The road to the development of ZnO doped with group III elements and hydrogen

By Nang T Tran (Ecosolar International)

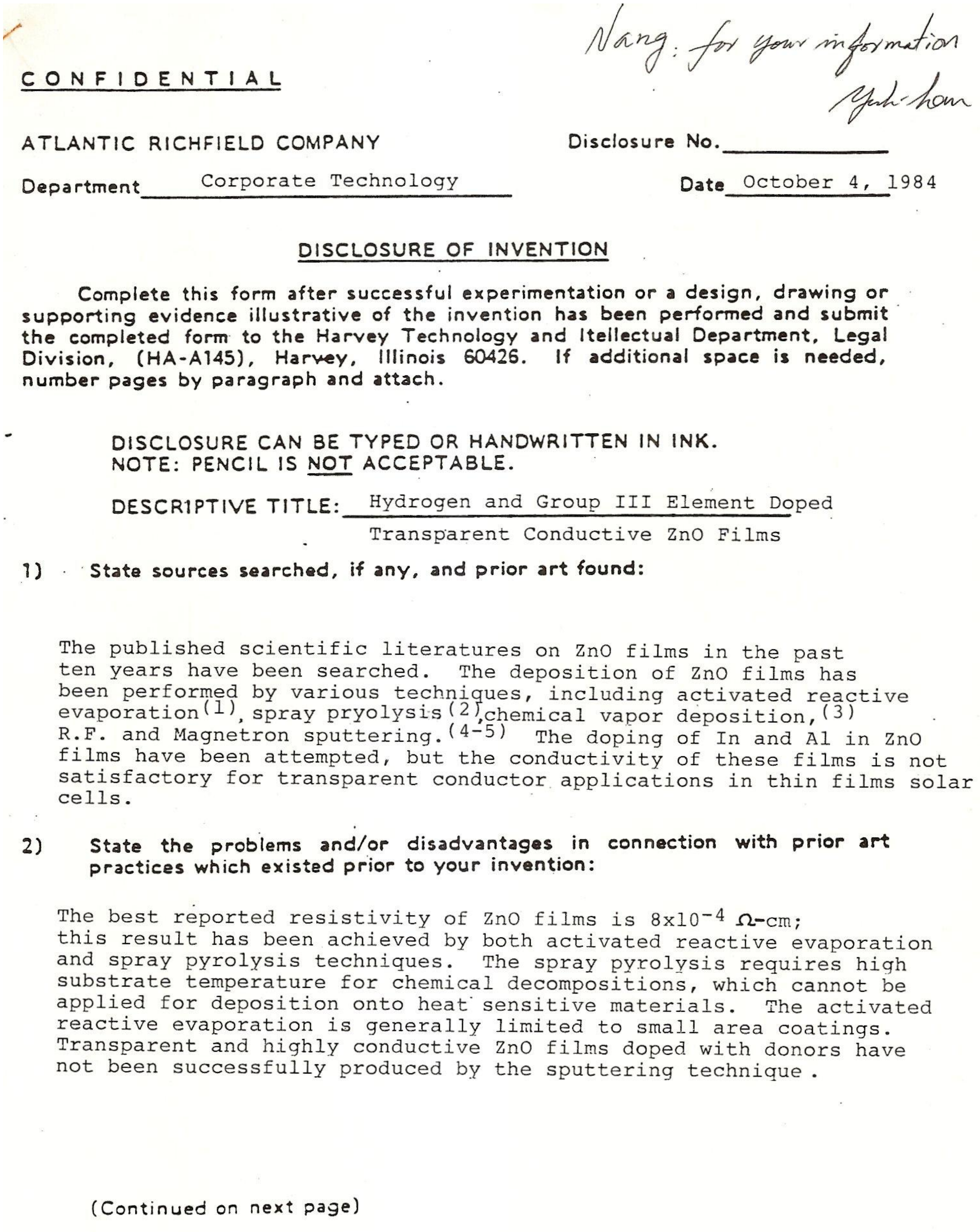
Zinc oxide (ZnO) films doped with group III elements (ZnO-III) and hydrogen that had been developed by Nang Tran and his colleague, Yu-Han Shing in 1983 while they were working at Atlantic Richfield Company (ARCO) has been increasingly used in many optoelectronic applications. One of them is the photovoltaic (PV) solar energy, a new millennium industry which has fast growing market, potential accessibility to the billions of people worldwide, and is environmentally sound as a "green" source of energy. This new type of oxide has many valuable attributes: indium –free therefore cheaper, non-toxic, zinc source abundance, stability against hydrogen, low process temperature, a good balance between conductivity and transmission. Since its introduction to the PV solar community, several laboratories have adapted and studied this new type of oxide as a front contact, back contract, buffer layer for their research and development of solar cells. In the case of thin film solar cells, most of the commercial modules of amorphous silicon, microcrystalline/ nanocrystalline silicon and copper indium gallium selenide have at least one layer of ZnO-III in the device structures.

In this article, I'd like to walk you back to the road that led us to the invention of sputtered ZnO doped with group III elements anh hydrogen. Back in the early of 1980's, our company (ARCO Solar) was in the business of producing thin film solar panels and we needed an alternative transparent conducting oxide which could perform better than indium tin oxide and tin oxide films. ZnO had been known to the scientific community and prepared using different techniques such as activated evaporation [1], spray pyrolysis [2], sputtering [3] and CVD [4]. The produced films had good transparency but its bulk resistivity was still not good enough, which had prevented it from being used as an effective transparent conducting oxide film.

Under these circumstances, on March 14, 1983, Yu-Han Shing (my suvervisor at that time) and I got the assignment from our managers to find a way to improve performance of ZnO films. After several meetings and discussions, two weeks later, in April, we had come up with the idea of doping ZnO with group III elements and hydrogen. The optimum resistivity of hydrogen doped films was achieved by Nang Tran on May 18, 1983. Subsequent Ga, In, Al, In and B doping were performed in the month of August and September, 1983 also by Nang Tran. Hydrogen- doped ZnO films were produced at ambient temperatures, which is suitable to temperature sensitive materials, whereas ZnO doped with groups III elements were deposited at elevated temperatures. We were able to achieve ZnO films which had a low bulk resistivity in the range of 10^{-4} Ω-cm , low absorption therefore could be made thicker for a given transmittance. This oxide is an n-type material; its conductivity is caused by the substitution of Zn^{2+} ions with group ions for example Al^{3+} ions, releasing excess electrons into the conduction band. For the sake of simplicity, let's call the oxide family having III elements ZnO -III., ZnO doped with aluminum AZO ; ZnO doped with boron BZO; whereas GZO is referred to as zinc oxide doped with gallium . The obtained ZnO-III is a high band gap material which is non-toxic, stable against chemically reactive hydrogen (like plasma environment) , less expensive , abundant in zinc source , low process temperature , has a low absorption coefficient , and high transmission , therefore can be made thick (2- 3 μm) for better conductivity; those are distinctive features that have not been readily realized with indium tin oxide (ITO) and fluorine -or sometimes doped with antimony- doped tin oxide (FTO), the two TCO's that have dominated the optoelectronic industry in the last forty years. This was the first success in producing effective ZnO films with extrinsic elements during the sputtering process.

The ARCO's group had further incorporated this new type of oxide as a front contact layer, a back contact and a buffer layer in the development of amorphous silicon single junction (MTF modules), copper indium diselenide single-junction solar cells, transparent solar cells, copper indium diselenide- amorphous silicon tandem cells (BCLIPSE modules), MTF cell/ single crystal silicon tandem (ECLIPSE modules) ; some of them exhibited among the best conversion efficiencies at that time. Since then, many laboratories in the solar energy community have adapted this oxide in their research and development of thin film solar cells.

A magnetron sputtering system had been employed to deposit ZnO films at ambient temperature. The sheet resistance of 8 Ω/square and a bulk resistivity of 6.4×10^{-4} Ω-cm had been achieved for hydrogen doped ZnO of a thickness of 8,000 A. Ga and Al doped ZnO films had a bulk resistivity of 4.9×10^{-4} Ω-cm and 8.7×10^{-4} Ω-cm, respectively. Details were discussed in the Disclosure of Invention on October 4, 1984 (Figures 1-4 , attached). A Ga- doped ZnO film of a thickness of 2.5 μm having a sheet resistance of 3 Ω/square and an optical transparency of 84% was obtained. As far as the sputtering process was concerned, in the beginning, we started our doping experiments in ZnO by placing solid pieces of group III elements (Al, Ga, In, B) on ZnO target and sputtered up. Once we found optimized contents in terms of electrical and optical performance, we sent the desired compositions out to Demetron Inc. to have the sputtering targets made. We also used diborane and organometallic gases such as trimethyl aluminium (TMA), trimethyl gallium (TMGa) for the doping purposes. Co-sputtering was also employed to deposit ZnO films. A patent was filed on June 4, 1985 and awarded on November 18, 1986 (US patent 4,623,3601). The main claims 1 & 15 of this patent are shown in Fig. 5.



Nang: for your information

CONFIDENTIAL

ATLANTIC RICHFIELD COMPANY

Disclosure No.

Department Corporate Technology

Date October 4, 1984

DISCLOSURE OF INVENTION

Complete this form after successful experimentation or a design, drawing or supporting evidence illustrative of the invention has been performed and submit the completed form to the Harvey Technology and Itellectual Department, Legal Division, (HA-A145), Harvey, Illinois 60426. If additional space is needed, number pages by paragraph and attach.

DISCLOSURE CAN BE TYPED OR HANDWRITTEN IN INK.
NOTE: PENCIL IS NOT ACCEPTABLE.

DESCRIPTIVE TITLE: Hydrogen and Group III Element Doped Transparent Conductive ZnO Films

1) **State sources searched, if any, and prior art found:**

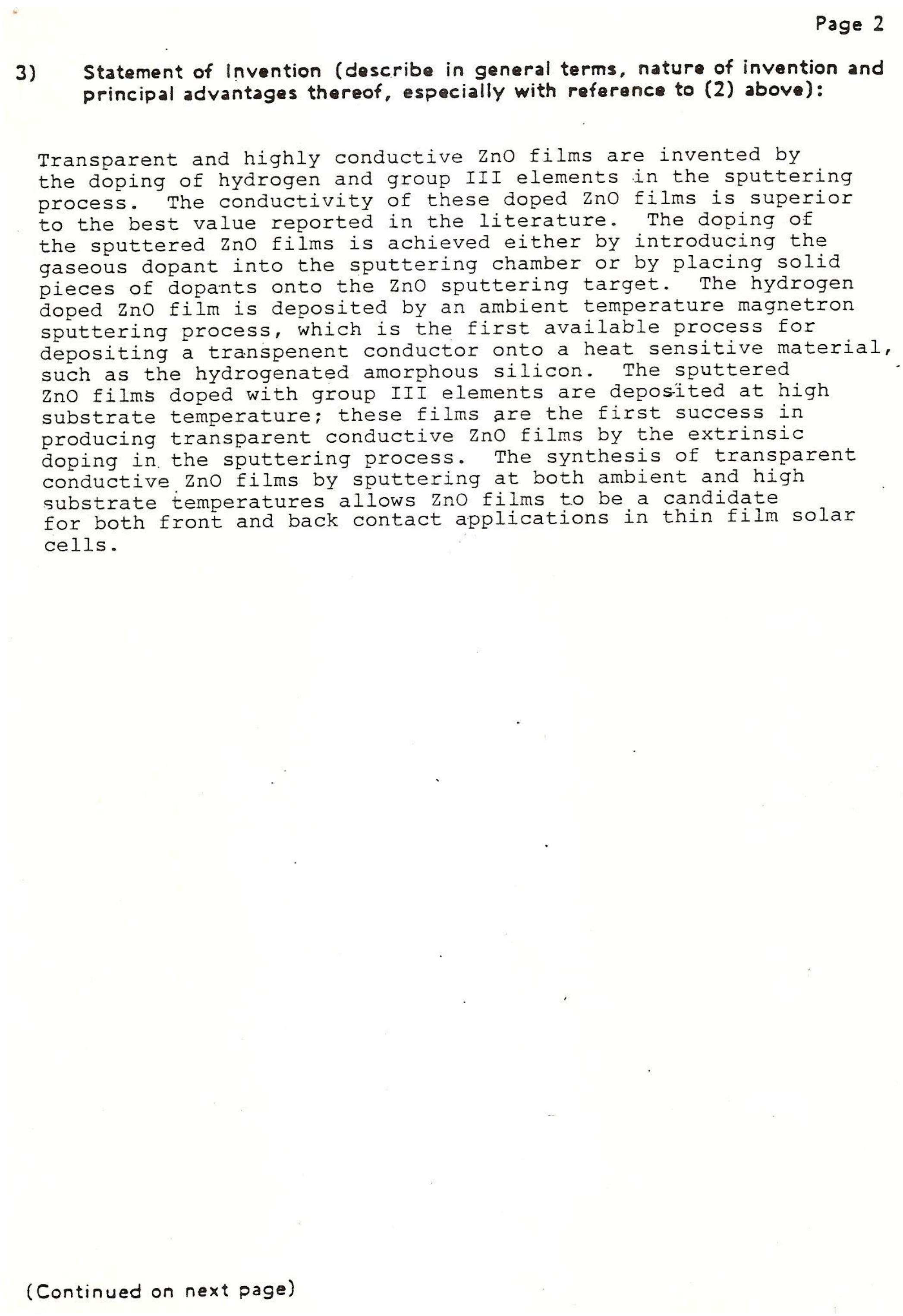
The published scientific literatures on ZnO films in the past ten years have been searched. The deposition of ZnO films has been performed by various techniques, including activated reactive evaporation(1), spray pryolysis(2), chemical vapor deposition,(3) R.F. and Magnetron sputtering.(4-5) The doping of In and Al in ZnO films have been attempted, but the conductivity of these films is not satisfactory for transparent conductor applications in thin films solar cells.

2) **State the problems and/or disadvantages in connection with prior art practices which existed prior to your invention:**

The best reported resistivity of ZnO films is $8x10^{-4}\ \Omega$-cm; this result has been achieved by both activated reactive evaporation and spray pyrolysis techniques. The spray pyrolysis requires high substrate temperature for chemical decompositions, which cannot be applied for deposition onto heat sensitive materials. The activated reactive evaporation is generally limited to small area coatings. Transparent and highly conductive ZnO films doped with donors have not been successfully produced by the sputtering technique .

(Continued on next page)

Fig. 1 : Disclosure of invention of ZnO doped with hydrogen and group III elements (page 1)



3) **Statement of Invention (describe in general terms, nature of invention and principal advantages thereof, especially with reference to (2) above):**

Transparent and highly conductive ZnO films are invented by the doping of hydrogen and group III elements in the sputtering process. The conductivity of these doped ZnO films is superior to the best value reported in the literature. The doping of the sputtered ZnO films is achieved either by introducing the gaseous dopant into the sputtering chamber or by placing solid pieces of dopants onto the ZnO sputtering target. The hydrogen doped ZnO film is deposited by an ambient temperature magnetron sputtering process, which is the first available process for depositing a transpenent conductor onto a heat sensitive material, such as the hydrogenated amorphous silicon. The sputtered ZnO films doped with group III elements are deposited at high substrate temperature; these films are the first success in producing transparent conductive ZnO films by the extrinsic doping in the sputtering process. The synthesis of transparent conductive ZnO films by sputtering at both ambient and high substrate temperatures allows ZnO films to be a candidate for both front and back contact applications in thin film solar cells.

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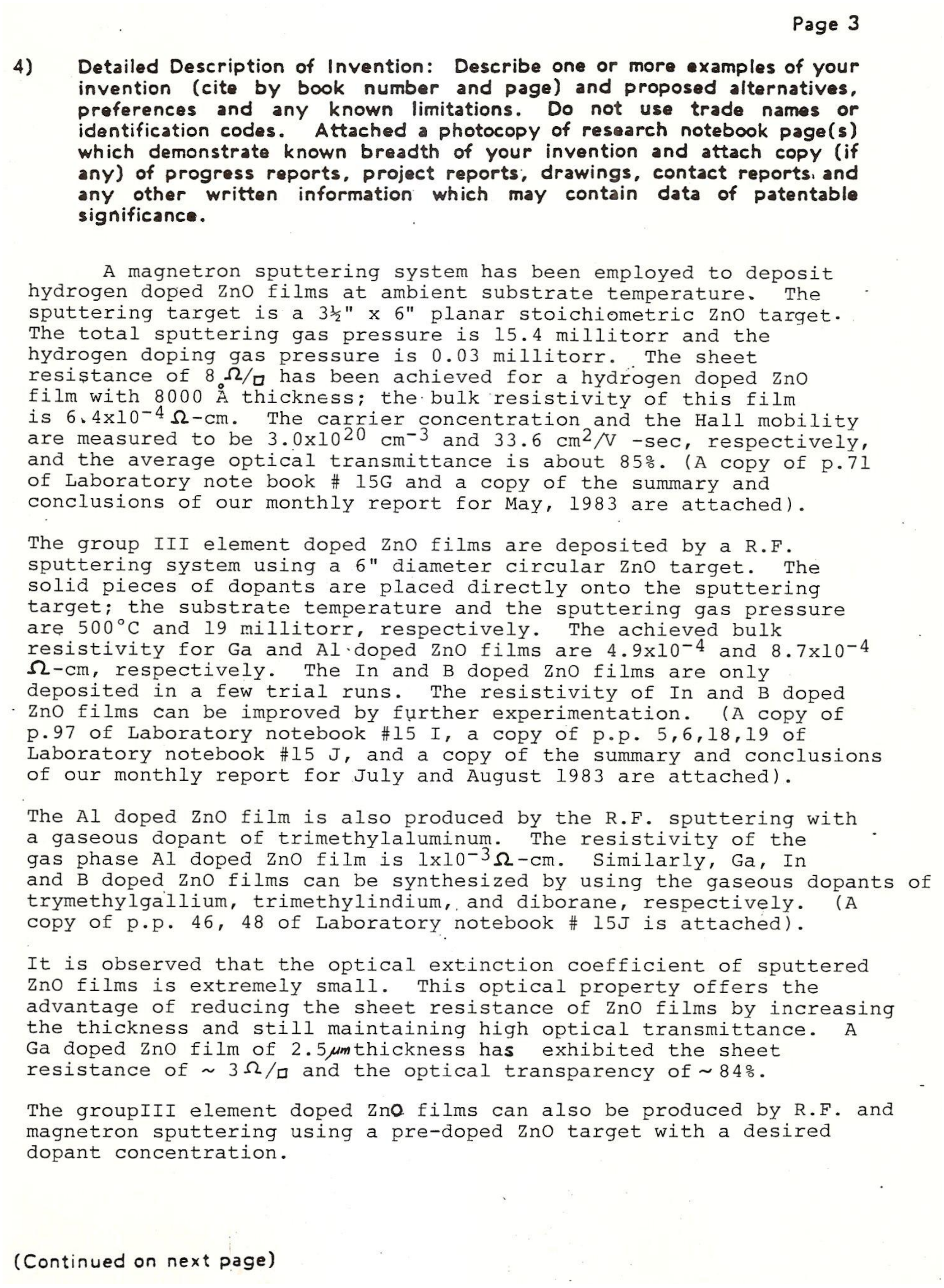
Fig. 2 : Disclosure of invention of ZnO doped with hydrogen and group III elements (page 2)



4) **Detailed Description of Invention: Describe one or more examples of your invention (cite by book number and page) and proposed alternatives, preferences and any known limitations. Do not use trade names or identification codes. Attached a photocopy of research notebook page(s) which demonstrate known breadth of your invention and attach copy (if any) of progress reports, project reports, drawings, contact reports, and any other written information which may contain data of patentable significance.**

A magnetron sputtering system has been employed to deposit hydrogen doped ZnO films at ambient substrate temperature. The sputtering target is a 3½" x 6" planar stoichiometric ZnO target. The total sputtering gas pressure is 15.4 millitorr and the hydrogen doping gas pressure is 0.03 millitorr. The sheet resistance of 8 Ω/□ has been achieved for a hydrogen doped ZnO film with 8000 Å thickness; the bulk resistivity of this film is $6.4\text{x}10^{-4}$ Ω-cm. The carrier concentration and the Hall mobility are measured to be $3.0\text{x}10^{20}$ cm^{-3} and 33.6 cm^2/V -sec, respectively, and the average optical transmittance is about 85%. (A copy of p.71 of Laboratory note book # 15G and a copy of the summary and conclusions of our monthly report for May, 1983 are attached).

The group III element doped ZnO films are deposited by a R.F. sputtering system using a 6" diameter circular ZnO target. The solid pieces of dopants are placed directly onto the sputtering target; the substrate temperature and the sputtering gas pressure are 500°C and 19 millitorr, respectively. The achieved bulk resistivity for Ga and Al doped ZnO films are $4.9\text{x}10^{-4}$ and $8.7\text{x}10^{-4}$ Ω-cm, respectively. The In and B doped ZnO films are only deposited in a few trial runs. The resistivity of In and B doped ZnO films can be improved by further experimentation. (A copy of p.97 of Laboratory notebook #15 I, a copy of p.p. 5,6,18,19 of Laboratory notebook #15 J, and a copy of the summary and conclusions of our monthly report for July and August 1983 are attached).

The Al doped ZnO film is also produced by the R.F. sputtering with a gaseous dopant of trimethylaluminum. The resistivity of the gas phase Al doped ZnO film is $1\text{x}10^{-3}$ Ω-cm. Similarly, Ga, In and B doped ZnO films can be synthesized by using the gaseous dopants of trymethylgallium, trimethylindium, and diborane, respectively. (A copy of p.p. 46, 48 of Laboratory notebook # 15J is attached).

It is observed that the optical extinction coefficient of sputtered ZnO films is extremely small. This optical property offers the advantage of reducing the sheet resistance of ZnO films by increasing the thickness and still maintaining high optical transmittance. A Ga doped ZnO film of 2.5μm thickness has exhibited the sheet resistance of ~ 3 Ω/□ and the optical transparency of ~ 84%.

The groupIII element doped ZnO films can also be produced by R.F. and magnetron sputtering using a pre-doped ZnO target with a desired dopant concentration.

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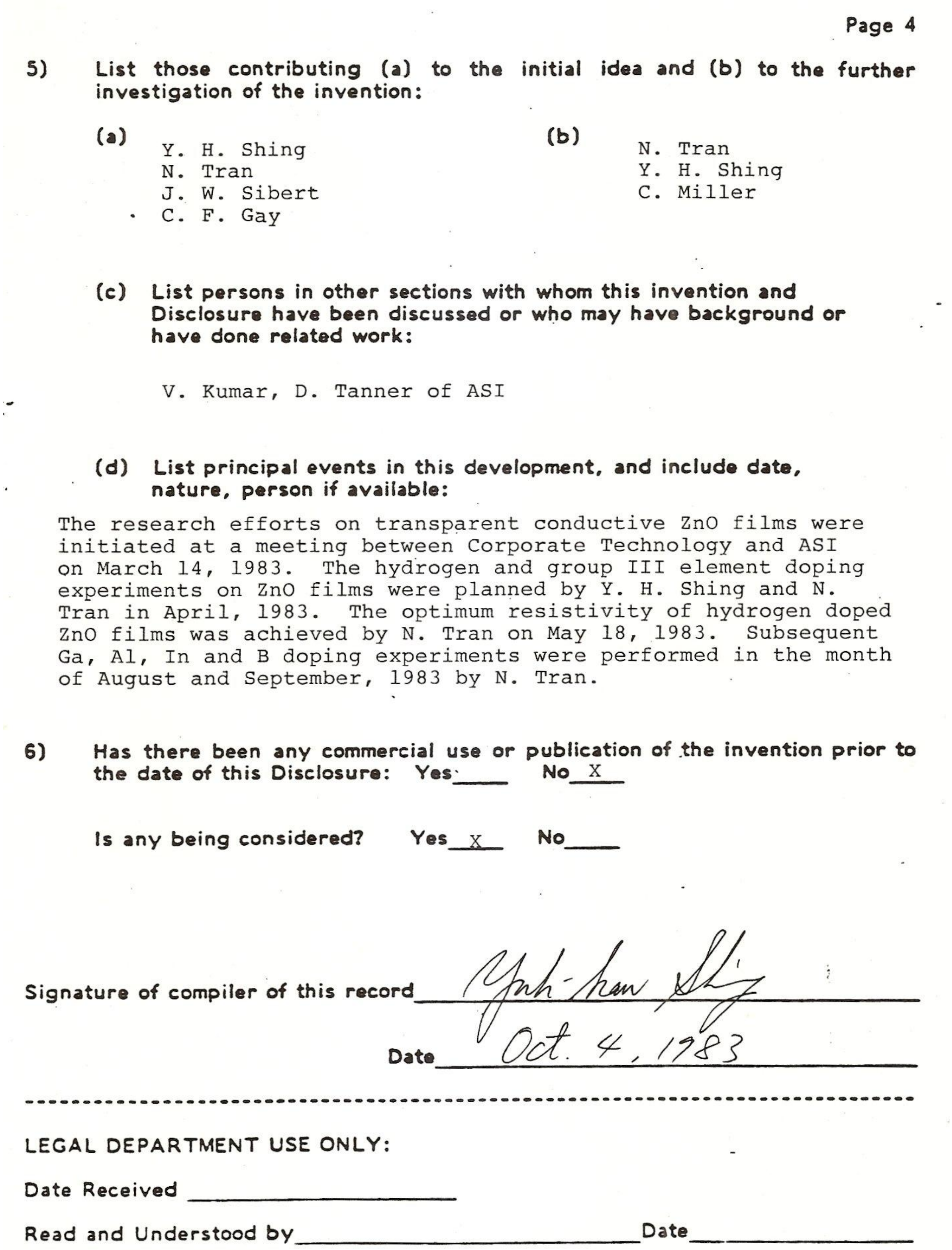
Fig. 3 : Disclosure of invention of ZnO doped with hydrogen and group III elements (page 3)



5) List those contributing (a) to the initial idea and (b) to the further investigation of the invention:

(a)
- Y. H. Shing
- N. Tran
- J. W. Sibert
- C. F. Gay

(b)
- N. Tran
- Y. H. Shing
- C. Miller

(c) List persons in other sections with whom this invention and Disclosure have been discussed or who may have background or have done related work:

V. Kumar, D. Tanner of ASI

(d) List principal events in this development, and include date, nature, person if available:

The research efforts on transparent conductive ZnO films were initiated at a meeting between Corporate Technology and ASI on March 14, 1983. The hydrogen and group III element doping experiments on ZnO films were planned by Y. H. Shing and N. Tran in April, 1983. The optimum resistivity of hydrogen doped ZnO films was achieved by N. Tran on May 18, 1983. Subsequent Ga, Al, In and B doping experiments were performed in the month of August and September, 1983 by N. Tran.

6) Has there been any commercial use or publication of the invention prior to the date of this Disclosure: Yes ____ No X

Is any being considered? Yes X No ____

Signature of compiler of this record Yuh-han Shing

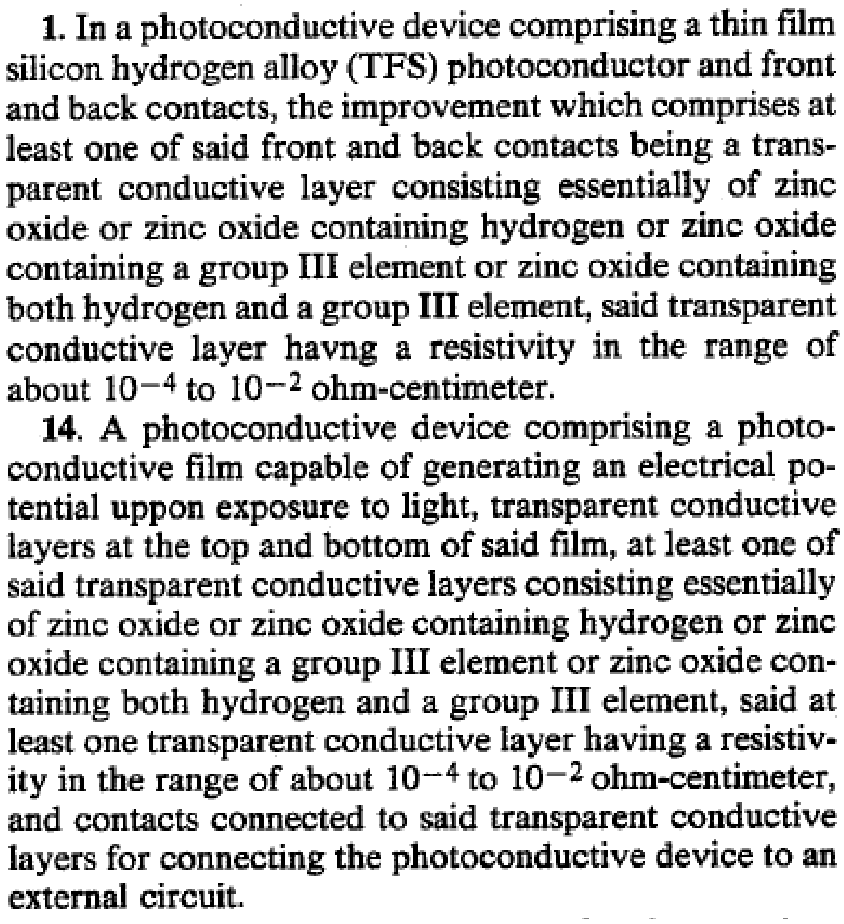
Date Oct. 4, 1983

LEGAL DEPARTMENT USE ONLY:

Date Received ____________________

Read and Understood by ____________________ Date ____________________

Fig. 4 : Disclosure of invention of ZnO doped with hydrogen and group III elements (page 4)

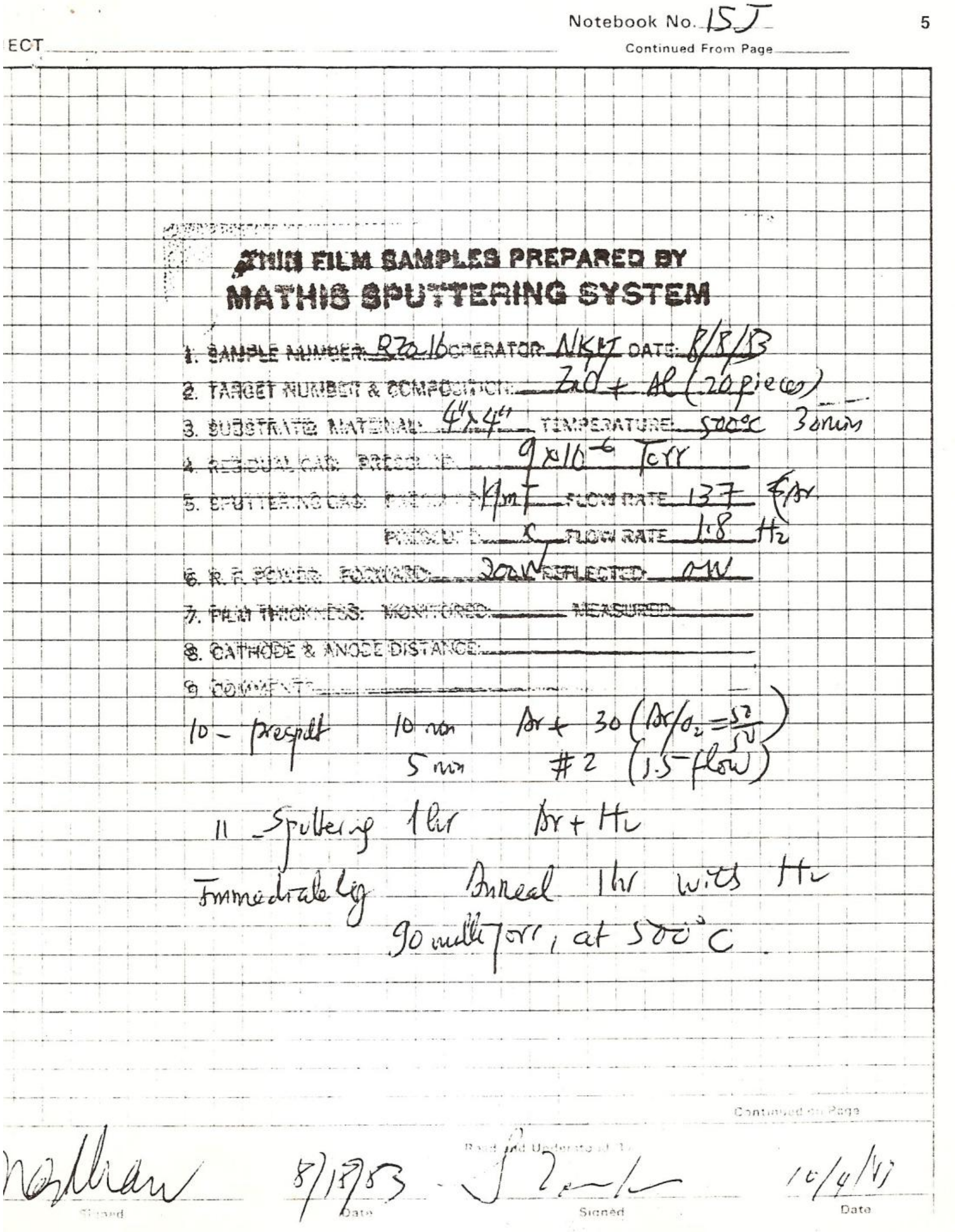


1. In a photoconductive device comprising a thin film silicon hydrogen alloy (TFS) photoconductor and front and back contacts, the improvement which comprises at least one of said front and back contacts being a transparent conductive layer consisting essentially of zinc oxide or zinc oxide containing hydrogen or zinc oxide containing a group III element or zinc oxide containing both hydrogen and a group III element, said transparent conductive layer havng a resistivity in the range of about 10^{-4} to 10^{-2} ohm-centimeter.

14. A photoconductive device comprising a photoconductive film capable of generating an electrical potential uppon exposure to light, transparent conductive layers at the top and bottom of said film, at least one of said transparent conductive layers consisting essentially of zinc oxide or zinc oxide containing hydrogen or zinc oxide containing a group III element or zinc oxide containing both hydrogen and a group III element, said at least one transparent conductive layer having a resistivity in the range of about 10^{-4} to 10^{-2} ohm-centimeter, and contacts connected to said transparent conductive layers for connecting the photoconductive device to an external circuit.

Fig. 5. The main claims of US patent 4,623,601

Experimental conditions were recorded in the laboratory notebook , as shown in Figs 6-10:



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Notebook No. 15J

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THIN FILM SAMPLES PREPARED BY
MATHIS SPUTTERING SYSTEM

1. SAMPLE NUMBER: RZo16 OPERATOR: NKT DATE: 8/8/83
2. TARGET NUMBER & COMPOSITION: ZnO + Al (20 pieces)
3. SUBSTRATE MATERIAL: 4"x4" TEMPERATURE: 500°C 30 min
4. RESIDUAL GAS PRESSURE: 9x10⁻⁶ Torr
5. SPUTTERING GAS: PRESSURE 4mT FLOW RATE 137 Ar
PRESSURE 5 FLOW RATE 1.8 H_2
6. R. F. POWER: FORWARD: 200W REFLECTED: 0W
7. FILM THICKNESS: MONITORED: MEASURED:
8. CATHODE & ANODE DISTANCE:
9. COMMENTS:

10 - presputt 10 min Ar + 30 (Ar/O_2 = 52/5)
5 min #2 (1.5 flow)

11 - Sputtering 1 hr Ar + H_2

Immediately Anneal 1 hr with H_2
90 milli Torr, at 500°C

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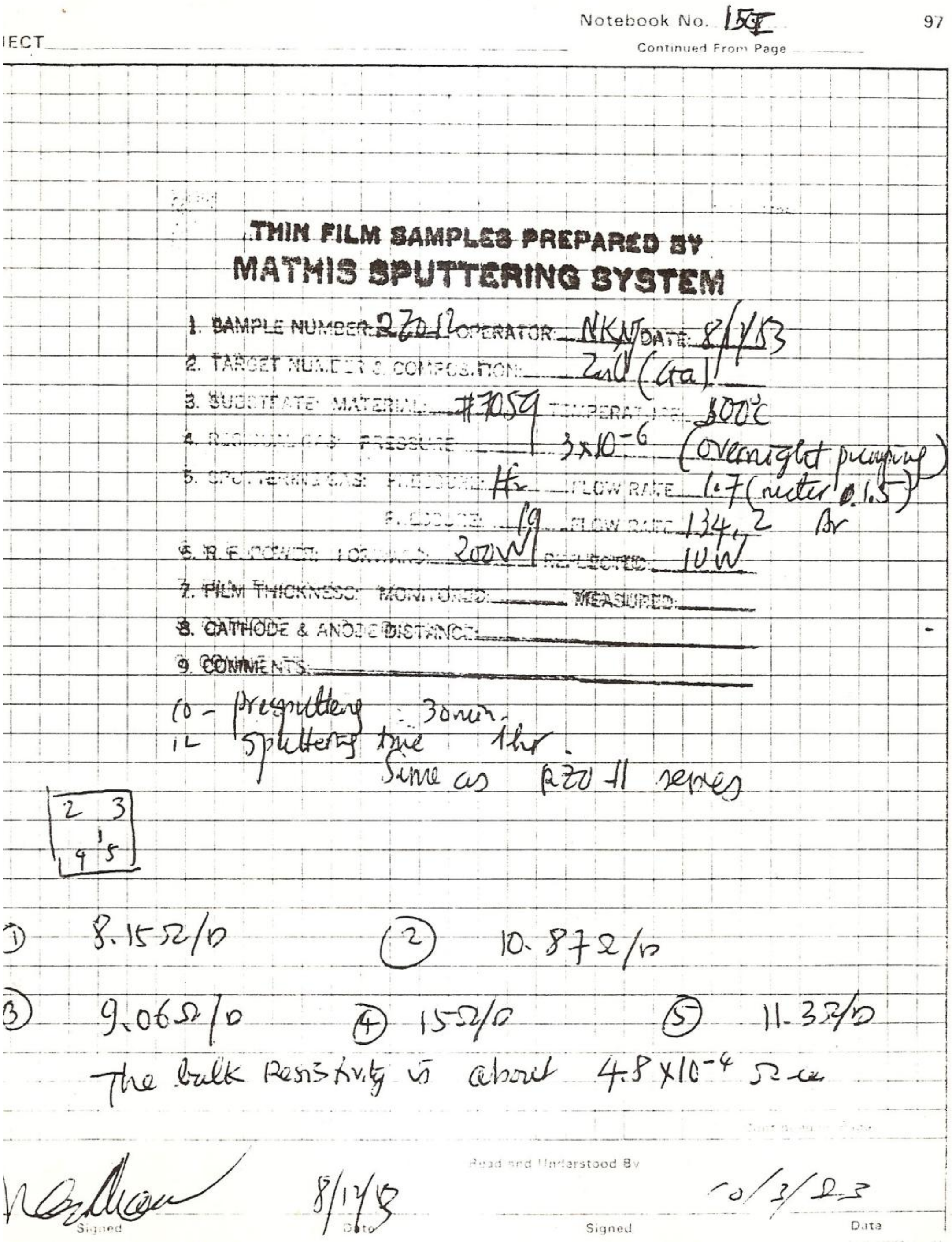
Nathan 8/18/83

Read and Understood by

10/4/83

Signed Date Signed Date

Fig. 6: Al-doped ZnO film was deposited, using a RF sputtering system with ZnO target and 20 pieces of aluminum by Nang Tran on August 18, 1983, witnessed and signed by Sarkiss Zoumalan on October 4, 1983. Page 5, Lab. notebook 15 J.



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Notebook No. 15C

97

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THIN FILM SAMPLES PREPARED BY
MATHIS SPUTTERING SYSTEM

1. SAMPLE NUMBER: RZO12 OPERATOR: NKN DATE: 8/12/83
2. TARGET NUMBER & COMPOSITION: ZnO (Ga)
3. SUBSTRATE MATERIAL: #7059 TEMPERATURE: 300°C
4. RESIDUAL GAS PRESSURE: 3×10^{-6} (overnight pumping)
5. SPUTTERING GAS: PRESSURE: H_2 FLOW RATE: 1.7 (meter 0.15)
PRESSURE: 19 FLOW RATE: 134.2 Ar
6. R.F. POWER: FORWARD: 200W REFLECTED: 10W
7. FILM THICKNESS: MONITORED: ______ MEASURED: ______
8. CATHODE & ANODE DISTANCE: ______
9. COMMENTS: ______

10 - Presputtering : 30 min.
11 Sputtering time 1hr.
Same as RZO 11 series

2 3
1
4 5

① 8.15 $\Omega/\square$ ② 10.87 $\Omega/\square$

③ 9.06 $\Omega/\square$ ④ 15 $\Omega/\square$ ⑤ 11.3 $\Omega/\square$

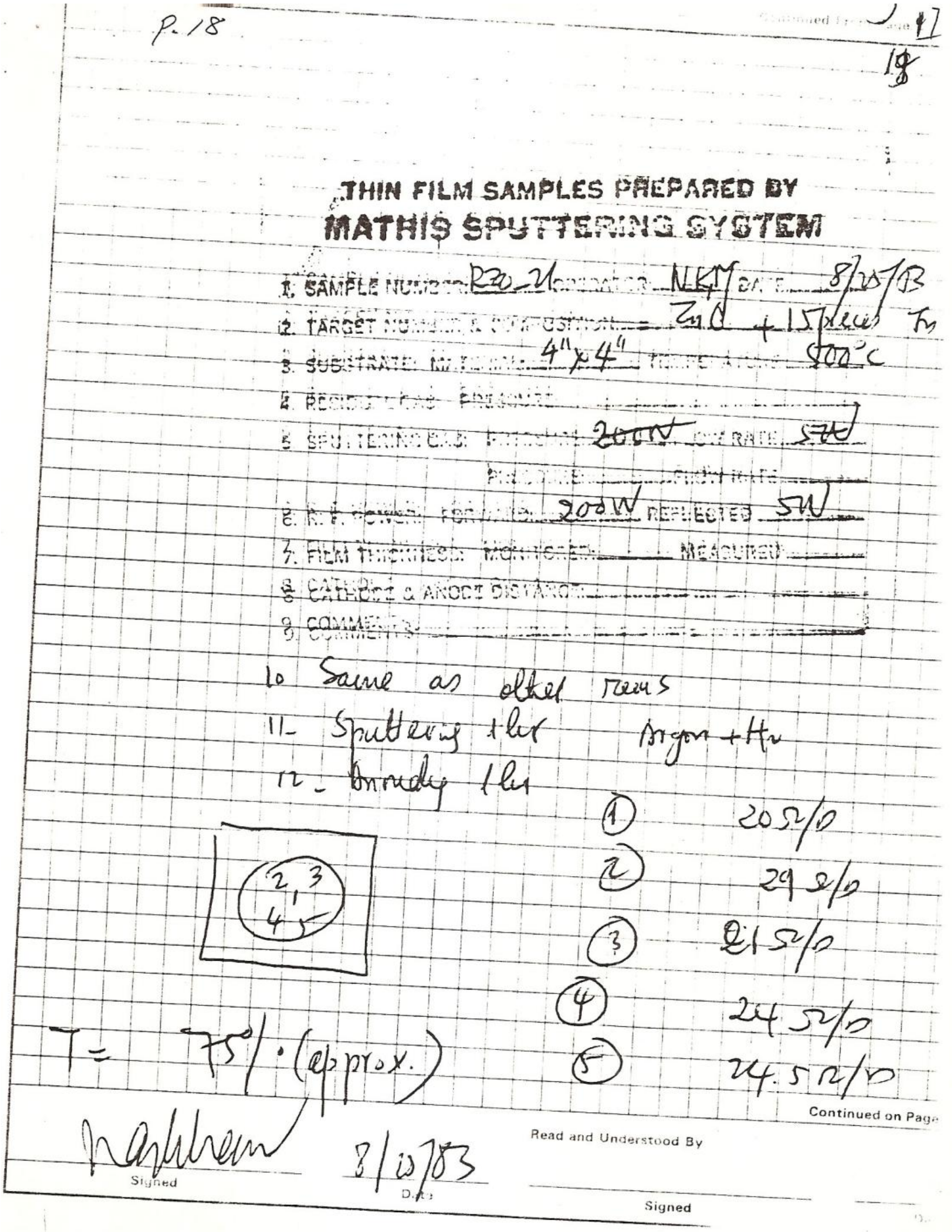
The bulk Resistivity is about 4.8×10^{-4} Ω-cm

Signed 8/12/83 Date

Read and Understood By

Signed 10/3/83 Date

Fig. 7: Ga- doped ZnO film was deposited, using a RF sputtering system with ZnO target and Ga pieces by Nang Tran on August 12, 1983, witnessed and signed by Sarkiss Zoumalan on October 3, 1983. Page 97, Lab. notebook 15 C.



P. 18

Continued From Page 17

18

THIN FILM SAMPLES PREPARED BY
MATHIS SPUTTERING SYSTEM

1. SAMPLE NUMBER R20-21 OPERATOR NKT DATE 8/28/83
2. TARGET NUMBER & COMPOSITION ZnO + 15 pieces In
3. SUBSTRATE: MATERIAL 4"x4" TEMPERATURE 300°C
4. RESIDUAL GAS PRESSURE
5. SPUTTERING GAS: PRESSURE ~~200W~~ FLOW RATE ~~5W~~
PRESSURE ___ FLOW RATE ___
6. R.F. POWER: FORWARD 200W REFLECTED 5W
7. FILM THICKNESS: MONITORED ___ MEASURED ___
8. CATHODE & ANODE DISTANCE ___
9. COMMENTS: ___

10 Same as other runs
11- Sputtering 1 hr Argon + H2
12 - Annealing 1 hr

①	20Ω/□
②	29Ω/□
③	21Ω/□
④	24.5Ω/□
⑤	24.5Ω/□

T = 75% (approx.)

8/28/83

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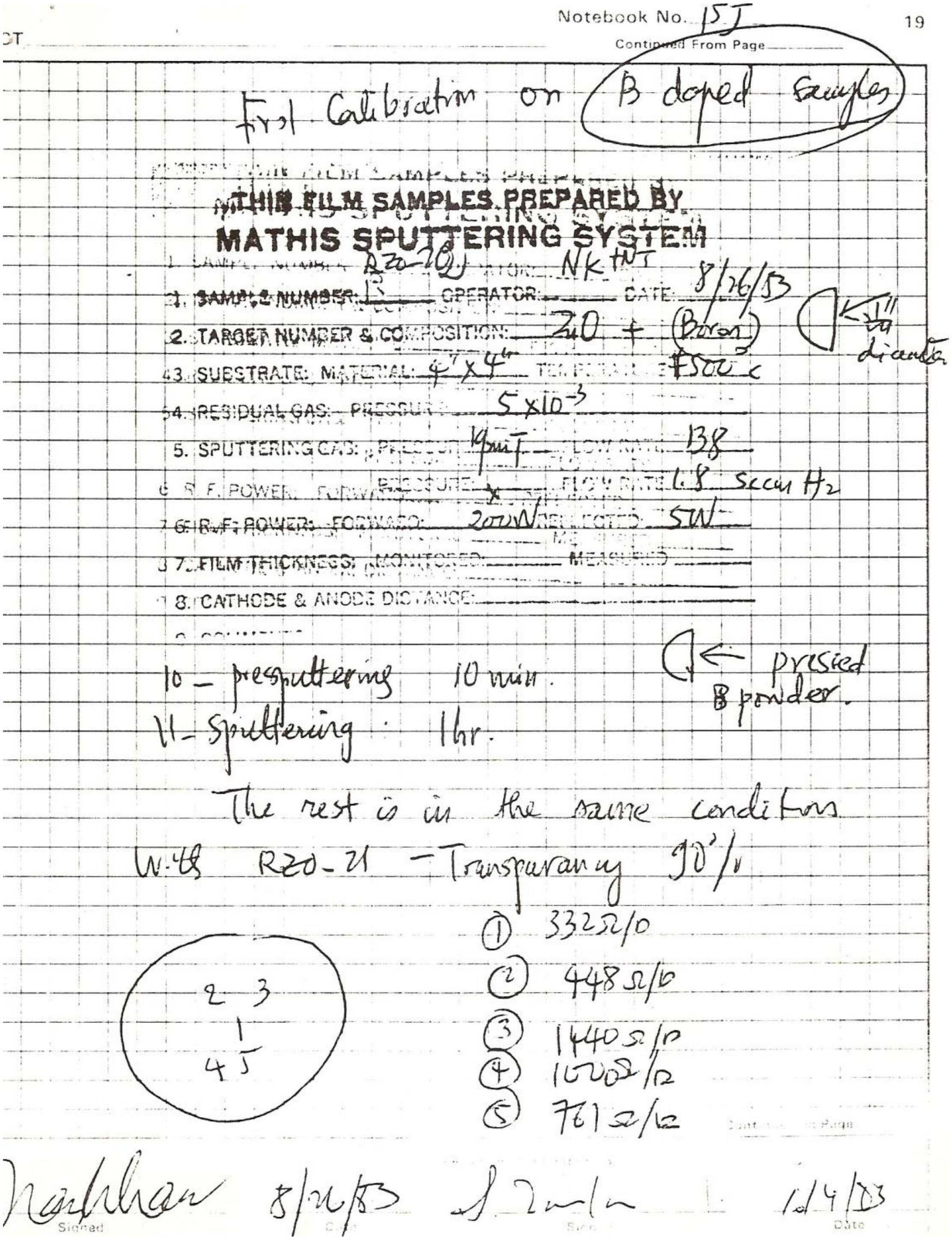
Read and Understood By

Signed

Date

Signed

Fig. 8: In- doped ZnO film was deposited, using a RF sputtering system with ZnO target and 15 In pieces by Nang Tran on August 28, 1983. Page 18, lab. notebook 15 J.



Notebook No. 15J   19

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First Calibration on B doped samples

THIS FILM SAMPLES PREPARED BY

MATHIS SPUTTERING SYSTEM

1. SAMPLE NUMBER: RZO-20 OPERATOR: NK TNT DATE: 8/26/83
2. TARGET NUMBER & COMPOSITION: ZO + (Boron)
3. SUBSTRATE: MATERIAL: 4"x4" TEMPERATURE: 500°c
4. RESIDUAL GAS: PRESSURE: 5×10^{-3}
5. SPUTTERING GAS: PRESSURE: 19mT FLOW RATE: 138

PRESSURE: x FLOW RATE: 1.8 sccm H_2

6. R.F. POWER: FORWARD: 200W REFLECTED: 5W
7. FILM THICKNESS: MONITORED: MEASURED:
8. CATHODE & ANODE DISTANCE:
9. COMMENTS

1/4" diameter

10 – presputtering 10 min.

← pressed B powder.

11 – sputtering : 1hr.

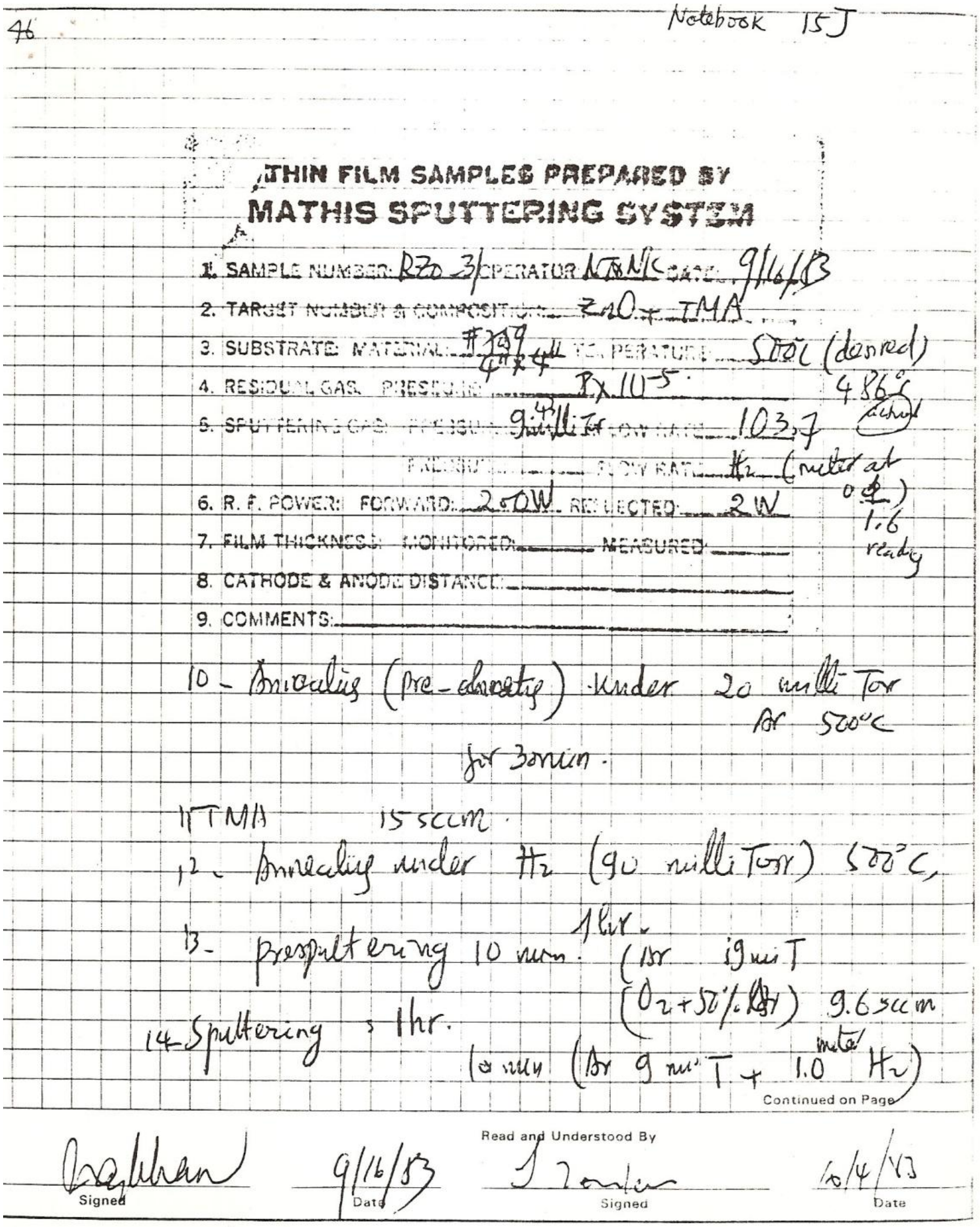
The rest is in the same conditions with RZO-21 – Transparency 90%

2 3
1
4 5

① 332Ω/□
② 448Ω/□
③ 1440Ω/□
④ 1020Ω/□
⑤ 761Ω/□

Signed 8/26/83 Date 10/4/83

Fig. 9: ZnO film doped with B was deposited, using a RF sputtering system with ZnO target and boron pieces by Nang Tran on August 26, 1983 and witnessed by Sarkiss Zoumalan on October 4, 1983. Page 19, lab. notebook 15 J.



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Notebook 15J

THIN FILM SAMPLES PREPARED BY
MATHIS SPUTTERING SYSTEM

1. SAMPLE NUMBER: RZO 3 OPERATOR NTN/C DATE: 9/16/83
2. TARGET NUMBER & COMPOSITION: ZnO + TMA
3. SUBSTRATE: MATERIAL: #7059 4"×4" TEMPERATURE: 500°C (desired) 486°C (actual)
4. RESIDUAL GAS PRESSURE: 8×10-5
5. SPUTTERING GAS: PRESSURE: 9.43 milliTorr FLOW RATE: 103.7
PRESSURE: ____ FLOW RATE: H_2 (meter at 0.4) 1.6 reading
6. R. F. POWER: FORWARD: 250W REFLECTED: 2W
7. FILM THICKNESS: MONITORED: ____ MEASURED: ____
8. CATHODE & ANODE DISTANCE: ____
9. COMMENTS: ____

10 - Annealing (pre-deposition) under 20 milli Torr Ar 500°C for 30min.

11 TMA 15 sccm.

12 - Annealing under H_2 (90 milliTorr) 500°C, 1hr.

13 - presputtering 10 min. (Ar 9 mT (O2+50% Ar) 9.6 sccm

14 - Sputtering 1hr. 10 mT (Ar 9 mT + 1.0 meter H_2)

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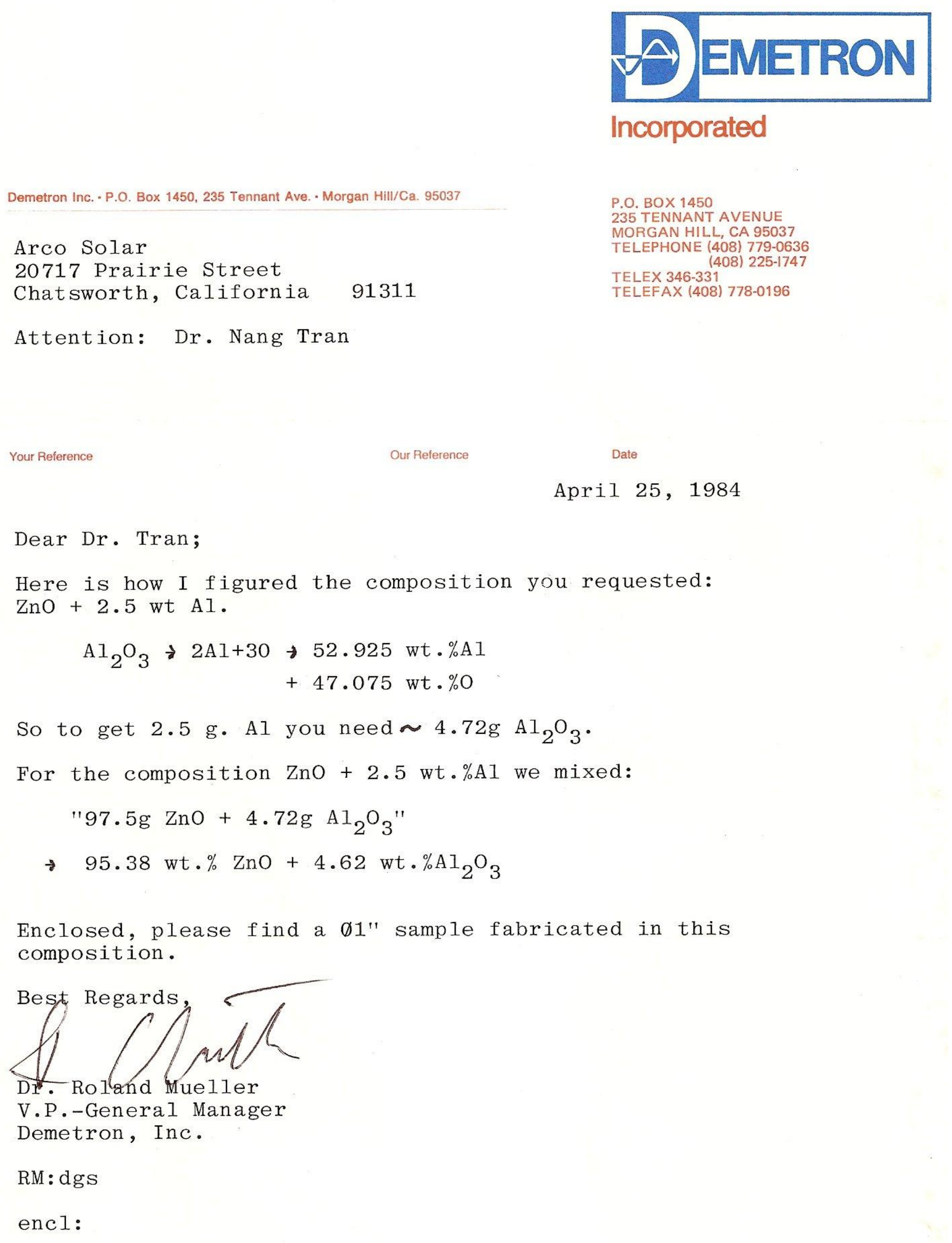
Read and Understood By

Signed 9/16/83 Date

Signed 10/4/83 Date

Fig. 10: Al- doped ZnO film was deposited, using a RF sputtering system with ZnO target and trimethyl aluminium (TMA) by Nang Tran on September 16, 1983 and witnessed by Sarkiss Zoumalan on October 4, 1983. Page 46, lab. notebook 15 J.

Once we were able to find the optimized composition of the dopants, sputtering ZnO targets premixed with group III elements were sent out to Demetron to have sputtering targets made, as shown in the correspondence between Dr. Rolland Mueller and me in Fig. 11.



DEMETRON
Incorporated

Demetron Inc. • P.O. Box 1450, 235 Tennant Ave. • Morgan Hill/Ca. 95037

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235 TENNANT AVENUE
MORGAN HILL, CA 95037
TELEPHONE (408) 779-0636
(408) 225-1747
TELEX 346-331
TELEFAX (408) 778-0196

Arco Solar
20717 Prairie Street
Chatsworth, California 91311

Attention: Dr. Nang Tran

Your Reference

Our Reference

Date

April 25, 1984

Dear Dr. Tran;

Here is how I figured the composition you requested:
ZnO + 2.5 wt Al.

$$Al_2O_3 \rightarrow 2Al+3O \rightarrow 52.925 \text{ wt.\%Al} + 47.075 \text{ wt.\%O}$$

So to get 2.5 g. Al you need ~ 4.72g Al_2O_3.

For the composition ZnO + 2.5 wt.%Al we mixed:

"97.5g ZnO + 4.72g Al_2O_3"

→ 95.38 wt.% ZnO + 4.62 wt.%Al_2O_3

Enclosed, please find a Ø1" sample fabricated in this composition.

Best Regards,

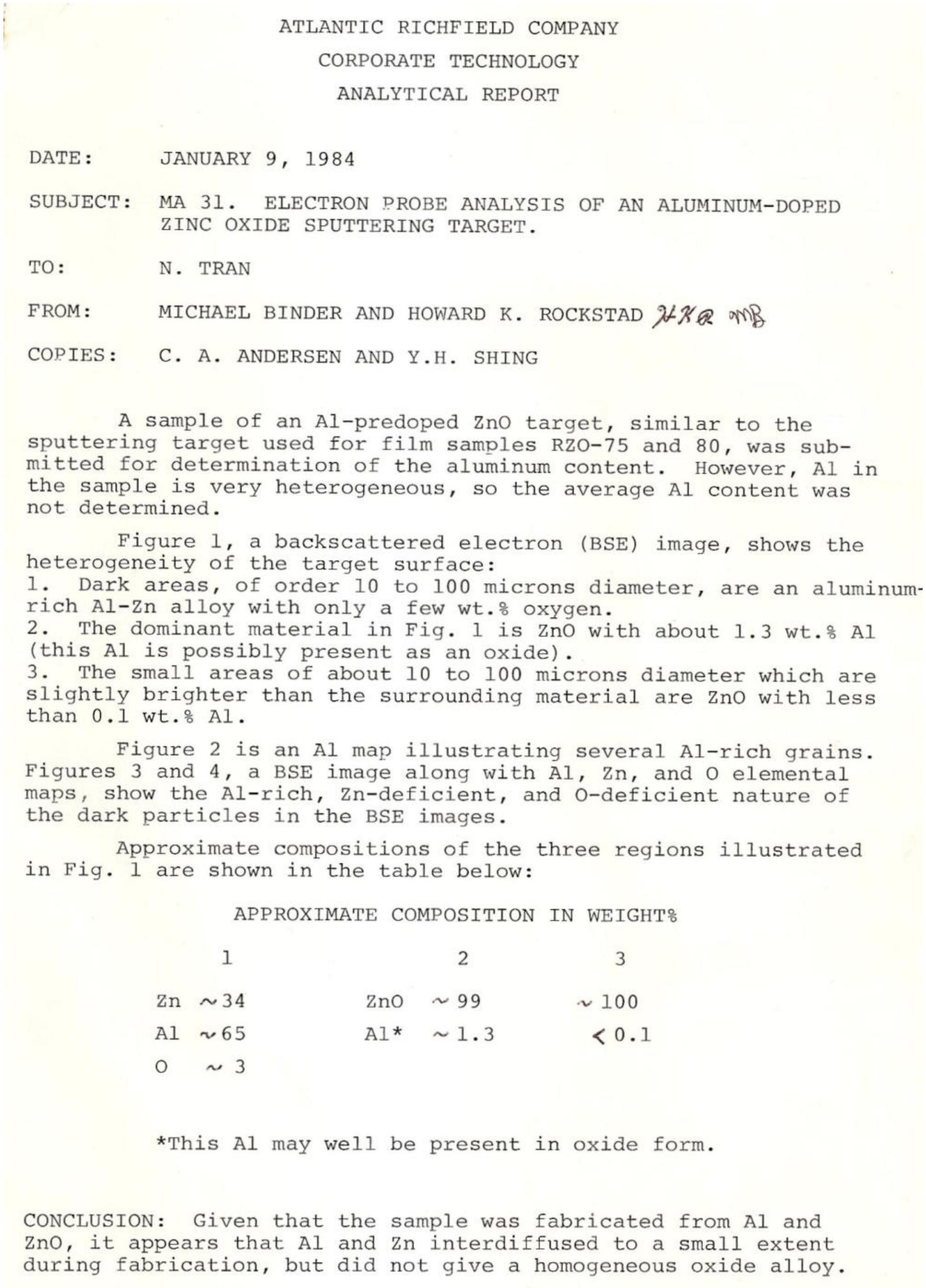
Dr. Roland Mueller
V.P.-General Manager
Demetron, Inc.

RM:dgs

encl:

Fig. 11: Correspondence between N. Tran and R. Mueller on the Al -doped ZnO sputtering target.

Electron probe analysis of the Demetron's Al-predoped ZnO sputtering target is shown in Figs. 12 and 13



ATLANTIC RICHFIELD COMPANY
CORPORATE TECHNOLOGY
ANALYTICAL REPORT

DATE: JANUARY 9, 1984

SUBJECT: MA 31. ELECTRON PROBE ANALYSIS OF AN ALUMINUM-DOPED ZINC OXIDE SPUTTERING TARGET.

TO: N. TRAN

FROM: MICHAEL BINDER AND HOWARD K. ROCKSTAD HKR MB

COPIES: C. A. ANDERSEN AND Y.H. SHING

A sample of an Al-predoped ZnO target, similar to the sputtering target used for film samples RZO-75 and 80, was submitted for determination of the aluminum content. However, Al in the sample is very heterogeneous, so the average Al content was not determined.

Figure 1, a backscattered electron (BSE) image, shows the heterogeneity of the target surface:
1. Dark areas, of order 10 to 100 microns diameter, are an aluminum-rich Al-Zn alloy with only a few wt.% oxygen.
2. The dominant material in Fig. 1 is ZnO with about 1.3 wt.% Al (this Al is possibly present as an oxide).
3. The small areas of about 10 to 100 microns diameter which are slightly brighter than the surrounding material are ZnO with less than 0.1 wt.% Al.

Figure 2 is an Al map illustrating several Al-rich grains. Figures 3 and 4, a BSE image along with Al, Zn, and O elemental maps, show the Al-rich, Zn-deficient, and O-deficient nature of the dark particles in the BSE images.

Approximate compositions of the three regions illustrated in Fig. 1 are shown in the table below:

APPROXIMATE COMPOSITION IN WEIGHT%

	1		2	3
Zn	~34	ZnO	~99	~100
Al	~65	Al*	~1.3	< 0.1
O	~ 3			

*This Al may well be present in oxide form.

CONCLUSION: Given that the sample was fabricated from Al and ZnO, it appears that Al and Zn interdiffused to a small extent during fabrication, but did not give a homogeneous oxide alloy.

Fig. 12 : Electron probe analysis of Demetron's Al-predoped ZnO sputtering target (from Howard Rockstad and Michael Binder, Jan. 9, 1984)

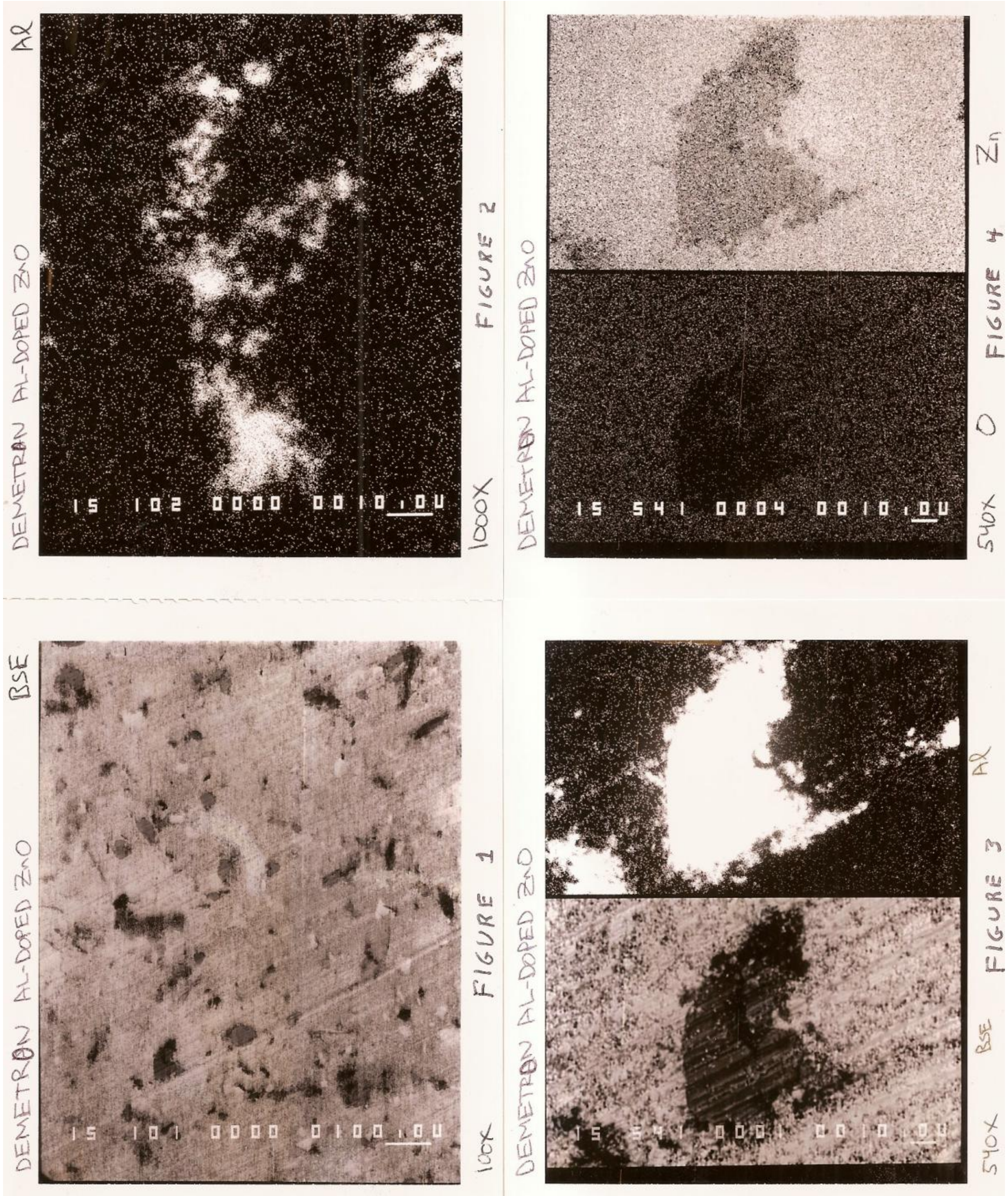


Fig. 13 : Back scattered electron images of Demetron's Al-predoped ZnO sputtering target (from Howard Rockstad and Michael Binder, Jan. 9, 1984)

SIMS data of sputtered ZnO films with different dopants Al and H are shown in Figs. 14-15.

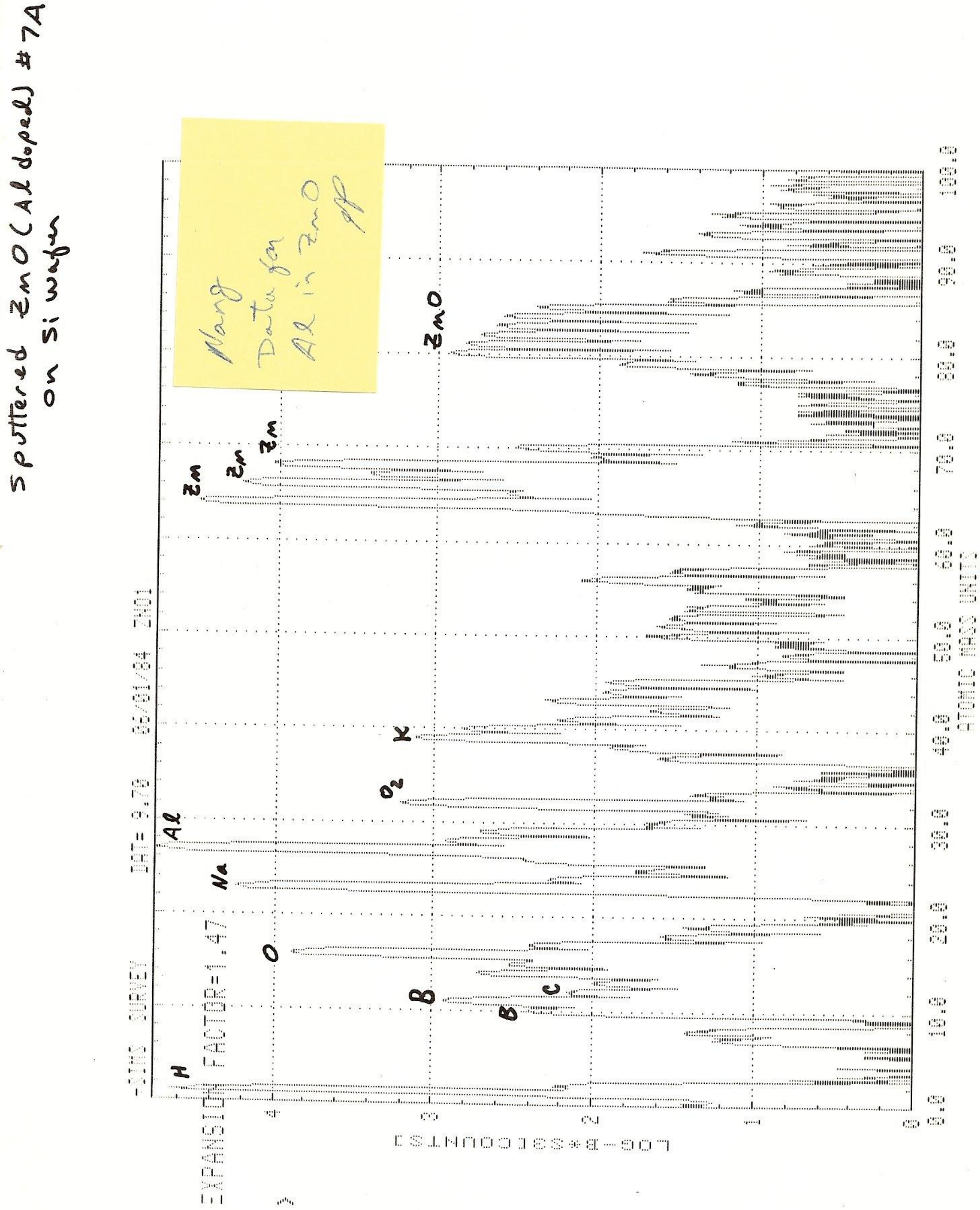


Fig. 14: SIMS data of sputtered Al- doped ZnO film on a silicon substrate.

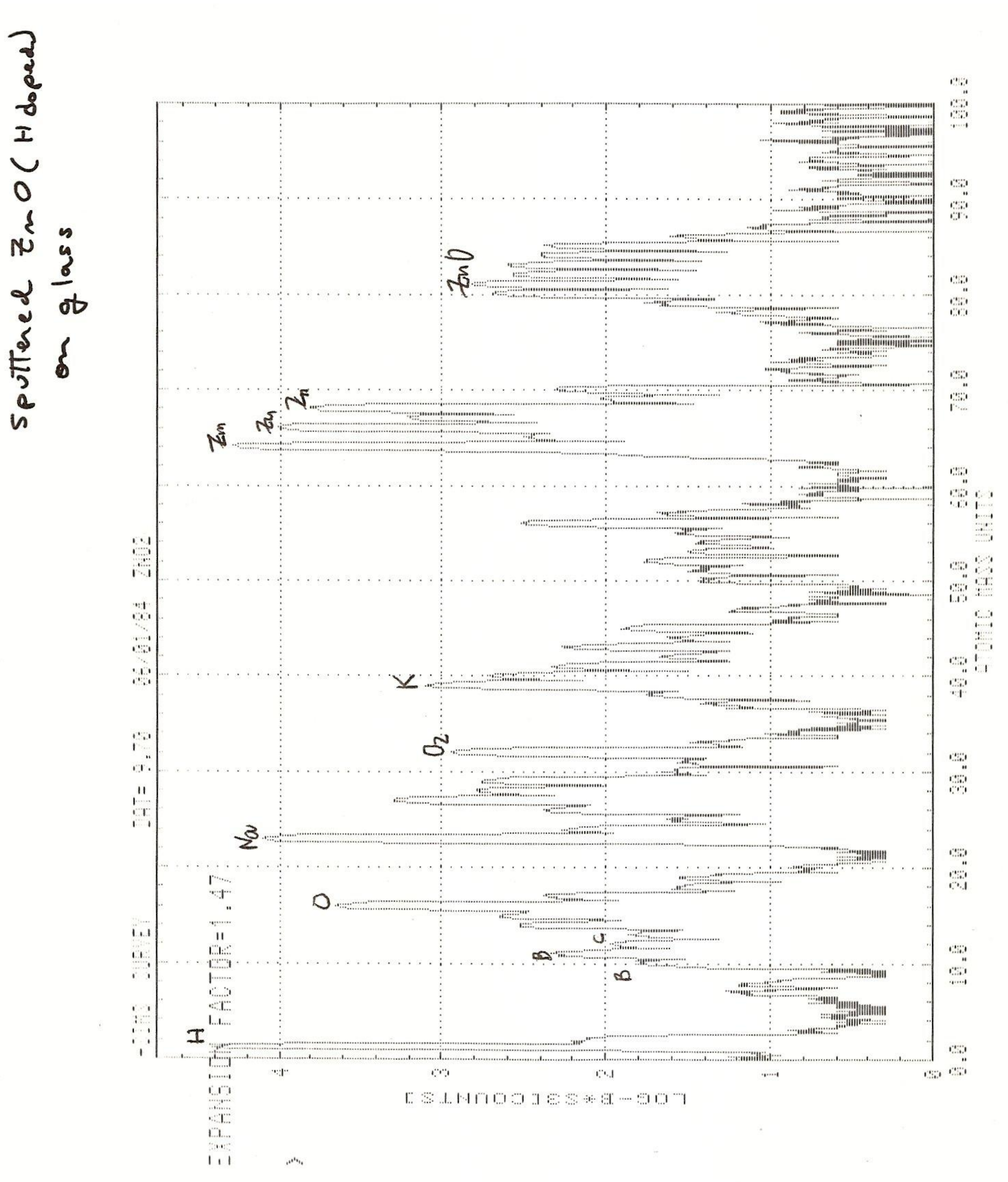


Fig.

Figure15: SIMS data of sputtered H- doped ZnO film on a glass substrate.

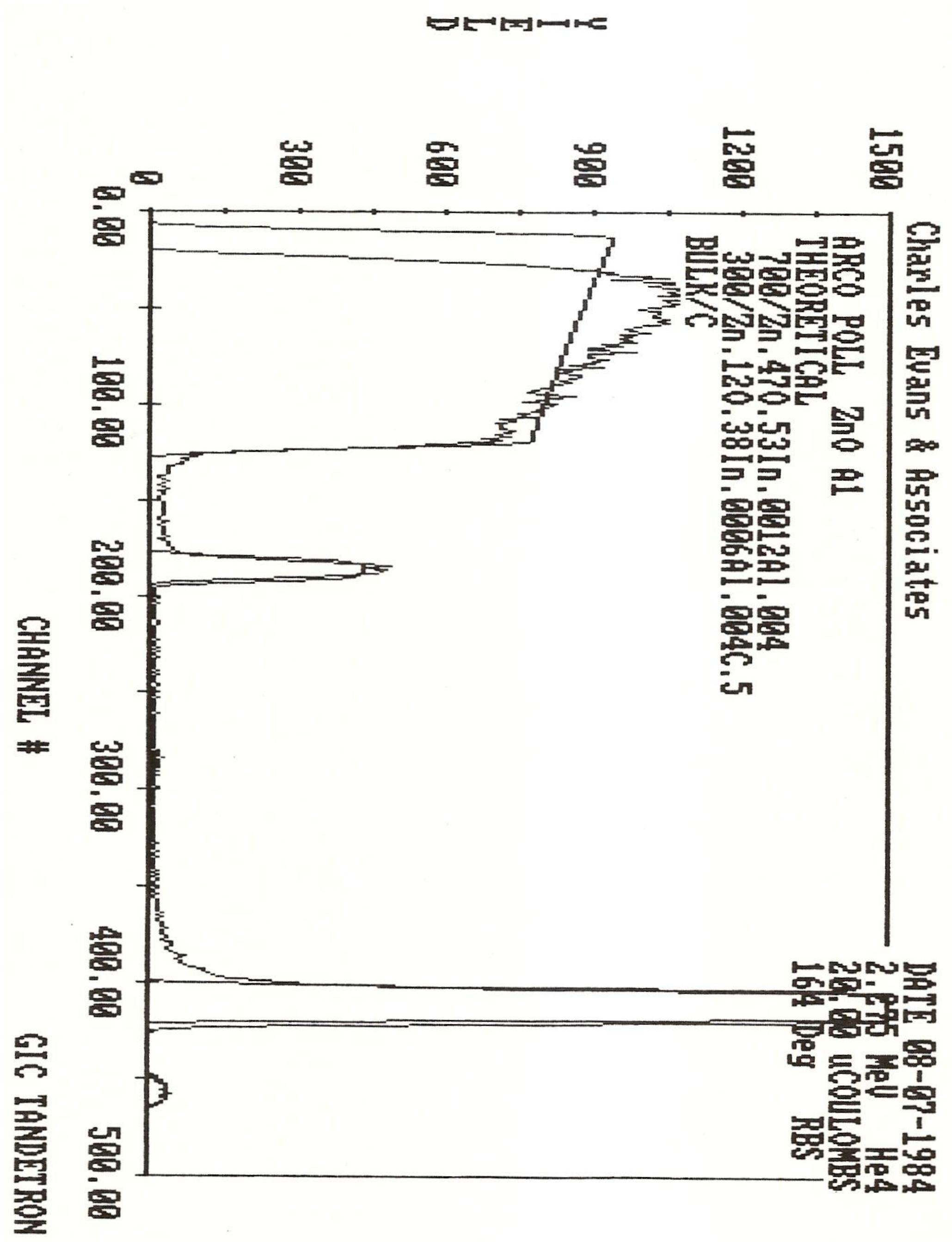
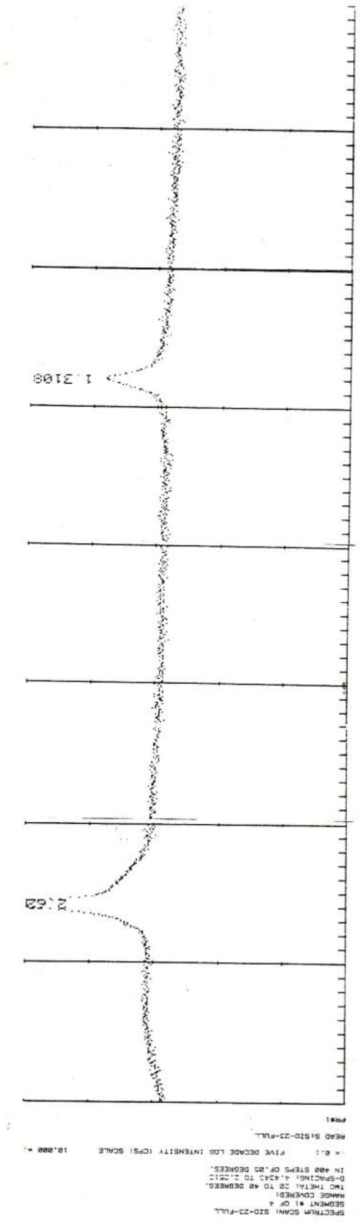


Fig. 16: Rutherford Backscattering Analysis of sputtered Al- doped ZnO (data from Charles Evans & Associates, via Garry Pollock, August 07, 1984)

Figs. 17-19 show XRD data of ZnO films doped with Al, Ga and hydrogen.



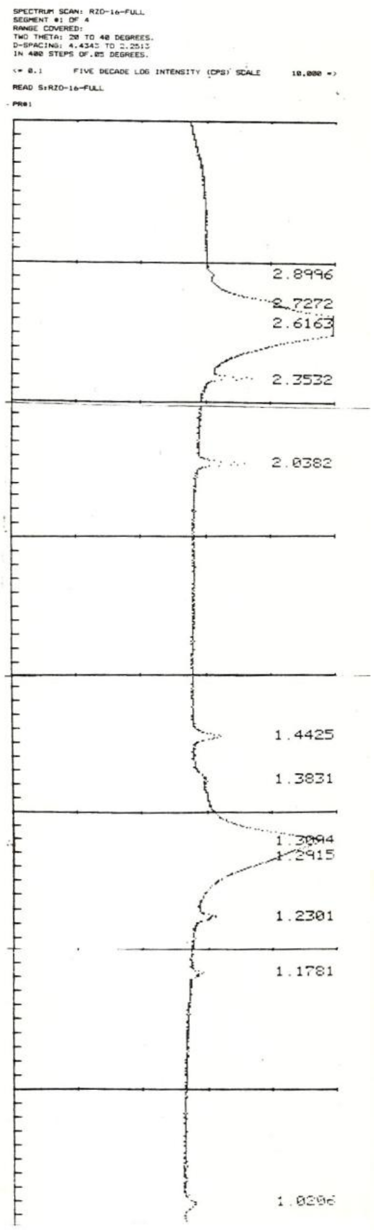
```
SZO-23-FULL***H DOPED ZNO FILM 3800 ANGS                    2 NOV 1983

SUMMARY OF IDENTIFIED PEAKS

TWO-THETA    D-SPACING    NET INTENSITY    REL. HEIGHT

34.18        2.62          28436            100
71.95        1.3108        568.72           2
```

Fig. 17: XRD data of sputtered H-doped ZnO film (From Sarkiss Zoumalan, Nov. 2, 1983)

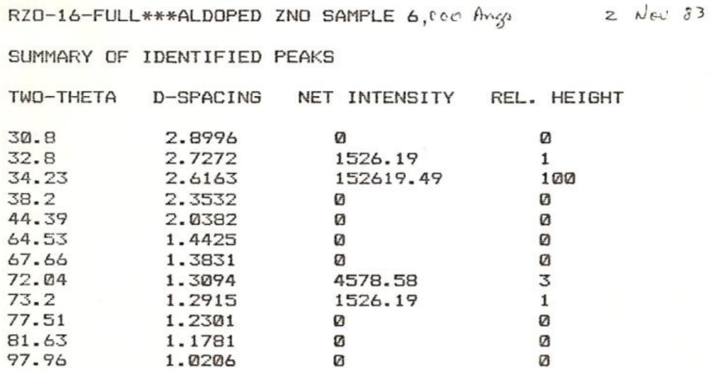


```
SPECTRUM SCAN: RZO-16-FULL
SEGMENT #1 OF 4
RANGE COVERED:
TWO THETA: 20 TO 40 DEGREES.
D-SPACING: 4.4343 TO 2.2513
IN 400 STEPS OF.05 DEGREES.

<= 0.1        FIVE DECADE LOG INTENSITY (CPS) SCALE        10,000 =>

READ S:RZO-16-FULL

- PR#1
```



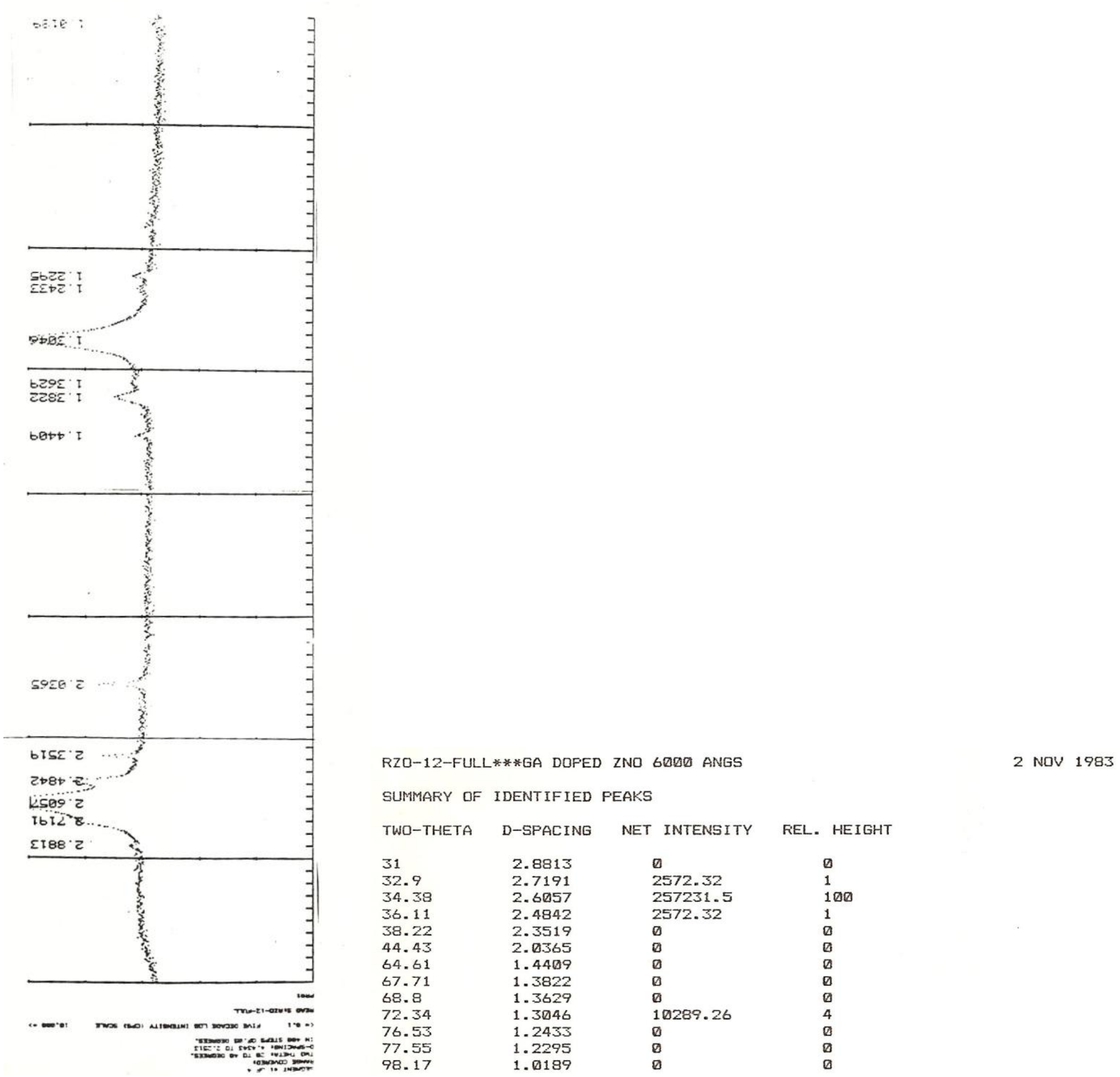
```
RZO-16-FULL***ALDOPED ZNO SAMPLE 6,000 Angs          2 Nov 83

SUMMARY OF IDENTIFIED PEAKS

TWO-THETA    D-SPACING    NET INTENSITY    REL. HEIGHT

30.8          2.8996         0               0
32.8          2.7272         1526.19         1
34.23         2.6163         152619.49       100
38.2          2.3532         0               0
44.39         2.0382         0               0
64.53         1.4425         0               0
67.66         1.3831         0               0
72.04         1.3094         4578.58         3
73.2          1.2915         1526.19         1
77.51         1.2301         0               0
81.63         1.1781         0               0
97.96         1.0206         0               0
```

Fig. 18: XRD data of sputtered Al- doped ZnO – 7,000 A (From Sarkiss Zoumalan, Nov. 2, 1983)



```
RZO-12-FULL***GA DOPED ZNO 6000 ANGS                              2 NOV 1983

SUMMARY OF IDENTIFIED PEAKS

TWO-THETA   D-SPACING   NET INTENSITY   REL. HEIGHT

31          2.8813        0                0
32.9        2.7191        2572.32          1
34.38       2.6057        257231.5         100
36.11       2.4842        2572.32          1
38.22       2.3519        0                0
44.43       2.0365        0                0
64.61       1.4409        0                0
67.71       1.3822        0                0
68.8        1.3629        0                0
72.34       1.3046        10289.26         4
76.53       1.2433        0                0
77.55       1.2295        0                0
98.17       1.0189        0                0
```

Fig. 19: XRD data of sputtered Ga- doped ZnO film (From Sarkiss Zoumalan, Nov. 2, 1983)

Figs. 20-23 summarizes properties of sputtered Al- doped ZnO (AZO), gallium- doped (GZO) and indium- doped ZnO (IZO) films.

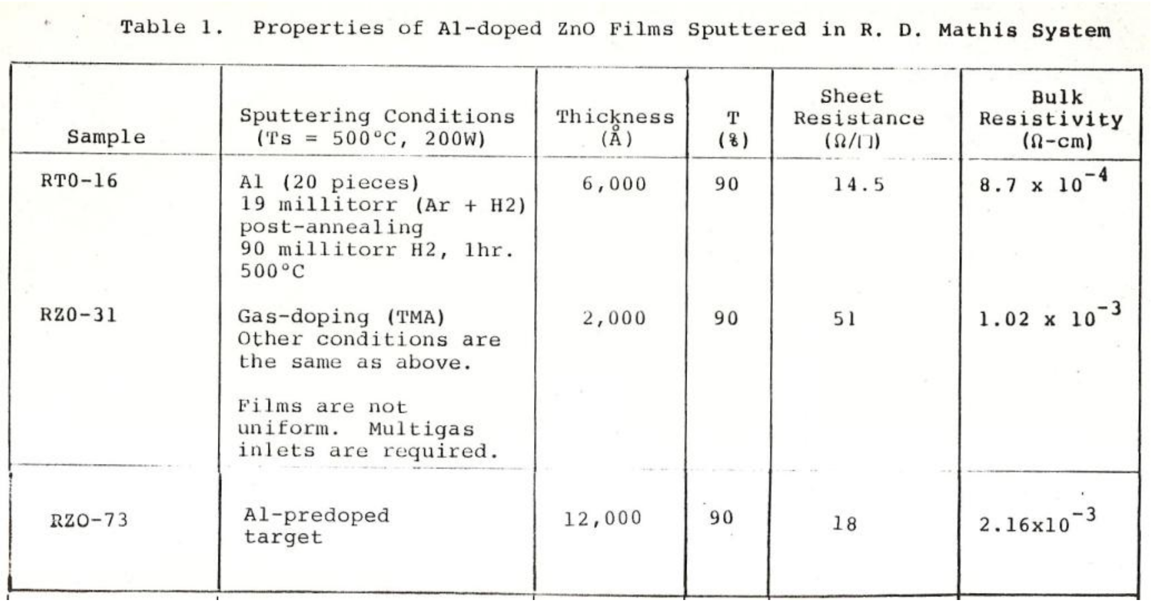


Table 1. Properties of Al-doped ZnO Films Sputtered in R. D. Mathis System

Sample	Sputtering Conditions (Ts = 500°C, 200W)	Thickness (Å)	T (%)	Sheet Resistance (Ω/□)	Bulk Resistivity (Ω-cm)
RTO-16	Al (20 pieces) 19 millitorr (Ar + H2) post-annealing 90 millitorr H2, 1hr. 500°C	6,000	90	14.5	8.7×10^{-4}
RZO-31	Gas-doping (TMA) Other conditions are the same as above. Films are not uniform. Multigas inlets are required.	2,000	90	51	1.02×10^{-3}
RZO-73	Al-predoped target	12,000	90	18	2.16×10^{-3}

Fig. 20: Properties of Al-doped ZnO films

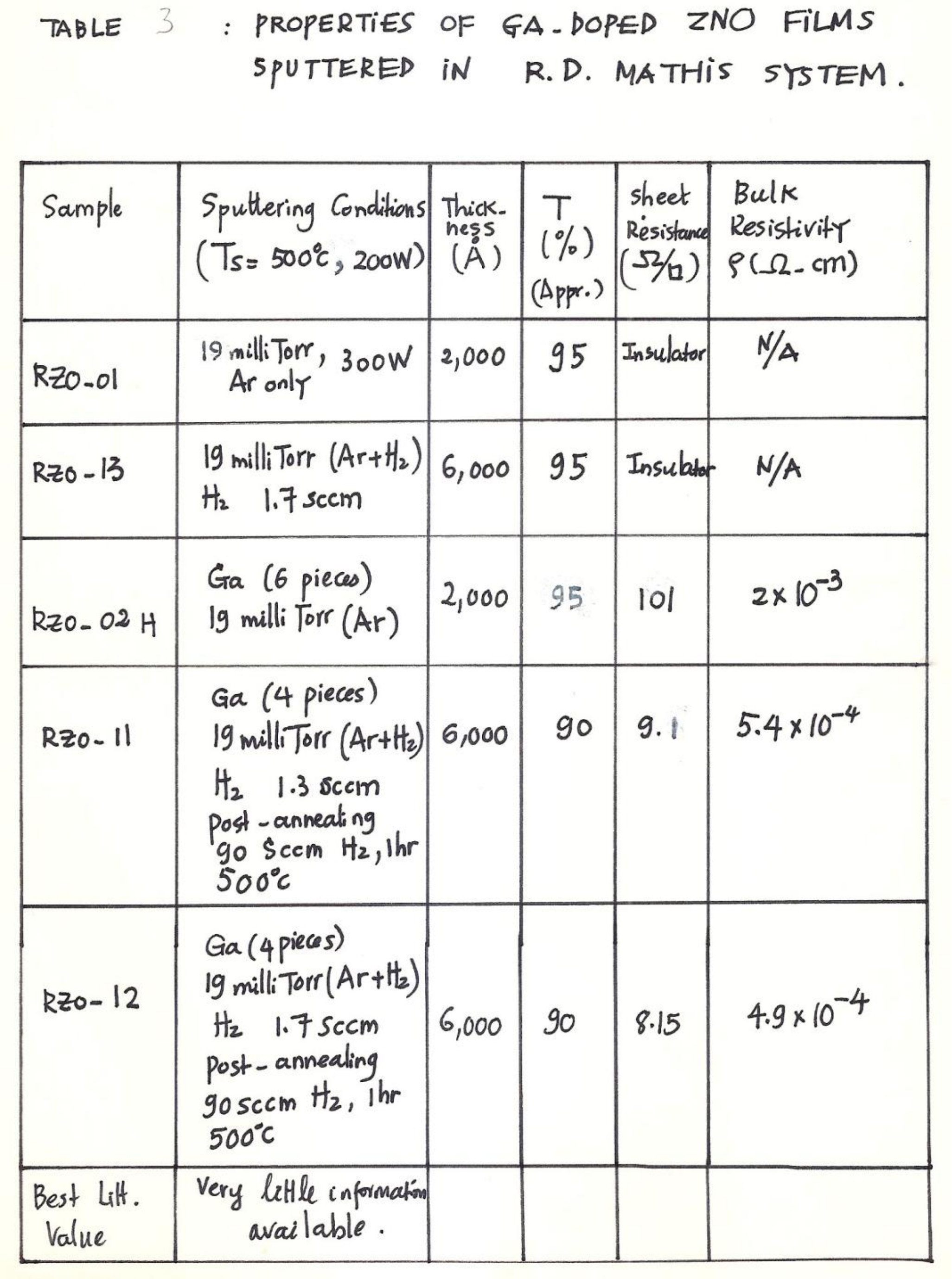


TABLE 3 : PROPERTIES OF GA-DOPED ZNO FILMS
SPUTTERED IN R.D. MATHIS SYSTEM.

Sample	Sputtering Conditions (T_S= 500°C, 200W)	Thickness (Å)	T (%) (Appr.)	Sheet Resistance (Ω/□)	Bulk Resistivity ρ (Ω-cm)
RZO-01	19 milliTorr, 300W Ar only	2,000	95	Insulator	N/A
RZO-13	19 milliTorr ($Ar+H_2$) H_2 1.7 sccm	6,000	95	Insulator	N/A
RZO-02 H	Ga (6 pieces) 19 milli Torr (Ar)	2,000	95	101	2×10^{-3}
RZO-11	Ga (4 pieces) 19 milliTorr ($Ar+H_2$) H_2 1.3 sccm post-annealing 90 sccm H_2, 1hr 500°C	6,000	90	9.1	5.4×10^{-4}
RZO-12	Ga (4 pieces) 19 milliTorr ($Ar+H_2$) H_2 1.7 sccm post-annealing 90 sccm H_2, 1hr 500°C	6,000	90	8.15	4.9×10^{-4}
Best Litt. Value	Very little information available.				

Fig. 21: Properties of Ga-doped ZnO films

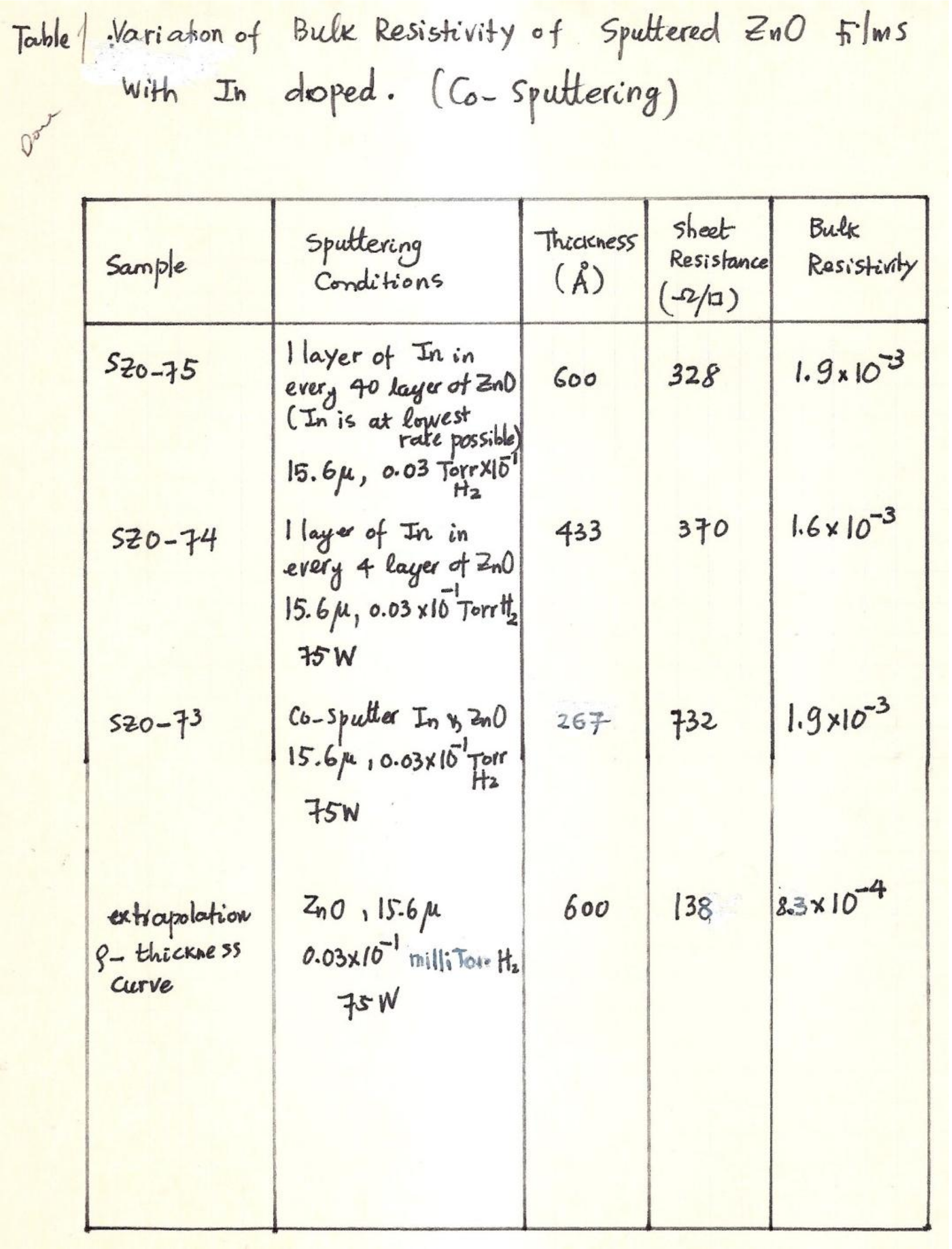
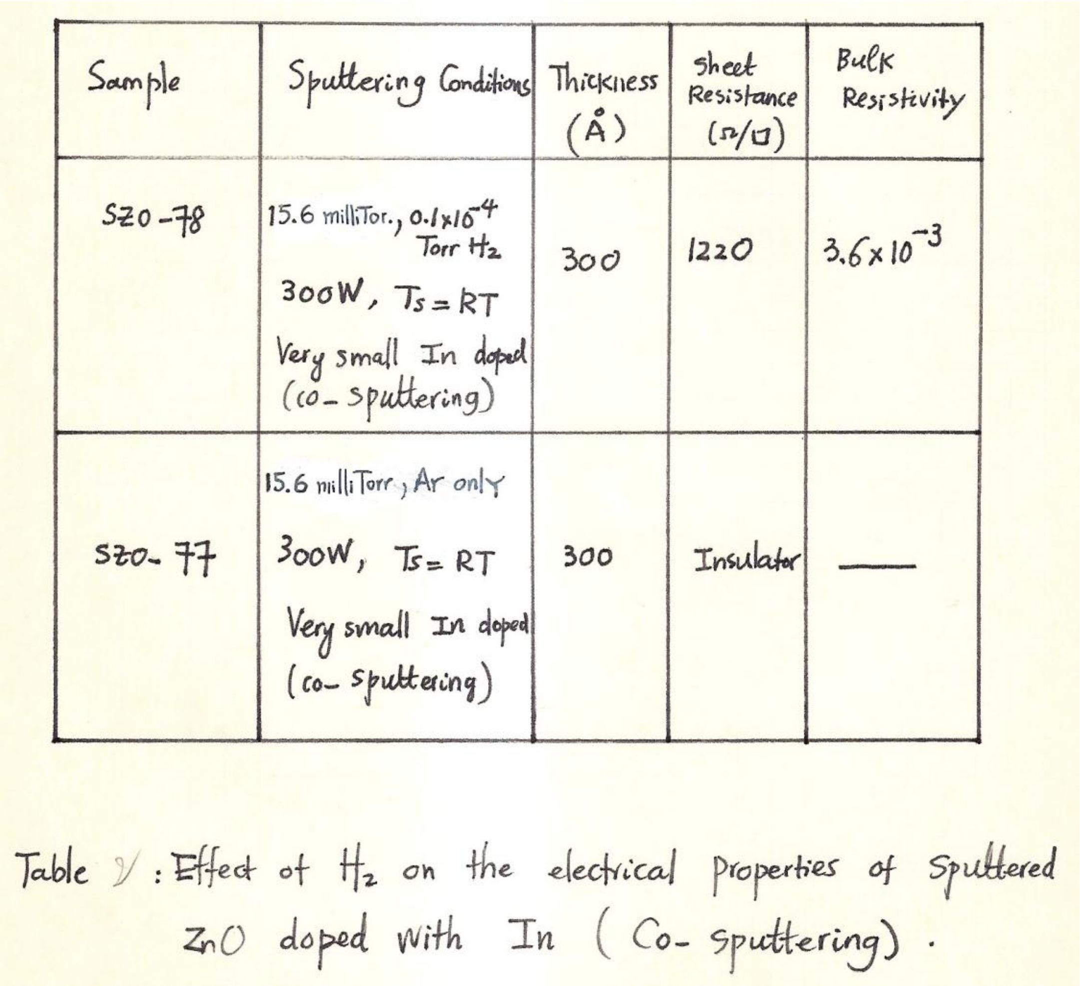


Table 1 Variation of Bulk Resistivity of Sputtered ZnO films With In doped. (Co-Sputtering)

Done

Sample	Sputtering Conditions	Thickness (Å)	Sheet Resistance (Ω/□)	Bulk Resistivity
SZO-75	1 layer of In in every 40 layer of ZnO (In is at lowest rate possible) 15.6μ, 0.03 Torr $\times 10^{-1}$ H_2	600	328	1.9×10^{-3}
SZO-74	1 layer of In in every 4 layer of ZnO 15.6μ, 0.03×10^{-1} Torr H_2 75W	433	370	1.6×10^{-3}
SZO-73	Co-sputter In & ZnO 15.6μ, 0.03×10^{-1} Torr H_2 75W	267	732	1.9×10^{-3}
extrapolation ρ- thickness curve	ZnO, 15.6μ 0.03×10^{-1} milliTorr H_2 75W	600	138	8.3×10^{-4}

Fig. 22: Properties of In-doped ZnO films



Sample	Sputtering Conditions	Thickness (Å)	Sheet Resistance (Ω/□)	Bulk Resistivity
SZO-78	15.6 milliTor., 0.1×10^{-4} Torr H_2 300W, T_s = RT Very small In doped (co-sputtering)	300	1220	3.6×10^{-3}
SZO-77	15.6 milliTorr, Ar only 300W, T_s = RT Very small In doped (co-sputtering)	300	Insulator	—

Table V : Effect of H_2 on the electrical properties of Sputtered ZnO doped with In (Co-sputtering) .

Fig. 23: Properties of In-doped ZnO films (continued)

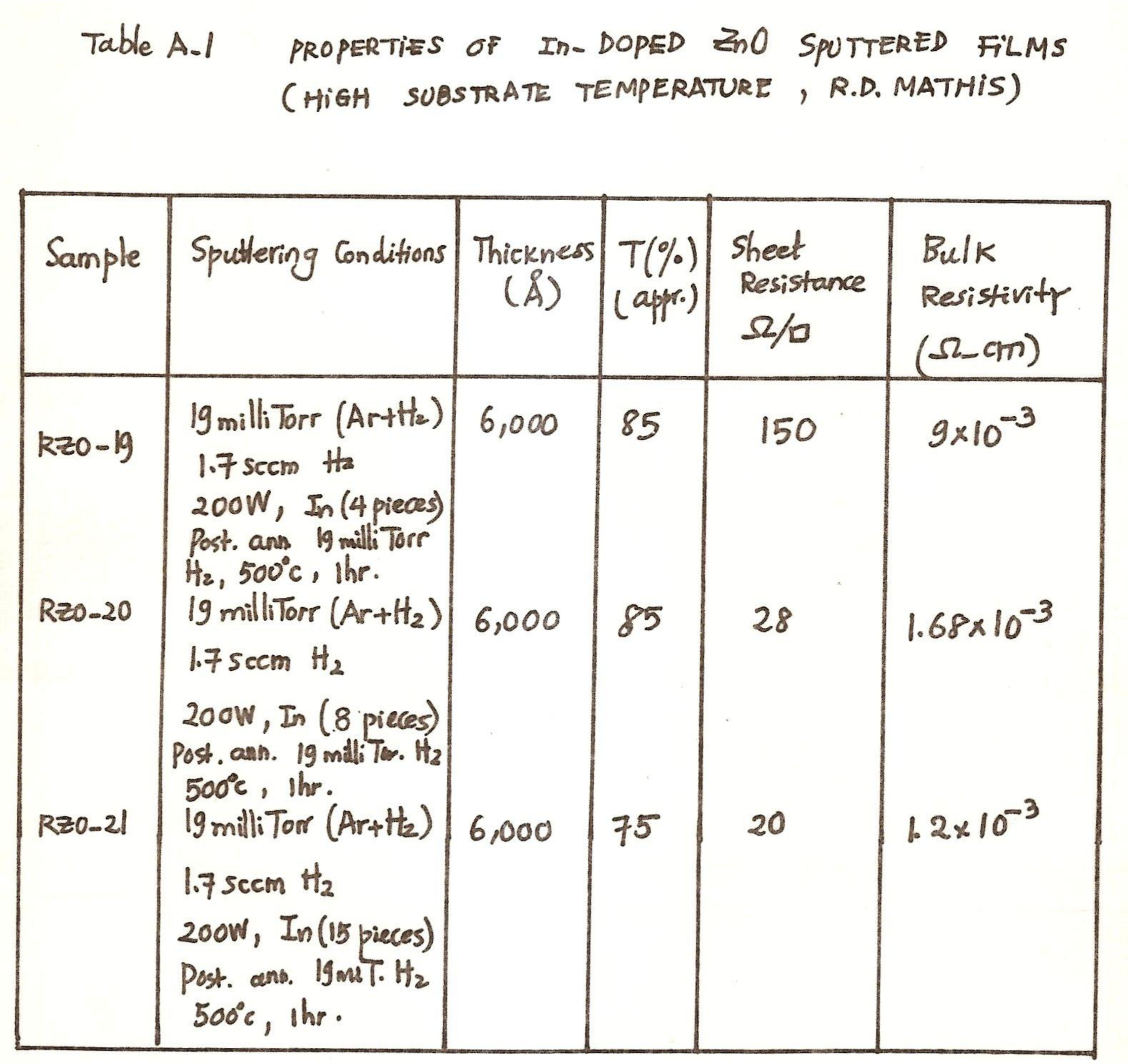


Table A-1 PROPERTIES OF In-DOPED ZnO SPUTTERED FILMS (HIGH SUBSTRATE TEMPERATURE, R.D. MATHIS)

Sample	Sputtering Conditions	Thickness (Å)	T(%) (appr.)	Sheet Resistance Ω/□	Bulk Resistivity (Ω-cm)
RZO-19	19 milliTorr ($Ar+H_2$) 1.7 sccm H_2 200W, In (4 pieces) Post. ann. 19 milliTorr H_2, 500°c, 1hr.	6,000	85	150	9×10^{-3}
RZO-20	19 milliTorr ($Ar+H_2$) 1.7 sccm H_2 200W, In (8 pieces) Post. ann. 19 milliTor. H_2 500°c, 1hr.	6,000	85	28	1.68×10^{-3}
RZO-21	19 milliTorr ($Ar+H_2$) 1.7 sccm H_2 200W, In (15 pieces) Post. ann. 19mT. H_2 500°c, 1hr.	6,000	75	20	1.2×10^{-3}

Fig. 24: Properties of In-doped ZnO films (continued)

Transmittance, reflectance and absorption of undoped ZnO films and ZnO films doped with group III elements and hydrogen are shown in Figs. 25- 32.

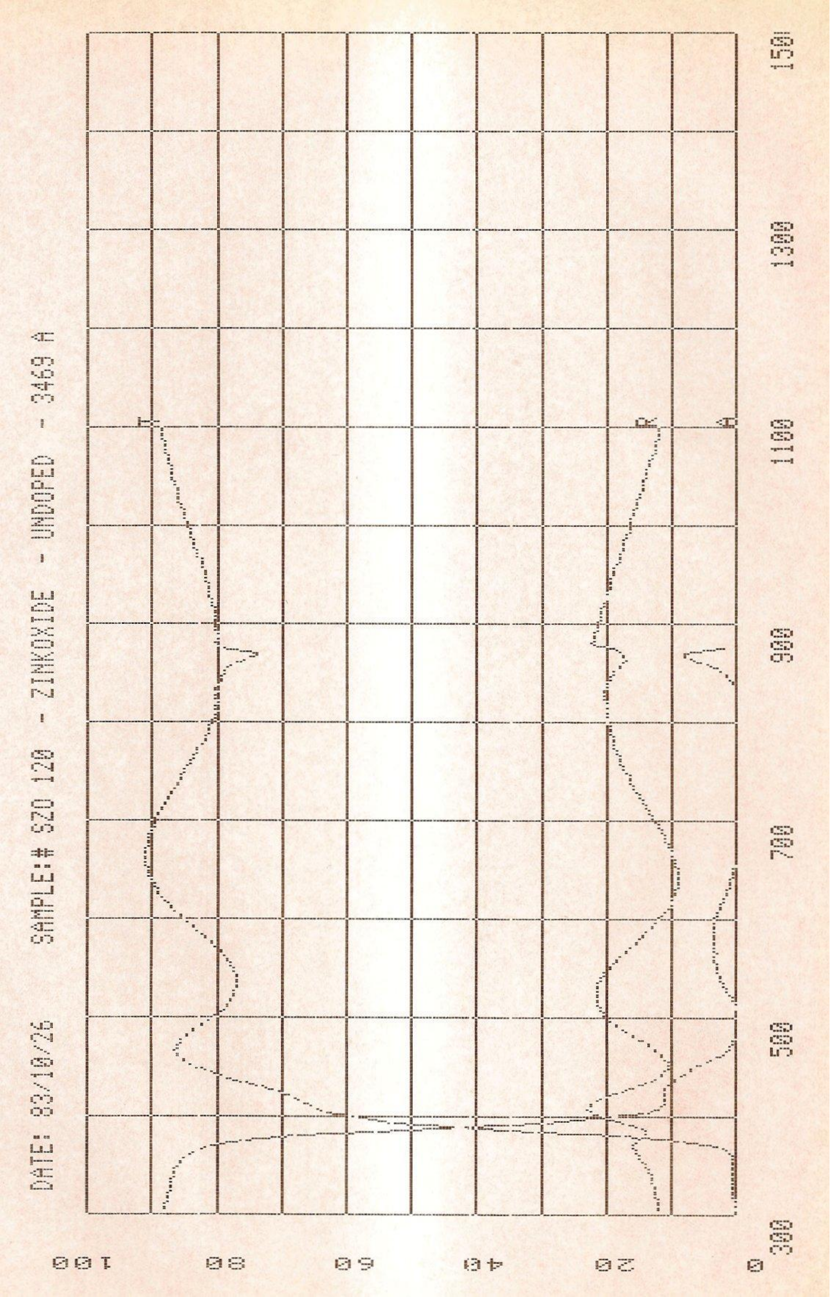


Fig. 25. Transmittance, reflectance and absorption of undoped sputtered ZnO films (thickness= 3,469 A)

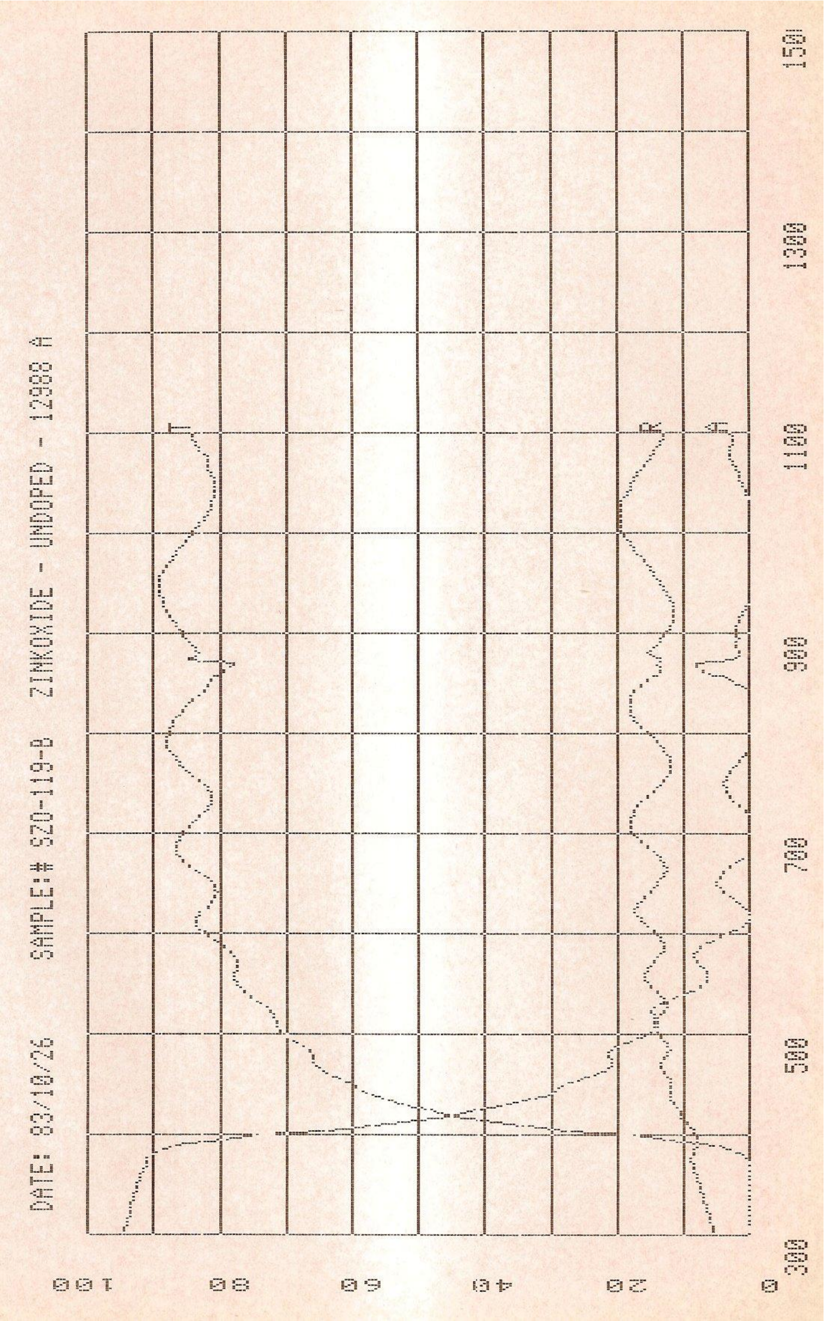


Fig. 26. Transmittance, reflectance and absorption of undoped sputtered ZnO films (thickness= 12,998 A)

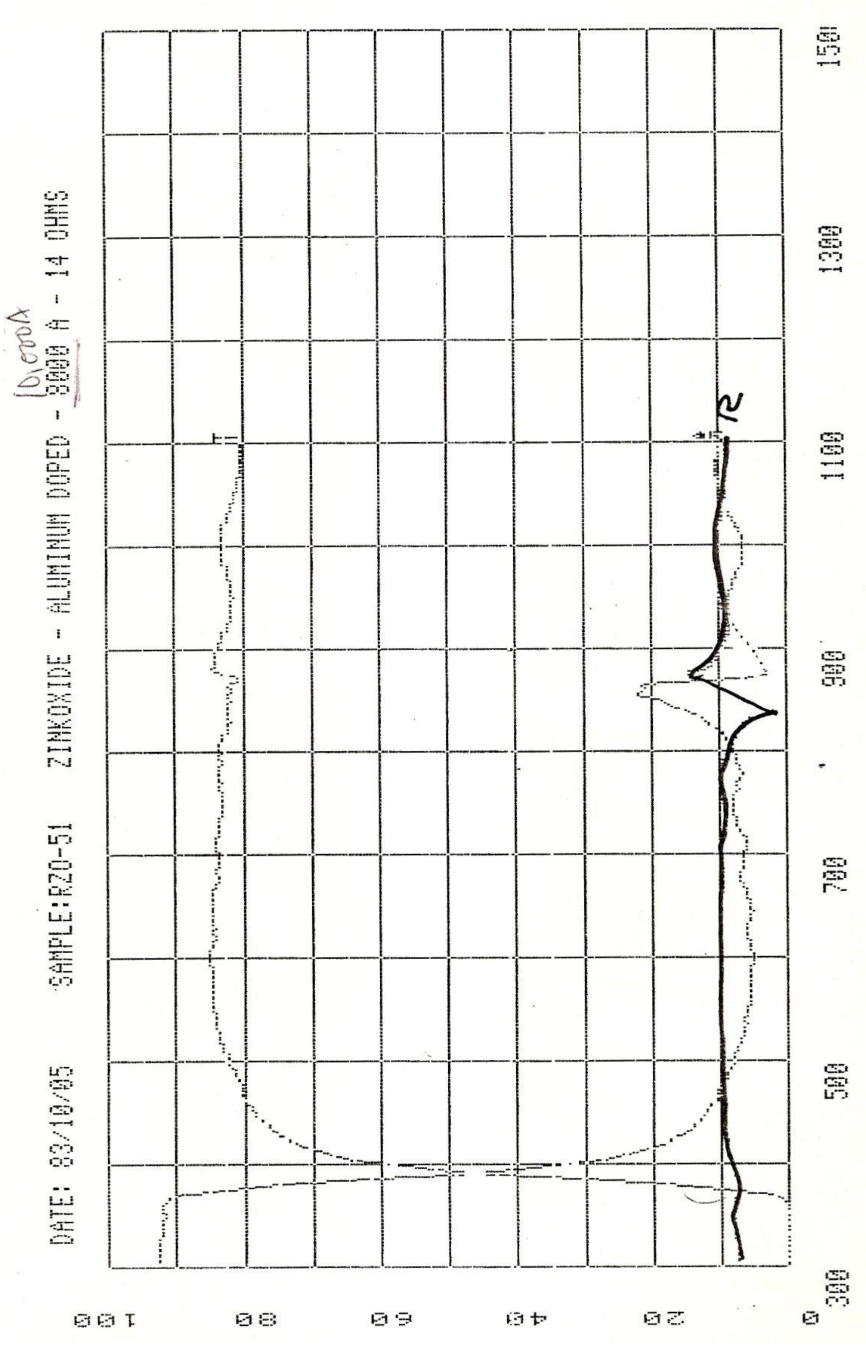


Fig. 27. Transmittance, reflectance and absorption of sputtered Al-doped ZnO films (thickness= 10,000 A)

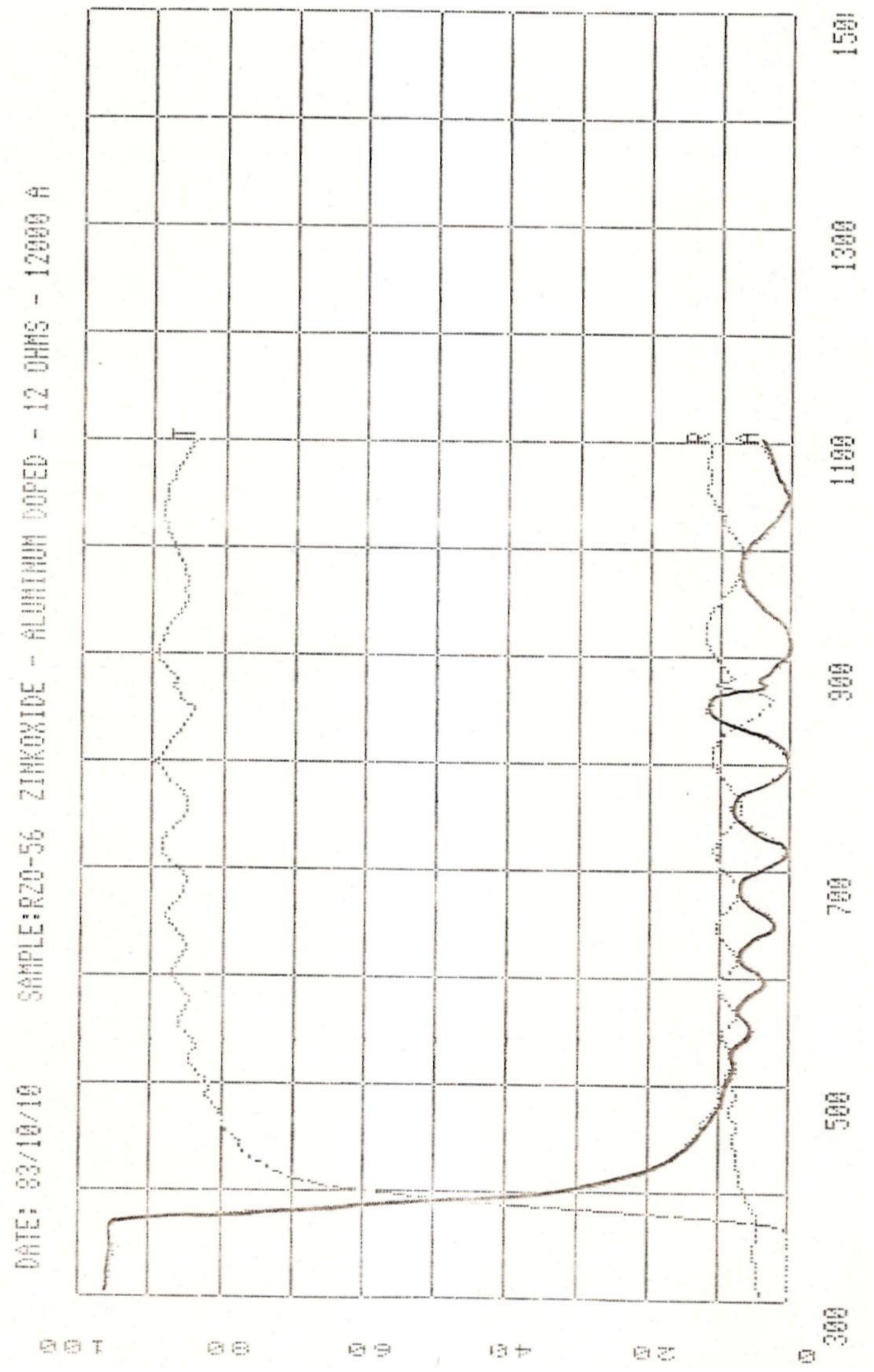


Fig. 28. Transmittance, reflectance and absorption of sputtered Al-doped ZnO films (thickness= 12,000 A)

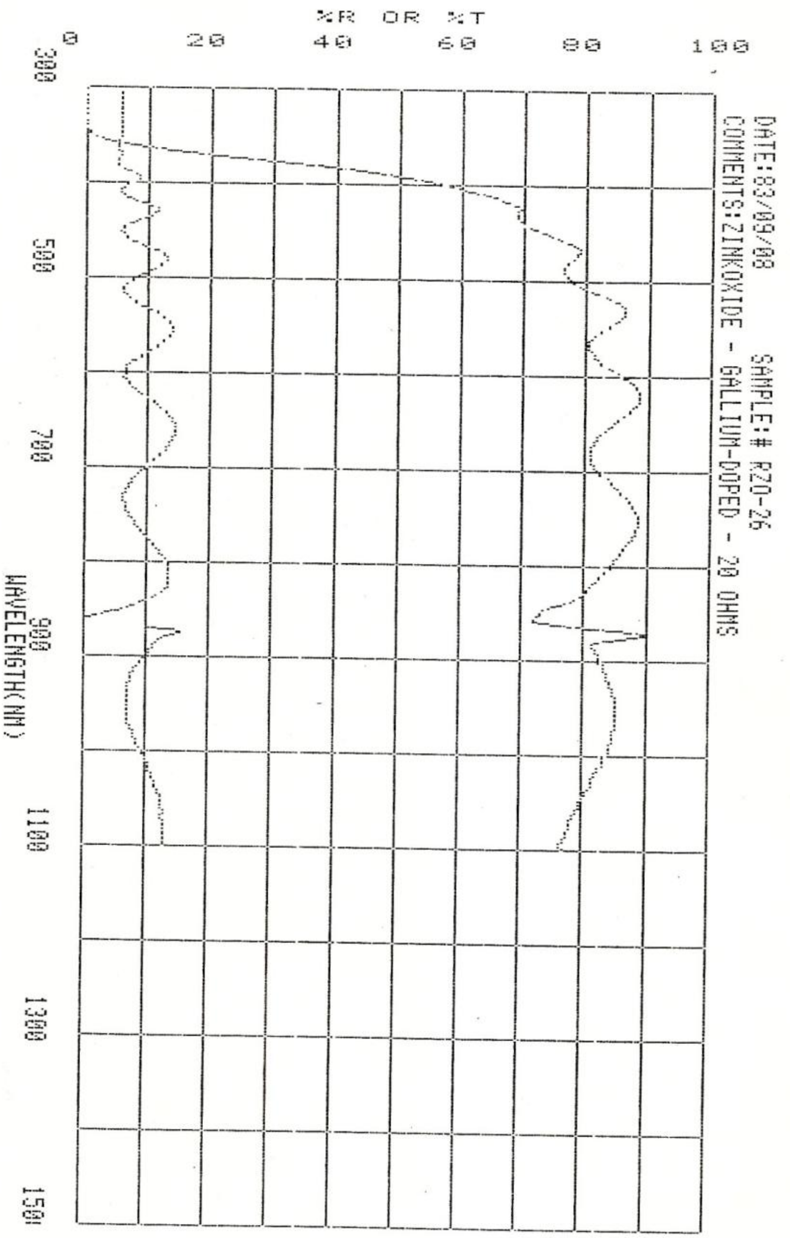
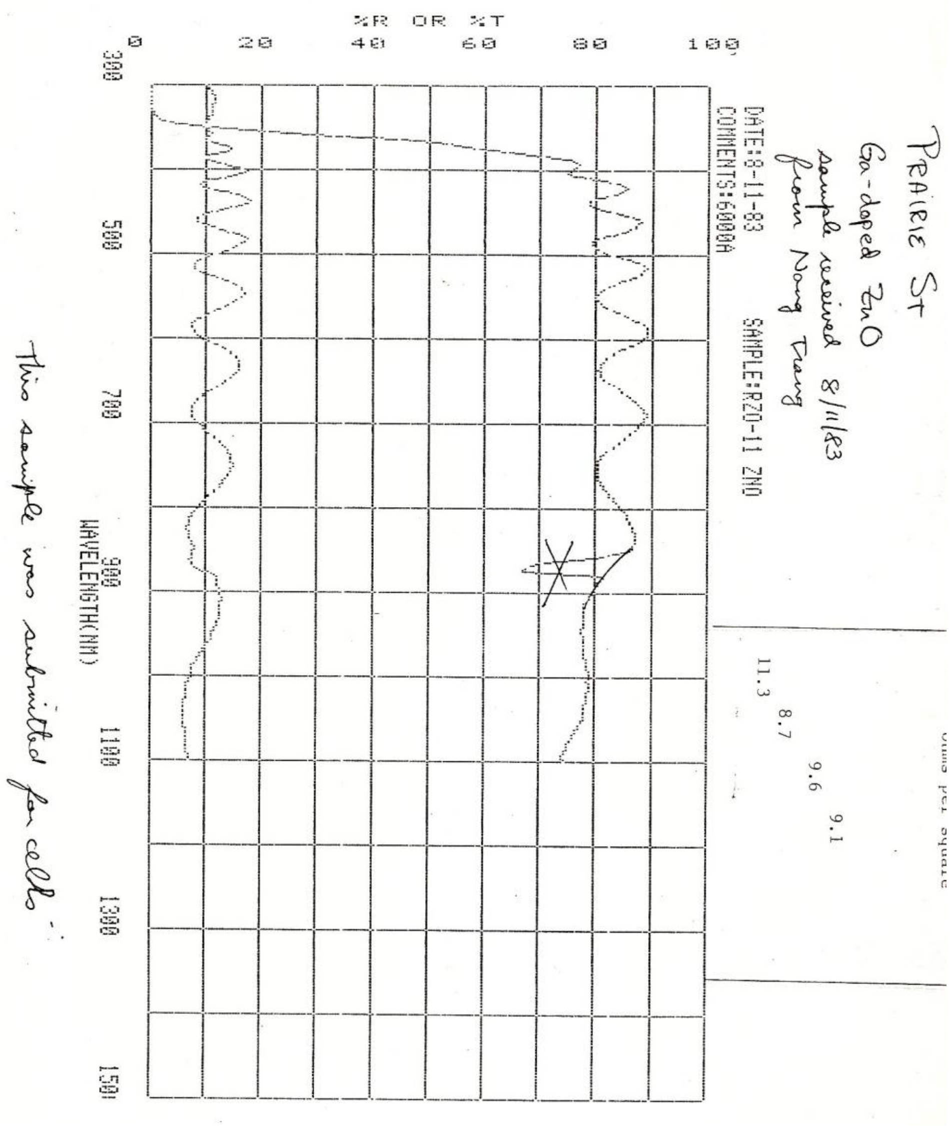


Fig. 29:. Transmittance, reflectance and absorption of sputtered Ga-doped ZnO films



PRAIRIE ST
Ga-doped ZnO
sample received 8/11/83
from Nong Trang

This sample was submitted for cells

Fig. 30. Transmittance, reflectance and absorption of sputtered Ga-doped ZnO films (continued)

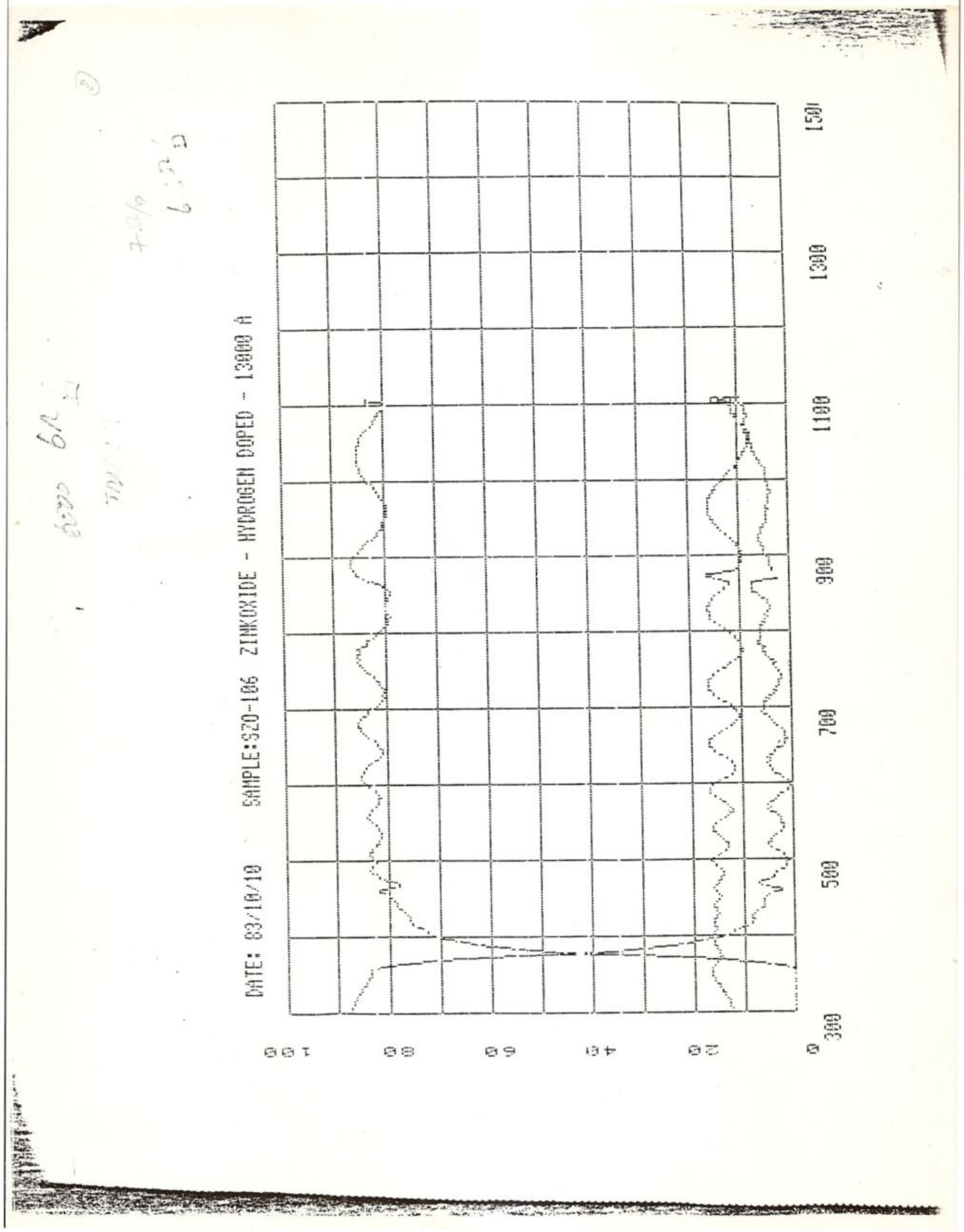


Fig. 31:. Transmittance, reflectance and absorption of sputtered hydrogen-doped ZnO films (thickness= 13,000 A)

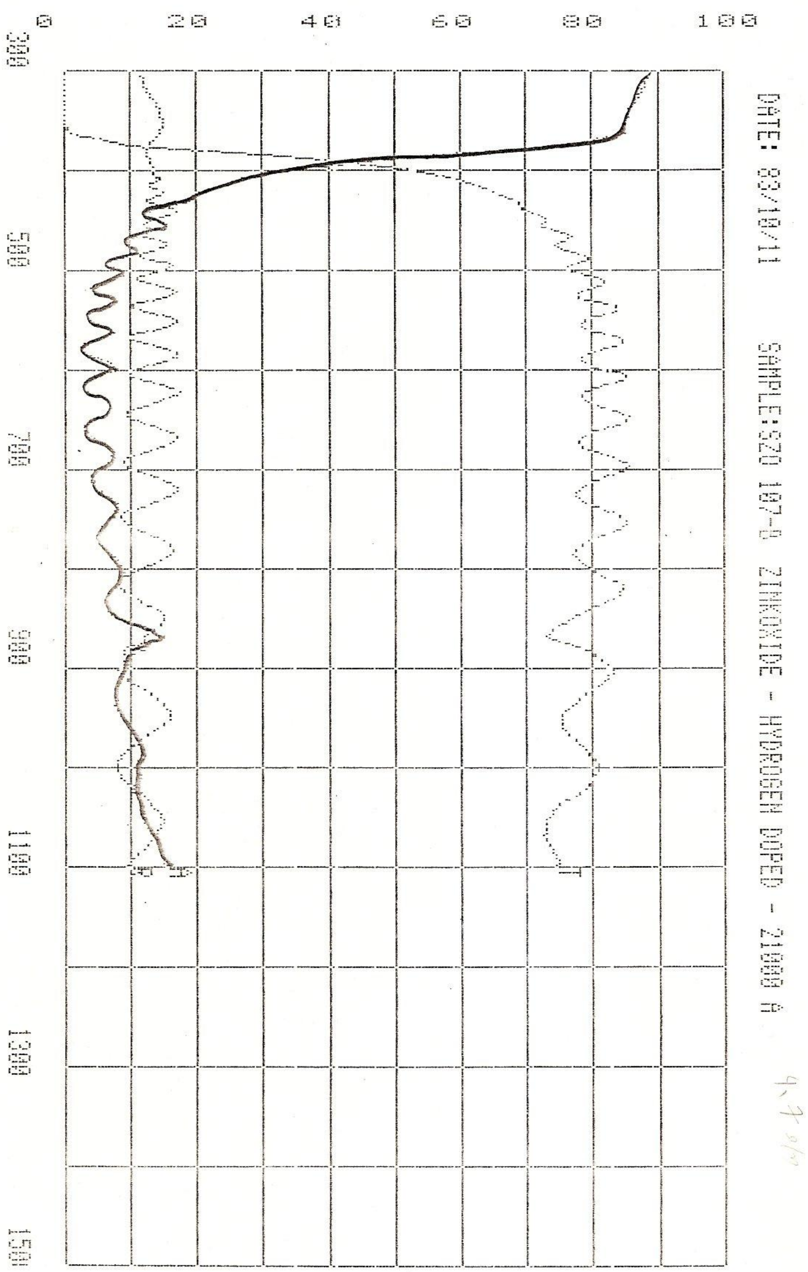


Fig. 32. Transmittance, reflectance and absorption of sputtered hydrogen -doped ZnO films (thickness= 21,000 A)

Fig.33 shows variation of bulk resistivity of ZnO films as a function of the hydrogen partial pressure whereas Fig. 34 shows transmission, reflection and absorption of the sputtered films.

Fig. 35 shows carrier concentration and mobility of the films.

Illuminated current- voltage characteristics of ZnO/CdS/CuInSe2 and ZnO/pin amorphous silicon solar cell with ZnO as a top electrode are shown in Figs. 36 and 37, respectively.

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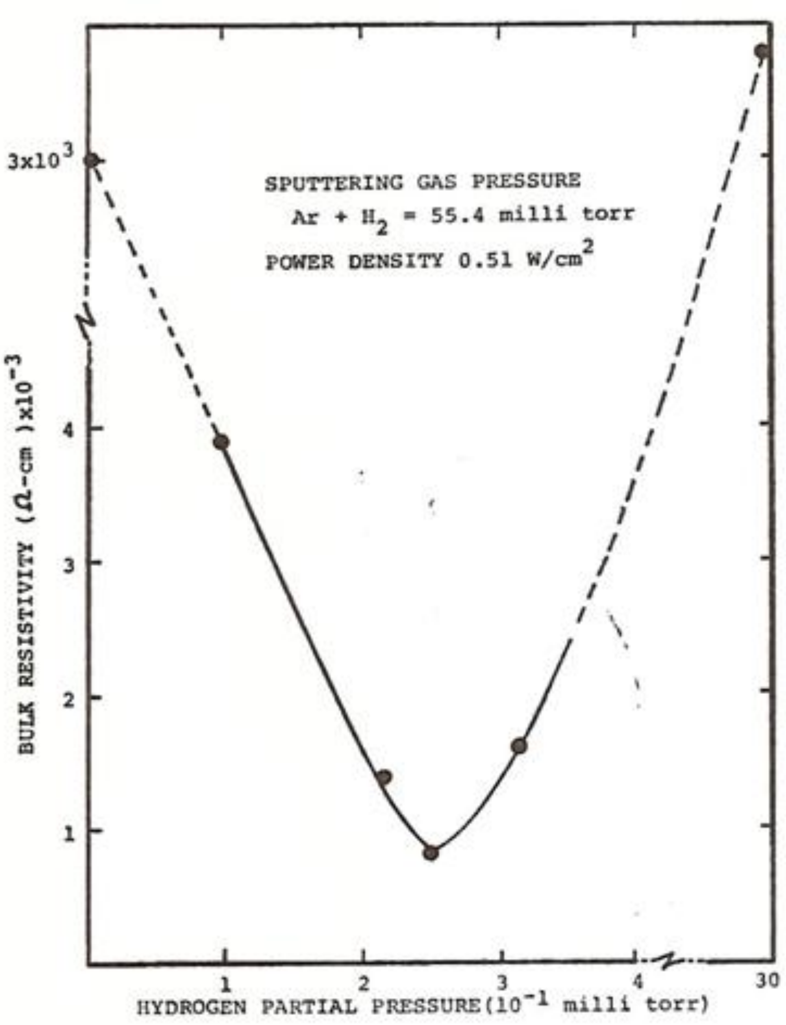


Fig. 33: Graph showing the resistivity of magnetron sputtered ZnO films as a function of the hydrogen partial pressure.

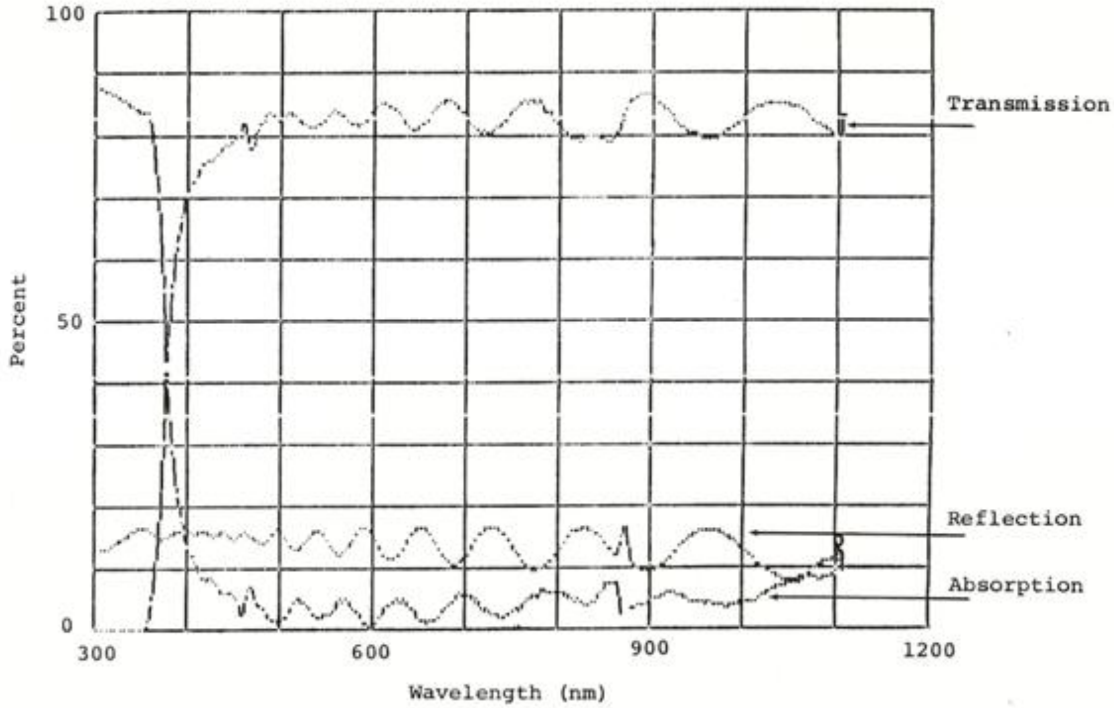


Fig. 34: Optical transmission, reflection and absorption of sputtered ZnO films as function of the wavelength.

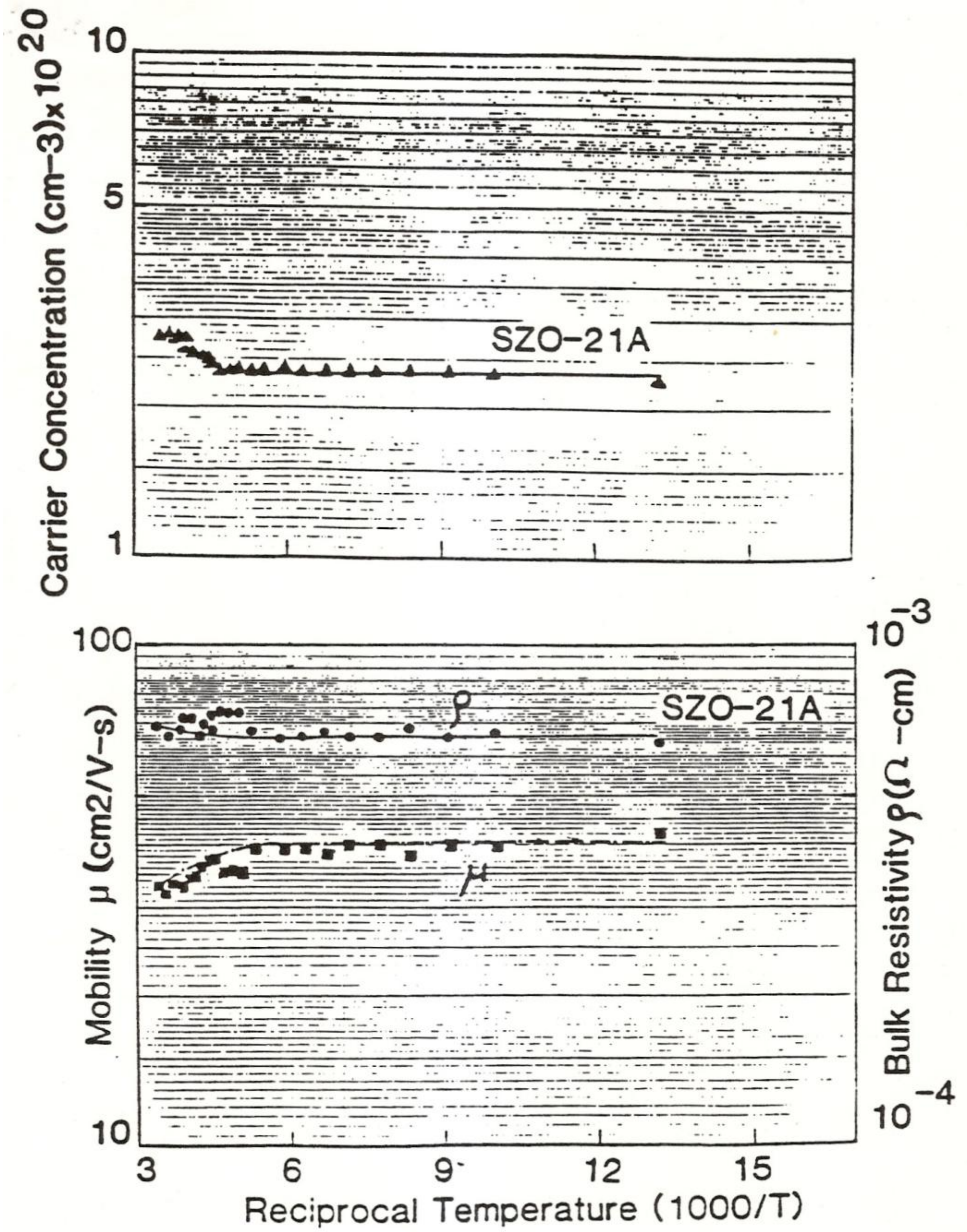
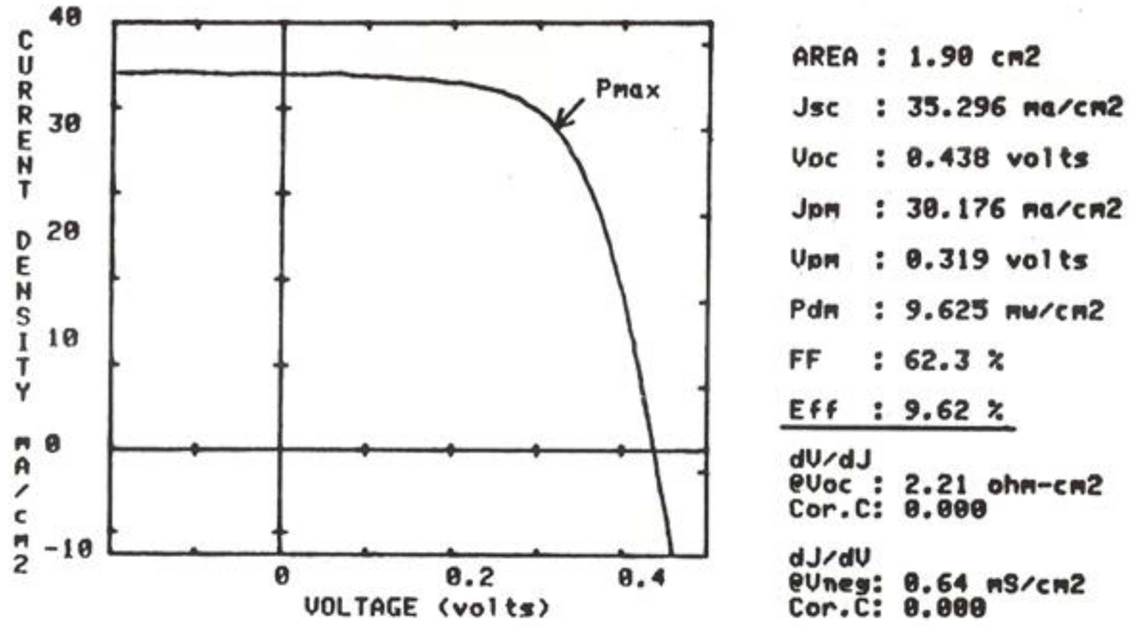


Fig. 35: Temperature dependence of Hall mobility, carrier concentration, and resistivity of sputtered ZnO films.



AREA : 1.90 cm2
Jsc : 35.296 ma/cm2
Voc : 0.438 volts
Jpm : 30.176 ma/cm2
Vpm : 0.319 volts
Pdm : 9.625 mw/cm2
FF : 62.3 %
Eff : 9.62 %

dV/dJ
@Voc : 2.21 ohm-cm2
Cor.C: 0.000

dJ/dV
@Vneg: 0.64 mS/cm2
Cor.C: 0.000

Fig. 36: Illuminated current-voltage characteristics of ZnO/CdS/CuInSe2 solar cell.

The device structure shown in Fig. 36 had been fabricated upon a glass substrate. The sputtered ZnO film (of which the properties shown in Figs 33 - 35) was deposited onto the evaporated CdS/CuInSe2 stack of films at an ambient substrate temperature. A 9.6% conversion efficiency was achieved for a solar cell of an area of 1.9 cm2.
Current-voltage characteristics of polysilicon and silicon solar cells with sputtered ZnO doped with Al or Ga are shown in Figs. 37-40.

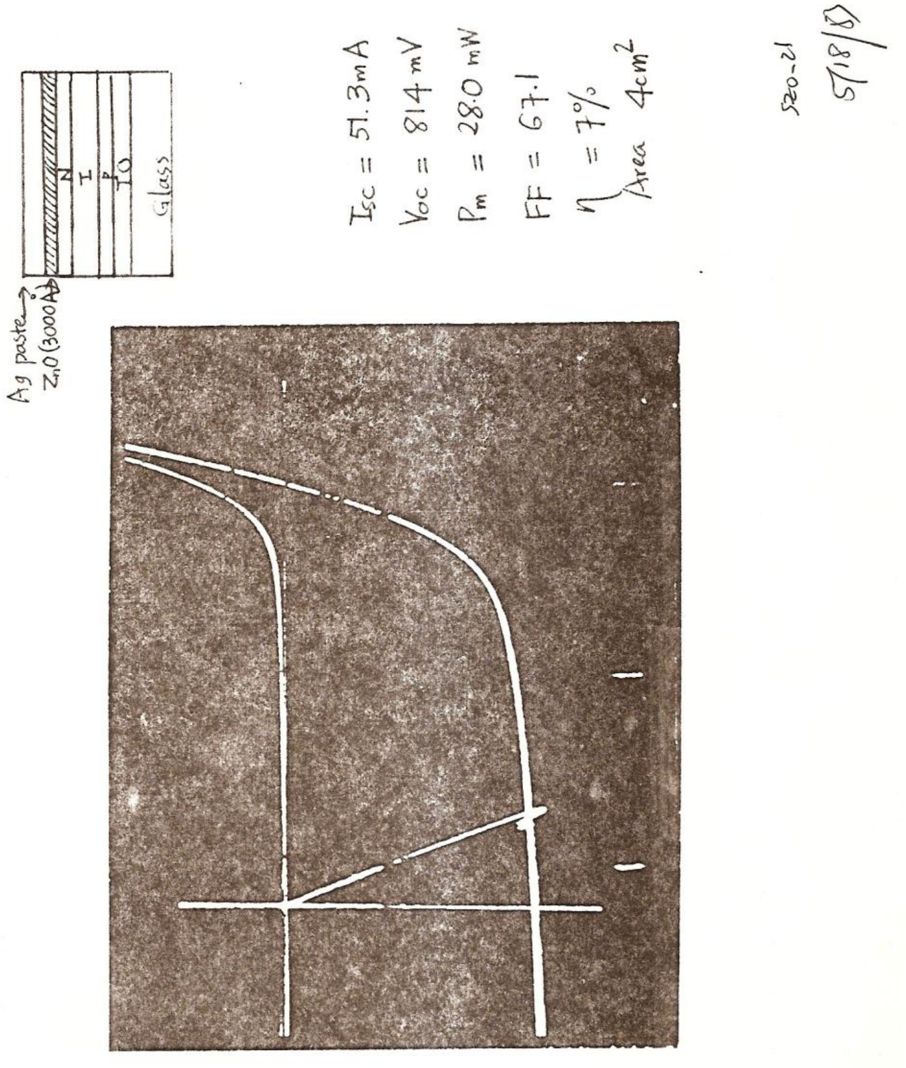
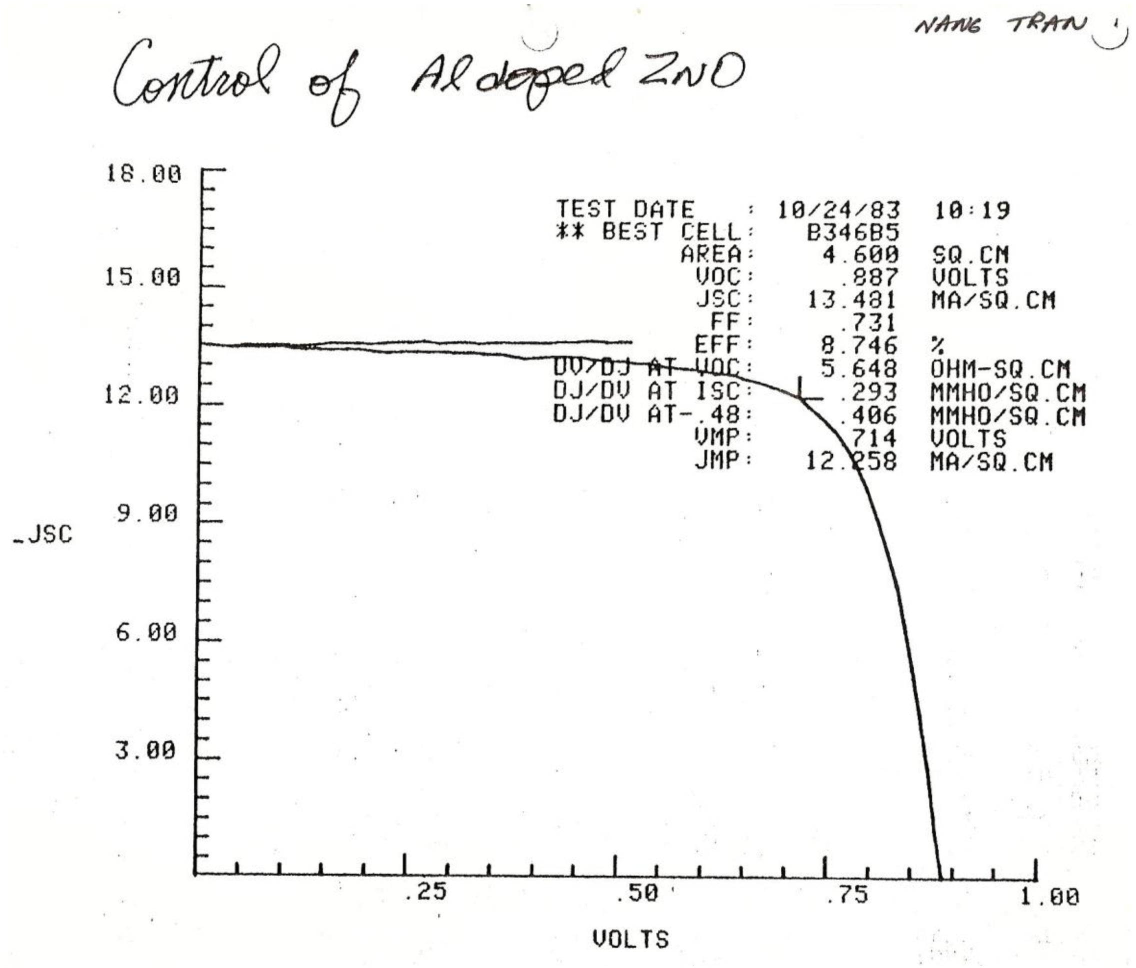


Fig.37: Illuminated current-voltage characteristics of ZnO/pin amorphous solar cell (area = 4 cm^2)



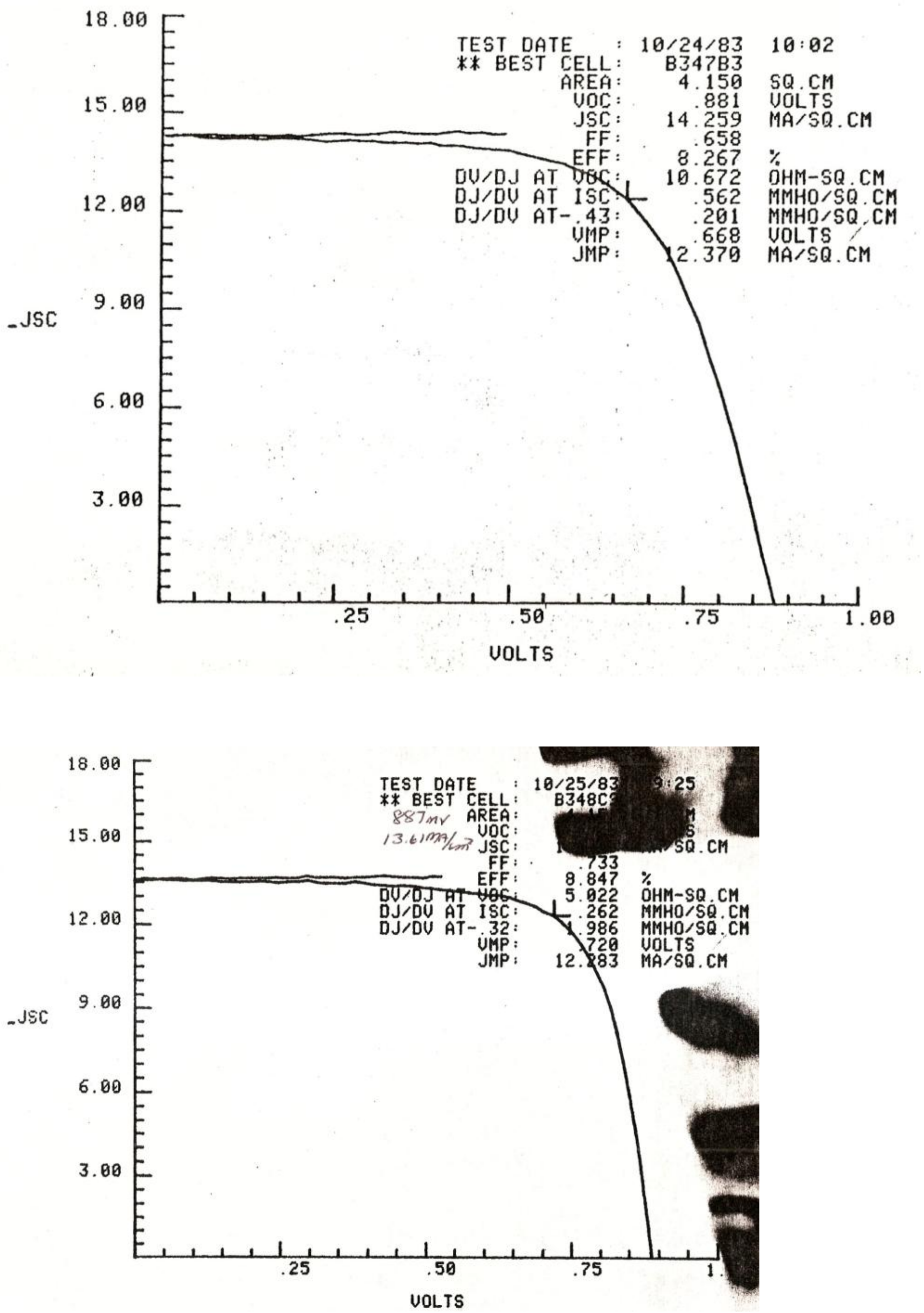
NANG TRAN

Control of Al doped ZnO

TEST DATE : 10/24/83 10:19
** BEST CELL: B346B5
AREA: 4.600 SQ.CM
VOC: .887 VOLTS
JSC: 13.481 MA/SQ.CM
FF: .731
EFF: 8.746 %
DV/DJ AT VOC: 5.648 OHM-SQ.CM
DJ/DV AT ISC: .293 MMHO/SQ.CM
DJ/DV AT-.48: .406 MMHO/SQ.CM
VMP: .714 VOLTS
JMP: 12.258 MA/SQ.CM

Fig.38: Illuminated current-voltage characteristics of Al- doped ZnO / pin amorphous solar cell (area = 4.6 cm^2)

Control GA doped ZnO



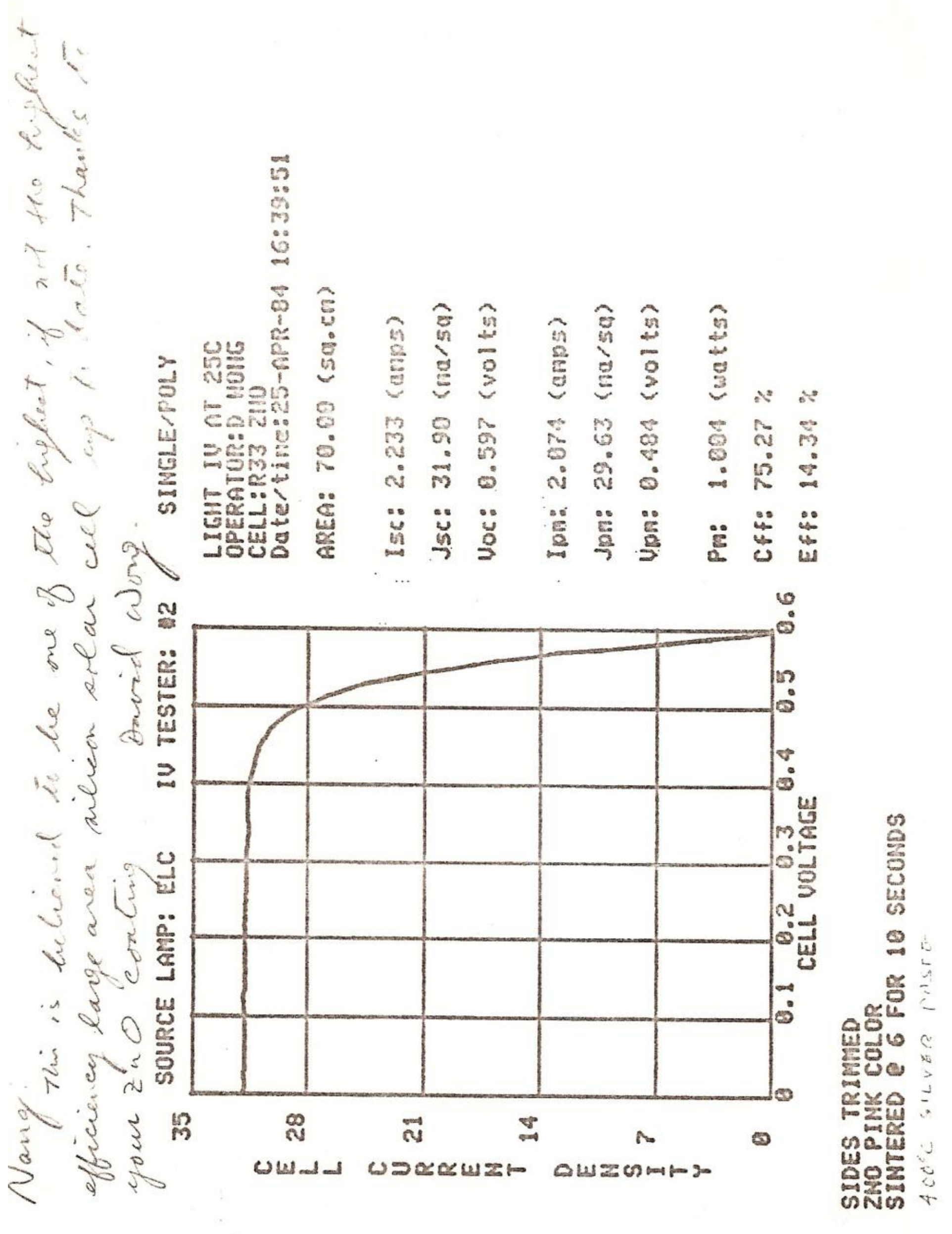
```
TEST DATE    : 10/24/83  10:02
** BEST CELL:   B347B3
        AREA:    4.150   SQ.CM
         VOC:     .881   VOLTS
         JSC:   14.259   MA/SQ.CM
          FF:     .658
         EFF:    8.267   %
DV/DJ AT VOC:   10.672   OHM-SQ.CM
DJ/DV AT ISC:     .562   MMHO/SQ.CM
DJ/DV AT-.43:     .201   MMHO/SQ.CM
         VMP:     .668   VOLTS
         JMP:   12.370   MA/SQ.CM
```

```
TEST DATE    : 10/25/83 [illegible]9:25
** BEST CELL:   B348C[illegible]
        AREA:  [illegible]         M
         VOC:  [illegible]         S
         JSC:   1[illegible]    SQ.CM
          FF:     .733
         EFF:    8.847   %
DV/DJ AT VOC:    5.022   OHM-SQ.CM
DJ/DV AT ISC:     .262   MMHO/SQ.CM
DJ/DV AT-.32:    1.986   MMHO/SQ.CM
         VMP:     .720   VOLTS
         JMP:   12.283   MA/SQ.CM
```

887mv

13.61mA/cm²

Fig. 39: Illuminated current-voltage characteristics of Ga- doped ZnO / pin amorphous solar cell (area = 4.15 cm^2)



Nang, This is believed to be one of the highest, if not the highest efficiency large area silicon solar cell up to date. Thanks to your ZnO coating.

David Wong

SOURCE LAMP: ELC IV TESTER: #2 SINGLE/POLY

LIGHT IV AT 25C
OPERATOR:D WONG
CELL:R33 ZNO
Date/time:25-APR-84 16:39:51

AREA: 70.00 (sq.cm)

Isc: 2.233 (amps)
Jsc: 31.90 (ma/sq)
Voc: 0.597 (volts)

Ipm: 2.074 (amps)
Jpm: 29.63 (ma/sq)
Vpm: 0.484 (volts)

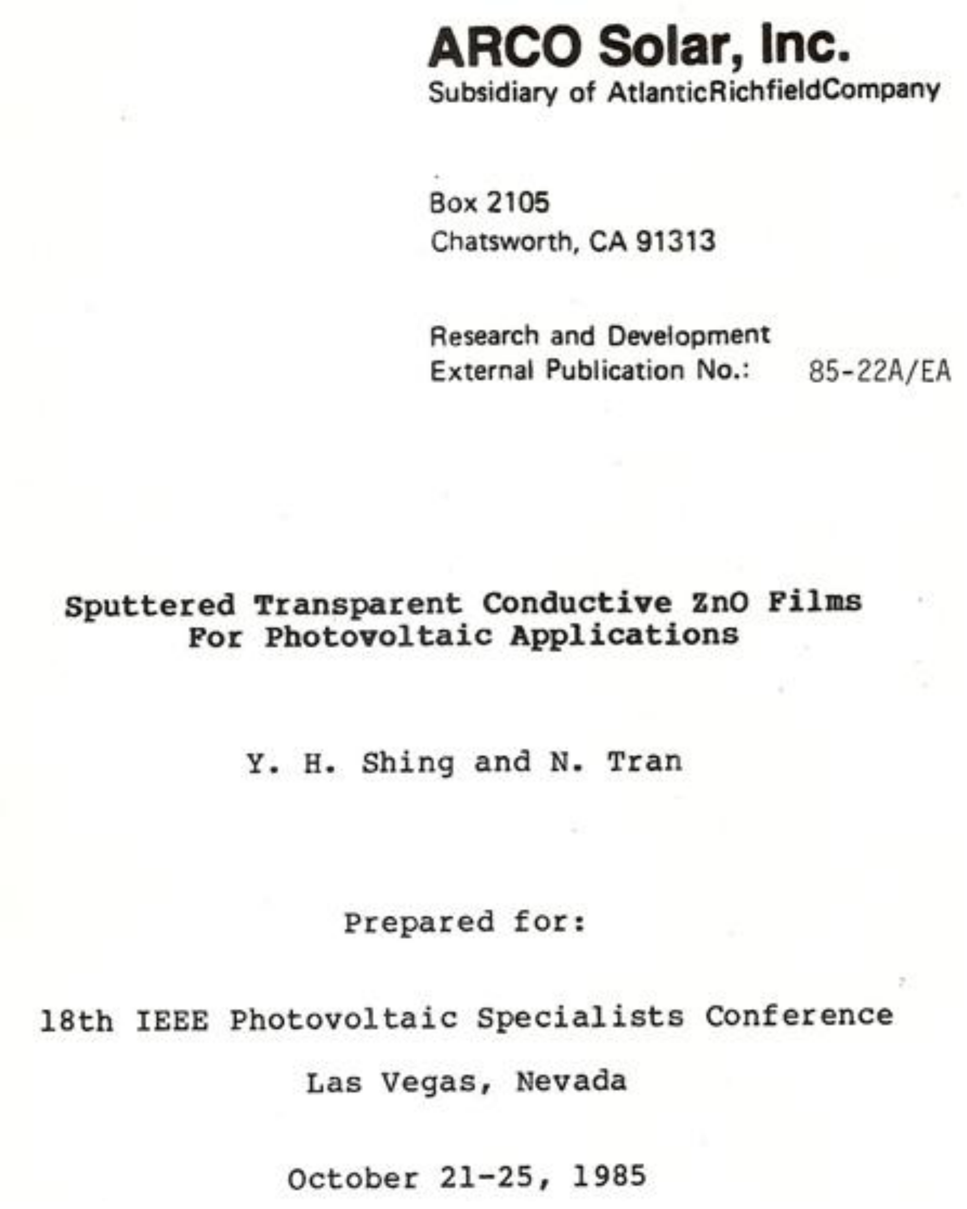
Pm: 1.004 (watts)
Cff: 75.27 %
Eff: 14.34 %

SIDES TRIMMED
ZNO PINK COLOR
SINTERED @ 6 FOR 10 SECONDS
400°C silver paste

Fig. 40: Illuminated current-voltage characteristics of Al- doped ZnO / polysilicon solar cell (area = 70 cm^2)

After the success of sputtered ZnO films as a front and back contact of solar cells, I was assigned to work on transferring the ZnO deposition process from Torr-Vac sputtering system to CPA in-line sputtering system. In August, 1984, I was able to demonstrate a hydrogen-doped ZnO film which had a bulk resitivity of 6 x 10^{-4} Ω-cm and MTF amorphous silicon solar with this ZnO as a front contact exhibited a conversion efficiency of 6.7 % (an area of 4 cm^2). I was also involved in the initial stage of setting up the CVD system for making ZnO films where diethyl zinc, trimethyl aluminum/or diborane and water vapor were used as reacting gases.

Yu-Han and I submitted a paper to 18th IEEE Photovoltaic Specialists Conference to be held in Las Vegas , October 21-25, 1985 (see Fig. 41) with the abstract shown in Fig. 42. Four and a half years of “fun” and “challenges” with ARCO (Fig. 43) had passed by so fast. On January 15 , 1985, I left the company and the sunny California to pursue my other opportunity in Minnesota.



ARCO Solar, Inc.
Subsidiary of AtlanticRichfieldCompany

Box 2105
Chatsworth, CA 91313

Research and Development
External Publication No.: 85-22A/EA

Sputtered Transparent Conductive ZnO Films
For Photovoltaic Applications

Y. H. Shing and N. Tran

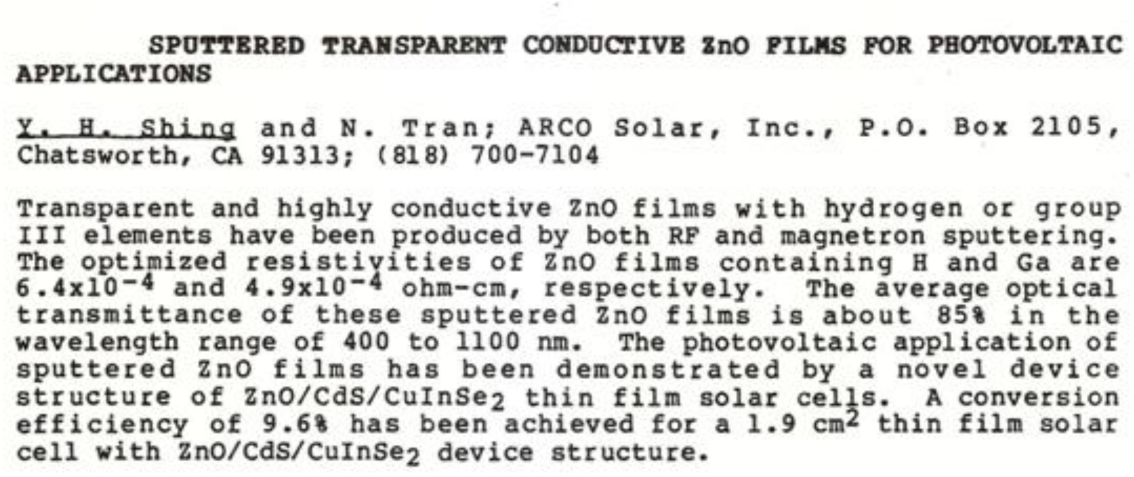
Prepared for:

18th IEEE Photovoltaic Specialists Conference

Las Vegas, Nevada

October 21-25, 1985

Fig. 41. The front page of the document we submitted to the conference committee of IEEE Specialists Conference.



SPUTTERED TRANSPARENT CONDUCTIVE ZnO FILMS FOR PHOTOVOLTAIC APPLICATIONS

Y. H. Shing and N. Tran; ARCO Solar, Inc., P.O. Box 2105, Chatsworth, CA 91313; (818) 700-7104

Transparent and highly conductive ZnO films with hydrogen or group III elements have been produced by both RF and magnetron sputtering. The optimized resistivities of ZnO films containing H and Ga are 6.4×10^{-4} and 4.9×10^{-4} ohm-cm, respectively. The average optical transmittance of these sputtered ZnO films is about 85% in the wavelength range of 400 to 1100 nm. The photovoltaic application of sputtered ZnO films has been demonstrated by a novel device structure of $ZnO/CdS/CuInSe_2$ thin film solar cells. A conversion efficiency of 9.6% has been achieved for a 1.9 cm^2 thin film solar cell with $ZnO/CdS/CuInSe_2$ device structure.

Fig. 42. Abstract of the paper we submitted to the conference.

Fig. 43. At the opening ceremony of the 1st International Photovoltaic Science and Engineering Conference, Nov. 15-18, 1984 in Kobe, Japan. I am the first person on the left, T.Dyer (at the center) and Charlie Gay (VP of ARCO Solar, on the right).

References

[1] J.H. Morgan and D.E. Brodie, Can. J. Phys. 60, 1387 (1982).
[2] J. Aranovich, A. Ortiz and R.H. Bube, J. Vac. Sci. Technol. 16, 994 (1979).
[3] J.B. Webb, D.F. Williams and M. Buchanan, Appl. Phys. Lett. 19, 640 (1981).
[4] F.T.J. Smith, Appl. Phys. Lett. 43, 1108 (1983).