxide was thought to be the source of this charge. As predicted by computer simulations, a 6% efficient MIS-IL solar cell was fabricated.

Tantalum oxide films were also prepared by spinning an alcoholate (TANTALUMSILICAPFILM) on silicon substrates. Positive oxide charge densities of up to $3 \times 10^{12}$ charges/cm$^2$ were measured in the "as-spun" solution. MIS-IL solar cells fabricated using this film resulted in total area efficiencies greater than 16% for some cells. This is the highest efficiency ever reported for this structure. Total area efficiencies of up to 12% were also measured for MIS-IL tantalum oxide cells on polycrystalline substrates, suggesting the possibility of cheaper processing. The current efficiency of both of these cells was close to unity over most of the useable spectrum. Computer simulation of the I-V curve for the singlecrystalline cell implied a minority carrier lifetime as high as 50 $\mu$s in the bulk. Also ILSCEL predicted that poor conversion
efficiencies would be achieved if a stencil mask was used to deposit
the grid, a result which was demonstrated experimentally. Unfortunately,
the film reacts slowly with the atmosphere forming charge neutral Ta₂O₅
and SiO₂. Encapsulation in an inert environment was found to slow this
process somewhat, but more work is necessary to achieve complete stab-
ilization. As a first step towards this goal, the nature of the solution
and the oxide charge were investigated.

5.3 Recommendations for Future Work

Based on the theoretical and experimental results reported in
this thesis, several recommendations for future work become evident:

1) MIS-IL solar cells on polycrystalline substrates

have great promise to be a cost effective replace-
ment to the diffused junction solar cell. A text-
urizing etch for the front surface should be empl-
yoyed to determine the efficiency limit for the
tantalum oxide cell. Perhaps a back surface field
should also be incorporated. (see below)

11) The trade-off between the minority carrier lifetime

and the advantages of a back surface field should
be investigated.

111) Because of the great potential of TANTALUMSILICA-

FILM, a chemist should work on the problem of

stability. This individual should also attempt to
synthesize other organometallic compounds with high,
stable charge densities.
iv) Other commercial antireflective films deserve research. For instance, using TITANUMSILICAFILM on one MIS cell obtained a total area efficiency of 14.2% before it "died". (Not published)

v) Some of the newer inks used in the screen printing industry should be investigated for possible use in MIS-IL cells. Such an advance would reduce production cost considerably, paving the way to a completely automated process.

vi) A better method of applying TANTALUMSILICAFILM to large wafers should be investigated.
Perhaps Plasma etching could be used to define the metal grid.
REFERENCES


[66] V. Sulway, private communication.


APPENDIX "A"

BASIC LISTING FOR THE TRS-80 SOLAR CELL TESTER

Most of the photovoltaic testing for this work was done using an automated tester controlled by a Radio Shack TRS-80 microcomputer. The controlling software for this computer had not yet been developed when I started this thesis; therefore, I undertook it myself. Because of the real need to document such work, this appendix has been included.

The program accepts as inputs the air mass, and the area of the solar cell. A complete characterization (Voc, Isc, Pmax, efficiency, F.F.) takes only about 25 seconds to complete. The tester has the ability to force current through the cell and to sense the resulting voltage.

Flow charts for the various program sections are outlined in figures A.1, A.2 and A.3. It should be noted that more sophisticated numerical methods involving slope sensing and maximization routines were attempted, but the high level of noise that the solar cell produced caused erroneous results. The software described is a compromise between noise, speed, and accuracy. Numerical offsets have been included to compensate for DAC inaccuracies on the current outputs, and for ADC offset in the voltage input.
Fig. A.1 Dark and light current - voltage routine.
\[ A = \sigma r_{01}^P r_{21}^P r_{21}^n - r_{10}^n r_{21}^P r_{21}^n \]  
(B.11)

\[ B = \sigma (r_{21}^n + r_{10}^n r_{21}^P) - r_{21}^P - r_{10}^P r_{10}^n r_{21}^n \]  
(B.12)

\[ C = \sigma r_{10}^n - r_{10}^P \]  
(B.13)

Solutions to equation B.6 are in general complex, i.e;

\[ Z = r \exp(j\phi) \]  
(B.14)

Using Newton's method for root finding, the program determines the solution with the value of ln(r) closest to zero. This yields the correct value for the refractive index of the film, while the thickness is found using equation (B.5).

No appreciable inaccuracies are introduced by the calculations. The complex refractive index of the silicon at 5461 Å is not used, but this does not appear to affect the accuracy of the results. The program is very fast, yielding answers in under a minute. Step by step instructions for use are given below.

1. Store Angle of Incidence \( \phi_0 \) [Degrees] STO 4
2. Store Refractive Index \( n_2 \) (4.051) STO 9 of Silicon
3. Store Constant \( 10^5 \) EEEX 5
4. Store constant \( 4\pi \) STO I

P S

ENT
ONE=0.0
TWO=SHORT CIRCUIT CURRENT
(IN BINARY FORM)
CENT=TWO/2.

POW1=POWER AT I=CENT
POW2=POWER AT I=CENT
PLUS 25,
(OBTAINED BY
FORCING THE CURRENT
AND MEASURING THE
VOLTAGE)

POW1>POW2?

TWO=CENT+25
CENT=(ONE+TWO)/2

ONE=CENT
CENT=(ONE+TWO)/2.

TWO-ONE>60?

CALCULATE THE MAXIMUM POWER BETWEEN POINTS ONE AND TWO.

DISPLAY THE MAXIMUM POWER

Fig. A.3 Maximum power point routine.
PROGRAM DEVELOPED BY R. NORTH
DEPARTMENT OF ELECTRONICS
CARLETON UNIVERSITY

CLS:PRINTCHR$(23):PRINT:INPUT"INPUT 1 FOR AM1, 0 FOR AMO
"A$:PRINT
11 IF A$="1" THEN Z=92.5:ZZ=.52 ELSE Z=135.3:ZZ=.37
12 OUT 183,147:OUT 187,128:OUT 191,128:OUT 184,0:OUT
168,0:OUT 186,0:OUT 190,0:OUT 182,0:OUT 185,8:OUT 189,0
13 INPUT"INPUT THE CELL AREA IN CM**2 ";AREA
15 N=0:W=0
16 PRINT"THE PHOTODIODE READING SHOULD BE":PRINT;ZZ;" VOLTS":
PRINT"THE PHOTODIODE READING IS ":
17 FOR VIN=1 TO 10
18 COSUB 5000;V=100*V;V=INT(V);V=V/100
19 PRINT @768,V;PRINT@778," VOLTS":
20 NEXT VIN
22 OUT 185,2
23 CLS:PRINTCHR$(23)
24 MAIN CONTROLLING PROGRAM
30 PRINT" SOLAR CELL TESTER":PRINT"--------------------"
40 PRINT:PRINT"1- DARK I-V PLOT"
50 PRINT:PRINT"2- ILLUMINATED I-V PLOT"
60 PRINT:PRINT"3- SHORT CIRCUIT CURRENT"
70 PRINT" OPEN CIRCUIT VOLTAGE"
80 PRINT" MAXIMUM POWER POINT"
90 PRINT:PRINT"4- TERMINATE TESTING"
91 PRINT:INPUT" WHICH TEST DO YOU WANT?";D
92 IF D>4 OR D<1 THEN PRINT"*** PLEASE ENTER 1 TO 6 ONLY ***":GOTO91
93 IF D=4 THEN CLS:OUT 189,0:END
100 CLS:PRINTCHR$(23):PRINT" AVAILABLE CURRENT RANGES":
PRINT"--------------------"
105 PRINT:PRINT:PRINT"A... 2 MA":PRINT:PRINT"B... 20 MA":
PRINT:PRINT"C... 200 MA":PRINT:PRINT"D... 1000 MA":PRINT
110 INPUT"ENTER DESIRED CURRENT RANGE";R$;
114 IF R$<"A" OR R$>"D" THEN 120
115 GOTO 125
120 PRINT"PLEASE ENTER LETTER FORM A TO D":GOTO110
125 ON D GOTO 200,1000,2000,93
200 DARK I-V ROUTINE
201 W=1:N=0
207 IF R$="A" THEN OUT 189,1:OFF=-3.313308182E-6:MU=1.013847026:
RA=2:GOTO 211
208 IF R$="C" THEN OUT 189,3:OFF=-1.35169258E-3:MU=.9747551009:
RA=200:GOTO 211
209 IF R$="D" THEN OUT 189,4:OFF=-1.70816099E-3:MU=.9919037489:
RA=1000:GOTO 211
210 IF R$="E" THEN OUT 189,2:OFF=-6.362213182E-5:MU=1.0097468847:
RA=20:GOTO 211
211 N=INT(N)
220 VIN=N:GOSUB6000
230 OUT188,LO:OUT190,HI:GOSUB5000
231 IF (V2-V)>0.05 THEN W=3
232 IF (V2-V)>0.005 THEN W=1
240 VIN=INT(1024*V):GOSUB 6000
245 PRINT@644,"CURRENT: '';OFF+(MUL*N*RA/1024):;PRINT@684,"MA":
PRINT;"VOLTAGE: "V; "VOLTS";
246 V2=V
250 OUT184,LO:OUT186,HI
251 IF N=0 THEN PRINT:PRINT:PRINT;"PUT DOWN THE PLOTTER PEN ";N=:CLS:PRINTCHR$(23)
260 IF V*0 THEN N=N+W:GOTO 211
270 CLS:PRINT:PRINT:PRINTCHR$(23):PRINT"PLEASE LIFT PLOTTER PEN AND HIT ENTER TO CONTINUE"
280 INPUT N$:OUT 188,0:OUT 190,0:GOTO 23
1000 ILLUMINATOR I-V ROUTINE
1001 N=2:GOTO2000
1020 OUT 185,8:GOSUB 1000:PRINTCHR$(23):PRINT"PHOTODIODE VOLTAGE IS:";
PRINT;V;OUT 185,2:PRINT
1031 IF (I*1024/RA) 750 THEN W=20:GOTO 1041
1032 IF (I*1024/RA) 500 THEN W=10:GOTO 1041
1033 IF (I*1024/RA) 250 THEN W=5 ;GOTO 1041
1034 W=1
1040 N=0:GOTO 211
2000 SHORT CIRCUIT CURRENT ROUTINE
2010 IF Rs="A" THEN OUT189,9:RA=2.0FF=-3.313308182E-6:MUL=1.013942026:
GOTO 2041
2020 IF Rs="B" THEN OUT189,10:RA=2.0FF=-6.362213182E-5:MUL=1.009746847:
GOTO 2041
2030 IF Rs="C" THEN OUT189,11:RA=200.0FF=-1.3516925E-3:
MUL=.9747551009:GOTO 2041
2040 IF Rs="D" THEN OUT189,12:RA=1000.0FF=1.708160999E-3:
MUL=.9919037489:GOTO 2041
2041 OUT 188,0:OUT 190,0:FOR V2=1 TO 29:NEXT V2:GOSUB 5000
2042 CLS:PRINTCHR$(23):PRINT"THE OPEN CIRCUIT VOLTAGE IS:
":PRINTV," VOLTS"
2043 PP=V;V2=V
2060 CENT=0
2065 CENT=CENT+250
2066 IF CENT>1024 THEN 2150
2070 VIN=CENT:GOSUB6000
2071 OUT 188,LO:OUT 190,HI:FOR S=1 to 11:NEXT S:GOSUB 5000
2075 IF V*0 THEN GOTO 2065
2080 CENT=CENT-50
2085 VIN=CENT:GOSUB6000
2090 OUT 188,LO:OUT 190,HI:GOSUB 5000
2095 IF V*0 THEN GOTO 2080
2100 CENT=CENT+5
2105 VIN=CENT:GOSUB 6000
2110 OUT 188,LO:OUT 190,HI:GOSUB 5000
2115 IF V*0 THEN GOTO 2100
2120 CENT=CENT-10
2121 CENT=CENT+1
2125 VIN=CENT:GOSUB 6000
2126 OUT 188,LO:OUT 190,HI:GOSUB 5000
IF V<0 THEN I=OFF+(MUL*CENT*RA/1024):GOTO2130
GOTO 2121
PRINTCHR$(23);PRINT"THE SHORT CIRCUIT CURRENT IS ";I;" MA":
FF=FF*I;PRINT
OUT 188,0:OUT 190,0
IF N=2 THEN GOTO 1020
GOTO 4000
CLS:PRINTCHR$(23);PRINT:PRINT:PRINT:PRINT:PRINT:PRINT:SHORT CIRCUIT
CURRENT NOT FOUND IN THIS RANGE"
PRINT:PRINT:PRINT:HIT ENTER TO SELECT ANOTHER";INPUT" RANGE";N$:=
GOTO1000
MAXIMUM POWER POINT ROUTINE
XNE=0
TWO=1024*1/RA
TWO=INT(TWO)
CENT=INT(TWO/2)
VIN=INT(CENT):GOSUB 6000
OUT 188,LO:OUT 190,HI:GOSUB 5000
UNE=(OFF+(MUL*VIN*RA/1024))*V-
VIN=CENT:25:GOSUB 6000
OUT 188,LO:OUT 190,HI:GOSUB 5000
DEUX=(OFF+(MUL*VIN*RA/1024))*V
IF DEUX UNE THEN MAX =DEUX;COR=VIN;XNE=CENT;CENT=INT((XNE+TWO)/2);
GOTO 4070
IF DEUX UNE THEN MAX =UNE;CUR=CENT;TWO=VIN;CENT=INT((XNE+TWO)/2):
GOTO 4070
MAX=DEUX;CUR=CENT:GOTO 4075
IF(TWO-XNE)>60 THEN GOTO 4025
FOR N=XNE TO TWO
VIN=N:GOSUB 6000
OUT 188,LO:OUT 190,HI:GOSUB5000
POW=(OFF+(MUL*VIN*RA/1024))*V
IF MAX<POW THEN MAX=POW;CUR=N
NEXT N
PRINT"MAXIMUM POWER POINT IS: ";PRINTMAX;" MILLIWATTS":
FF=MAX/FF
PRINT"AT A CURRENT OF: ";
CUR=OFF+(MUL*CUR*RA/1024)
PRINT;CUR:" FF;PRINT
PRINT"THE EFFICIENCY IS: ";MAX*100/(AREA*Z);:
PRINT:"PERCENT";PRINT:" AND THE FILL FACTOR IS ";FF:INPUT A$
OUT 188,0:OUT 190,0:GOTO 23
ADC READ ROUTINE
OUT 182,255:OUT 182,0
A=INP(181):IF A AND 128 128 THEN 5020
B=INP(180):C=INP(181)AND 15
V=2.5-(5.0*(B+256*C)/4095)
V=(V+.0266934)/3.67691
RETURN
V TO BINARY CONVERT ROUTINE
V=ABS(VIN)
HI=INT(ABS(VIN/256))
6020  LO=INT(ABS(VIN - 256*HI))
6030  RETURN
APPENDIX "E"

ANALYSIS OF ELLIPSOLOGY MEASUREMENTS

The refractive index (n) and thickness (d) of thin transparent films on silicon are usually determined by using an ellipsometer. This instrument relies on the reflection of plane polarized light from the film to produce two measurements: Delta (\Delta) and PSI (\Psi). A graph of \Delta versus \Psi is then consulted to ascertain the thickness and refractive index of the film.

This graphical method may, however, be very inaccurate. In fact, for refractive indices greater than 2.0, the graph is quite useless. Because of this, it was necessary to develop a program to analyze the measurements obtained while doing this thesis. The algorithm was implemented on the Hewlett Packard model 97 calculator. This machine was chosen for its portability and the suitability of its architecture to handle complex arithmetic.

The refraction of the plane polarized light as it passes through the film is governed by Snell's Law:

\[ n_0 \sin \phi_0 = n_1 \sin \phi_1 = n_2 \sin \phi_2 \]  \hspace{1cm} (B.1)

The subscripts 0, 1 and 2 refer to the air, film and silicon respectively. All angles are measured with respect to the perpendicular.

The total reflection coefficient \( R^P \) and \( R^n \) for light polarized parallel (p) and perpendicular (n) to the plane of incidence
are given by:

\[
R_P = \frac{r_{01}^p + r_{12}^p}{1 + r_{01}^p r_{12}^p} Y \quad (B.2)
\]

\[
R_n = \frac{r_{01}^n + r_{12}^n}{1 + r_{01}^n r_{12}^n} Y \quad (B.3)
\]

\[
Y = \exp(j\varphi n_1 \cos(\varphi_1 d_1 / \lambda)) \quad (B.4)
\]

Where \( r_{01}^p, r_{12}^p, r_{01}^n, \) and \( r_{12}^n \) are the Fresnel reflection coefficients between air and film and between the film and substrate respectively.

\[
r_{01}^p = \frac{\sin \varphi_1 \cos \varphi_1 - \sin \varphi_0 \cos \varphi_0}{\sin \varphi_1 \cos \varphi_1 + \sin \varphi_0 \cos \varphi_0} \quad (B.5)
\]

\[
r_{01}^n = \frac{\sin \varphi_1 \cos \varphi_0 - \sin \varphi_0 \cos \varphi_1}{\sin \varphi_1 \cos \varphi_0 + \sin \varphi_0 \cos \varphi_1} \quad (B.6)
\]

\[
r_{12}^p = \frac{n_1 \cos \varphi_2 - n_2 \cos \varphi_1}{n_1 \cos \varphi_2 + n_2 \cos \varphi_1} \quad (B.7)
\]

\[
r_{12}^n = \frac{n_1 \cos \varphi_1 - n_2 \cos \varphi_2}{n_1 \cos \varphi_1 + n_2 \cos \varphi_2} \quad (B.8)
\]

The ellipsometer readings determine:

\[
\gamma = \tan \psi \exp(j\delta) = \frac{R_P}{R_n} \quad (B.9)
\]

From equations B.3 and B.9;

\[
AY^2 + BY + C = 0 \quad (B.10)
\]
Where:

\[ A = \rho r_{10}^p r_{21}^p r_{21}^n - r_{10}^n r_{21}^p r_{21}^n \]  \hspace{1cm} (B.11)

\[ B = \rho (r_{21}^n + r_{10}^n r_{21}^p) - r_{21}^p - r_{10}^p r_{10}^n r_{21}^n \]  \hspace{1cm} (B.12)

\[ C = \rho r_{10}^n - r_{10}^p \]  \hspace{1cm} (B.13)

Solutions to equation B.6 are in general complex, i.e;

\[ Z = r \exp(j\delta) \]  \hspace{1cm} (B.14)

Using Newton's method for root finding, the program determines the solution with the value of \( \ln(r) \) closest to zero. This yields the correct value for the refractive index of the film, while the thickness is found using equation (B.4).

No appreciable inaccuracies are introduced by the calculations. The complex refractive index of the silicon at 5461 Å is not used, but this does not appear to affect the accuracy of the results. The program is very fast, yielding answers in under a minute. Step by step instructions for use are given below.

1. Store Angle of Incidence \( \theta_0 \) [Degrees] STO 4

2. Store Refractive Index \( n_2 (4.051) \) STO 9

3. Store Constant 10^5

4. Store constant 48

EE 5

STO I

PS

ENT
(4 con't)

5. Store wavelength of light used [Angstroms] 

6. Store Delta [Degrees]

7. Store Tan(PSI) [Degrees]

8. Input Guess for \( n_1 \) \( \text{GBS C} \)

9. Program Calculates \( n_1 \) and thickness in Angstroms, for new case go to step 6.

H1. P. 97 PROGRAM LISTING

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109.
051 SIN
052 RCIC
053 GSB7
054 RCL4
055 SIN
056 RCL4
057 GSB1
058 STO5
059 RCLC
060 SIN
061 RCL4
062 GSB7
063 RCL4
064 SIN
065 RCLC
066 GSB1
067 STO6
068 RCL4
069 SIN
070 RCL9
071 ÷
072 SIN
073 STO3
074 RCLD
075 X=\ Y
076 GSB7
077 RCL9
078 RCLC
079 GSB1
080 STO7
081 RCLD
082 RCLC
083 GSB7
084 RCL9
085 RCL3
086 GSB1
087 STO8
088 RCLB
089 RCL5
090 RCL7
091 x
092 RCL8
093 x
094 RCLA
095 x
096 \( \rightarrow R \)
097 RCL7
098 GSB8
099 STO0
100 X=\ Y
101 STO1
102 \( \uparrow S \)
103 RCLB
104 RCLA
105 RCL6
106 RCL5
107 x
108 RCL7
109 x
110 RCL8
111 +
112 x
113 \( \rightarrow R \)
114 RCL7
115 -
116 RCL5
117 GSB8
118 X=\ Y
119 RCL1
120 \( - \frac{B \pm \sqrt{B^2 - 4AC}}{2A} \)
121 X=\ Y
122 RCL0
123 2
124 x
125 \( \div \)
126 CHS
127 equation
128 \( \rightarrow R \) \( AY^2 + BY + C = 0 \)
129 STO6
130 STO8
131 STO9
132 STO7
133 R\( \uparrow \)
134 \( \rightarrow B \)
135 \( \rightarrow X \)
136 X=\ Y
137 2
138 x
139 X=\ Y
140 \( \rightarrow R \)
141 STO2
142 \( \rightarrow R \)
143 STO3
144 \( \uparrow S \)
145 RCLB
146 RCL6
147 RCLA
148 x
149 \( \rightarrow R \)
150 RCL5
151  -
152  \rightarrow P
153  P=S
154  RCL0
155  \div
156  X=Y
157  RCL1
158  -
159  \rightarrow R
160  \rightarrow SP
161  ST-2
162  \rightarrow S
163  ST-3
164  RCL3
165  RCL2
166  \rightarrow P
167  X
168  X=Y
169  2
170  \div
171  X=Y
172  \rightarrow R
173  ST+6
174  ST-8
175  \rightarrow S
176  ST*7
177  ST-9
178  RCL7
179  RCL6
180  \rightarrow F
181  LN
182  RCL9
183  RCL8
184  P=S
185  \rightarrow P
186  LN
187  X=Y
188  \rightarrow S
189  X=Y?
190  GTO0
191  \rightarrow S
192  X=Y
193  STOE
194  X=Y
195  RTN
196  *LBL0
197  \rightarrow S
198  STQB
199  \rightarrow 4
200  RTN

Comments:

201  *LBL1
202  GSB7
203  \rightarrow F
204  +
205  \rightarrow S
206  -
207  \rightarrow 4
Subroutines for repetitious steps in main program

210  *LBL7
211  COS
212  x
213  ENT
214  DEG
215  RTN
216  *LBL8
217  RCL6
218  x
219  RCL8
220  x
221  -
222  \rightarrow P
223  R=S
224  RTN

Calculate

181  LN
182  RCL9
183  RCL8
184  P=S
185  \rightarrow P
186  LN
187  X=Y
188  \rightarrow S
189  X=Y?
Find smallest
190  GTO0
191  \rightarrow S
192  X=Y
193  STOE
Store
194  X=Y
195  RTN
196  *LBL0
197  \rightarrow S
198  STQB
199  \rightarrow 4
200  RTN
APPENDIX "C"

DETAILED MIS-IL CELL FABRICATION SCHEDULE

A. Select and Measure Wafers (to characterize substrate)
   - material: 1/2" diameter, p type 111 silicon wafers
   - scribe identification numbers on front, near edge of wafer
   - measure wafer thickness with micrometer
   - measure wafer resistivity with four-point probe

B. Prefurnace Clean (to prepare slices for evaporation)
   - 5 minute boil in trichloroethylene (tric)
   - 15 minute etch in hot Caro's acid
   - 10 minute rinse in flowing de-ionized (DI) water
   - 5 minute etch in concentrated nitric acid (HNO₃) at 75-80°C
   - 10 minute DI water rinse
   - 2 minute etch in 10% hydrofluoric acid (HF)
   - 10 minutes DI water rinse
   - blow wafer dry with clean nitrogen gas (N₂)

C. Back-Metallization (to make contact to the back of the cell)
   - carefully place the wafers with back surface up on a evaporator plate--avoid scratching fronts.
   - load plate into Bell jar, draw a vacuum
   - deposit 10 KΩ of aluminum at - 15 Ω/sec
- release vacuum, unload and inspect wafers

D. Sintering (to obtain good ohmic contacts)
- furnace temperature = 450°C - gas flow = 2 l/min N₂
- 5 minute warm up - 30 second push - 15 minute sinter
- 60 second pull - 5 minute cool, unload

E. Front Surface Etch (to remove thin oxide)
- load teflon dropper with concentrated H.F.
- swirl over fronts of wafer
- rinse for 5 minutes - go directly to oxidation

F. Oxidation (to grow thin MIS oxide)
- blow slices dry with N₂
- load slices on boat with fronts up
- furnace temperature = 450°C - gas flow = 2 l/min O₂
- 5 minute warm up, 30 second push, 10 minute run
- 5 minute cool, test thickness of oxide using ellipsometer

G. Front Metallization (to form MIS contact)
- load slices immediately after oxidation onto evaporator plate
- draw vacuum
- deposit 20 Å of aluminum at - 15 Å/second
- release vacuum, unload and inspect wafers

H. Lithography (to define metal grid pattern)
- 30 minute prebake at 200°C
spin negative photoresist on front
- 20 minute bake at 85°C
- remove wafers, align mask and expose
- expose, develop, blow dry with N₂ - inspect
- 30 minute post bake at 145°C just prior to etching

I. Metal Etch (to remove unwanted Aluminum)
- etch wafers in concentrated phosphoric acid (H₃PO₄) at 55-60°C
  agitating constantly for 1 minute
- rebake at 145°C for 10 minutes to prevent photoresist from lifting
- continue etching in phosphoric until all aluminum is removed
- 10 minute DI rinse
- inspect under microscope

J. Photoresist Removal (prior to spinning on oxide)
- 10 minute in J-100 microstrip at 100-110°C
- 30 minute DI water rinse
- blow dry

K. Spin-On Tantalum Oxide (to make solar cell)
- remove tantalum oxide solution from refrigerator
- bake slices for 30 minutes at 200°C to remove moisture
- clean eyedropper, remove slices
- spin-on solution at - 4000 RPM
- inspect under microscope
- test for photovoltaic output
END

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FIN