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TITLE OF THESIS/TITRE DE LA THÈSE INVESTIGATION OF THICK-FILM CONTACTING
PROCEDURES FOR SILICON SOLAR CELLS

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INVESTIGATION OF THICK-FILM CONTACTING PROCEDURES)
FOR SILICON SOLAR CELLS

by

Stephen S. Winterton, B.Eng.

A thesis 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

January 1981

The undersigned recommend to the Faculty of Graduate Studies
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"INVESTIGATION OF THICK-FILM CONTACTING PROCEDURES FOR
SILICON SOLAR CELLS"

submitted by Stephen Scott Winterton in partial fulfillment of the
requirements for the degree of Master of Engineering.

Prof. R.E. Thomas
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February, 1981

ABSTRACT

In this study, a thick-film contacting procedure for n^+/p silicon solar cells has been developed to achieve uncorrected AM1 efficiencies of 12-14% (15-17% when corrected for residual reflectance and shading). Techniques for measuring important contact properties, and an original analytical model of solar cell operation, have been developed for the purpose of characterizing these solar cells. Finally, an original fabrication process has been proposed, which should in principle make junction diffusion and contact firing proceed simultaneously. While the principle has not yet proven feasible, promising efficiencies (7%) and a great reduction in the number of required process steps have been demonstrated.

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I would like to thank my thesis supervisor, Professor Raye Thomas, for helping to define the scope and direction of this work. I would further like to thank Tony Armstrong, Gary Salter, Lyall Berndt and Dr. Ed Norman - presently, or until recently, with the Carleton Electronics Research Laboratory (CERL) - for helpful discussions and valuable technical advice. For preparing the photomasks used, and carrying out much of the device fabrication, I would like to thank Eleanor Armstrong, Jessie McAinsh and Shirley Woodward at CERL. I would also like to express my gratitude to Bob Boynton and Blair MacLaurin of Bell-Northern Research, for their helpful advice and assistance with some of the fabrication and measurements.

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LIST OF PRINCIPAL SYMBOLS AND ABBREVIATIONS

The following is not a complete list of symbols used in the text, since most are defined when they are first introduced, while others are in such general use that they do not require explanation.

A	Area
AM1	Air mass one
b	Base (as subscript)
B	Bus bar (as subscript)
c	Contact or solar cell (as subscript)
e	Emitter (as subscript)
E	Electric field
η	Efficiency
F	Grid finger (as subscript); also, shading (or shadowing) factor
I	Current
I_{sc}	Short-circuit current
j	Current density
j_L	Photocurrent density
j_o	Diode saturation current density
k	Boltzmann's constant
L	Length
m	Metal (as subscript)
n	Junction perfection factor
q	Electronic charge
r	Radius

LIST OF PRINCIPAL SYMBOLS AND ABBREVIATIONS (cont'd)

R	Resistance
R_s	Series resistance
R_{sh}	Shunt resistance
ρ	Bulk resistivity
ρ_c	Contact resistivity
ρ_D	Sheet resistivity
S	Spacing
t	Thickness
T	Absolute temperature
V	Voltage
V_{oc}	Open-circuit voltage
V_T	Thermal voltage (i.e. kT/q)
w	Width
x	Distance

CHAPTER 1

INTRODUCTION

1.1 Background

Terrestrial sunlight contains more energy, in the form of light and heat, than is now consumed by mankind in any form. Solar cells can aid in tapping some of this vast energy resource, since they convert sunlight directly into electricity; in striking contrast with the power generation methods in use today, solar cell generated electricity is fuel-free, pollution-free, safe and reliable. Despite these advantages and desirable qualities, solar cells are presently so expensive to manufacture that large-scale power production is not a realistic application. However, many researchers are confident that radical changes in manufacturing technology - scheduled to make their appearance in this decade - will make solar cell electricity cost-competitive with electricity generated by conventional means [1].

The manufacture of solar cells using single-crystal silicon wafers with diffused junctions, is the oldest and best understood of solar cell fabrication technologies. Until recently, vacuum processes such as evaporation and sputtering were used almost exclusively to form the electrodes of such solar cells; however, cheaper techniques such as electroless plating and "screen-printing" (properly thick-film contacting) are now being investigated [1,2]. Further research and development of diffused-junction monocrystalline silicon technology may not be the most promising direction for low-cost solar cell

research to take (e.g. Cu_2S -CdS, polycrystalline silicon and induced junctions represent intrinsically cheaper approaches [1,3]), yet it is widely believed to be capable of achieving low-cost goals (e.g. EFG silicon ribbon [1]). Thus, the development of a contacting technique applicable to this technology is a useful undertaking; improvements in contacting techniques may yet be secured in the general areas of increased manufacturing throughput, increased solar cell efficiency and reliability, and decreased manufacturing labour, energy consumption and materials costs.

In 1978, the Carleton Electronics Research Laboratory (CERL) undertook, under contract to the National Research Council of Canada (NRC), to develop a complete low-cost solar cell array technology [4]. Single-crystal silicon solar cells with diffused junctions and thick-film contacts were to be a principal feature of the demonstration arrays of that study. This thesis originated because no research had yet been conducted at CERL into thick-film contacting processes, or solar cell contacts, per se.

1.2 Purpose of Study

The primary objective of this thesis was to develop means for manufacturing solar cells with thick-film electrodes, having high efficiency; this basic statement of aim is expanded on, below.

- 1) Thick-film contacts are applied in the form of an "ink" or "paste", containing silver and glass particles and organic liquids. As there are many commercially available ink formulations, the first goal was to select inks which would perform well in the present application.

- 2) The next step was to develop a contacting process, and to characterize the results of that process. Methods for characterizing solar cell contacts, and methods for modelling solar cells, required investigation.
- 3) It was anticipated that alterations in the contacting process already developed would achieve only small efficiency gains or cost reductions. The feasibility of a technique - original to this study - which would form the junction and (sinter) the contacts simultaneously, was to be investigated; if proven feasible, the implementation of this technique in production would substantially lower production costs.

1.3 Thesis Organization

In Chapter 1, the subject, scope and outline of this thesis are described. Chapter 2 develops an original model of solar cell operation in which the current-voltage characteristics and certain details of construction are related. The optimization of a thick-film contacting process is taken up in Chapter 3, and the results of this process are characterized in Chapter 4 with the aid of the theory developed in Chapter 2. Chapter 5 considers prospects for improvement in the contacting process, while Chapter 6 gives the conclusions and recommendations of the thesis.

CHAPTER 2

SOLAR CELL ELECTRICAL MODELLING

2.1 Introduction

In this chapter, an original model of the solar cell is developed which relates the electrical characteristics to details of construction. This new model will be used in Chapter 4 for the characterization of solar cells fabricated in this thesis. The present section provides a motivation for study of this isolated aspect of the solar cell theory.

2.1.1 Simple Solar Cell Model

Figure 2.1 shows plan and section views of a typical solar cell structure. Usually 5 to 10% of the top surface of the solar cell is covered with a gridded metal contact; because of this, there is a direct loss of power by reflection (i.e., shading or shadowing factor, F). Away from the top contact, a fraction of the incident sunlight is lost - also by reflection - but an antireflection coating minimizes the importance of this loss. The bulk of the light enters the semiconductor, where sufficiently energetic photons (i.e., energy exceeding the bandgap) create mobile electron-hole pairs by ionization of atoms in the lattice. The electric field associated with the depletion region sweeps a proportion of these light-generated charge carriers from one neutral region to the other, producing a photocurrent of density, j_L . The remaining light-generated carriers are lost by

FIGURE 2.1 Plan and section views of typical solar cell structure (not to scale).

FIGURE 2.2 Simple electrical model of the solar cell.

recombination at charged lattice sites (e.g., impurity ions, crystallographic defects, unsatisfied surface bonds).

A load connected to the solar cell causes a "dark current" to flow in opposition to the photocurrent - usually by the mechanisms of injection or depletion-region recombination. If one of these two components dominates, the density of the dark current is given by

$$j_0(e^{(V/n V_T)} - 1)$$

where j_0 is the saturation value of the current density, V is the junction voltage, V_T is the thermal voltage and n is the junction perfection factor. The latter is unity for the mechanism of injection, and in excess of unity for the mechanism of depletion-region recombination (e.g., $n=2$ for the idealized situation of one trap level at the center of the forbidden band [1]). The dark current can be increased if there are diffusion spikes of n-type dopant or top contact metal, or if the junction is shunted at the cell edges because of surface leakage. The excess current in such cases can be modelled by a resistance, R_{sh} , in shunt with the junction (or diode) [1]. In addition, voltage drops arise from current flow through the emitter, base, top contact grid and contact interfaces, and the net effect can be modelled by a resistance, R_s , in series with the junction [1,5,6,7].

The terminal characteristics of the solar cell in this model are then given by

$$I_c = [j_L(1-F) - j_0(e^{\frac{V_c + I_c R_s}{n V_T}} - 1)]A_c - \frac{V_c + I_c R_s}{R_{sh}} \quad (2.1)$$

where I_c is the solar cell terminal current, V_c is the solar cell terminal voltage and A_c is the total area of the top surface of the solar cell. The model is illustrated by means of a schematic circuit diagram in Figure 2.2.

Three operating points of the solar cell are of particular interest from a performance point of view, corresponding to the short-circuit, open-circuit and maximum generated power conditions. The three parameters of short-circuit current, open-circuit voltage and efficiency (i.e., the ratio of maximum power generated to incident light power), which are determined at these operating points, are the most often used measures of solar cell quality.

2.1.2 Problems with the Simple Model

There are several deficiencies in the simple model of the solar cell just described. Shunt resistance and junction perfection factors are often grossly different from values anticipated on a theoretical basis [1]. Furthermore, in theory, high values of junction perfection factor should coincide with high open-circuit voltages; in practice, the dark current is always found to increase with junction perfection factor in such a way as to maintain or lower the open-circuit voltage. This observation is quantitatively inexplicable on the basis of existing theories of the dark current [1]. Finally, where good contacting procedures are used, a current-dependent series resistance should not occur. Nevertheless, several workers have observed this phenomenon [8].

It has been shown [9,10] that at least some of the serious shortcomings of the simple model can be eliminated, if account is taken of the spatial variation of junction voltage accompanying lateral current flow in the diffused emitter and top contact grid. A method of analyzing this distributed series resistance effect has been developed in this thesis and will shortly be presented.

2.1.3 The Need for Improved Analysis

Shading and series resistance problems have historically been aggravated for the thick-film contact [11,12]. Distributed series resistance effects are known to be important for large area (i.e. low cost) solar cells under terrestrial sunlight [10]. In view of these facts, there is a special need in this thesis to be able to correlate series resistance factors with solar cell performance in the presence of distributed series resistance effects. Numerical techniques can be used to model such effects, and have been employed by many workers in solar cell simulation programs [3,9,10,13]. However, present computer simulations of solar cells have serious deficiencies. Two drawbacks which have been pointed out [1] are the necessity of including many heuristic assumptions and approximations which are not well founded on observations, and the time-consuming nature of obtaining and interpreting solutions. While these deficiencies do not rule out the use of numerical methods, they at least make the use of simple analytical techniques preferable.

2.2 Method of Analysis

At the present time, no equations giving the solar cell terminal characteristics in the presence of distributed series resistance effects are possible for generalized solar cell or contact grid geometries. For this reason, the method of analysis which has been developed will be illustrated for the simple example of a solar cell with rectangular geometry. Some possible generalizations will be suggested, but their development is left for later work.

2.2.1 Formulation of the Equations

Figure 2.3 illustrates the geometry of the problem to be solved. The equations governing current flow are the same regardless of the condition of operation, or of the region of the solar cell under description (i.e., illuminated or dark; emitter, grid finger or bus bar). Assuming one-dimensionality and injection dominated dark current, these equations are, as illustrated in Figure 2.4:

$$\frac{d}{dx} I(x) = W(j - j_0(e^{\frac{V(x)}{V_T}} - 1)) \quad (2.2)$$

and

$$\frac{d}{dx} V(x) = - \frac{\rho_{\square}}{W} I(x) \quad (2.3)$$

where W is the width of the region, j is the density of the current which enters the region uniformly and in a direction normal to the plane of the junction, $\rho_{\square}$ is the sheet resistivity of the layer, and $V(x)$ and $I(x)$ are respectively the junction voltage, and the current

FIGURE 2.3 Plan and section views of solar cell section under analysis.

FIGURE 2.4 Equivalent circuit for an infinitesimal solar cell element (of width W and length Δx).

in the layer, at a distance x from the origin. The latter is selected so that

$$I(0) = 0 \quad (2.4)$$

Hence, for the emitter and grid fingers, the origins have been marked as A and B on Figure 2.3, while for the analysis of the bus bar, the origin lies at the opposite end from that where an electrical interconnection is made to the solar cell.

This formulation of equations is consistent with the work of Therez [13] and Bobbio et al [14] among others (i.e., these, or more general two-dimensional expressions underlie all good numerical simulations, although they may not appear explicitly).

2.2.2 Solution of the Boundary Value Problem

Equations (2.2) and (2.3) may be combined into a single equation:

$$\frac{d^2}{dx^2} V(x) = -\rho_{\square} (j - j_0 (e^{\frac{V(x)}{V_T}} - 1)) \quad (2.5)$$

which can be integrated to obtain, after substituting (2.3) and (2.4)

$$I^2(L) = \frac{2W^2 j_0 V_T}{\rho_{\square}} \left[\left(1 + \frac{j}{j_0}\right) \frac{V(0) - V(L)}{V_T} - \left(e^{\frac{V(0)}{V_T}} - e^{\frac{V(L)}{V_T}}\right) \right] \quad (2.6)$$

where L is the length of the region, and $V(0)$ and $V(L)$ are the junction voltages at its boundaries. Furthermore, $I(x)$ may be given in terms of a Maclaurin Series expansion

$$I(x) = \sum_{m=0}^{\infty} \frac{I^{(m)}(0)}{m!} x^m$$

$$\sim I(0) + I^{(1)}(0)x$$

Assuming that

$$I^{(1)}(0) \sim \frac{I(L)}{L}$$

yields

$$I(x) = \frac{I(L)}{L} x \quad (2.7)$$

One can determine an exact solution for $I(x)$ by using Eqns. (2.2), (2.3) and (2.4) to find the coefficients of the complete series.

However, the present approximate approach yields more useful results.

Using Eqn. (2.3),

$$\int_{V(0)}^{V(L)} dV(x) = \int_0^L \left(- \frac{\rho_{\square} I(x)}{W} \right) dx$$

with Eqn. (2.7) yields

$$V(0) - V(L) = \left(\frac{\rho_{\square} L}{2W} \right) I(L) \quad (2.8)$$

The same result has been obtained by Wolf [5], who used the form of the term in brackets for the effective contributions to series resistance of the emitter and grid finger.

Using Eqns. (2.6) and (2.8), equations giving the current, I_e , exiting or entering the emitter at the grid finger edge, the current,

I_F , exiting or entering the grid finger at the bus bar, and the current, I_B , exiting or entering the solar cell at the bus bar interconnect, can be determined. These equations are given explicitly in Table 2.1. To estimate the overall solar cell characteristics, one must solve these equations in turn for I_e , I_F and I_B . It is important to note that the highest junction voltage in each region - $V(0)$ in Eqn. (2.8) - is the same for all regions, given fixed conditions at the terminals.

2.2.3 Nonidealities

Fang and Hauser [9] have shown, using numerical calculations and measurements, that after accounting for distributed series resistance effects there remains a residuum of series resistance which can be lumped (R_s). This probably arises in the contact interfaces and base of the cell. To a first order approximation, the writer finds this to be

$$R_s \sim \frac{\rho_{c,e}}{(1-F)A_c} + \frac{\rho_{c,b}}{A_c} + \frac{k\rho_b t_c}{A_c} \quad (2.9)$$

where $\rho_{c,e}$ and $\rho_{c,b}$ are the contact resistivities (i.e., in units of $\Omega\text{-cm}^2$) at the front and back contacts, ρ_b is the base resistivity, t_c is the cell thickness, and $k \sim \frac{1}{2}$ for illumination and ~ 1 for dark conditions. This is consistent with the series resistance approach [5,6,7], although usually no distinction is made between illuminated and dark conditions when estimating base resistance; the distinction is a natural one, and traces to the "uniform" generation of current throughout the thickness of the cell when the cell is illuminated.

Conditions Region	Illuminated Cell	Dark Cell
Emitter	$I_e^2 = (j_o + j_L) w_e L_e I_e - \frac{2w_e^2 j_o V_T}{\rho_{e,e}} \left(e^{\left(\frac{\rho_{e,e} L_e I_e}{2w_e V_T} \right)} (e^{(V_e/V_T)} - 1) e^{(V_e/V_T)} \right)$	$I_e^2 = \frac{2w_e^2 j_o V_T}{\rho_{e,e}} (1 - e^{-\left(\frac{\rho_{e,e} L_e I_e}{2w_e V_T} \right)}) \left(\frac{V_e}{V_T} \right) e^{(V_e/V_T)}$
Grid Finger	$I_F^2 = (j_o w_F L_F + 2I_e) I_F - \frac{2w_F^2 j_o V_T}{\rho_{F,m}} \left(e^{\left(\frac{\rho_{F,m} L_F I_F}{2w_F V_T} \right)} (e^{(V_F/V_T)} - 1) e^{(V_F/V_T)} \right)$	$I_F^2 = \frac{2w_F^2 j_o V_T}{\rho_{F,m}} (1 - e^{-\left(\frac{\rho_{F,m} L_F I_F}{2w_F V_T} \right)}) \left(\frac{V_F}{V_T} \right) e^{(V_F/V_T)}$
Bus Bar	$I_B^2 = (j_o w_B L_B + N_F I_F) I_B - \frac{2w_B^2 j_o V_T}{\rho_{B,m}} \left(e^{\left(\frac{\rho_{B,m} L_B I_B}{2w_B V_T} \right)} (e^{(V_B/V_T)} - 1) e^{(V_B/V_T)} \right)$	$I_B^2 = \frac{2w_B^2 j_o V_T}{\rho_{B,m}} (1 - e^{-\left(\frac{\rho_{B,m} L_B I_B}{2w_B V_T} \right)}) \left(\frac{V_B}{V_T} \right) e^{(V_B/V_T)}$

Table 2.1. Current-voltage characteristics at different points in the solar cell.

More precise determinations of series resistance may be necessary in practical cases. It is important to note that a back contact will fill a large fraction, not all, of the back surface area. Furthermore, only a small area of the back contact will itself be contacted by an external interconnection. The consequent contribution to residual series resistance of lateral current flow in these regions, can easily be larger than the terms in Eqn. (2.9). Also, because of current crowding at the top contact, Eqn. (2.9) will generally overestimate contact resistance. For cases in which better accuracy is required, References [7,15] will be particularly valuable.

The overall solar cell characteristics are given by:

$$I_c = I_B + k' V_B / R_{sh} \quad (2.10)$$

$$V_c = (1 + R_s / R_{sh}) V_B + k' I_B R_s \quad (2.11)$$

where a shunt resistance, R_{sh} , has been assumed, and where $k' = -1$ for illumination and $+1$ for dark conditions, and I_c and V_c are respectively the terminal solar cell current and voltage.

2.2.4 Closing Remarks

The objective in this section has been to illustrate methods, rather than to give general solutions. There are several possibilities for improving the results given, so that the model applies even better to real solar cells:

- (1) to ensure that the one-dimensional (lateral) current flow and effective resistance representations are realistic, the regions can be broken up into short and wide rectangular strips

(2) dark currents comprising injection, depletion-region recombination and even tunneling could be incorporated into this model - a sum of several exponentials, rather than a single exponential, will then appear in the right-hand side of Eqn. (2.2).

The development of these or other possible generalizations is left for later work.

2.3 Verification of the Model

A glance at Table 2.1 shows that if the present model is correct, very different behaviour can be expected for real solar cells than is anticipated by the simple theory discussed at the beginning of this chapter. It will now be shown for the emitter region that in the limiting cases where the effective series resistance or the current become very small, or very large, the new model gives correct results.

For the illuminated emitter (see Table 2.1)

$$I_e^2 = (j_o + j_L) W_e L_e I_e - \frac{2W_e^2 j_o V_T}{\rho_{n,e}} \left(e^{\left(\frac{\rho_{n,e} L_e I_e}{2W_e V_T} \right)} - 1 \right) e^{\left(\frac{V_e}{V_T} \right)}$$

or

$$I_e = (j_o + j_L) W_e L_e - j_o W_e L_e e^{\left(\frac{V_e + \frac{\rho_{n,e} L_e I_e}{2W_e}}{V_T} \right)} \left[\frac{2W_e V_T}{\rho_{n,e} L_e I_e} \left(1 - e^{-\left(\frac{\rho_{n,e} L_e I_e}{2W_e V_T} \right)} \right) \right]$$

As effective emitter resistance or emitter current become very small, the term in square brackets approaches unity, and

$$I_e \sim (j_L - j_o) \left(e^{\left(\frac{V_e + \rho_{n,e} L_e I_e / 2W_e}{V_T} \right)} - 1 \right) W_e L_e$$

exactly as in Wolf's theory for the illuminated emitter [5].

For the emitter under dark conditions,

$$I_e^2 = \frac{2W_{e,o}^2 V_T}{\rho_{\square,e}} \left(1 - e^{-\left(\frac{\rho_{\square,e} L_e I_e}{2W_{e,o} V_T}\right)} \right) e^{\left(\frac{V_e}{V_T}\right)} - j_o W_{e,o} L_e I_e$$

As the effective emitter resistance or emitter current becomes large

$$I_e \sim \sqrt{\frac{2W_{e,o}^2 V_T}{\rho_{\square,e}}} e^{\left(\frac{V_e}{2V_T}\right)}$$

This equation has been given by Fang and Hauser [9] (although their approach could not be extended to the illuminated case), and has been confirmed by them on the basis of measurements and numerical calculations.

2.4 Conclusions

The model developed in this chapter clearly has greater validity, and can be expected to have greater accuracy, than the lumped series resistance approach [1,5,6,7]. One obvious consequence of the present model is that it makes possible the formulation of better contact grid design rules than those which are presently in use [1,5]. Improvements in the theory so that two-dimensional problems of arbitrary solar cell shape and contact grid geometry can be treated would also be of great practical value in the design of better solar cells. Research into these questions will hopefully be undertaken as a consequence of this investigation.

CHAPTER 3

THICK-FILM CONTACTING PROCESS3.1 Introduction

The thick-film solar cell contact is not new; it was successfully demonstrated for the first time by Ralph [2], in 1975. Recent research has resulted in several innovations in the technique, but little has been reported in the literature concerning the optimization of results. This chapter examines one implementation of the technique, and describes efforts to optimize it in this thesis; subsequent chapters will consider process characterization and prospects for improvement.

3.1.1 The Process

Thick-film technology has been used for many years to integrate conductors, resistors, capacitors and silicon "chips" on ceramic substrates [16,17]. More recently, it has been applied to solar cell contacting; several fabrication processes have been developed, with most of these incorporating established thick-film techniques and materials. However, the different approaches are, in chemical and physical terms, quite dissimilar. The process investigated in this thesis was developed along lines recommended by Lin et al [12].

The thick-film contact is applied in a three-stage process consisting of screen-printing, firing and contact activation. In screen-printing, an ink or paste containing fine particles of silver

and borosilicate glass suspended in a liquid organic medium, is pushed through a stencil of the desired contact shape onto the non-contacted solar cell. The ink is then fired - a high temperature heat treatment which drives off the organics and melts the glass component of the ink. Some of the glass wets the silver grains, yet allows them to fuse together to give a low volume resistivity. The remainder of the glass falls to the metal-semiconductor interface where it forms an adherent bond, but where it can also give rise to a high contact resistivity. For this reason, the contact may require activation after the firing treatment to reduce the high resistance arising at the glassy interfacial layer. Lin et al [12] have suggested a dip in hydrofluoric acid for this purpose, although they have not given details.

3.1.2 Purpose of Investigation

Little has been reported in the literature about the effects of process variations upon the performance of solar cells when using the thick-film contacting process. For the Carleton Electronics Research Laboratory (CERL), the author has studied commercially available inks [4] and has selected two - Engelhard E-460A and E-422D - for contacting, respectively, the n-type emitter and p-type base of a solar cell [18]. Based on this study, a contacting procedure has been developed [18,19] which results in satisfactory quality solar cells when using these inks. The present investigation seeks to determine optimal firing and activation procedures for the contacts. Fabrication details, where not given explicitly, are to be found in Appendix 1 and Reference

[18], while solar cell testing procedures have been previously described by Norman [3] (measurements of solar cell performance in this investigation were made at 295°K).

3.2 Firing Temperature

In the first experiment, one solar cell was prepared and fired isochronally; significant fabrication details and results are given in Table 3.1. During testing, it was noted that the application of a small reverse bias to the solar cell would sometimes cause a shift to increased currents to occur in the measured current-voltage characteristics (this is noted in the table as "I-V characteristics unstable"). Furthermore, it was observed that the contact material adhered poorly to the silicon when low firing temperatures were used. From the table, the optimum firing temperature appears to be ~750°C, but the efficiency without contact activation is very low.

Since dipping of a solar cell in hydrofluoric acid is known to activate the thick-film contact [12], it was decided to test the effects of firing temperature and HF dip time simultaneously in order to determine the optimum firing temperature. A 1% HF solution was used to allow for extended dipping times and to give good control over the process. To ensure that the results were practically useful, only elevated temperatures which would give satisfactory contact adhesion were investigated. From the results given in Table 3.2, it can be seen that efficiency is maximized for a firing temperature of 650°C, and probably for HF dip times in excess of those tested.

Firing Temperature (°C) ±5°C	Firing Time (min.)	Total Furnace Time (min.)	I _{sc} (mA)	V _{oc} (mV)	Uncorrected η _{AM1} (%)	Comments
405	12	22	~0.03	~525	<0.05	IV characteristics unstable
505	11	20	6	570	0.05	
550	11	20	18	570	0.2	
605	11	25	61	570	0.5	
650	11	25	133	570	1.0	
700	10	22	251	565	2.1	IV characteristics stable
745	11	22	296	548	3.1	
800	11	23	172	507	1.4	

Table 3.1. Effect of firing temperature upon solar cell performance (cell C-1, isochronal firing, no contact activation).

Solar Cell	Firing Temperature (°C) ±5°C	Firing Time (min.)	Total Furnace Time (min.)
C-2	650	5	17
C-3	700	5	17
C-4	755	5	19
C-5	800	5	21
C-6	850	5	19
		5	17-21

Solar Cell	Uncorrected AMI Efficiencies (%)						Comments
	HF Dip Time (sec)	0	30	45	60	75	
C-2		0.6	5.4	7.4	9.5	10.2	IV characteristics unstable for dip times shorter than 30 seconds
C-3		0.4	5.9	8.0	9.4	9.7	
C-4		5.9	7.6	7.8	7.9	7.9	
C-5		5.6	5.6	5.7	5.7	5.7	IV characteristics stable
C-6		5.6	5.6	5.5	5.6	5.5	

Table 3.2. AMI efficiency of solar cells as a function of firing temperature and HF dip time.

Illuminated current-voltage characteristics after contact activation are shown in Figure 3.1. The loss of short-circuit current with increasing firing temperature indicates loss of lifetime in the base region of the cell. This was confirmed by means of solar cell collection efficiency (i.e., ratio of the number of carriers collected to the number capable of being collected - i.e., the number of photons with energy exceeding the bandgap - at a given wavelength) measurements. Figure 3.2 shows the results of these measurements for the cells fired at the lowest and highest temperatures studied. The poor long-wavelength response of the cell fired at 850°C confirms that there is a loss of electron lifetime in the base. This is not surprising as silver is a fast-diffusing and lifetime-killing impurity in silicon. The improved short-wavelength response of the same cell is probably due to the reduced surface recombination velocity and decreased reflectance accompanying thermal oxidation.

3.3 HF Dip Time

Table 3.3 shows that for a 1% HF solution, the optimum dip time is roughly 3 minutes. A partial loss of front contact material occurs very quickly after this optimum time is exceeded. The current-voltage characteristics of Figure 3.3 show that the effect of increasing HF dip time is to reduce series resistance in the solar cell. This implies that the step introduces F^- into the glassy layer, thereby reducing interface resistance.

It should be noted that there is a substantial difference between the results (i.e., dipping times required to maximize solar cell

FIGURE 3.1 Solar cell current-voltage characteristics as a function of firing temperature (after contact activation).

FIGURE 3.2 Effect of firing temperature upon collection efficiency (measurements normalized to give a maximum of unity. Measurements locally averaged in figure to eliminate "noise").

HF Dip Time (seconds)	Uncorrected AM1 Efficiency (%)	Comments
0	0.2	
30	3.2	
60	6.7	
90	9.1	
120	9.8	
150	10.0	
180	10.2	
210	10.0	
240	-	
270	-	partial failure by adhesion loss

Table 3.3. Effect of HF dip time upon solar cell efficiency (cell C-7 : fired for 5 min. at 640°C, total furnace time 17 min.).

FIGURE 3.3 Effect of HF dip time upon the solar cell electrical characteristics (cell C-7).

efficiency) of Tables 3.2 and 3.3. This is probably largely due to an acceleration of the activation effect, caused by passing high currents (i.e., in excess of the short-circuit current, by reverse-biasing the cell) through some of the cells during testing. Additional minor differences between the results could be a consequence of slightly different firing conditions, or HF solution strengths.

3.4 Firing Time

The importance of firing time was investigated next. From the results presented in Table 3.4, it is clear that firing time is much less significant than temperature in determining contact quality. This is consistent with what is usually found for passive thick-film devices [16]. However, there does appear to be a small loss of performance with extended firing time. These results and the behaviour of open-circuit voltage in Table 3.1 tend to confirm the presence of junction shunting - probably caused by diffusion of silver into the depletion region. The optimum firing time is about 5 minutes, with a total furnace time of 15 minutes being satisfactory.

3.5 Ink Selection

Inks have been selected [4,18], although the test methods used did not unambiguously favour the choices made. The problem was that the test methods devised were not proven prior to the experimental ink selection study, and in service they proved to be less than completely satisfactory. Table 3.5 gives some details on the inks under test, and presents the major conclusions of the ink selection study;

Solar Cell	Firing Temperature ($^{\circ}\text{C}$) $\pm 5^{\circ}\text{C}$	Firing Time (min.)	Total Furnace Time (min.)	1% HF Dip Time (min.)	I_{sc} (mA)	V_{oc} (mV)	Uncorrected η_{AM1} (%)
C4, C-12, C-13	640-645	5-6	14-19	3	496-519	592-593	9.8-10.6
C-8	650	15	26	3	512	593	10.5
C-9	645	32	42	3	500	588	9.8

Table 3.4. Effect of firing time upon solar cell performance.

Where Ink is to be Used	Ink	Supplier	Reason for Outright Rejection	Marginal Cause for Rejection
n-Si	E-460A	Engelhard		
n-Si	E-422C	Engelhard	narrowest grid finger which can be printed is 10mils (other inks can attain 5mils)	higher sheet resistivity than E-460A at 5mil grid finger widths
n-Si	7713	Dupont		higher contact resistivity than E-422D
p-Si	E-422F	Engelhard		
p-Si	E-422D	Engelhard		
p-Si	4929	Dupont	use not compatible with firing tempera- tures necessary for the front contact	

Table 3.5. Results of prior ink selection study [4,18].

these results are drawn from References [4,18]. The purpose of the present investigation is to justify, on the basis of solar cell performance measurements, the ink choices made in that earlier study.

The results of Table 3.6 confirm that the use of the pair of inks selected results in the best observed solar cell performance. Although there is a large gain in short-circuit current when the ink, E-460A, is replaced by the ink, 7713, there is no gain in efficiency.

3.6 Conclusions

In this chapter, the effects of firing and contact activation conditions upon solar cell performance have been studied. It has been shown that:

- 1) Increases of firing temperature in the range from 650°C to 850°C lead to lifetime killing in the base and loss of short-circuit current. At temperatures below 650°C , adhesion of the contacts to silicon becomes poor. An optimum firing temperature of 650°C has been determined.
- 2) Increased firing time causes a small decrease in solar cell performance through junction shunting. A total furnace time of 15 minutes with a firing time of 5 minutes has proven quite adequate from the point of view of resulting contact quality, and allows for a reasonable process throughput.
- 3) Contact activation is necessary to develop the highest possible efficiency in solar cells fired at 750°C or below.

Solar Cells	Front Contact Ink	Back Contact Ink	Firing Temperature ($^{\circ}\text{C}$) $\pm 5^{\circ}\text{C}$	Firing Time (min.)	Total Furnace Time (min)	1% HF Dip Time (min)	I_{sc} (mA)	V_{oc} (mV)	Uncorrected η_{AM1} (%)
C4, C-12, C-13	E-460A	E-422D	640-645	5-6	14-19	3	496-519	592-593	9.8-10.6
C-14	E-460A	E-422F	645	5	17	3	479	588	9.6
C-15*	7713	E-422D	640	6	18	3	550	572	9.7

* Estimated results for full cell from results for one-half cell.

Table 3.6. Effect of ink selection upon solar cell performance.

A dip of 3 minutes in 1% HF seems best for the optimum firing conditions discussed. The use of a low strength HF solution gives good control over the process, and ensures safety and low material costs.

- 4) Close tolerances on all aspects of the contact firing and activation steps are necessary in order to repeatedly manufacture high efficiency solar cells. Tolerances of $\pm 5^{\circ}\text{C}$ on firing temperature, ± 1 minute on firing time, ± 2 minutes on total furnace time and ± 5 seconds on HF dip time (the HF solution should be made up in several liter quantities) are easily attainable goals, and in view of the results, are not excessively stringent.
- 5) The selection of inks made on a previous occasion [4,18] has been justified on the basis of solar cell performance measurements, and
- 6) A solar cell contacting procedure has been developed which produces solar cells, with 9.8 to 10.6% uncorrected AMI efficiency (or 15.4 to 16.7% AMI efficiency, when corrected for reflection and contact coverage). With currently available antireflection coating techniques [18], solar cells with uncorrected efficiencies of 12.3 to 14.4% should be manufacturable.

In addition, it is clear that several areas require research. Completely adequate adhesion and reliability tests have yet to be defined. With a good test for adhesion, it could be determined whether

lower firing temperatures were practical. If this were the case, increased efficiency, lower process cost and reduced energy payback times may be realized (Dupont 7713 should not be overlooked in the event that lower firing temperatures are investigated). A good test for reliability is necessary to determine whether such mechanisms as silver electromigration, and F^- etching of the glassy interface layer, will practically limit the service life of thick-film contacted solar cells.

CHAPTER 4

PROCESS CHARACTERIZATION

4.1 Introduction

The most important factors to be considered in developing a contacting procedure for solar cells are contact geometry, metal bulk resistivity, contact resistivity and contact-semiconductor adherence [1,20]. The first three factors mentioned influence power loss in the solar cell, as has been discussed in Chapter 2, while contact-semiconductor adherence determines whether or not the contacting procedure is a practical one. This chapter examines the four factors in turn, describing measurement techniques, and then giving measured results for several materials. In Section 4.7, the relevant factors are correlated with solar cell performance using the theory of Chapter 2.

This chapter is mainly concerned with the technical aspects of measurement; theoretical considerations are given in Appendices 2, 3 and 4 for contact geometry, metal bulk resistivity and contact resistivity, respectively.

4.2 Experiments

Table 4.1 gives important details of sample fabrication. Thick-film contacts were prepared in the same way as the solar cell contacts of Chapter 3. Evaporated aluminum and silver contacts were included as the control samples, because their properties have been reasonably well established.

Contacts Fabricated at	Contact Material	Contact on Si-type	Screened with	Sintering or Firing Temperature	Comments
CERL	Evaporated aluminum (2μ thick)	n ⁺ or p	N/A	450°C	Blistered-probably evolution of trapped moisture as gas during sintering
CERL	Evaporated silver (1μ thick)	n ⁺	N/A	450°C	Poorly adherent; 30% nitric acid etchant leaves ragged edges
BNR	E-460A	n ⁺	325 mesh; 45° mesh to pattern angle*	650°C	
BNR	E-422D	p	250 mesh	650°C	
CERL	E-460A	n ⁺	325 mesh; 45° mesh to pattern angle*	650°C	
CERL	E-422D	p	250 mesh	650°C	

* Results in better line definition than parallel alignment of pattern and mesh [21].

Table 4.1. Details of sample fabrication.

4.3 Contact Geometry

Thick-film contacts are much poorer than evaporated or plated contacts in terms of the variability of contact geometry, and how well it conforms to design. Despite this well-known fact, the factor of contact geometry has not been investigated in the relevant literature.

4.3.1 Assessment Techniques

A test pattern, used for investigating geometrical effects in both thick-film and evaporated contacts, is shown in Figure 4.1. Details of the techniques used to measure contact width and thickness are given in Table 4.2; the techniques used - microscopy and profilometry - were found to be completely satisfactory for the purposes of this study.

4.3.2 Results

The poor definition of thick-film contacts relative to evaporated contacts is clearly demonstrated in Figure 4.2; generally, the minimum width of continuous thick-film contacts has been found to be 5 mils. In a quantitative comparison of thick-film and evaporated contacts, Figure 4.3 shows average measured widths and thicknesses as a function of designed contact width, for narrow evaporated (aluminum) and thick-film (E-460A) contacts.

A fit to the data of the original theory of thick-film contact geometry developed in Appendix 2, is also shown in Figure 4.3. In the theory, the dimensions of fired contacts - width, W , and thickness, t , - are related to the designed contact width, W_d (actually, to the width of the contact as measured on the photomask), by

A photomask of the pattern was prepared at 25X reduction from rubylith artwork. Mask dimensions were 0.16 mils smaller than designed.

FIGURE 4.1 Test patterns for assessment of contact geometry (scale: 1mm to 1 mil).

Factor Under Measurement	Measurement Technique	Where Measured	Smallest Resolvable Detail	Repeatability	Comments
Thickness of as-screened and as-dried contacts*	Microscope with calibrated focusing knob	BNR	1μ	Not measured ⁺	Method good but factor useless because of shrinkage during firing
Thickness of fired contacts	profilometry	BNR	1000A ^c or better	Not measured ⁺	Chart data inconvenient to work with
Width of fired contacts	Travelling microscope	CERL	0.01 mils (1/4 μ)	0.07 mils (1-3/4 μ)	Measure for contact metal only (not surrounding glass)

* Of large area contacts not displayed in Figure 4.1.

+ Said to be good [21]

Table 4.2. Contact geometry assessment techniques.

(a) evaporated aluminum contacts, designed to be 2 and 4 mils wide.

(b) thick-film - 7713 ink fired at 620°C - contacts, designed to be 4 and 5 mils wide.

FIGURE 4.2 Photomicrographs of (a) evaporated and (b) thick-film contacts to silicon.

(a)

(b)

FIGURE 4.3 Measured contact (a) width and (b) thickness as a function of designed width.

$$W = \sqrt{\frac{t_{\text{lim}}}{k_t} (W_d - W_c)} \quad (4.1)$$

and

$$t = \sqrt{t_{\text{lim}} k_t (W_d - W_c)} \quad (4.2)$$

for narrow lines, and

$$W = W_d - W_c \quad (4.3)$$

$$\text{and } t = t_{\text{lim}} \quad (4.4)$$

for wide lines. The transition between the two types of behaviour is

$$W_d = \frac{t_{\text{lim}}}{k_t} + W_c \quad (4.5)$$

with the factors W_c , t_{lim} and k_t being independent of geometry, but not of fabrication process conditions. The fit can be seen to be excellent.

4.4 Metal Bulk Resistivity

Sheet resistivities of a few $\text{m}\Omega/\square$ have been reported [11,22] in previous studies of silver-borosilicate glass inks applied to solar cell contacting. However, contact thickness is not constant, and bulk resistivity is therefore a more meaningful quantity.

4.4.1 Measurement Techniques

Some devices used to assess metal bulk resistivity in this study are illustrated in Figure 4.4(a), where probe positions numbered

a

b

c

d ("semi-infinite" strip)

(a) some test patterns (scale: 2mm to 5 mils)

(b) test circuit

FIGURE 4.4 Metal bulk resistivity measurement methods.

in the figure correspond to the test circuit shown in Figure 4.4(b). Details on these and the remaining devices under test are given in Table 4.3. Repeatability of voltage measurements at "constant" current was good, with a $\pm 0.5\%$ spread due to current error, and $\pm 5\mu\text{V}$ due to meter limitations. With care, the current error can be further reduced, although testing proceeds more slowly.

Determination of metal bulk resistivity using such measurements requires only simple calculations. First, a resistance in parallel with the device resistance, due to current flow in the semiconductor sheet, must be extracted. The method of correction is straightforward. Table 4.3 gives correction factors, which are explicitly determined in Appendix 3. Once this correction is carried out, measured aspect ratios and thicknesses determined by the methods of Section 4.3.1 are applied to the corrected resistance, yielding the bulk resistivity of the metal.

Thick-film contacts which are fired without proper furnace ventilation are found to have a high bulk resistivity [16]; this phenomenon is evidenced by discoloration of the normally white contacts. Too high test currents used with the device of highest aspect ratio can lead to local melting at irregularities in the contact, and high apparent resistivities. For the samples tested, this was found to occur at a test current of 10mA - a current density of the order of $1\text{kA}/\text{cm}^2$.

Device	Aspect Ratio	Device Description	Tested With	Voltmeter Used	Semiconductor* Resistance in Parallel with Metal Resistance
a	40	See Fig. 4.2	manipulable probe multiprobe IC tester	Fluke 8300A DVM ⁺ or Fluke 8000A DMM	0.61 $\rho_{\square}$
b	25.2	See Fig. 4.2	Four-point-probe resistivity test rig (50 mil probe spacings)	Fluke 8300A DVM ⁺ or Fluke 8000A DMM	0.22 $\rho_{\square}$
c	4.0	See Fig. 4.2	"	Fluke 8300A DVM	0.22 $\rho_{\square}$
d	3.3	See Fig. 4.2	"	"	3.30 $\rho_{\square}$
e ^s	0.34	200 mil dia. circle	"	"	0.34 $\rho_{\square}$
f	0.22	one-half of 1.75" dia. circle	"	"	0.22 $\rho_{\square}$

* Sheet resistivity $\rho_{\square}$

+ Fluke 8300A DVM has 1 μ V resolution; Fluke 8000A DMM has 0.1mV resolution.

Table 4.3. Details of metal bulk resistivity testing.

4.4.2 Results

Table 4.4(a) shows that measurements made using different devices give substantially the same results. It also shows that resistivity is independent of geometry for thick-film contacts.

Table 4.4(b) gives resistivity estimates by material. The resistivities of evaporated metals are seen to be significantly larger than their accepted bulk values, primarily because bulk material is more dense than evaporated material. The thick-film contacts have higher resistivities than evaporated silver contacts, largely because of their granular microstructure (see grain sizes in Table 4.4(b), and an illustration in Figure 4.5), and partly because of the small fraction of aluminum in E-422D ink (i.e., ~6% of metal [4]). The granular microstructure of thick-film contacts is also responsible for their white colour.

4.5 Contact Resistivity

This factor, measured in units of $\Omega\text{-cm}^2$, represents the most useful quantitative approach to the study of ohmic metal-semiconductor contacts. If current flows in a direction largely normal to the contact plane, the contact resistivity divided by the contact area gives an effective "contact resistance". More general current flow problems representative of real situations may be treated by the methods of Berger [15].

Contact resistivity has not been adequately assessed for thick-film contacts in the literature - inaccurate measurement techniques

Material	Resistivity Measured Using Different Devices						Resistivity as a Function of Contact Geometry			
	a	b	c	d	e	f	(device cross-section) ($\mu\Omega\text{-cm}$)			
Evap Al	-	4.0	3.7	3.7	4.0	4.2	-	-	-	-
Evap Ag	-	1.9	1.8	-	1.9	-	-	-	-	-
E-460A	3.9	3.8	3.4	3.6	3.9	-	3.9	3.6	3.9	-

(a) Resistivities are independent of device used, or contact geometry.

Material	Measured Resistivity ($\mu\Omega\text{-cm}$)	Accepted Bulk Resistivity [23] ($\mu\Omega\text{-cm}$)	Average Measured Grain Size (μ) Variability $\sim \pm 100\%$
Evap Al	3.9 ± 0.8	2.74	-
Evap Ag	1.9 ± 0.5	1.61	2.3
E-460A	3.7 ± 0.8	N/A	3.8
E-422D	~ 4.7	N/A	6.3

(b) Resistivities and grain sizes by material.

Table 4.4. Measured metal bulk resistivities.

FIGURE 4.5 SEM photomicrograph of thick-film contact
(7/13 ink fired at 650°C. Magnification:
X1200; tilt angle:70°).

have been used [11,12,18,22] or results have been reported having meaningless units [17,22,24]. Riemer [20] has described a plausible measurement technique for application to thick-film contacts, but has not given results.

4.5.1 Measurement Techniques

In this work, two types of devices were used to measure contact resistivity. One is shown in Figure 4.6(a); the three configurations of measurement used with this device are shown in Figure 4.6(b). It can be shown (see Appendix 4) that the contributions from semiconductor sheet resistivity, ρ_D , and contact resistivity, ρ_C , to the resistances measured for each circuit configuration are

$$R_A = \frac{\rho_D}{2\pi} \ln \left(\frac{S+W/2}{W} \right) + \frac{\rho_C}{W^2} \quad (4.6)$$

$$R_B = \frac{\rho_D}{2\pi} \ln \left(2 \frac{(2S-W/2)}{W} \right) + \frac{\rho_C}{W^2} \quad (4.7)$$

and

$$R_C = \frac{\rho_D}{\pi} \ln 2 \quad (4.8)$$

where S is the spacing of the contact pads, and W is the square root of the contact pad area. Contact pads are generally rounded at the corners rather than square, so that their area is given by

$$W^2 = W_0^2 - (4-\pi) \left[\frac{\sqrt{2}W_0 - \delta}{2(\sqrt{2}-1)} \right]^2 \quad (4.9)$$

where W_0 and δ are defined in Figure 4.6(c). Using these equations,

(a) test pattern (scale: 2mm to 5 mils)

(b) test circuits A,B and C

(c) true contact pad shape

essentially no current
flows in the
semiconductor beyond
this ring

(d) improved test pattern (scale: 2mm to 5 mils)
-400 to 400 MA

(e) test circuit for improved test pattern (D)

FIGURE 4.6 Contact resistivity test methods.

measurements from test circuit C can be used to eliminate the semiconductor sheet resistivity components of R_A and R_B , thereby yielding a contact resistivity estimate.

In this technique, the contact resistivity component can be so small with respect to the sheet resistivity component of R_A and R_B , that an accurate estimate of contact resistivity is a practical impossibility. In a similar method employed by Terry and Wilson [25], use was made of smaller and more closely spaced contacts. This would "amplify" the contact resistivity component, but their test pattern is too small to apply to thick-film contact testing. The use of a three probe configuration adds a random component (i.e., the resistance of the common probe) to the measured values of R_A and R_B . This resistance cannot be extracted from the measurements, although the problem can be avoided by using a test rig with at least four movable probes. In summary then, the technique of Figure 4.6(b) may be used to determine whether contact resistivity will cause an excessive or negligible power loss in a solar cell, but it can not be used to accurately estimate contact resistivity.

The second technique used in this study is illustrated in Figure 4.6(d), where probe positions numbered in the figure correspond to the test circuit shown in Figure 4.6(e); this method is similar to a technique advocated by Riemer [20]. Voltage repeatability was found to include $\pm 5\%$ due to current error and "forming" (see below), and $\pm 5\mu V$ owing to the meter limitations already mentioned.

This method is free of both of the major problems encountered in the first method described. The measured resistance is, in fact, mainly due to contact resistivity

$$R_D = \frac{\rho_c}{2\pi rW} \quad (4.10)$$

where measured dimensions for r and W should be used in the equation. A more complex form for R_D involving contact geometry, metal bulk resistivity and semiconductor sheet resistivity may be necessary for detailed interpretation of the measurement (see Appendix 4).

A general problem with contact resistivity measurements is that the test current can alter contact resistivity ("forming"); large currents have been found to substantially reduce the contact resistivity of thick-film contacts (see Chapter 5). For this reason, one should generally begin by testing at low currents, and use only test currents which reflect solar cell conditions. In addition, measurements should be carried out in the absence of light to avoid photovoltaic effects.

4.5.2 Results

Results from the first technique described are given in Table 4.5. Generally, these demonstrate that contact resistivity is inaccurately estimated by the technique. Measurements presented for evaporated aluminum are several orders of magnitude higher than values previously reported in the literature (i.e., due to the common probe resistance). Measurements for thick-film contact materials are inconsistent with the results of Chapter 3 - that is, they are unreal-

Material	Contact to Si-Type	Measured Contact Resistivity ($m\Omega\text{-cm}^2$)	Contact Resistivity Reported in the Literature [15] ($m\Omega\text{-cm}^2$)
Evap. Al	n^+	3	3×10^{-4} to 10^{-2}
	p	10	
E-460A*	n^+	7	N/A
E-422D*	p	60	N/A

* No HF dip.

Table 4.5. Contact resistivity measurements by simple technique.

istically low. In Chapter 3, it was shown that solar cell performance without contact activation was very poor, which implies a large value of contact resistivity. The probable cause of the low values observed when contact resistivity is measured directly, is the use of high test currents (several A/cm^2) and the forming phenomenon.

Figure 4.7 shows the contact resistivity of an activated contact as a function of current density, as measured by the second measurement technique. Positive currents correspond to a field direction pointing from the metal to the semiconductor - the case for an n^+/p solar cell under illumination. These measurements show the contacts to be non-ohmic, when observed over a wide range of operating currents. However, the operating point of the contact under expected service conditions would be confined to a small region about the origin. For all practical purposes, such a contact may be treated as if it were ohmic [15,26]. The reduction of contact resistivity by the various "activation" methods (i.e., dipping in HF, "forming" and firing at high temperatures), is attributed speculatively to the introduction of traps (fluorine or silver ions) into the thick insulating borosilicate glass layer (see Fig. 4.5) lying between the metal and semiconductor, and the consequent promotion of tunneling.

FIGURE 4.7 Improved contact resistivity measurements
(E-460A ink fired at 650°C ; $2\frac{1}{2}$ min dip
in 1% HF).

The results presented here show that the contact resistivity of fired and activated E-460A ink to n^+ -silicon is about $33\mu\Omega\text{-cm}^2$, for current densities typical of solar cells. Similarly, the contact resistivity of fired and activated E-422D ink to p-silicon is expected to be lower than $60\text{m}\Omega\text{-cm}^2$.

4.6 Contact-Semiconductor Adherence

Accurate determination of the load or stress required to separate contact and semiconductor requires elaborate interconnection techniques, expensive and elaborate equipment to strain the contact at a constant rate and destructive tests of many samples [16,17,27]. A qualitative test called the "scotch-tape test" [16] eliminates many of the drawbacks of the quantitative approach; Lamneck et al [28] have given a method for producing quantitative adherence figures from the results of this test.

4.6.1 Assessment Technique

In the scotch-tape test, cellulose tape is applied firmly to the contacts and pulled rapidly to cause failure. No special contact shape is required. According to the scheme of Lamneck et al [28], a contact which resists the test completely is rated as 5, while one which has little or no resistance to the test is rated as 0. Intermediate gradings for degrees of resistance to the test are possible.

4.6.2 Results

Thick-film contact materials (not dipped in hydrofluoric acid) and evaporated aluminum were found to be very strongly adherent (rating, 5). Evaporated silver was very poorly adherent (rating, 0); this is well known in the literature [1,28] and owes to the poor adherence of silver to native silica, which is difficult to remove completely. It was not determined how adherence rated for thick-film contacts after activation. However, probing of the solar cell contacts during measurement of the IV characteristics did not damage the contacts, and this is a good indication that adherence is satisfactory.

4.7 Correlation with Solar Cell Performance

Distributed series resistance effects in the top contact grid are known to be small for typical solar cells operating under one-sun conditions [9]. This is advantageous, because only one equation (modified by series and shunt resistance effects) is then required to predict the complete illuminated solar cell IV characteristics - namely, the equation describing illuminated emitter characteristics given in Table 2.1. For the present modelling problem, light-generated and diode saturation current densities were deduced from measured shading factor, open-circuit voltage and short-circuit current. Furthermore, an effective emitter length of one-half of the grid finger spacing was used, and an effective emitter width was determined to maintain the proper total cell area (i.e., the product of the total number of emitter regions and the effective emitter area, corrected for shading).

Shunt resistance was determined from the slope of the measured illuminated solar cell IV characteristics at zero bias. Series resistance incorporated an effective resistance for the grid metal (17.1mΩ), base (1.7mΩ) and contact interfaces (3.7mΩ), calculated according to the methods of Chapter 2. In addition, the effect upon series resistance of the use of a small base contact, was accounted for by the following means. If one determines the voltage drop in the non-contacted portion of the base according to Fourier Series Methods [7], the effective resistance found by dividing this voltage by the current flowing, is

$$\frac{1}{2} \frac{\rho_b}{\pi t_c} \left[\frac{1}{2} \ln \left(\frac{b}{a} \right) - \frac{1 - \left(\frac{a}{b} \right)^2}{4} \right]$$

where ρ_b is the base resistivity, t_c is the cell thickness, b is the cell radius and a is the contact radius (note: the premultiplying factor of 1/2 has the same significance as that appearing in the base resistance term of Eqn. (2.9)). A similar effect will arise in the emitter. For the solar cells studied in this thesis, these components of series resistance are very important (88.5mΩ).

It can be seen in Figure 4.8, that the electrical characteristics predicted on this basis give an accurate fit to measured results (the error bars show the spread of measured results for several cells under test); presumably, even better correspondence would be obtained with a complete model of distributed series resistance effects, although this would be more difficult to obtain. These preliminary results suggest that if the problems of low back surface area coverage and low shunt resistance could be eliminated, a 17% improvement in efficiency would be

FIGURE 4.8 Measured and predicted illuminated solar cell electrical characteristics.

realized. These and other possibilities for improvement will be taken up in Chapter 5.

4.8 Conclusions

In this chapter, practical techniques for measuring important solar cell contact properties have been developed and demonstrated. These methods could be used to monitor process results on a regular basis, and thereby ensure the maintenance of high quality. They could also be used to guide the development of new contacting techniques.

Thick-film and evaporated contact geometries have been shown to be completely different; in the former, there is significant deviation from mask dimensions, and much variability in size from sample to sample. A model has been developed (Appendix 2) which quantitatively accounts for deviations from mask dimensions; the phenomenon could therefore be compensated for during contact grid design.

Metal bulk resistivity has been found to be independent of contact geometry. However, contact thickness generally increases with contact width; the consideration of different grid finger or bus bar widths in design should therefore account for the altered metal sheet resistivities to be encountered.

Following an appropriate contact activation step, the interface resistivity of thick-film contacts is of small importance, and could be neglected when designing the solar cell contacts.

CHAPTER 5

PROSPECTS FOR IMPROVEMENT IN THE CONTACTING PROCESS

5.1 Introduction

This chapter begins by considering the prospects for raising the solar cell efficiency or lowering the process cost, through relatively small changes in the fabrication procedure of Chapter 3. A major change in that procedure, permitting junction formation and contact sintering to be carried out at the same time, is introduced. Results of an experimental investigation of some of these process alterations are then described.

5.2 Improvements Through Minor Process Alterations

According to theory, a silicon solar cell can produce no more than $42.5\text{mA}/\text{cm}^2$ of short-circuit current under AM1 sunlight [1]. The solar cells studied in this thesis had uncorrected short-circuit currents of $25.5\text{mA}/\text{cm}^2$. After correction for reflectance (42.9%) and shading (8.28%), this short-circuit current becomes $39.8\text{mA}/\text{cm}^2$. Although reflectance has probably been overestimated, the result is excellent, with only slight prospects for improvement. The use of an arsenic, rather than a phosphorus spin-on-emulsion dopant-source, might increase the short-circuit current slightly through better atomic matching to the silicon lattice, and the consequent reduction of bulk and surface recombination at the emitter [1].

The solar cell open-circuit voltage of 592mV given in Chapter 3 is very high, suggesting a diode saturation current of $1.9 \times 10^{-12} \text{ A/cm}^2$. Simple theory [1,29] gives a value of $9.8 \times 10^{-12} \text{ A/cm}^2$ for this current based on the known base doping density of $6 \times 10^{15} / \text{cc}$ and a representative lifetime [1] of $10 \mu\text{s}$. A much higher lifetime (hundreds of μs) could account for the difference between measured and predicted values. However, although a somewhat higher value of lifetime than that assumed could exist in the base, the fabrication process for the cells would suggest that several hundred microseconds are improbable. More likely, the difference between results is due to the formation of a back-surface-field-region - a highly doped p-layer between the base and back contact - due to the aluminum contained in the back contact ink. This back-surface-field would confine electrons in the base, away from the back contact, increasing their probability of collection, and thereby lowering diode saturation current and increasing short-circuit current. A net increase in open-circuit voltage results. Needless to say, much improvement in the open-circuit voltage is not likely to be realized.

Base and contact resistivity presently account for $5.5 \text{ m}\Omega$ of solar cell series resistance, when calculated according to the methods of Chapter 2. In fact, base resistance must be significantly higher than this, due to the relatively small proportion of the back surface covered with contact material (78%) and the lateral current flow effects discussed in Chapter 2. A larger contact, subject to the need to avoid short-circuiting any solar cells (i.e., which have slightly variable diameter from cell to cell) would probably improve the solar cell efficiency noticeably.

Metal sheet resistivity may be decreased by increasing the thickness of the front contact grid. For this purpose, an altered screen-printing procedure [16] or a follow-up plating and/or solder-dipping process [11,17] are possibilities. It should be possible, especially in the event that metal sheet resistivity is decreased, to reduce shading loss through altered contact grid design, and thereby improve efficiency.

Shunt resistance is presently an important source of loss in these solar cells. Since no investigation of this factor was made in this thesis, the source of low shunt resistance is not certain. As discussed in Chapter 2, low shunt resistances are not necessarily associated with contacting procedure.

The present antireflection coating technique, making use of a spin-on titania-silica formulation, results in 25 to 36% improvement in short-circuit current over a bare cell [18]. An improved procedure - for example, incorporating a step to texturize the silicon surface before diffusion [1], and using a potassium or sodium hydroxide solution as the etchant - would raise these figures to about 34 to 40% - a substantial gain.

Finally, there is some scope for cost-cutting throughout the fabrication procedure. The identification and elimination of unnecessary steps, and reducing the duration of necessary steps in the process, would require a fairly involved investigation; but may yield a substantial improvement in economy.

5.3 Simultaneous Diffusion and Sinter Concept

A flow diagram for the solar cell fabrication process used in this thesis is shown in Figure 5.1. Also shown is a possible alternative scheme, which would reduce the number of required process steps. In particular, the proposed scheme would eliminate one of two high temperature heat treatments, and the need to etch away the silica dopant source and diffusion mask after diffusion. It would also eliminate the need to activate contacts and the antireflection coating step. Substantial cost reductions would result if this scheme were proven viable.

It should be stressed that the success of this procedure hinges on the ability of the silica-film dopant-source to retard the diffusion of silver into the silicon, and prevent junction-shunting. It should also be noted that silica is a poor antireflection coating material [1], so that some loss in solar cell efficiency can be anticipated.

5.4 Experiments

Experiments have been carried out on possible modifications to the present solar cell fabrication process. These include alternative contact activation and antireflection coating techniques, and the simultaneous diffusion and sinter concept just outlined. Although none of the new methods has yet proven reliable, results obtained to date are promising.

5.4.1 Alternative Contact Activation Technique

As has already been discussed in Chapter 4 (Section 4.5), the passage of high currents through a solar cell reduces contact resist-

(a) Present process

* The film will act as an in-situ passivating layer and antireflection coating

(b) Simultaneous diffusion and sinter

Figure 5.1. Comparison of (a) present and (b) a proposed simultaneous diffusion and sinter process.

ivity. One solar cell was tested to determine whether this principle could be applied in a practical procedure. Figure 5.2, which gives the results, shows the method to be capable of improving solar cell efficiency well above that of a solar cell with "as-fired" contacts. If currents and times can be optimized, the method could eliminate the cost of chemicals, improve the safety aspect and shorten the duration of contact activation, compared with the present hydrofluoric acid dipping treatment. A detailed study of the method is therefore to be recommended.

5.4.2 Alternative Antireflection Coating Technique

Two solar cells were treated by a technique described by Gonsiorawski [30]. In this, a high-quality dark blue silica film is grown electrochemically by dipping a solar cell with contacts into a 3 HF:1 H₂O₂ solution for 5 seconds (followed by rinsing). The step was found to deposit an antireflection coating on the solar cell surface; however, cell performance was poor, as shown in Table 5.1. This is attributed to the hydrofluoric acid in the solution attacking the borosilicate glass layer, which "glues" the metal and semiconductor together.

It might be possible, if the solar cell contacts have been fired at higher temperatures*, to achieve high efficiency solar cells when using this antireflection coating technique. The simplicity of the procedure and the high quality of the coating obtained [30] recommend adoption of the procedure wherever possible.

* This was not investigated further because a non-optimum firing sequence can cause substantial efficiency loss.

FIGURE 5.2 Improved solar cell electrical characteristics achieved by "forming".

Cell	Firing Temp (°C)	Firing Time (min)	Total Furnace Time (min)	Dip Time (sec)	Film Colour	I _{sc} (mA)	V _{oc} (mV)
C-10	645	5	16	2-3	brown-blue	159	458
C-11	640	6	17	3-4	blue-purple	17	318

Table 5.1. Solar cell performance after antireflection coating step.

5.4.3 Simultaneous Diffusion and Sinter

This method was found in practice to be inconsistent with low baking temperatures (see Figure 5.1), as shown in Table 5.2. It was found, for baking temperatures below 650°C, that the spin-on-emulsion dopant-source was dissolved or penetrated by the applied contact ink, as evidenced by colour changes in the film around the contact grid after screen-printing.

To determine if the method had any promise, baking was carried out at the usual diffusion temperature of 900°C. Table 5.2, which gives fabrication details and results, shows that high short-circuit currents and open-circuit voltages are possible, although the highest uncorrected AMI efficiency achieved was only 7%. One must consider that silica is a poor antireflection coating when interpreting this result. Generally speaking, best solar cell performance corresponded with the achievement of good film colour (blue), uniformity and transparency, and was achieved for short firing times of up to 5 minutes; extensive firing times of 15 to 45 minutes resulted in poor performance cells, with discoloured and cloudy film appearance especially in the vicinity of contact material. These results are promising, despite the fact that the diffusion and sinter are not really simultaneous (i.e., see advantages in Section 5.3). It is to be recommended that this approach be investigated in more detail.

Cell	Baking Conditions	Diffusion/ Firing Temperature (°C)	Firing Time (min)	Total Furnace Time (min)	I _{sc} (mA)	V _{oc} (mV)
9	200°C	880	17	39	60	194
P35*	650°C 20 min	900-910	3	18	62	50
P36	650°C 20 min	900	<1/2	8	7	247

* Fired four times up to a total of 45 minutes: I_{sc} < 111mA, V_{oc} < 152mV.

(a) Low baking temperature

Cell	Baking Temperature (°C)	Baking Time (min)	Total Furnace Time (min)	Firing Temp (°C)	Firing Time (min)	Total Furnace Time (min)	I _{sc} (mA)	V _{oc} (mV)	Uncorrected AMI Eff. (%)
10	895-900	17	30	890	16	29	496	358	3.4
11	900	16	28	900-905	4	22	411	276	1.9
12	910	5	21	890	4	21	470	538	6.8

(b) High baking temperature

Table 5.2. Results with simultaneous diffusion and sinter.

5.5 Conclusions

In this chapter, prospects for improvement in the fabrication process of Chapter 3 have been considered. Results obtained to date are only moderately promising, and more work is required to develop truly practical methods.

Contacts may be activated by passing high currents* through the solar cells for a few minutes. The procedure has not been optimized, although high short-circuit currents and open-circuit voltages have been demonstrated to be possible. Using this rather than the hydrofluoric acid dipping procedure, would eliminate chemical costs, improve the safety aspect and probably reduce labour time.

An alternative antireflection coating treatment has been described which would eliminate some of the labour time and materials costs involved in the present method. Unfortunately, its use is not consistent with low contact firing temperatures (650°C), although it may be compatible with a higher temperature (non-optimal) firing cycle.

The simultaneous diffusion and sinter method has not yet been made "simultaneous", but efficiencies of 7% have been demonstrated, with already a considerable reduction of process steps. Recent results in the literature [31,32] suggest that a titania-based rather than silica-based spin-on dopant-source would be more compatible with the aims of this process; furthermore, titania is an excellent antireflection

* Several A/cm².

coating material [1]. Success in this area would decrease solar cell cost greatly, and the prospects for success would appear to be good.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary of the Work

In this study, a thick-film contacting procedure for solar cells has been developed. The effects of using different thick-film inks, firing temperatures and times, and contact activation conditions have been studied, and optimized process conditions have been identified which yield solar cells with uncorrected AMI efficiencies of 12.3 to 14.4%. Major limitations in these cells are low shunt resistance (source not identified), non-optimal grid and back contact designs, and non-optimal antireflection coating techniques.

Practical methods have been developed for characterizing solar cell contacts in terms of contact geometry, metal bulk resistivity, contact resistivity and contact-semiconductor adherence. Furthermore, a one-dimensional non-linear theory of solar cell operation has been developed and validated, which is more sensitive to the quality of contacts than closed-form models employed in the past. These results have been applied to characterization of the solar cells in this report.

Finally, a new procedure has been proposed, in which junction diffusion and contact sintering are, in principle, carried out simultaneously. The feasibility of the principle has not yet been demonstrated; however, research into the technique thus far has achieved a solar cell efficiency of 7%. Alternative contact activation and

antireflection coating methods have also been investigated, but require more research to match the quality of present methods.

6.2 Recommendations for Future Work

The application of silver thick-film inks to solar cell contacting incurs high materials costs. For this reason, the investigation of non-noble metal inks, although not in widespread use in the thick-film industry [16,17], is recommended. The study of aluminum inks is especially recommended, because aluminum is capable of forming ohmic contacts to n^+ - or p-type silicon, and of forming a back-surface-field [1]. In this case, the need for small-area solderable silver ink overprints to make soldered interconnections possible is well-known [2, 22,32]. However, the technical difficulty and labour-intensive nature of soldering interconnections [16,17,19,33] strongly recommends the investigation of welding processes as a potential interconnection technique for solar cells.

Further investigation of the simultaneous diffusion and sinter process is highly recommended. In this investigation, a simpler implementation of the principle which is now proposed, should be examined. In the envisaged procedure, aluminum ink would be screen-printed over the surface of an n-type silicon wafer, and fired at a high temperature (in an inert ambient) to form a p^+/n solar cell. A contact grid could then be defined using screen-printed photoresist, and formed by selective etching. This implementation of the scheme offers several advantages in addition to those outlined in Chapter 5, including the avoidance of

shunting problems, and the achievement of high short-circuit currents expected to accompany the use of aluminum dopant [1]. The use of lithium to dope the base would further improve short-circuit current because of its high- and "recoverable" - lifetime properties [1].

Finally, further development of the theory of solar cell operation originated in this thesis is to be recommended. Walker's analysis of stellar gravitation [34] may give some valuable insight into the two-dimensional problem and a possible solution. Implementation of such results in a computer program for contact grid design would do much to expedite photovoltaic research and development.

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APPENDIX 1

FABRICATION NOTES

A1.1 Silicon Solar Cells with Thick-Film ContactsA. Select Wafers

- 2" diameter, 300 μ thick, p-type (boron-doped), 1.8-2.6 Ω -cm,
<100> orientation
- scribe 1D on backs, near edge, to be legible after contacting

B. Prefurnace Clean

- details standard

C. Spin-on Emulsions

- bake wafers 20 minutes at 200°C
- cool
- apply 6 drops of SILICAFILM (Emulsitone Company) to backs of wafers and spin for 18 seconds at 3000 rpm
- bake 15 minutes at 100°C; 20 minutes at 200°C
- cool
- apply 5 to 6 drops of EMITTER SOLUTION N-250 (Emulsitone Company) to fronts of wafers and spin for 18 seconds at 3000 rpm
- bake 15 minutes at 100°C; 20 minutes at 200°C
- cool

D. Diffusion

- load wafers into boat with like coated sides facing each other

- warm up for 5 minutes
- push for 3 minutes
- leave for 15 minutes in furnace hot-zone at 900°C (oxygen ambient)
- pull for 5 minutes
- cool for 5 minutes

E. Etch Silica Films

- 3-5 minutes in 10% HF
- 10 minute rinse in DI water
- 5 minutes in Caro's acid
- 10 minute rinse in DI water
- 1 minute in 10% HF
- 10 minute rinse in DI water
- vapour dry
- if stained, repeat steps using fresh Caro's acid

NOTE: - diffused layer properties measured at this point are:
 junction depth = 0.4μ , sheet resistivity = $34 \pm 2\Omega/\square$

F. Screen-Print Conductive Inks

- screen top contact grid using E-460A ink (Engelhard)
- dry for 10 minutes in air
- bake 15 minutes at 175°F
- screen back contact using E-422D ink (Engelhard)
- dry for 10 minutes in air
- bake 15 minutes at 175°F

NOTE: - remove ink from screen and screen-printer parts between ink changes, and after completing all steps, using xylene

G. Fire the Contacts

- 5 minute warmup and push
- 9 minutes fire at 650°C (air ambient)
- 5 minutes pull and cool
- see Section A1.3

H. Contact Activation

- dip 3 minutes in 1% HF
- 10 minute rinse in DI water
- vapour dry

I. Antireflection Coating

- bake wafers 30 minutes at 200°C
- cool
- apply drops of TITANIUM SILICA FILM C (Emulsitone Company) to fronts of wafers and spin for 15 seconds at 4500 rpm
- bake 15 minutes at 100°C; 15 minutes at 200°C
- cool

A1.2 Silicon Solar Cells with Simultaneous Diffusion and Contact Sinter

A,B,C - as in Section A1.1, steps A, B and C

D. Spin-on Emulsion Bake

- 7½ minutes warmup and push
- 5 minutes bake at 900°C (air ambient)
- 7½ minutes pull and cool

E. Screen-Print Conductive Inks

- as in Section A1.1, step F, except 7713 (Dupont) and E-422F (Engelhard) supplant E-460A and E-422D (Engelhard) inks, respectively

F. Fire the Contacts

- as in Section A1.2, step D

A1.3 Experimental Firing Procedure (Calibration)

- NOTE:
- see Figure A1.1
 - adjust furnace controls to give roughly the desired temperature
 - push test rig to furnace hot-zone and measure hot junction voltage using the voltmeter
 - measure cold junction temperature using the thermometer
 - determine hot-zone temperature (i.e., add voltage equivalents of hot- and cold-junction temperatures, and find temperature equivalent of this voltage using the standard chromel-alumel thermocouple tables)
 - if necessary, adjust the furnace controls to get closer to the desired temperature and repeat steps above
 - adjust "chart rate" to be 100 (± 5) sec/cm, if using centimeter graph paper to record firing profiles
 - short-circuit Y-input of X-Y recorder, and mark "0°C level on convenient line of graph paper
 - connect thermocouple and adjust scale of Y-input voltage to give a convenient correspondence between °C and centimeters

(a) test rig

(b) electronics

FIGURE A1.1 Experimental firing procedure equipment.

The chromel-alumel thermocouple was chosen for this work because of its excellent linearity. At 900°C, it produces 37.36mV. A simple proportionality assumed between temperature and voltage gives maximum errors of +6°C near 300°C, and -2.5°C near 750°C. This scheme gives reliable furnace profiles (i.e. temperature-time graphs) for moderately slow test rig push and pull rates; the accuracy of the scheme is limited by the thermal inertia of the test rig when fast push or pull rates are used. A convention adopted in reporting results is that the time needed to go from 100°C to the peak temperature and back is total furnace time; the time needed to go from the peak temperature less 25°C, to the peak temperature and back, is firing time.

A1.4 Screen Preparation

A. Prepare Emulsion Sensitizer

- add 125g of ammonium bichromate to 1 liter of warm DI water
- stir until all crystals are dissolved
- store in a capped container

B. Prepare Sensitized Emulsion

- add 25mls of sensitizer solution to 125mls of NAE DAR PHOTOEMULSION EZ-32 in a 150ml beaker
- stir well
- store in the beaker, with an opaque flexible plastic cover surrounding the beaker to keep out light, and keep in a moderate temperature and humidity environment

NOTE: - this preparation has a limited shelf-life of weeks at most. As it polymerizes, as evidenced by "sludge" formed at the bottom of the beaker, dispose and prepare fresh material as needed

C. Clean Screens to be Coated

- place screen face down in a developing tray
- pour on NAZ DAR EZ-STRIPP 202 and leave to soak for 15 minutes to remove most of photoemulsion
- rinse screen under running water and dry
- remove remaining emulsion by rubbing vigorously with dextilose paper dipped in acetone. keep using fresh paper
- use a strong spray of water (i.e., from narrow laboratory type outlet) to rinse; dry
- if necessary, repeat steps

D. Coat Screens

- work in a dimly lit room (e.g., a 300W tungsten lamp operated at 30V with a rheostat makes a suitable working light)
- remove any lint or dust on the screen using compressed air or nitrogen
- pour a small amount of emulsion on the bottom of the screen (i.e., side of screen touching substrate during screen-printing)
- spread over surface using a soft-bladed spatula
- alternately work emulsion from top to bottom of screen, scrape off excess emulsion and spread over the bottom of the

screen using the spatula, until a thin, uniform coating results with no uncovered areas on the screen; if worked too long, emulsion will dry and tear from the screen

- dry 10 minutes at 40 to 50°C

E. Exposure/Development

- work in a dimly lit room - see step D
- clean photomask with Q-tips and isopropyl alcohol to remove any fingerprints
- remove any dust and lint from photomask and screen using compressed air or nitrogen
- place screen, top facing down, on a sturdy laboratory bench
- place photomask, emulsion side touching screen, at the centre of the screen, and secure with two small pieces of scotch tape placed at opposite corners
- position the 300W tungsten lamp directly above the screen, with 10" (25cm) between the bottom of the lamp and the surface of the screen being exposed (bottom)
- adjust lamp voltage to 100V, and expose for 7½ minutes
- reduce lamp voltage to 30V, remove photomask, and remove unexposed photoemulsion with a strong maintained spray of water

An opening may appear in the emulsion corresponding to the position of the edges of the photomask during exposure. This can be eliminated in a two-step exposure. Re-exposing the screen after development may extend screen life.

2 2
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APPENDIX 2

THICK-FILM CONTACT GEOMETRY

In this appendix, the author develops a theoretical model of thick-film contact geometry; experimental results are presented which largely confirm the theory.

A2.1 The Mechanics of Screen-Printing

The essentials of screen-printing are contained in the sequence of diagrams of Figure A2.1. Details of the screen are given in (a) of the figure. A charge of ink is placed on the screen, which is bolted to the screen-printer (Figure A2.1(b)), and a tapered blade, called a "squeegee", pushes the ink across the screen surface. At the same time, the squeegee exerts a downward force, deflecting the screen so that it contacts the substrate to be printed upon (Figure A2.1(c)). Ink is pushed into the open volume of the screen (Figure A2.1(d)) and thence into contact with the substrate. As the squeegee passes, the original shape of the screen is restored; some ink is left in contact with the substrate in the form of dots (Figure A2.1(e)), while some is carried away with the screen. The dots of ink coalesce when left to level in air at room temperature (Figure A2.1(f)), while a subsequent oven drying step removes volatile components in the ink and allows for further screen-printing steps as required. Firing eliminates the remaining volatile ink components, and causes more volume shrinkage by compaction of the glass/metal volume.

(a) bottom view of screen

1) cast aluminum frame, 2) threaded hole for bolting screen to screen-printer, 3) raised portion of frame where epoxy binds screen to frame, 4) stainless steel mesh coated with photo-emulsion, 5) stencil - an open area formed in screen by photolithography.

screen-printing (b) elements, (c) action

1) printing platform, 2) substrate, 3) breakaway, 4) frame, 5) squeegee, 6) ink, 7) downward pressure, 8) forward motion.

(d) close-up views of stencil

1) stainless steel mesh wire, 2) open volume, 3) emulsion coating, 4) bottom of screen, 5) emulsion coating, 6) emulsion build-up, 7) open volume, 8) stainless steel mesh wire.

(e) dots of ink printed on substrate

(f) ink dot coalescence after levelling in air

* typical mesh area $5 \times 5 \text{ in}^2$; usable area $3 \times 3 \text{ in}^2$
 ** substrate held down by vacuum and positioned against fixed alignment markers

FIGURE A2.1 Elements of the screen-printing process.

A simple theory to determine the geometry of thick-film contacts will now be given. For further details on screen-printing, drying and firing, leading to a better qualitative understanding, the reader's attention is directed to References [16,17].

A2.2 A Theory of Screen-Printing

Suppose that a long rectangular pattern of width, w_d (it will be assumed that the designed width of the pattern and the stencil width are the same) is to be screened; what results is a nearly rectangular shape of width, w , and thickness, t . The following assumptions will be made in relating the three factors:

- 1) increases in pattern width, w_d , are accompanied by proportional increases in deposit volume (per unit length), wt
- 2) there is a lower limit, w_c , on the size of patterns which can be screened
- 3) deposit thickness, t , increases in proportion to deposit width, w , for narrow lines, and is constant for wide lines
- 4) wide lines are accurately screened, and
- 5) all screen-printing conditions except pattern geometry are fixed.

Assumptions 1 and 4 are a priori reasonable, while 2 and 3 quantify the changing relative importance of ink-screen and ink-substrate adherence, and the differing deflection of the screen mesh by the squeegee (i.e., because of emulsion build-up) for different line widths.

Taken in order, assumptions 1, 2 and 3 yield

$$d(wt) = k_v dw_d \quad (A2.1)$$

$$wt = 0, w_d < w_c \quad (A2.2)$$

and

$$t = \begin{cases} k_t w, & w < t_{\text{lim}}/k_t \\ t_{\text{lim}}, & w > t_{\text{lim}}/k_t \end{cases} \quad (A2.3)$$

where k_v , w_c , k_t and t_{lim} are constants. Using Eqns. (A2.1) and (A2.2)

$$\int_0^{wt} d(wt) = k_v \int_{w_c}^{w_d} dw_d$$

or

$$wt = k_v (w_d - w_c) \quad (A2.4)$$

By assumption 4,

$$w \sim w_d - w_c, w > t_{\text{lim}}/k_t$$

which, by Eqn. (A2.4), gives

$$t \sim k_v, w > t_{\text{lim}}/k_t$$

Thus, $k_v = t_{\text{lim}}$. For narrow lines, $w_d < \frac{t_{\text{lim}}}{k_t} + w_c$,

$$w = \sqrt{\frac{t_{\text{lim}}}{k_t} (w_d - w_c)} \quad (A2.5)$$

and

$$t = \sqrt{t_{\text{lim}} k_t (w_d - w_c)} \quad (A2.6)$$

while for wide lines, $w_d > \frac{t_{lim}}{k_t} + w_c$,

$$w = w_d - w_c \quad (A2.7)$$

and

$$t = t_{lim} \quad (A2.8)$$

The constants w_c , k_t and t_{lim} must be determined empirically. Also, wet (i.e., as-screened), dry and fired contact dimensions should be described by these equations, although different constants may be necessary (assumption 5).

A2.3 Comparison of Theory and Observations

Figure A2.2 shows agreement between theoretical and measured fired thick-film contact widths and thicknesses, for narrow-line behaviour (i.e., as designed, the lines were 5 to 15 mils wide) and several inks. To obtain theoretical results, the constants w_c , k_t and t_{lim} were obtained from the data, and results were then forecast using Eqns. (A2.5) and (A2.6), as a function of designed line width. Figure A2.2(a) is based on a much larger set of data than Figure A2.2(b), and correlation is much better for this reason. On the basis of Figure A2.2(a), it may be concluded that the theory is accurate for this width-regime.

For somewhat wider devices (i.e., as designed, 25 mils wide), agreement between measured and theoretical (same constants as above) results is much poorer (see Table A2.1). This only implies that there is a gradual region of transition between narrow- and wide-line behaviour, rather than the single point in the simple theory developed here, and is not a serious defect.

(a)

(b)

FIGURE A2.2 Predicted versus measured contact (a) width, (b) thickness (narrow line behaviour).

Ink	Measured Width (mils)	Narrow Line Theory Prediction (mils)	Wide Line Theory Prediction (mils)	Transition Between Two Types of Behaviour (mils)
E-460A	22.5	17.5	21.5	17.6
E-422C	18.4	15.4	16.4	23.0
7713	22.0	17.7	20.6	19.6
E-422F	24.3	20.0	21.2	22.6
E-422D	21.7	17.3	18.3	23.1

Table A2.1. Predicted vs measured contact width (intermediate line width behaviour).

sheet resistivity is several orders of magnitude smaller than that of the semiconductor.

A4.2 Analysis of Device 1

In this measurement technique, illustrated in Figure A4.1, the device (in (a)) is tested with three circuits, as shown in (b). The true shape of the contacts is not square, but rounded at the corners, as in (c); their area is w^2 , where

$$w^2 = w_0^2 - (4-\pi) \left[\frac{\sqrt{2} w_0 - \delta}{2(\sqrt{2}-1)} \right]^2 \quad (\text{A4.2})$$

The measured voltage, V , in each circuit configuration will include in addition to any drop at the contact interface a component due to current flow in the semiconductor, ΔV :

$$V = I \frac{\rho_c}{2w} + \Delta V$$

where I is the test current. Although contact resistance is generally a complicated function of contact resistivity, metal and semiconductor sheet resistivities and geometry, the technique being discussed is too crude to warrant a better estimation than ρ_c/w^2 .

To evaluate the voltage drop ΔV for each test circuit configuration, it will be assumed that the electric field in the semiconductor, E , due to current entering or exiting via a probe, is

$$E = \pm \frac{\rho_a I}{2\pi x}$$

where x is the distance from the probe (placed at the contact pad center)

a

b

c

d ("semi-infinite" strip)

device e: 200 mil dia circle; device f: one-half of 1.75" dia circle.
 note: in testing devices d, e and f for this thesis, a four-point-probe scheme was used, with probes spaced at 50 mils.

(a) devices (scale 2mm to 5 mils).

(b) "corners", "t's"

FIGURE A3.1 Metal bulk resistivity measurement method.

Thus, the appropriate values for R_s are $3.3\rho_{\square}$, $0.34\rho_{\square}$ and $0.22\rho_{\square}$ for devices d, e and f, respectively, where $\rho_{\square}$ is the semiconductor sheet resistivity. For devices b and c, the appropriate value of R_s is $\frac{\ln 2}{\pi} \cdot \rho_{\square}$ or $0.22\rho_{\square}$ - the same as would be measured by the conventional four-point probe technique, as can be readily seen. The correction in the case of device a is approximately $\frac{1}{\pi} \ln\left(\frac{235}{35}\right)\rho_{\square}$ or $0.61\rho_{\square}$; this is not obvious, but it is determined in the same way as for devices b and c.

A3.3 Geometry Correction

Devices d, e and f will, in general, be well-defined whereas devices a, b and c - particularly in the case of thick-film contacts - will not. If the apparent sheet resistivity is $\rho'_{\square,m}$ the true sheet resistivity is $\rho'_{\square,m} w/w_d$, where w is the true width of the device and w_d is its designed value. Knowing the thickness, resistivity may then be readily calculated.

APPENDIX 4

CONTACT RESISTIVITY MEASUREMENT

In this appendix, the determination of contact resistivity using techniques described in this report is discussed.

A4.1 Background

Metal-semiconductor contacts generally display non-linear IV characteristics; however, for stresses typical of use conditions, the IV characteristics of so-called ohmic contacts may be treated as approximately linear. The contact in such cases is characterized by a contact resistivity, ρ_c ,

$$\rho_c = \frac{V_c}{j_c} \quad (\text{A4.1})$$

where V_c is the voltage dropped across the contact in response to a normally-directed current density, j_c .

For conditions of uniform current flow, the contact resistance is ρ_c/A_c , where A_c is the contact area. Current flow is generally non-uniform (i.e., crowding occurs over the contact area) and the determination of the relationship between contact resistivity and contact resistance involves the use of differential equations. The contact is actually a sandwich of three layers - metal of sheet resistivity, $\rho_{o,m}$, an interface of contact resistivity, ρ_c , and a semiconductor layer of sheet resistivity, ρ_o . In many cases, the metal may be treated as if it were an equipotential plane, because its

sheet resistivity is several orders of magnitude smaller than that of the semiconductor.

A4.2 Analysis of Device 1

In this measurement technique, illustrated in Figure A4.1, the device (in (a)) is tested with three circuits, as shown in (b). The true shape of the contacts is not square, but rounded at the corners, as in (c); their area is w^2 , where

$$w^2 = w_0^2 - (4-\pi) \left[\frac{\sqrt{2} w_0 - \delta}{2(\sqrt{2}-1)} \right]^2 \quad (\text{A4.2})$$

The measured voltage, V , in each circuit configuration will include in addition to any drop at the contact interface a component due to current flow in the semiconductor, ΔV :

$$V = I \frac{\rho_c}{2w} + \Delta V$$

where I is the test current. Although contact resistance is generally a complicated function of contact resistivity, metal and semiconductor sheet resistivities and geometry, the technique being discussed is too crude to warrant a better estimation than ρ_c/w^2 .

To evaluate the voltage drop ΔV for each test circuit configuration, it will be assumed that the electric field in the semiconductor, E , due to current entering or exiting via a probe, is

$$E = \pm \frac{\rho_s I}{2\pi x}$$

where x is the distance from the probe (placed at the contact pad center)

(a) device

(b) test circuit configurations A, B, C.

(c) true contact pad shape

x current entering pad
 • current leaving pad

A $\frac{\rho_c I}{W^2} \rightarrow \Delta V_A$

B $\Delta V_B \rightarrow \frac{\rho_c I}{W^2}$

C ΔV_C

(d) device analysis for different test circuit configurations

FIGURE A4.1 Contact resistivity measurement method (device 1).

to the point where the field is evaluated. Then, for each test circuit configuration, the electric field at any point along the line joining contact pad centers, is

$$E_A = \frac{\rho_{\square} I}{2\pi} \left[\frac{1}{x} - \frac{1}{x-S} \right]$$

$$E_B = \frac{\rho_{\square} I}{2\pi} \left[\frac{1}{x} - \frac{1}{x-2S} \right]$$

and

$$E_C = \frac{\rho_{\square} I}{2\pi} \left[\frac{1}{x} - \frac{1}{x-3S} \right]$$

where $x=0$ corresponds to the position of the probe at which current enters the semiconductor (Figure A4.1(d)). To find ΔV , these expressions are integrated over the relevant ranges; respectively, for A $[S+w/2, 2S]$, for B $[S, 2S-w/2]$ and for C $[S, 2S]$. For example,

$$\begin{aligned} \Delta V_A &= - \int_{S+w/2}^{2S} E_A \, dx \\ &= - \int_{S+w/2}^{2S} \left[\frac{\rho_{\square} I}{2\pi} \left(\frac{1}{x} - \frac{1}{x-S} \right) \right] dx \\ &= \frac{\rho_{\square} I}{2\pi} \ln \left(\frac{S+w/2}{w} \right) \end{aligned}$$

The measured resistances for each configuration are therefore:

$$R_A = \frac{\rho_{\square}}{2\pi} \ln \left(\frac{S+w/2}{w} \right) + \frac{\rho_c}{w} \quad (\text{A4.3})$$

$$R_B = \frac{\rho_D}{2\pi} \ln \left(\frac{2(2S-w/2)}{w} \right) + \frac{\rho_C}{2} \quad (A4.4)$$

and

$$R_C = \frac{\rho_D}{\pi} \ln 2 \quad (A4.5)$$

Despite the simplicity of the analysis, the resulting picture is in reasonable accord with measured results. If there is negligible contact resistance

$$R_A/R_C = \frac{\ln \left(\frac{S+w/2}{w} \right)}{2 \ln 2}$$

and

$$R_B/R_C = \frac{\ln \left(\frac{2(2S-w/2)}{w} \right)}{2 \ln 2}$$

Measured and theoretical resistance ratios are compared in Figure A4.2. These results show that the measured and theoretical resistance ratios tend to decrease with contact width, and that there is some contact resistance in the measurements.

A4.3 Analysis of Device 2

This problem (see Figure A4.3) has been mentioned by Berger [15], but not solved. If the metal is treated as an equipotential, the solution for the contact resistance, using Berger's approach, is

$$R_C = \frac{\rho_D}{2\pi\alpha r_2} \left[\frac{I_0(\alpha r_3)k_1(\alpha r_3) + I_1(\alpha r_3)k_0(\alpha r_3)}{I_1(\alpha r_2)k_1(\alpha r_3) - I_1(\alpha r_3)k_1(\alpha r_2)} \right]$$

where, $\alpha = \sqrt{\rho_D/\rho_C}$, and I_0 , k_0 , I_1 and k_1 are modified Bessel functions of

FIGURE A4.2 Resistance ratios as a function of contact width.

(a) device

(b) test circuit

(c) device analysis

FIGURE A4.3 Contact resistivity measurement method (device 2).

first and second kind, and zeroth and first order. This equation must be solved numerically, as contact resistivity is an implicit function of contact resistance, semiconductor sheet resistivity and contact geometry.

The contribution to measured resistance of metal sheet resistivity may be approximately established by the following means. The current, i , flowing in the center ring, at an angle $\pi - \theta$ radians away from the voltage probe (Figure A4.3(c)) is

$$i = I \frac{\theta}{2\pi}$$

where I is the test current. The power loss in the ring is therefore

$$\begin{aligned} & \int_{-\pi}^{\pi} \left(I \frac{\theta}{2\pi} \right)^2 \cdot \rho_{\square, m} \frac{r_3 + r_2}{2(r_3 - r_2)} d\theta \\ &= \frac{\pi}{12} \rho_{\square, m} \frac{r_3 + r_2}{r_3 - r_2} I^2, \end{aligned}$$

and the effective resistance of the ring is approximately

$$\begin{aligned} & \frac{\pi}{12} \rho_{\square, m} \frac{r_3 + r_2}{r_3 - r_2} \\ &= \frac{\pi}{6} \rho_{\square, m} \frac{r}{w} \end{aligned}$$

For measurements presented in the body of the report (Section 4.5), this is actually larger than the measured resistance, V/I .

A proper solution would have to account for the positions of probes, as well as contact geometry, metal and semiconductor sheet resistivities and contact resistivity. However, there are good reasons for not extending the analysis further in this thesis:

- 1) the contact IV characteristics are strongly non-linear (Section 4.5), which leads to the conclusion that the interface electrical characteristics are a dominant factor determining measured resistance, and
- 2) estimating contact resistance by

$$\frac{\rho_c}{2\pi r w}$$

necessarily gives an upper bound on contact resistivity, because the power loss at the interface and the active area of the contact are overestimated.

END

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