

TRANSPARENT CONDUCTIVE COATINGS

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Materials with electrical conductivity and optical transparency are highly desirable in many optoelectronic applications including photovoltaics. Ultra-thin, semitransparent metal films have served the purpose in some situations but they suffer from a number of problems which seriously limit the performance of the resulting devices. In contrast, certain binary oxide semiconductors such as tin oxide (SnO_2) and indium oxide (In_2O_3) offer much better performance tradeoff in optoelectronics as well as better mechanical and chemical stability. These thin-film "transparent conductors" (TC) are essentially wide-bandgap (≈ 3.5 eV) degenerate semiconductors - invariably n-type - and hence are transparent to sub-bandgap (visible) radiation while affording high electrical conductivity due to the large free electron concentration (up to 10^{21} cm^{-3}).

The principal performance characteristics of TC's are, of course, electrical conductivity σ and optical transmission T , but a suitable figure of merit ϕ_{TC} for TC's has been shown to be the ratio T^{10}/R_s , where R_s is the sheet resistance of the TC [1,2]. It is found that ϕ_{TC} is much higher for the oxide semiconductors than the corresponding value for thin metal films. The TC's also have a refractive index of around 2.0 and hence act as very efficient antireflection (AR) coatings. For using TC's in surface barrier solar cells, the photovoltaic barrier is of utmost importance and so the work function or electron affinity of the TC is also a very important material parameter.

A large number of processes are available for depositing TC thin films [3], but for illustration the preparation of tin-doped indium oxide ($\text{In}_2\text{O}_3:\text{Sn}$) or the so-called indium-tin oxide (ITO) by a simple spray pyrolysis process and its use in fabricating an efficient surface barrier solar cell on silicon will be discussed at length [4]. It is found that the performance of the cell is strongly dependent on ITO preparation conditions, silicon surface preparation and the nature of carrier transport across the interface.

The method of deposition used for preparing the TC/Si surface barrier cell has drastic consequences on the photovoltaic barrier region and hence on the cell efficiency. To take an extreme example, ion-beam deposited ITO forms a barrier (and hence a good solar cell) on p-type Si, while spray and vacuum evaporation processes yield efficient cells on n-type Si [5]. It has also been found that the angle of deposition of SnO_2 has a strong bearing on the efficiency of the resulting $\text{SnO}_2/\text{n-Si}$ solar cell [6]. Similarly thermal annealing can also affect both the bulk and interfacial properties of these TC's.

Thermal [7] as well as photon [7,8] induced stresses can degrade the characteristics of solar cells by reducing the open-circuit voltage V_{OC} , short-circuit current density J_{OC} as well as the fill factor FF. Much further study is needed in this crucial area of environmental stability.

A number of problems remain unresolved in the field of transparent conductors, including such basic ones as the role of the 'dopant'. Easy as the preparation of these TC's is, comparing films prepared by different techniques under different conditions is often difficult, requiring thorough material characterization. In terms of fabricating highly efficient surface barrier solar cells, it may be convenient to alter the absorber semiconductor (substrate) surface by shallow ion implantation as done for metal-semiconductor Schottky barriers [9]. With further applications in optoelectronic detectors, and imaging devices, there is currently a great deal of interest in this field and numerous studies are in progress for improving the quality and controllability of the films, as well as basic understanding of this class and materials.

References

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6. T. Feng, A. K. Ghosh and C. Fishman, J. Appl. Phys., 50, 8070 (1980).
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1. INTRODUCTION
2. PROPERTIES OF TRANSPARENT CONDUCTORS(TC)
3. TC's IN SURFACE BARRIER SOLAR CELLS - SPRAY ITO/N-Si SOLAR CELL
4. INFLUENCE OF DEPOSITION CONDITIONS ON SOLAR CELL CHARACTERISTICS
5. STABILITY AND AGING OF TC's IN SOLAR CELLS
6. FUTURE DIRECTIONS AND PROBLEM AREAS

Transparent Conducting Films

DEFN. - VISIBLE TRANSPARENCY AND ELEC. CONDUCTIVITY.

CURRENT INTEREST - PHOTOVOLTAICS, SOLAR THERMAL, OPTOELECTRONICS.

PARAMETERS - TRANSMISSION T, CONDUCTIVITY σ

HISTORICAL - CdO(1907), AIRCRAFT WINDSHIELD DEICING(1940's), NESA GLASS.

APPLICATIONS -
 TRANSPARENT HEATERS
 DISPLAYS AND IMAGERS
 HEAT MIRRORS(IR REFLECTORS)
 ANTISTATIC AND SCRATCH-RESISTANT COATINGS
 ELECTROCHEMICAL STUDIES
 TRANSPARENT SUBSTRATES

PROPERTIES -
 ELECTRICAL RESISTIVITY
 OPTICAL TRANSMISSION Vs. λ
 ENVIRONMENTAL AND LIFE STABILITY
 CHEMICAL NATURE, STRUCTURE AND MORPHOLOGY
 CHEMICAL RESISTANCE AND ETCHABILITY
 INTERFACIAL AND BULK PROP.(WORK FUNCTION, ENERGY GAP,...)
 METHOD OF DEPOSITION

TYPES -
 1. ULTRA-THIN METALS(50 Å) - Au,Pt,Cu,Ag...
 2. WIDE-BANDGAP DEGENERATE SEMICONDUCTORS -
 OXIDE SEMICONDUCTORS - $\text{SnO}_2, \text{In}_2\text{O}_3, \text{CdO},$
 $\text{ZnO}, \text{Cd}_2\text{SnO}_4...$
 (DOPED OR UNDOPED)

Thin Metal Films

VACUUM EVAPORATION AND SPUTTERING - PROPERTIES DEPEND ON
FILM NUCLEATION AND COALESCENCE.

- A. DISCONTINUOUS FILMS - ISLAND STRUCTURE - LOW ,
LIGHT SCATTER, ACTIVATED CONDUCTION.
- B. CONTINUOUS FILMS - SIZE EFFECT, EXCESS IMPURITIES,
INSULATING PHASES.
- C. NUCLEATION-MODIFYING LAYERS - EG.: Bi_2O_3 MAKES
AU FILM MORE CONDUCTIVE.

Semiconducting Oxide Films

- NO NUCLEATION PROBLEM DUE TO CHEMICAL BONDING AT SURFACE.
 - CONDUCTION MECHANISM DIFFERENT FROM THAT OF METAL.
 - ALL N-TYPE SEMICONDUCTORS.
- A. BINARY OXIDES - ANION-DEFICIENT (OXYGEN VACANCY)
ELECTRON CONC. = $10^{17}-10^{21} \text{ cm}^{-3}$
RELATIVELY EASY TO OXIDIZE OR REDUCE.
 - B. DOPED OXIDES - SUBSTITUTIONAL CATIONS OF HIGHER
VALENCY, OR ANIONS OF LOWER
VALENCY (EG.: $\text{In}_2\text{O}_3:\text{Sn}$, $\text{SnO}_2:\text{F}$).
 - NO COMPOUND OR SOLID SOLUTION
OF SUBSTITUTIONAL CATION.
 - CARRIER SCATTERING;

IDEAL TRANSPARENT CONDUCTOR (TC) LOW m_e^* .
INSB: $m_e^* = 0.013 m_e$. SO $R_s = 0.5 \Omega/\text{SQUARE}$ & $T=95\%$
FOR $2 \mu\text{M}$ FILM DOPED TO 10^{19} cm^{-3} .
BUT BANDGAP $E_G = 0.17 \text{ eV}$. TOO LOW!

BANDGAP REQUIREMENT - $E_G \approx 3 \text{ eV}$.

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Methods of Preparation of Transparent Conductors

1. VACUUM EVAPORATION
2. REACTIVE EVAPORATION
3. EVAPORATION AND OXIDATION
4. SPUTTERING - DC, RF, ION-BEAM
5. REACTIVE SPUTTERING
6. CHEMICAL VAPOR DEPOSITION
7. SPRAY HYDROLYSIS

Oxide Semiconductors: Properties of Interest in Solar Cells

OXIDE SEMICONDUCTORS - PROPERTIES OF INTEREST IN SOLAR CELLS

1. WORK FUNCTION OR ELECTRON AFFINITY - HIGH FOR N-TYPE ABSORBERS, LOW FOR P-TYPE ABSORBERS.
2. WIDE BANDGAP (3 eV).
3. LOW ELEC. RESISTIVITY (SHEET RES. 10 OHMS/SQUARE).
4. HIGH OPTICAL TRANSMISSION.
5. INTERFACIAL MATCHING, ABSENCE OF SURFACE DAMAGE.
6. ENVIRONMENTAL AND LIFE STABILITY.
7. REFRACTIVE INDEX.

FUNCTIONS OF OXIDE SEMICONDUCTORS IN SURFACE BARRIER CELLS-

- A. FORMATION OF PHOTOVOLTAIC BARRIER
- B. PHOTOCURRENT COLLECTION
- C. LOW-RESISTANCE FRONT CONTACT REGION
- D. OPTICALLY TRANSPARENT WINDOW
- E. ANTIREFLECTION (AR) COATING

PROPERTIES OF IMPORTANT OXIDE SEMICONDUCTORS-

MATERIAL.	E_G (eV)	LATTICE	T(%)	n (CM^{-3})	μ_n ($CM^2/V-S$)	α (CM^{-1})
$IN_2O_3:SN$ (ITO)	~ 3.7	BCC ($A_0=10.12 \text{ \AA}$)	0.83	10^{20}	75	1200
SnO_2	~ 3.5	RUTILE ($A_0=4.74 \text{ \AA}$ $C_0=3.19 \text{ \AA}$)	0.85	8×10^{20}	10	1300

Fig. of Merit for Transparent Conductors

$$\phi_{TC} = T^0 / R_s$$

$$\phi_{TC} = \sigma t \exp(-10 \alpha t)$$

FOR GIVEN R_s

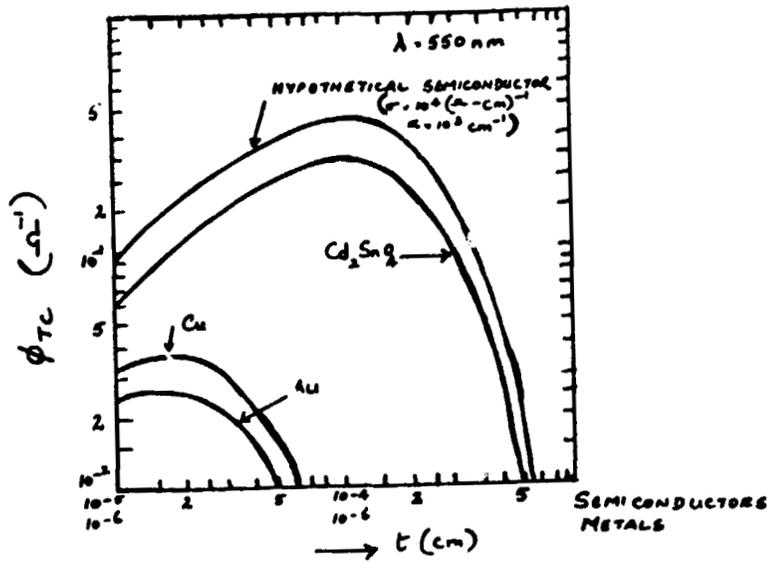
$$\phi_{TC} \propto \exp\left(-\text{CONST.} \frac{\alpha}{\sigma}\right)$$

$$\frac{\sigma}{\alpha} = \pi c n v^2 \tau^2 = \frac{\pi c n v^2}{e} \mu^2 m^*$$

SINCE $\mu = \frac{e \tau}{m^*}$

μ = MOBILITY
 τ = FREE CARRIER RELAXATION TIME
 n = REFRACTIVE INDEX
 m^* = EFFECTIVE MASS

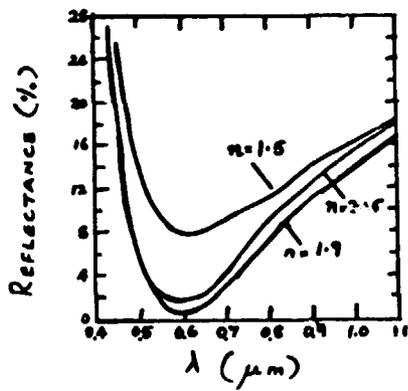
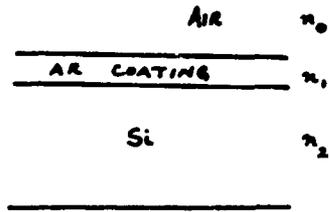
$\phi_{TC} \uparrow$ as $\mu \uparrow$ OR $m^* \downarrow$ SINCE $\mu \propto (m^*)^{-1.35}$



Ref. [1,2]

AR Coating

OPTIMIZATION OF POOR QUALITY



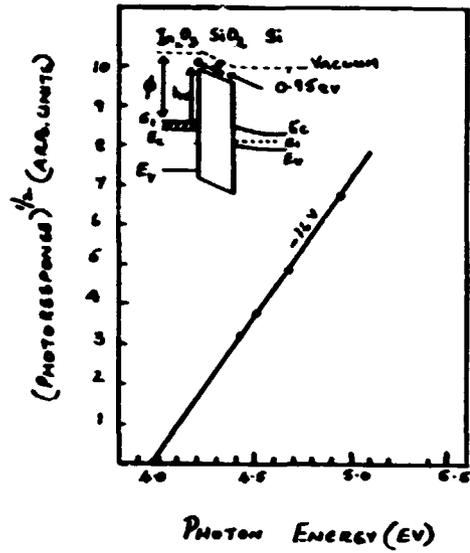
$n_2 = 3.5$ AT $1 \mu m$
 3.75 AT $0.75 \mu m$
 $n_1 = 1.9 - 2.3$

REFLECTANCE MIN. AT

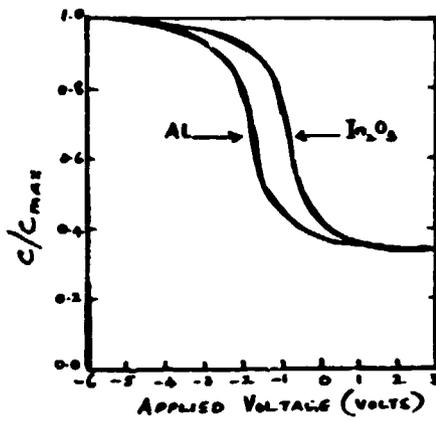
$$n_1 d_1 = (2m-1) \frac{\lambda_0}{4}$$

$R_{min} = 0$ FOR $n_1^2 = n_0 n_2$

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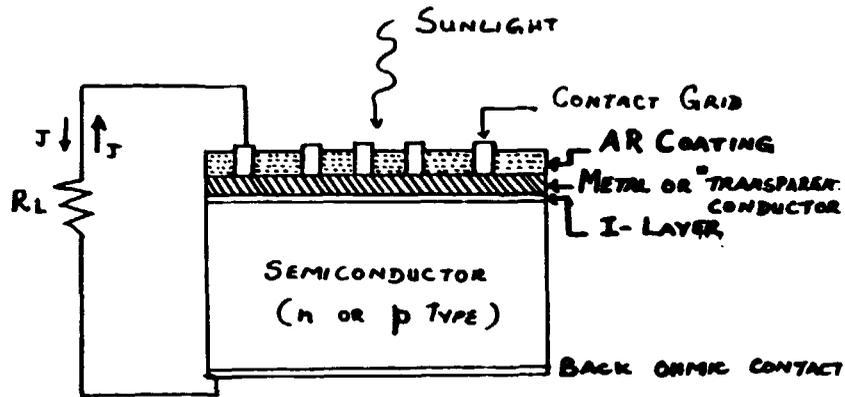


INTERNAL PHOTO-
EMISSION MEAS.
TO FIND WORK
FUNCTION/ELECTRON
AFFINITY OF
TRANSPARENT
CONDUCTOR



MOS/TCOS
CAPACITOR
C-V DATA

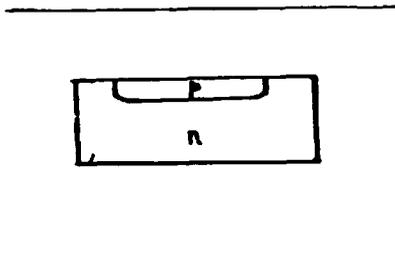
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SCHMATIC OF
SURFACE BARRIER SOLAR CELL
(MS, MIS, SIS)

Surface barrier cell -

only one semiconductor, p conductivity type, is used as absorber; the principal source of photovoltaic action is a depletion barrier at the surface.



Surface Barrier Solar Cells

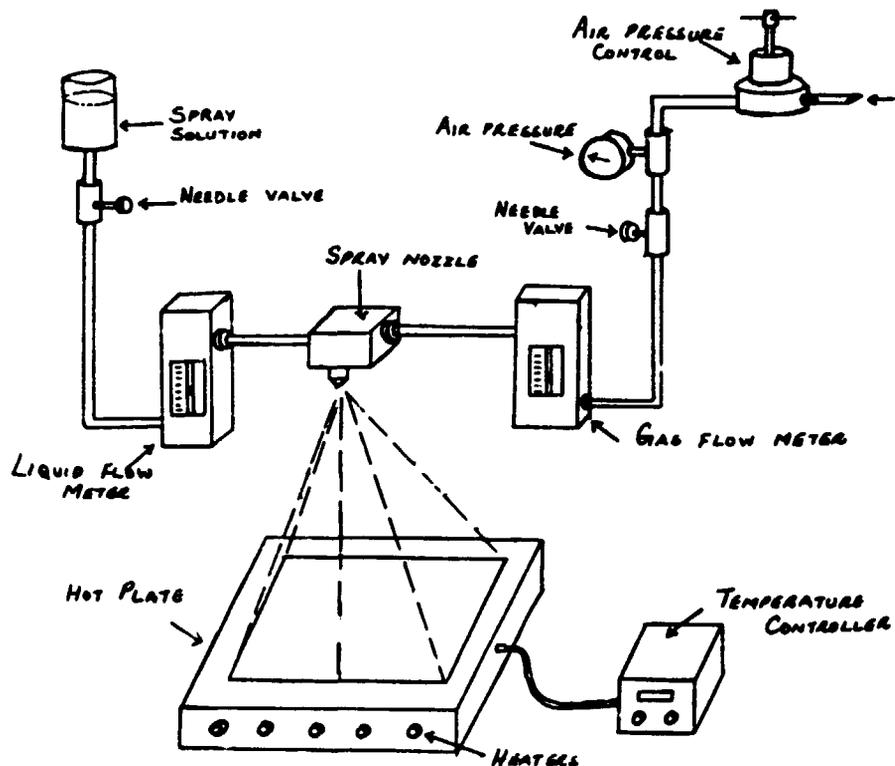
FEATURES -

1. SIMPLE FABRICATION
2. LOW TEMP. PROCESSING. So
NO MIN. CARRIER LIFETIME DEGRADATION (SINGLE XTAL)
NO GRAIN BOUNDARY DIFFUSION (POLY)
NO DECOMPOSITION (AMORPHOUS)
3. BETTER BLUE RESPONSE THAN P-N HOMOJUNCTION
4. USEFUL FOR ASSESSING NEW PHOTOVOLTAIC ABSORBER MATERIALS

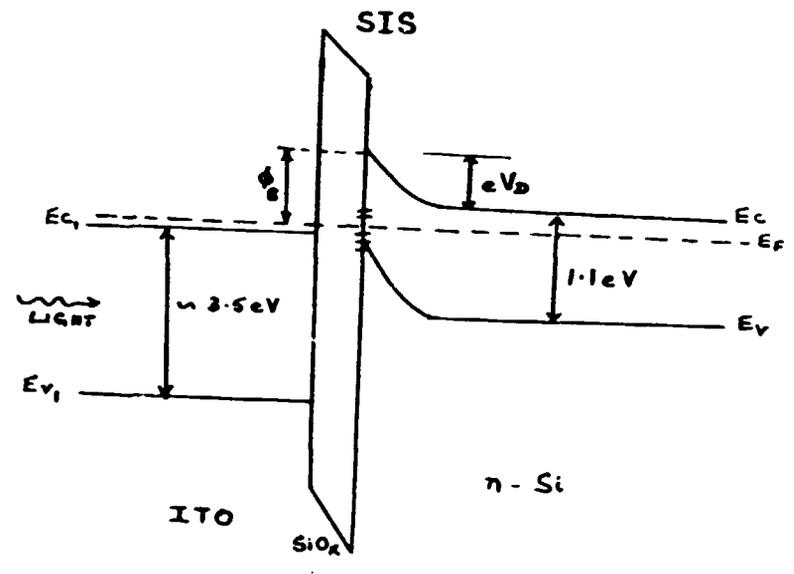
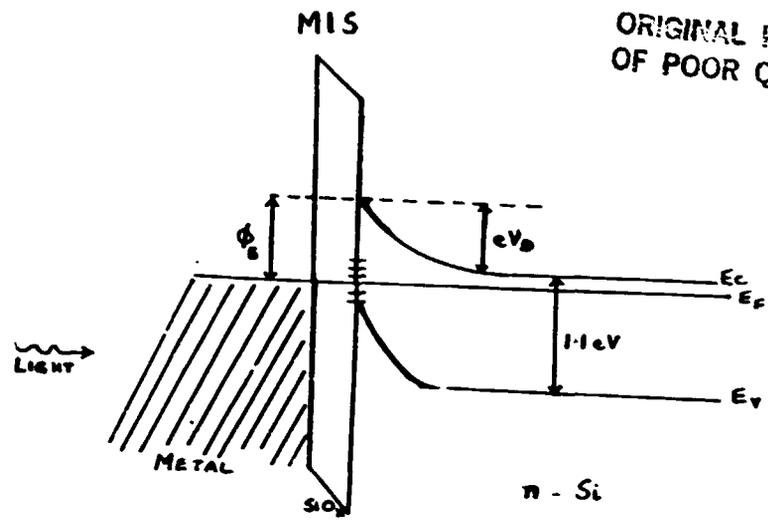
LIMITATIONS -

1. LOW V_{OC} - THERMIONIC EMISSION OR MULTI-STEP TUNNELING.
2. SHEET RESISTANCE/TRANSPARENCY TRADEOFF (J_{SC} VS. FF TRADE-OFF)
3. STABILITY AND AGING OF THIN FILMS.
4. POSSIBLE PHOTOGENERATED MINORITY CARRIER LOSS THROUGH INTERFACE TRAPS)

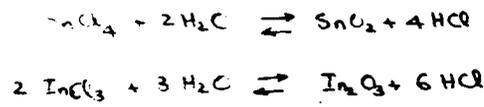
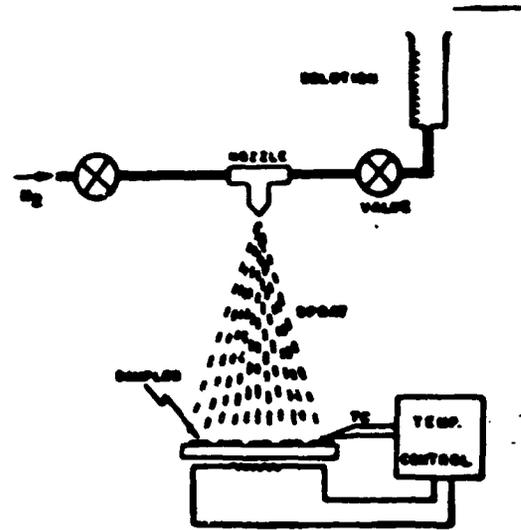
Spray Pyrolysis System



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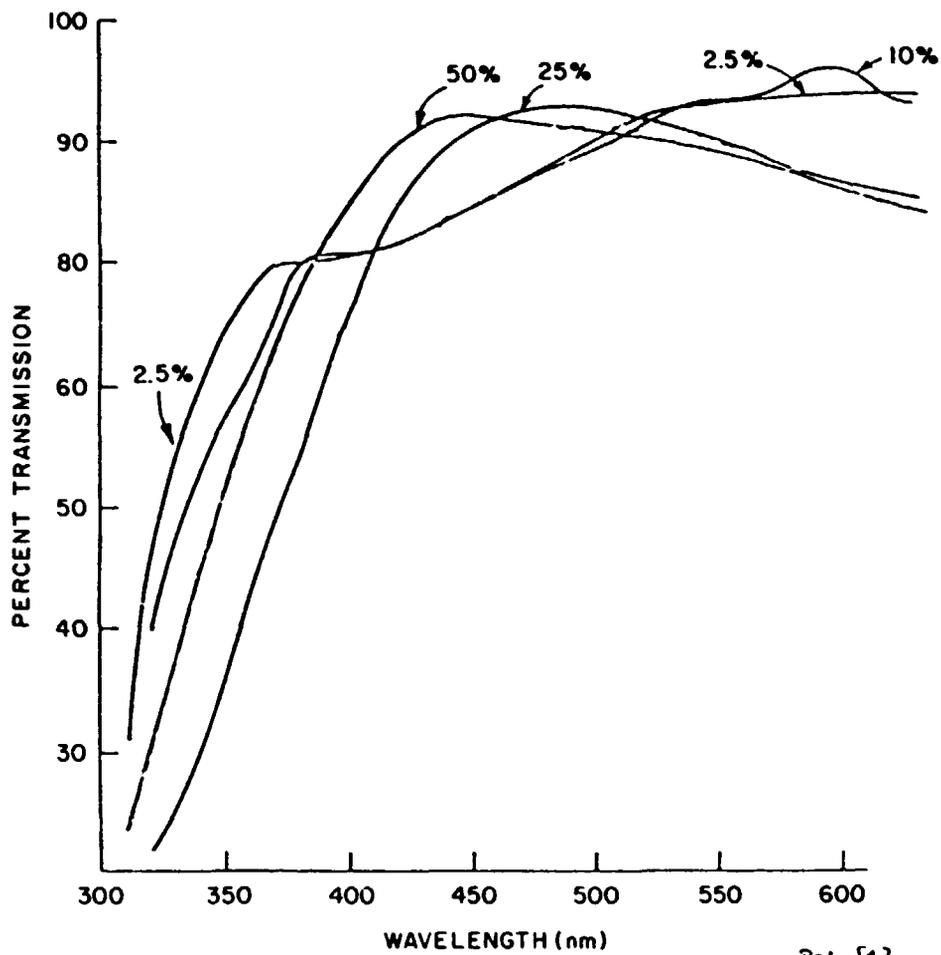
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ITO Resistivity as a Function of Chemical Composition

Weight % of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	Thickness (\AA)	Refractive Index	R (Ω/\square)	P (Ω/cm)
2.5	4200	1.9	25	1.1×10^{-3}
25	4700	2.1	270	1.3×10^{-2}
50	4300	2.2	335	1.4×10^{-2}

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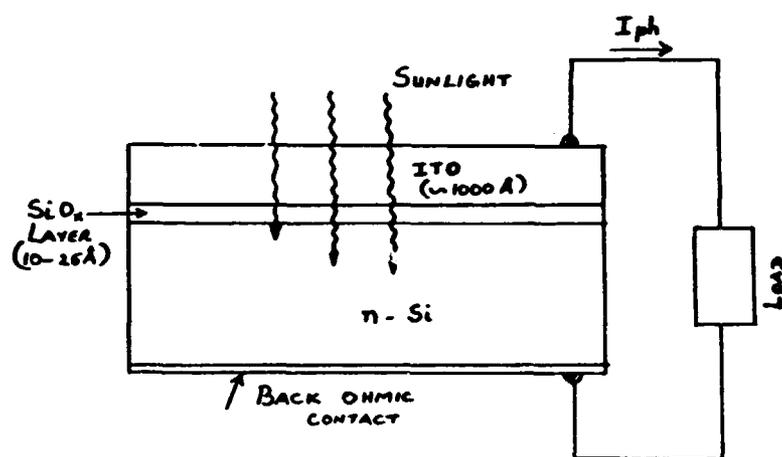


Ref. [4]

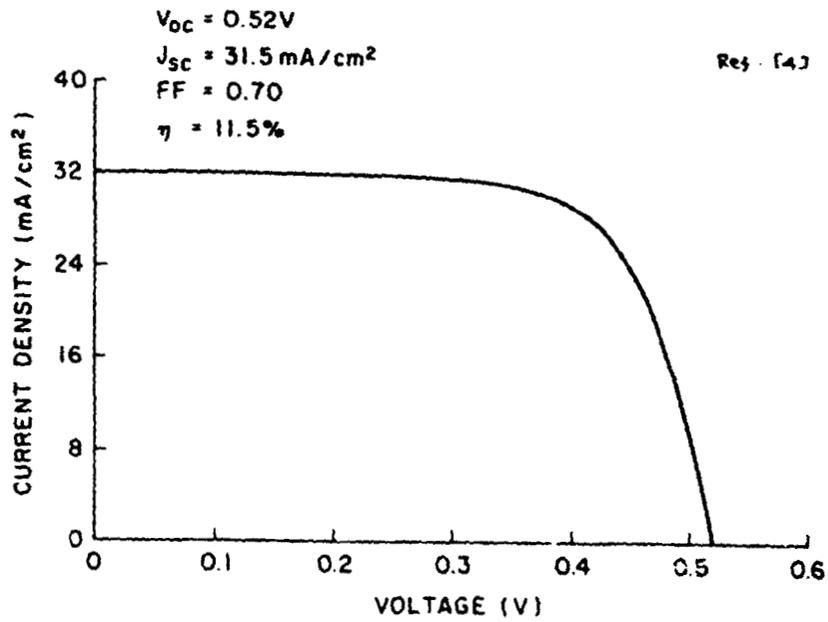
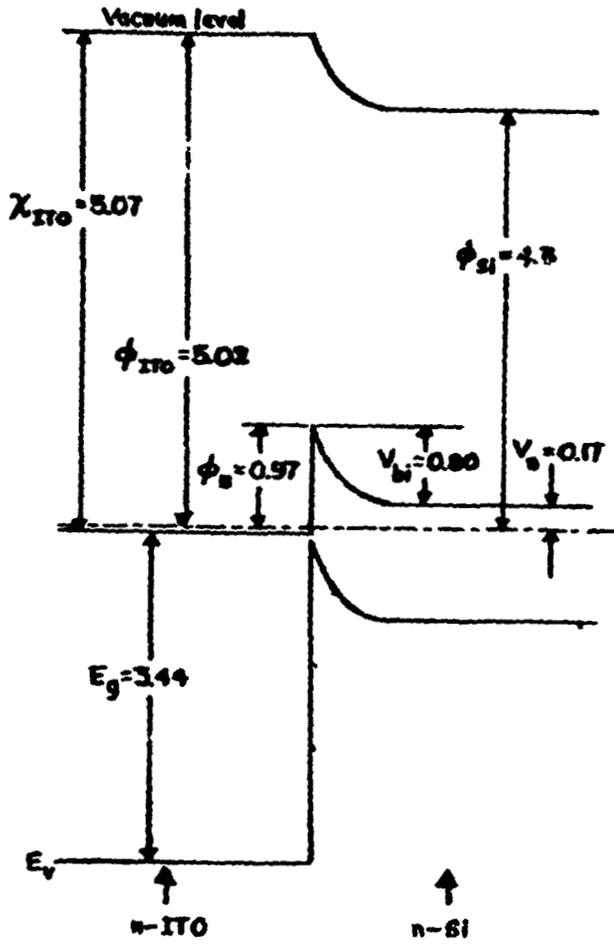
ITO Optical & Electrical Characteristics

1. ALLOY COMPOSITION CHOSEN FOR BEST OPTICAL TRANSMISSION, LOWEST ELECTRICAL RESISTANCE, AND BEST PHOTOVOLTAIC RESPONSE.
2. ITO BANDGAP IN THE RANGE 3.2 - 3.45 eV FOR VARYING COMPOSITION.
3. ELECTRON MICROGRAPH SHOWS POLYCRYSTALLINE FILM WITH 400-1000 Å GRAINS.
4. SPRAY ITO FORMS BARRIER CONTACT WITH N-TYPE Si AND OHMIC CONTACT WITH P-TYPE Si.

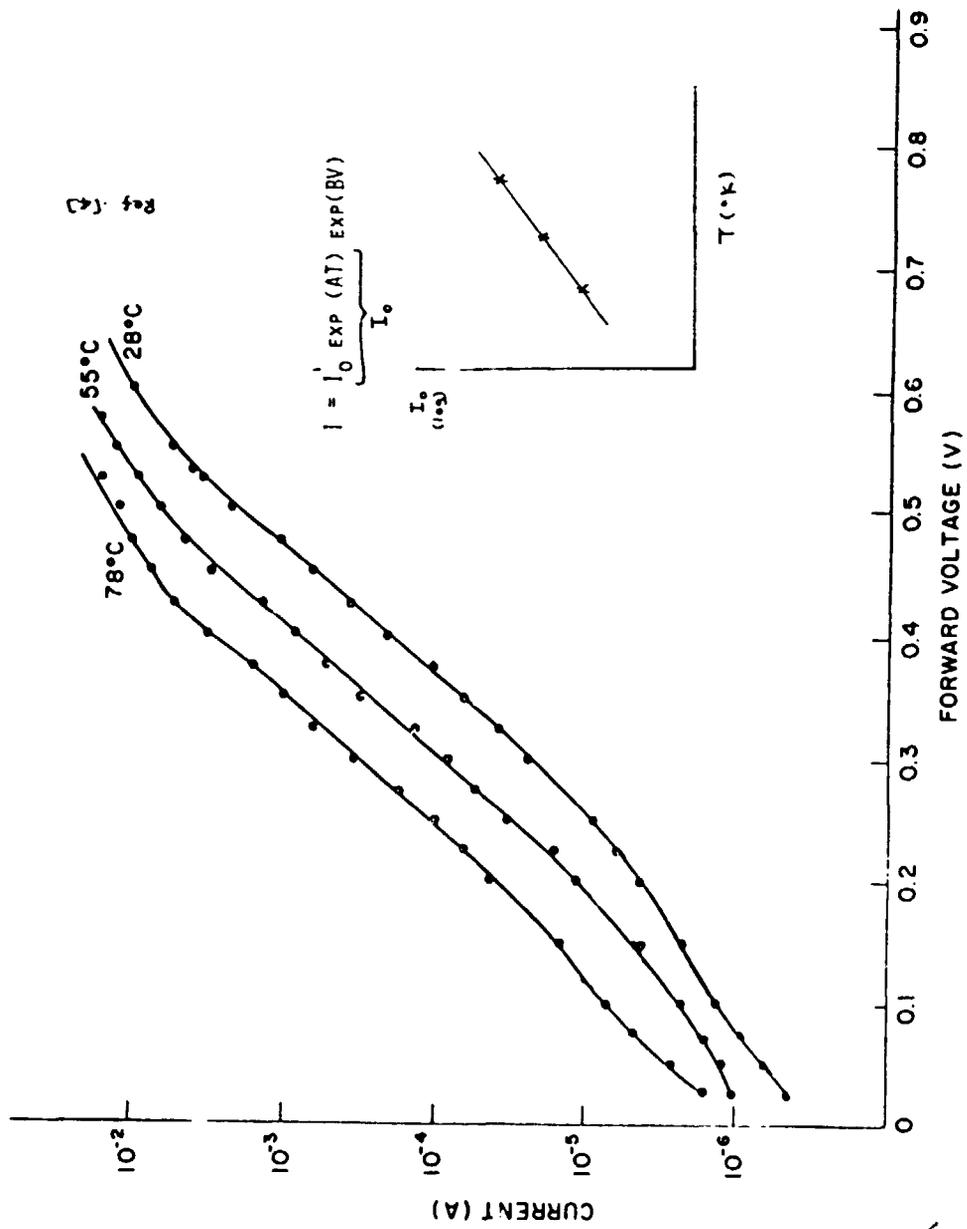
ITO-SiO_x-n-Si SIS Solar Cell



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Best Reported Performance of ITO—n-Si & SnO₂—n-Si Cells

(SPRAY PROCESS)

CELL TYPE.	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	EFFICIENCY(%)
ITO/n-Si (SINGLE XTAL Si)	30.2	0.626	0.73	13.7
SnO ₂ /n-Si (SINGLE XTAL Si)	29.1	0.615	0.615	12.3
ITO/n-Si (WACKER POLY Si)	29.8	0.557	0.67	11.2
SnO ₂ /n-Si (WACKER POLY Si)	26.6	0.56	0.68	10.1

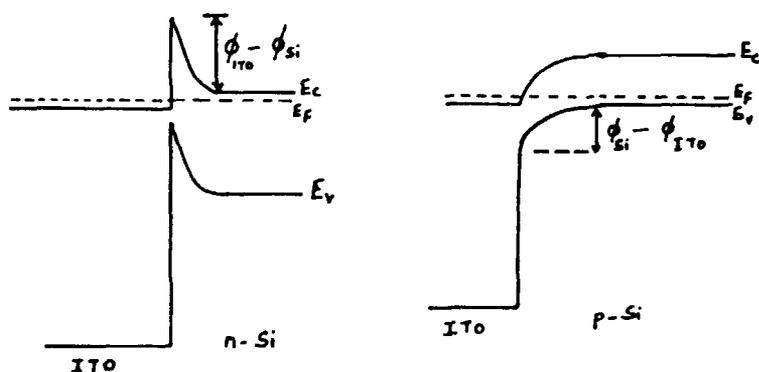
ITO—Si Heterojunction Anomaly

SPRAY OR ELECTRON-BEAM EVAPORATED ITO -

RECTIFYING JUNCTION ON n-Si (SOLAR CELL)
OHMIC CONTACT (LOW BARRIER) ON p-Si

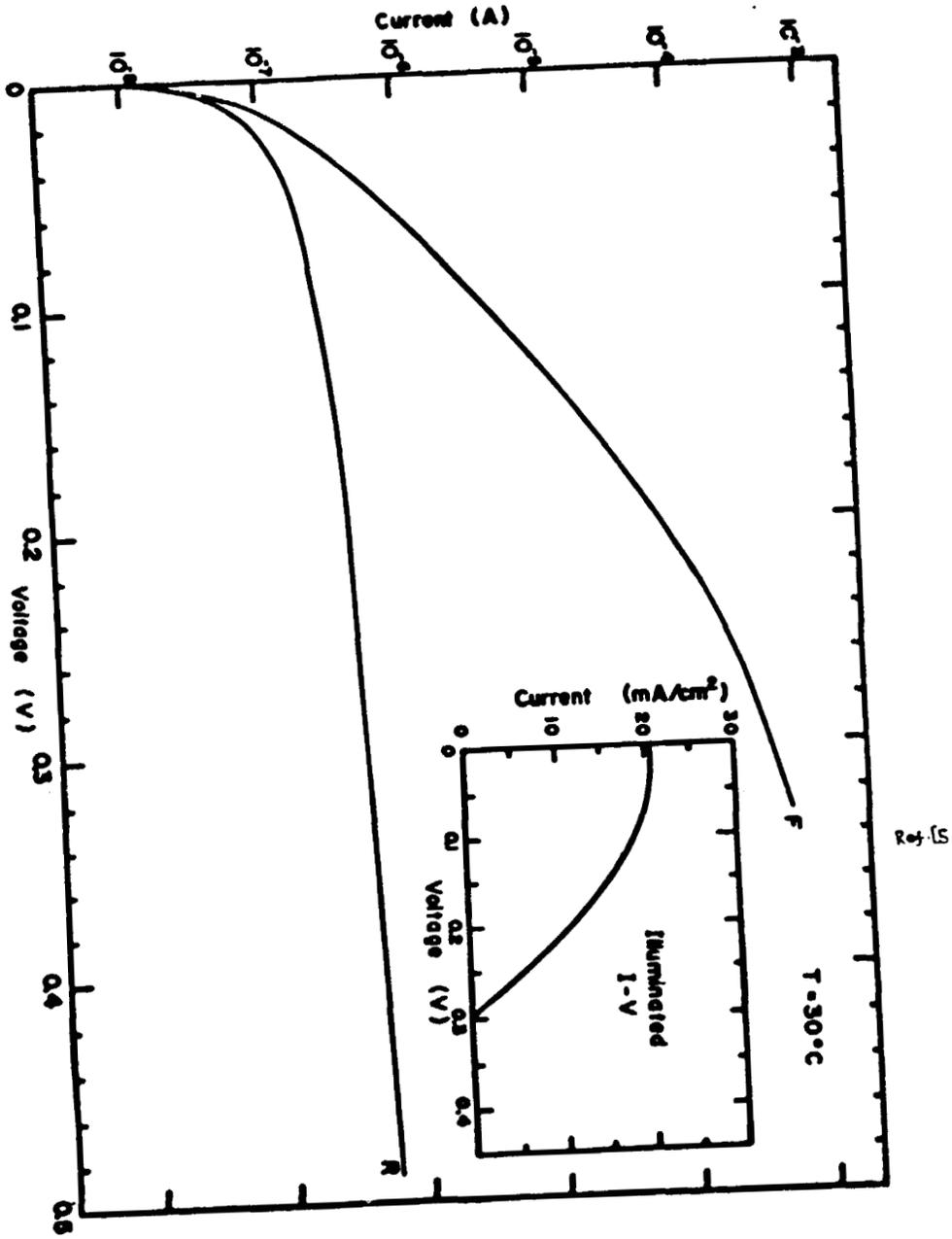
ION-BEAM SPUTTERED ITO -

RECTIFYING JUNCTION ON p-Si (SOLAR CELL)
OHMIC CONTACT (LOW BARRIER) ON n-Si

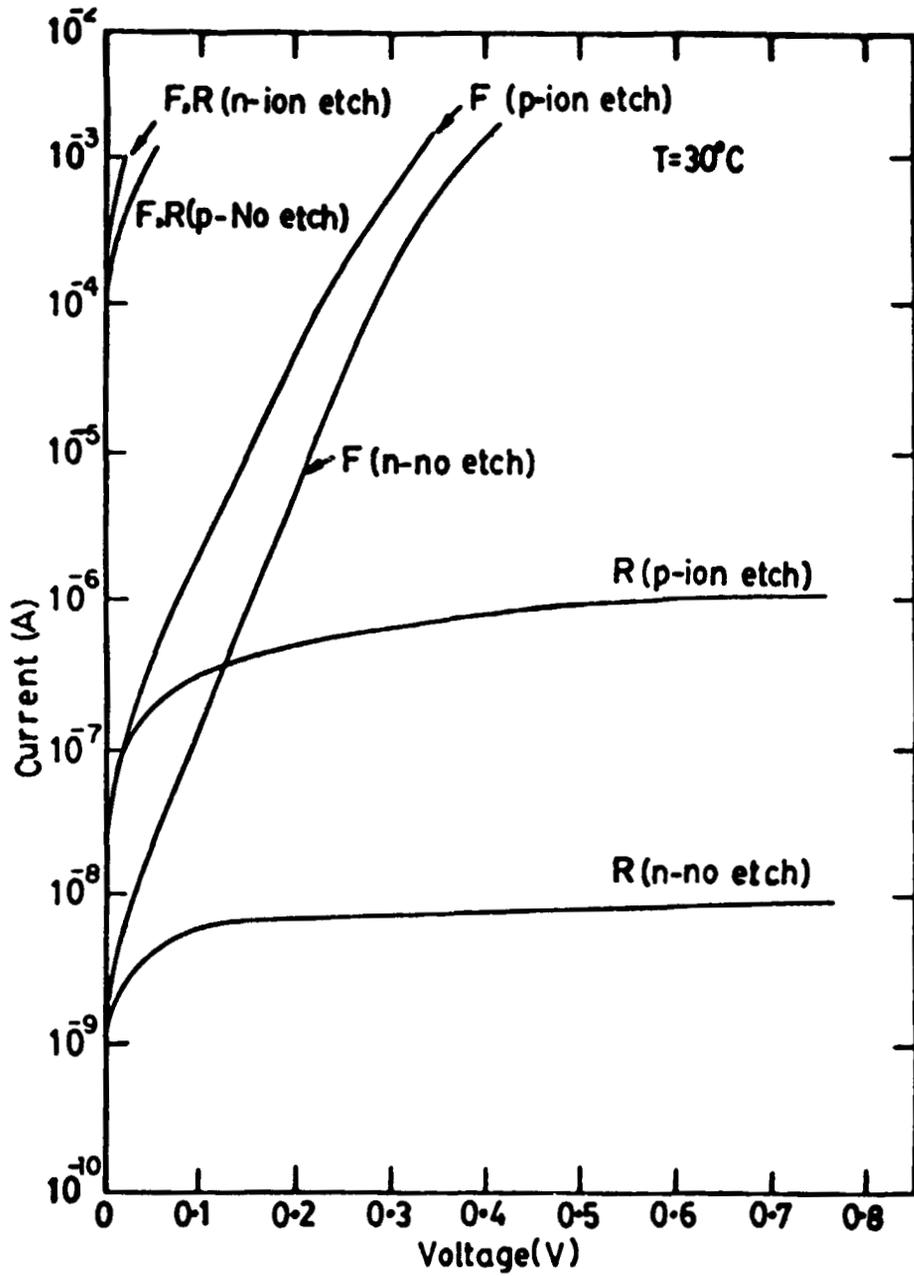


Ref. (5)

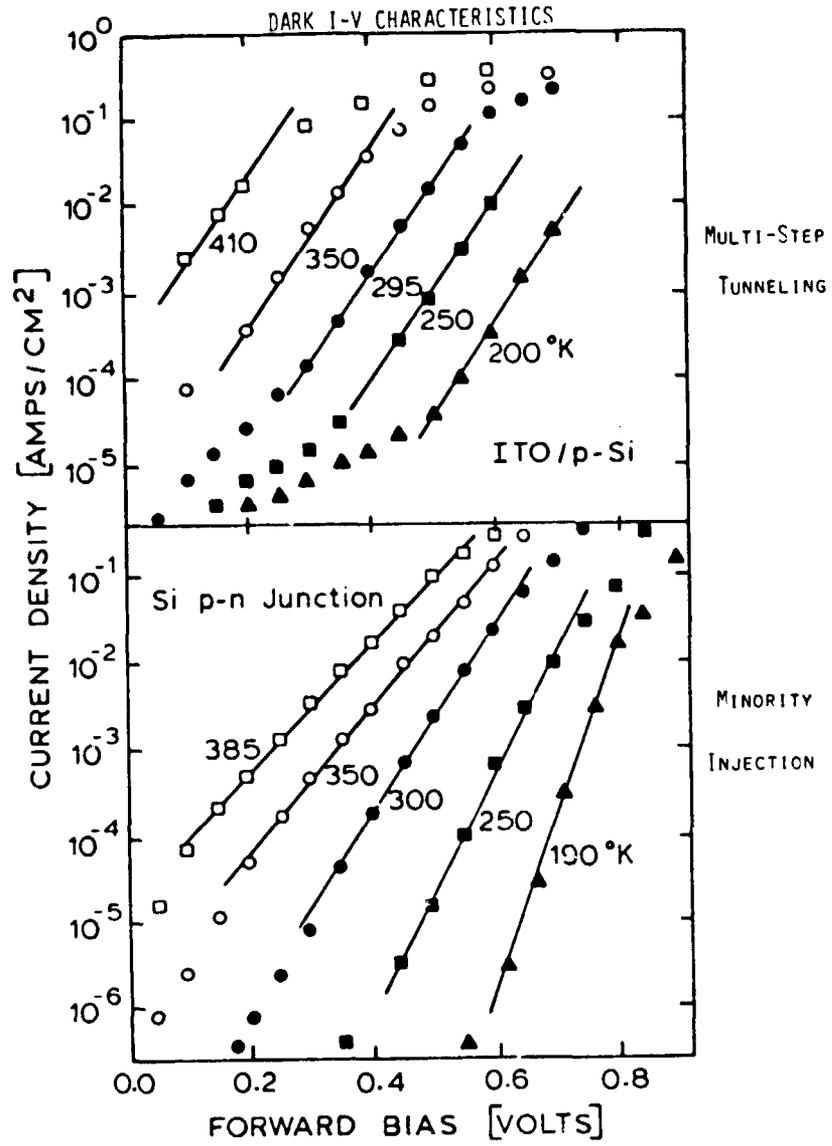
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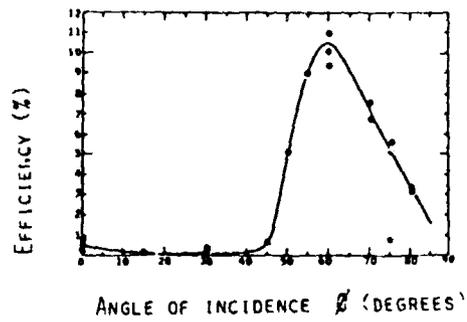
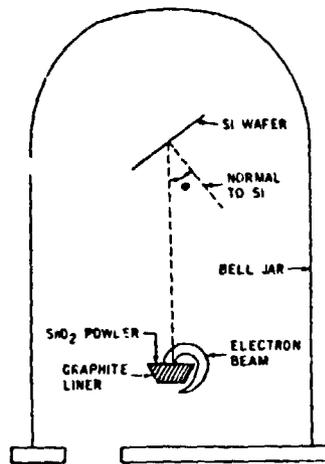
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Angle-of-Incidence Dependence of Electron-Beam-Deposited SnO₂-n-Si Cells

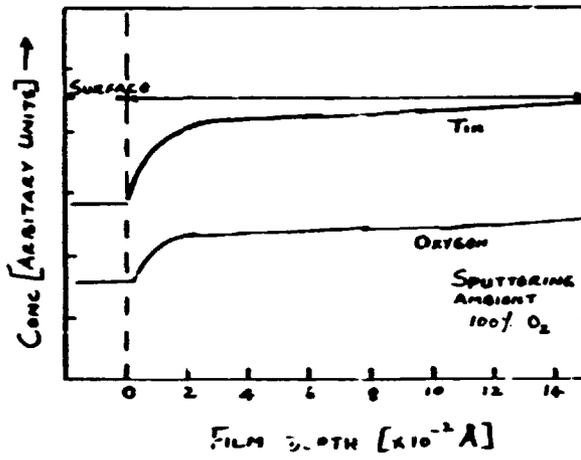


Ref. [c]

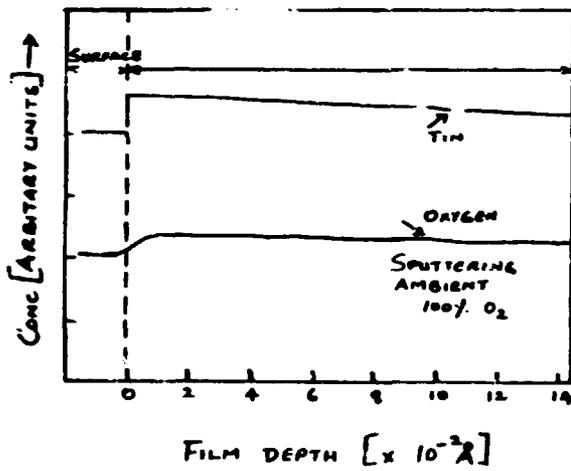
AES Profiles

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RF sputtered SnO₂



After heating
in air
for 200°C

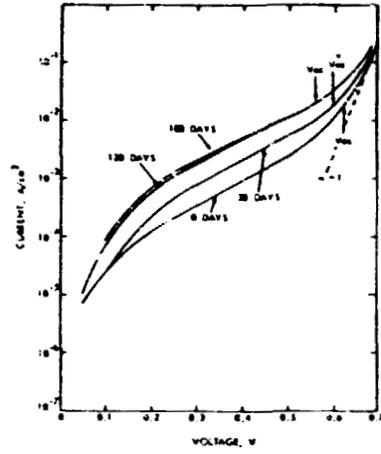


As sputtered

Ref. [7]

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Light-Induced Degradation of Spray SnO_2 -n-Si Cells



CHANGE IN DARK I-V CHRCS. DUE TO LIGHT

MECHANISM - CHARGE TRAPPING AT Si/SiO_2 INTERFACE WITH
RESULTANT CHANGE IN BARRIER HEIGHT.
DUE TO ULTRA-VIOLET COMPONENT.

Ref. [8]

Surface Barrier Height Control

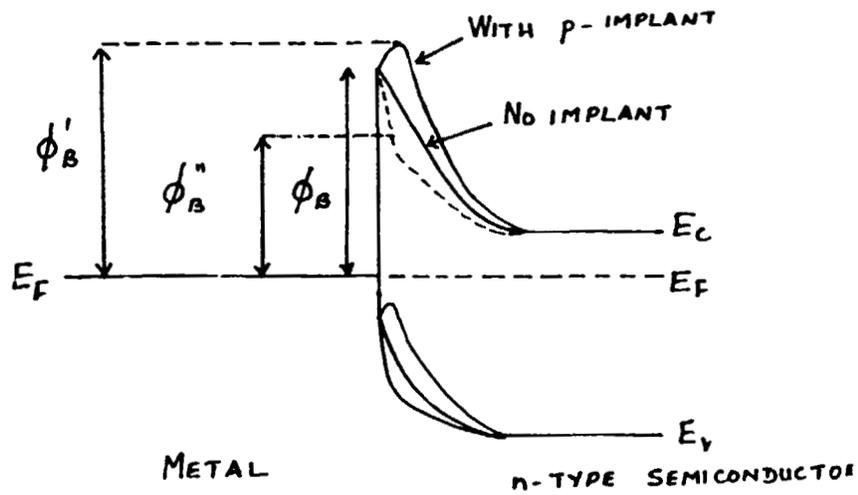
BARRIER HEIGHT ENHANCEMENT BY VERY SHALLOW ION
IMPLANT.

$\sim 50 - 150 \text{ \AA}$ PROJECTED RANGE

ION ENERGY 5 - 15 KEV

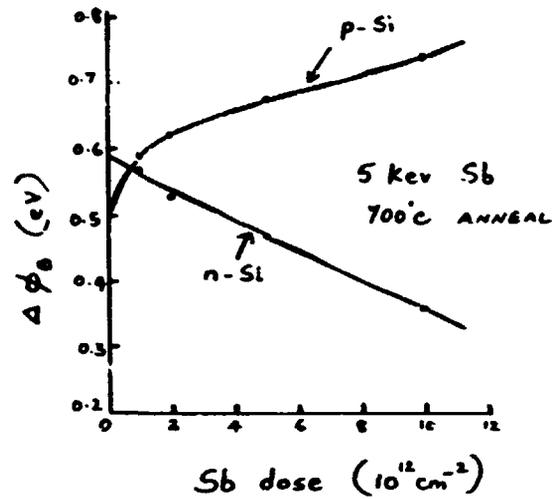
ION DOSE $10^{12} - 10^{13} \text{ cm}^{-2}$

IMPLANT ION TYPE - OPPOSITE TO SUBSTRATE CONDUCTIVITY TYPE
(DONOR FOR P-SUBSTRATE, ACCEPTOR FOR
N-SUBSTRATE), WITH LOW DIFFUSION CONST.



Ref. (9)

Barrier Height Change vs Shallow Implant Dose



Ref. [5]

Problem Areas

1. ROLE OF "DOPANTS"
2. INFLUENCE OF DEPOSITION CONDITIONS ON ELEC. INTERFACE
3. CONTROL OF PARAMETERS
4. CRITERIA FOR COMPARING FILMS PREPARED BY DIFFERENT TECHNIQUES
5. FURTHER AGING AND INTERFACE STABILITY STUDIES
6. AMORPHOUS TRANSPARENT CONDUCTORS ?

DISCUSSION

WOLF: When you list E, the transmission factor E, is that purely due to absorption or does that still include reflection?

ASHOK: That is due to absorption.

WOLF: Then it must be thickness dependent.

ASHOK: Yes, but we have to have--in order to have a good AR coating, you have to have about 1000 Angstroms. If you make it too thick, then it is going to increase even more.

SOMBERG: Have you have done any work with dual AR using a transparent conductor?

ASHOK: No, I am not aware of any. The two different transparent conductors have been tried for a different reason. One is used to form a good barrier and the other one to reduce surface reflection.

SOMBERG: I am just talking about optimizing the antireflection barriers. The other question is, why do you say you have to have a 1000-Angstrom-thick layer for a good AR, rather than something around 600 to 800 Angstroms?

ASHOK: It was a round figure. I just rounded it off without giving an exact figure.

GALLAGHER: In your enhanced work function graph, you showed work functions going up in the 7 to 8 region. Since the work function and the VOC is almost the same, what measurable VOCs did you get in those devices?

ASHOK: With the last viewgraph?

GALLAGHER: Yes.

ASHOK: I showed the change in the work function.

GALLAGHER: You got up to 0.7 --

ASHOK: It is not the work function. It is the body barrier height.

GALLAGHER: Oh, it's the barrier height, excuse me, I misunderstood.

WONG: I have a question on the fluorinated tin oxide. What kind of a conductor mechanism does fluorinated tin oxide utilize?

ASHOK: Well, it is similar to the other cases.

WONG: The reason I am asking this question is because tin oxide is n-type. The conductor mechanism is by oxygen vacancies, right? The available oxygen vacancies? By adding fluorine atoms -- fluorine is -1 -- you are actually occupying an ion vacancy rather than giving up an ion vacancy.

So actually I am thinking the opposite way -- so that you lose the conductivity that way.

ASHOK: No. It substitutes for an oxygen site.

WONG: Would the fluorine ion go into the oxygen vacancy? Because there is already oxygen vacancy there. So very easily it will go to the oxygen vacancy, and energetically is more favorable, so I would see the opposite mechanism going on. I know there is a more complicated answer but this is what I naively see.

ASHOK: I am not sure of the exact answer for that.

HOGAN: The light-and-temperature-induced changes -- are those independent of the method of the ITO fabrication?

ASHOK: Well, this one is on the straightforward system. I would think they would be comparable.

FIRESTER: Typically, for example, the sputtered ITO is unstable above the temperature in which it is sputtered. The resistivity goes up, depending on what the sputter temperature is.

WOLF: The substrate temperature?

FIRESTER: Yes.

QUESTION: What about light-intensity changes?

ASHOK: That is only to the interfaces. It is not to the bulk, I don't think. It is to the silicon-SnO₂ interface. It changes at the interface.

HOGAN: So that should be independent of the method of deposition?

ASHOK: I would think so, yes.

STEIN: There is another method of deposition that we have used, not for this purpose, but we make a metallo-organic composition that gives an ITO film. When printed and fired at between 550° and 600°C, the light transparency or transmission is higher than you have indicated in some of the films you have described. We have seen greater than 95%. The resistivity is not as low; sheet resistivity is in the order of 1000 ohms per square. You can modify that upward by quite a bit. You can't get much lower than 400 or 500--it's a function of firing temperature. The stability of these films is good to about 500°C, which more or less coincides with what our friend has said. They are sensitive to moisture. I don't know if the same is true in some of the films that you have described. The resistivity tends to increase with higher relative humidity, and it can be dried out and decreased. It seems to be reasonably reversible.

Q: Let me ask a general question. Where do you think this technology is going to challenge our standard systems? Will it be costly, will it be inefficient, or what do you think? Anyone can answer that.

ASHOK: Well, I think they are comparing two different things. If the efficiency can be boosted up, it obviously can be done when the open-circuit voltage problem can be handled separately by means of the surface treatment of silicon. But the material has to be grown with better transmission characteristics. But there is an interim tradeoff as we increase the conductivity. The plasma edge moves closer to the silicon band gap, and the plasma frequency increases as the electron concentration goes up. But if material can be developed with transmission in the range of 90%, in the range of interest, then it can be useful.

BURGER: What likelihood is there that you may turn up with newer or better transparent conductive coatings along the lines that you have been investigating? In other words, how broad could the field be, or is it a limited set of combinations and permutations?

ASHOK: Unfortunately, much of the information available in this whole field is still empirical. I think, in terms of understanding of the materials, it is comparable to amorphous silicon; probably amorphous silicon is better.

BURGER: I have one additional question. You mentioned that there was an optimal doping. How sensitive is that? I mean, is that a very narrow window or is it easy to achieve?

ASHOK: It can be easily achieved. It is not a problem.

SCHRODER: Who of the solar-cell manufacturers is using this technology?

ASHOK: For a production device?

SCHRODER: Yes, or some serious research.

ASHOK: I don't think anyone is using a pilot line, but at Exxon they have used it in their research.

FIRESTER: Photon Power is selling tin-oxide-coated glass, which is the first layer in their glass-tin-oxide CdS.

SCHWUTTKE: These are the 2% or 3% efficiency cells?

FIRESTER: I don't know what the efficiency is.

SCHRODER: Exxon is using it at least in R&D, and that is it. Are other companies that you are aware of?

ASHOK: I am talking about using it in single-crystal silicon. But as a thin film substrate, it is used.

SCHRODER: I am not talking about that.