

AD-A035 630

STANFORD UNIV CALIF SOLID-STATE ELECTRONICS LAB
TIN OXIDE AND RELATED OXIDES WITH REGARD TO COLD CATHODES.(U)
SEP 76 R A POWELL, W E SPICER

F/G 9/1
DAAG29-74-C-0022
NL

UNCLASSIFIED

ARO-12514.3-P

1 of 1
ADA035630



END

DATE
FILMED
3-77

ADA 035630

✓ 020-12514.3-7

12

**TIN OXIDE AND RELATED OXIDES
WITH REGARD TO COLD CATHODES**

FINAL REPORT

R.A. Powell and W.E. Spicer

September 15, 1976

**U.S. ARMY RESEARCH OFFICE
CONTRACT DAAG29-74-C-0022**

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED.

DDC
RECEIVED
FEB 16 1977
B

**SOLID-STATE ELECTRONICS LABORATORY
STANFORD ELECTRONICS LABORATORIES
STANFORD UNIVERSITY • STANFORD, CALIFORNIA**



The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 18 (ABO) (9) 12514.3-P	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 6 Tin Oxide and Related Oxides with Regard to Cold Cathodes		5. TYPE OF REPORT & PERIOD COVERED Final Report 1 April 1974-15 September 1976
7. AUTHOR(s) 10 R. A. Powell and W. E. Spicer		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Stanford University Stanford Electronics Laboratories Stanford, CA 94305		8. CONTRACT OR GRANT NUMBER(s) 15 DAAG29-74-C-0022
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 11 15 September, 1976
		13. NUMBER OF PAGES 33 (2) 400
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA		
18. SUPPLEMENTARY NOTES The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) 1. Cold Cathode 2. Tin Oxide 3. Indium-Tin-Oxide 4. Auger Spectroscopy 5. Photoemission Spectroscopy 6. Electron Emission 7. Field Emission 8. Secondary Emission		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The results of a study which was originated in order to provide fundamental knowledge of the emission mechanism for SnO ₂ cold electron emitters are reported. Instead of satisfactorily completing that objective, this work has brought into focus the fact that reports of practically important cold emission from such devices is based on a limited number of cathodes and that it has been impossible to reproduce these cathodes. As a result, no such cathodes were made available for		

20. (continued)

study under this program. Thus, the major finding of this work is that SnO_2 (or closely related In-Sn-Oxide) cold cathodes with large emission currents are anomalies which cannot be reproduced at will. Further, it is apparent that only if a major and extremely well thought out and expensive program is undertaken can substantial hope be given to producing such practical cathodes. It is not apparent to the present workers that such a program would be a good investment. Before that decision can be made, some essential groundwork should be done to determine if these cathodes can be economically incorporated into existing devices. Measurements of the spatial and energy spread of emitted electrons should have a high priority.

Despite the fact that a good emitter was never delivered to us, we studied structures such as those reported to have given good emission (some of which we fabricated) in order to gain insight into the emission and activation process. Considerable detailed data was obtained and a tentative model, closely related to those suggested previously, was developed. This model is based on the detailed analysis of the activated region obtained by the use of Auger electron spectroscopy with high spatial resolution.

END

TIN OXIDE AND RELATED OXIDES
WITH REGARD TO COLD CATHODES

FINAL REPORT

R. A. Powell and W. E. Spicer

September 15, 1976

U.S. ARMY RESEARCH OFFICE

CONTRACT DAAG29-74-C-0022

Stanford Electronics Laboratories
Stanford University
Stanford, Ca. 94305

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED.

ACCESSION for	
DTIC	White Section <input checked="" type="checkbox"/>
DDC	Soft Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/CLASSIFICATION CODES	
Dist. Avail. and SPECIAL	
A	

ABSTRACT AND CONCLUSION

The results of a study which was originated in order to provide fundamental knowledge of the emission mechanism for SnO_2 cold electron emitters are reported. Instead of satisfactorily completing that object, this work has brought into focus the fact that reports of practically important cold emission from such devices is based on a limited number of cathodes and that it has been impossible to reproduce these cathodes. As a result, no such cathodes were made available for study under this program. Thus, the major finding of this work is that SnO_2 (or closely related In-Sn-Oxide) cold cathodes with large emission currents are anomalies which can not be reproduced at will. Further, it is apparent that only if a major and extremely well thought out and expensive program is undertaken can substantial hope be given to producing such practical cathodes. It is not apparent to the present workers that such a program would be a good investment. Before that decision can be made, some essential groundwork should be done to determine if these cathodes can be economically incorporated into existing devices. Measurements of the spatial and energy spread of emitted electrons should have a high priority.

Despite the fact that a good emitter was never delivered to us, we studied structures such as those reported to have given good emission (some of which we fabricated) in order to gain insight into the emission and activation process. Considerable detailed data was obtained and a tentative model, closely related to those suggested previously, was developed. This model is based on the detailed analysis of the activated region obtained by the use of Auger electron spectroscopy with high spatial resolution.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
I. INTRODUCTION	1
II. PHOTOEMISSION STUDIES OF Sn, SnO ₂ , AND Sn + O ₂	1
III. COLD-CATHODES BASED ON ITO	2
A. Sample Preparation	3
B. Sample Activation	4
C. Sample Emission	6
IV. AUGER ELECTRON SPECTROSCOPY (AES)	9
A. SnO ₂ and In ₂ O ₃	9
B. ITO	12
C. Depth Profiles	14
1. The Effect of Temperature and Electric Field	14
2. The Necked-Down Region	16
V. THE SnO ₂ /ITO DATA BASE	18
VI. DISCUSSION	21
VII. SUMMARY	26
VIII. RECOMMENDATIONS	30
REFERENCES	32

ACKNOWLEDGMENT

We would like to express our appreciation for the ITO cathodes supplied by Leslie Wong and Prof. C. G. Fonstad, MIT, and for the emission measurements performed by Bernie Smith, U.S. Army Electronics Command, Ft. Monmouth. We especially want to acknowledge the assistance of John Rizzo in the preparation of ITO cathodes at Stanford and their Auger analysis.

I. INTRODUCTION

Hot cathodes have generally been used as electron emitters in vacuum technology; however, thermal effects, chemical interactions with the hot cathode, evolution of positive ions, etc. make them unattractive emitters for many device applications. For these cases a suitable cold-cathode is desired.

The possibility that strong cold-cathode emission could be obtained from suitably prepared tin dioxide (SnO_2) films was first reported by Russian workers (Elinson et al)¹ in 1964. This work was encouraging because electron emission currents, I_E , were large (~ 1 mA) and highly efficient at low voltages (> 10 V) and because the SnO_2 surface was chemically stable (i.e., as compared to cesium-activated surfaces). The major goal of our research program has been to understand the emission properties of cold-cathodes employing SnO_2 and to thereby provide guidance in the technical development and evaluation of practical cold-cathode devices. For reasons which will be discussed later, considerable effort was directed not only at SnO_2 but at cold-cathodes employing $\text{In}_2\text{O}_3/\text{SnO}_2$, i.e., indium-tin-oxide (ITO) films.

II. PHOTOEMISSION STUDIES OF Sn, SnO_2 , AND $\text{Sn} + \text{O}_2$

Ultraviolet photoemission studies of SnO_2 films prepared by chemical vapor deposition (CVD) at Beta Industries were carried out. Electronic properties of these CVD- SnO_2 films have already been reported in a previous technical report (Semi-Annual Report of March 31, 1975)³ and will not be repeated here. Beta Industries had reported that identically prepared CVD- SnO_2 films, when suitably patterned and activated, gave cold-cathode emission in agreement with Refs. 1 and 2. In addition to studies we have made on these films, both Sn and SnO_2 films prepared at Stanford by the evaporation of Sn and its subsequent oxidation were studied using photoemission. In summary, the quantum yield of Sn with exposures of as much as 4000 L oxygen (1 L = 1 Langmuir = 10^{-6} torr-sec) differs only slightly from that of the clean metal. The electron affinity, E_A , remained constant with exposure to O_2 at ~ 4.3 eV. The energy

distribution of photoemitted electrons (EDCs) from Sn with increasing exposure to oxygen above ~ 20 L are characterized by the growth of two peaks which were not present in the EDCs for the clean metal, located 2.9 and 4.8 eV below the Fermi level. We have associated this structure with the presence of SnO_2 . No sharp resonance which could be associated with adsorbed oxygen was seen. Uniformly reduced emission from metallic Sn states and a Fermi level as sharp as for the clean metal is observed in the EDCs at all oxygen exposures. In addition, no change in work function with oxygen exposure was detected. The effects of oxygen saturate for exposures $\gtrsim 4000$ L. We have suggested that, under the conditions used in this experiment, the oxygen penetrates beneath the surface forming SnO_2 and leaving metallic Sn on the surface. These results are discussed in detail in our paper in Surface Science 55, 681 (1976).⁴

III. COLD-CATHODES BASED ON ITO

Having completed the above background studies to characterize Sn, SnO_2 , and the interaction of Sn and O_2 , we prepared instrumentation to study cold-cathode emission from SnO_2 films. This phase of our research was undertaken with the understanding that Beta Industries would supply us with suitably emitting SnO_2 films. This was not done, frustrating our efforts to develop a basic understanding of the cold-cathode emission mechanism in such films and to perform critical experiments such as a measurement of the energy distribution of emitted electrons, $N(E)$. Too large a spread in energy of the emitted electrons, for example, could rule out the use of SnO_2 -based cold-cathodes for certain device applications. Elinson et al¹ have suggested that a critical experiment in understanding the process of electron emission from SnO_2 would be a determination of the electron affinity, E_A . We have obtained values of $E_A \cong 4.5$ eV for the CVD- SnO_2 samples studied from Beta Industries. No data on changes in E_A following the activation process were taken since suitably activated samples could not be obtained. The model we had earlier proposed for cold-cathode emission³ suggests that E_A is lowered following activation.

It became apparent in late summer of 1975 that Beta could not supply our need for samples and, in fact, Beta's contract was terminated in December 1975. Since no possibility of obtaining the expected SnO_2 emitters remained, we directed our attention to ITO. There were several reasons for this decision. (1) Strong electron emission had been reported in December 1975⁵ for patterned ITO films following the identical activation process used for SnO_2 films.^{1,2} The ITO emission current, however, was reported to be an order of magnitude larger than observed for SnO_2 at comparable film currents (1 mA of emission with only 10 mA film current). (2) In addition, only very low anode voltages (~ 300 V) were used with relatively large anode-to-emitter spacings (~ 2 cm). Thus, even though the basic physics of emission for ITO and SnO_2 was probably identical, ITO films promised to be more technically interesting. (3) ITO films can be fabricated by sputter deposition rather than by CVD as was the case for SnO_2 . Sputtering is by far the easier method and is expected to lead to emitters with more reproducible emission properties.

It should be stressed at this point that it was never our intention in undertaking a research program on SnO_2 and related oxides to fabricate cold-cathodes. In the case of SnO_2 , no capability existed at Stanford to reliably form and pattern CVD SnO_2 films. However, since sputter preparation could be performed at Stanford, the possibility existed for in-house preparation of ITO emitters. In order to overcome the difficulties mentioned above with obtaining SnO_2 samples, we have fabricated ITO samples at Stanford. This course of action meant that less time and effort could be spent on our primary task.

A. Sample Preparation

The ITO films were RF sputtered onto quartz slide substrates from a hot-pressed ceramic target. The sputtering target (obtained from Haselton Company) was a sintered mixture of 9 parts by weight In_2O_3 powder to 1 part SnO_2 powder. With a pressure of 20 microns argon and 2.5 KV on the target, a sputter deposition rate of ~ 4000 Å/hour was obtained. Typical films were ~ 2000 Å thick and highly conducting, i.e., resistivities were $\sim 4 \times 10^{-4}$ Ω-cm as measured with a four-point probe. Most transparent

metal oxides (Al_2O_3 , MgO , etc.) are highly insulating with resistivities $>10^8 \Omega\text{-cm}$. The value we obtained for the resistivity of sputtered ITO films compares favorably with literature values for such films.⁶

Two approaches were used in an attempt to produce the desired patterns in the films, viz the "H" or dumbbell pattern employed by Elinson et al¹ and subsequent workers.^{2,5,7,8} The crossbar or neck of the "H" has dimensions ~ 1 mm long by ~ 0.1 mm wide. In an effort to follow the procedure of Hartwell and Fonstad,⁵ photolithography was tried first. KTRF photo-resist was spun onto the ITO film, exposed through an H-shaped mask, and developed using standard procedures. Unfortunately, the unprotected ITO film could not be etched off using the recommended solvent--warm oxalic acid solution, 0.1 molar concentration.⁶ 2000 Å thick ITO films did not even dissolve after an hour in 0.3 molar, boiling oxalic acid! Suitable etchants for the ITO could be found, such as hot HCl, but these dissolved the KTRF as well so that the photolithographic approach was abandoned. Acceptable patterned films could be formed, however, by sputtering ITO over a carbon mask. For this procedure, a 1 mm wide vertical stripe of Alkadag (graphite dissolved in alcohol) was first painted onto a clean quartz slide and a 0.1 mm channel cut across the vertical stripe (Fig. 1). With a little practice, this could readily be done by hand under a binocular microscope. The ITO was then sputtered over the carbon mask. After dissolving the mask in alcohol, the desired H-shaped ITO film on quartz remained.

B. Sample Activation

Procedures for activating both SnO_2 and ITO cathodes have been reported in detail in the literature^{1,2,5,7,8} and were followed in the present work. Basically, a high-resistance region is formed in the neck by subjecting it to high temperatures and electric fields. In the present work, the high-resistance region was formed in the following manner: a voltage V_F was applied across the film and increased slowly. For $V_F \lesssim 50$ V (film currents $I_F \lesssim 50$ mA), the current I_F increased in an ohmic manner accompanied by an increase in film temperature. I_F increased in a nonlinear manner above ~ 50 mA, and by 100 mA the neck glowed bright orange (temperature $\gtrsim 600^\circ\text{C}$). The glow abruptly stopped in less

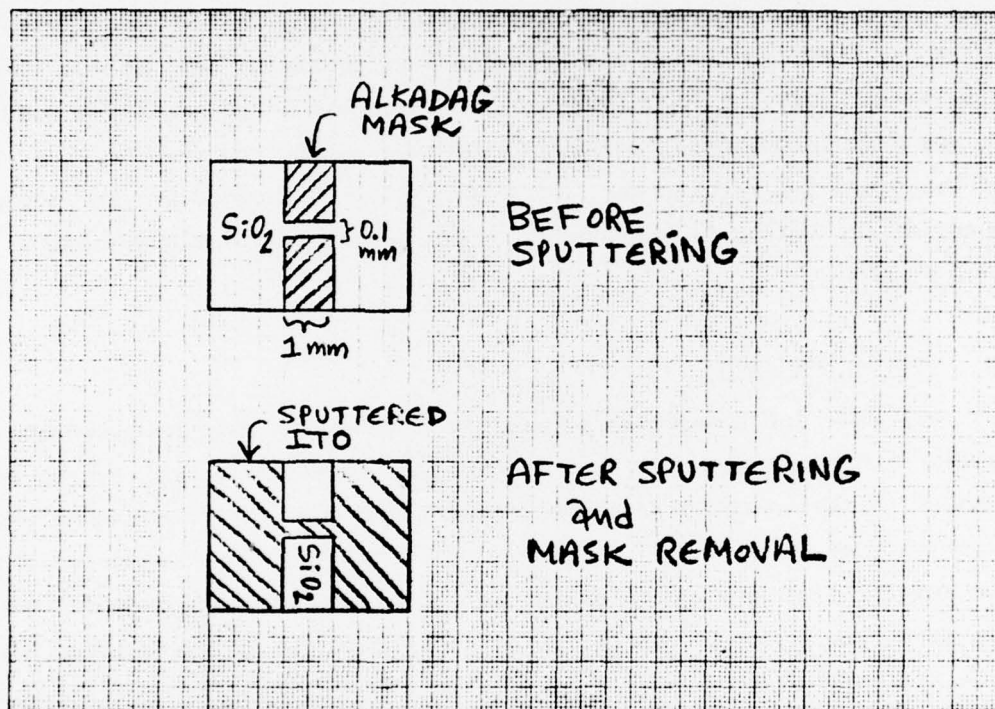


Fig. 1. PROCEDURE USED TO PATTERN ITO FILMS IN THE "H-SHAPED" CONFIGURATION.

than a minute accompanied by an equally abrupt decrease in I_F by several orders of magnitude. A typical ITO film might have an initial resistance $R_i = 100 \Omega$ and a resistance after activation $R_f = 10-100 K\Omega$. We will refer to ITO films which have been subjected to the above activation process as "activated" regardless of their cold-cathode emission properties.

Scanning Electron Microscope (SEM) photographs of an activated ITO film ($R_i = 68 \Omega$, $R_f = 600 K\Omega$) are shown in Fig. 2. The jagged break which has occurred across the neck is clearly seen as well as the cracked appearance of the film on either side of the break, probably the result of the high temperatures present in the neck during activation. The width of the break is ~ 5 microns. From the 2000X SEM photograph, the topography of the bottom of the break is seen to be rough and bumpy rather than smooth.

C. Sample Emission

The emission properties of activated ITO films have been reported by Hartwell and Fonstad (HF).⁵ The emitter testing circuit we used was similar to that used by HF and by workers who have reported cold-cathode emission from SnO_2 .^{1,2,7,8} Figure 3 presents a pictorial schematic of the emitter testing circuit which was placed in a diffusion-pumped bell jar (pressure $\lesssim 5 \times 10^{-6}$ torr). Electrical contacts to the emitter were made with silver paste.

In contrast to the strong emission reported by HF, all ITO we studied were extremely poor electron emitters. Most failed to emit at all, while those that did emit had unstable emission currents of $I_E \sim$ several microamp and brief lifetimes of several minutes. Parameters such as the emitter-to-collector spacing, D , and anode high voltage V_A were varied over a wide range ($D = 0.5-2$ cm, $V_A = 300-1500$ V) with little or no effect on emission. Similar results were obtained by workers at Ft. Monmouth who activated ITO samples which we prepared at Stanford and measured their emission properties.⁹ This argues against attributing the poor emission performance to our activation or measurement techniques. Extensive work was also performed on ITO films kindly prepared and supplied to us by Prof. C. G. Fonstad's research group at MIT, the workers



200X



500X



2000X

Fig. 2. SEM PHOTOGRAPHS OF THE NECKED-DOWN REGION OF AN ACTIVATED ITO CATHODE.

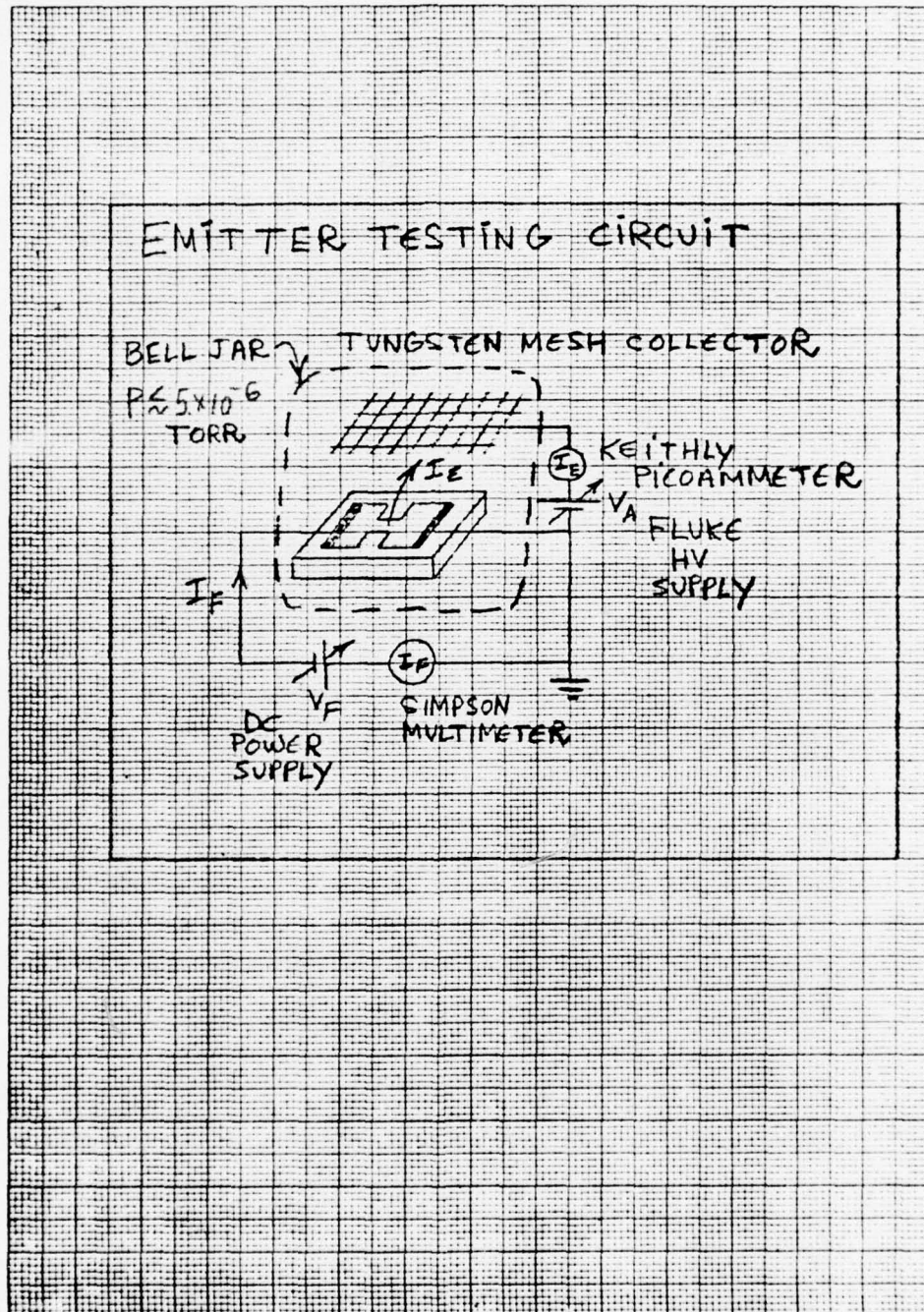


Fig. 3. SCHEMATIC OF THE CIRCUIT USED TO TEST EMISSION FROM ACTIVATED ITO CATHODES.

who had first reported strong, cold-cathode emission from such films. The emission characteristics of these samples were comparable to those fabricated at Stanford. In brief, we were unable to confirm the earlier results of HF that strong emission ($I_E \gtrsim 1 \text{ mA}$) can be obtained from ITO films.

IV. AUGER ELECTRON SPECTROSCOPY (AES)

AES is a technique which is particularly well-suited to the study of either SnO_2 or ITO cold-cathodes. There are two major reasons for this: (1) The prominent Auger transition energies for Sn, In, and O occur between 350-550 eV. Electrons in this energy range can be emitted without appreciable energy loss from electron-electron scattering only if they originate in the first few monolayers at the sample surface. Hence, with AES it should be possible to characterize the emitter surface and measure changes in surface composition which might occur following the activation process. (2) The spatial resolution in AES is determined by the primary electron beam spot size. For our Varian Associates AES system, spatial resolution is $\gtrsim 10$ micron. This should be sufficient to probe the necked-down region of the H-shaped emitters ($\sim 1000 \mu \times 100 \mu$) from which electron emission is believed to occur as well as the "break" which occurs in the neck following activation ($\sim 5 \mu$ wide).

A. SnO_2 and In_2O_3

AES studies of pure powders (99.999%) of SnO_2 and In_2O_3 were first carried out to aid in understanding the data from the more complex system expected in ITO films, $\text{In}_{2-x}\text{Sn}_x\text{O}_y$. AES spectra for SnO_2 and In_2O_3 are shown in Fig. 4 and 5, respectively. Data was taken on a Varian Associates high-resolution Auger spectrometer employing a single pass cylindrical mirror analyzer with energy resolution $\Delta E/E \sim 0.5\%$. The samples were cleaned by Ar^+ sputtering (2.5 KeV , $30 \mu\text{A}/\text{cm}^2$, 5×10^{-5} torr of Argon), and subsequent AES measurements were made at pressures $\lesssim 2 \times 10^{-10}$ torr. The derivative $dN(E)/dE = N'(E)$ of the number of Auger

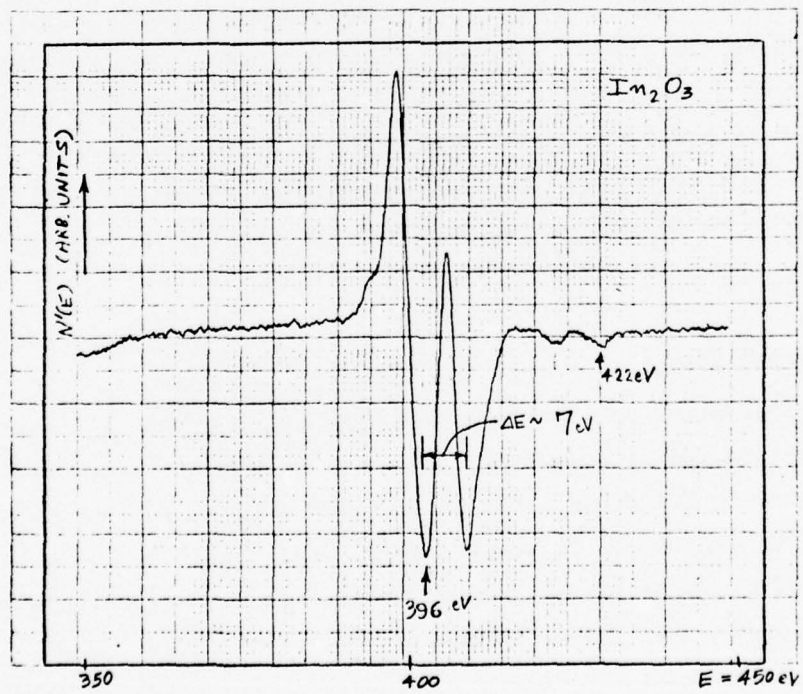
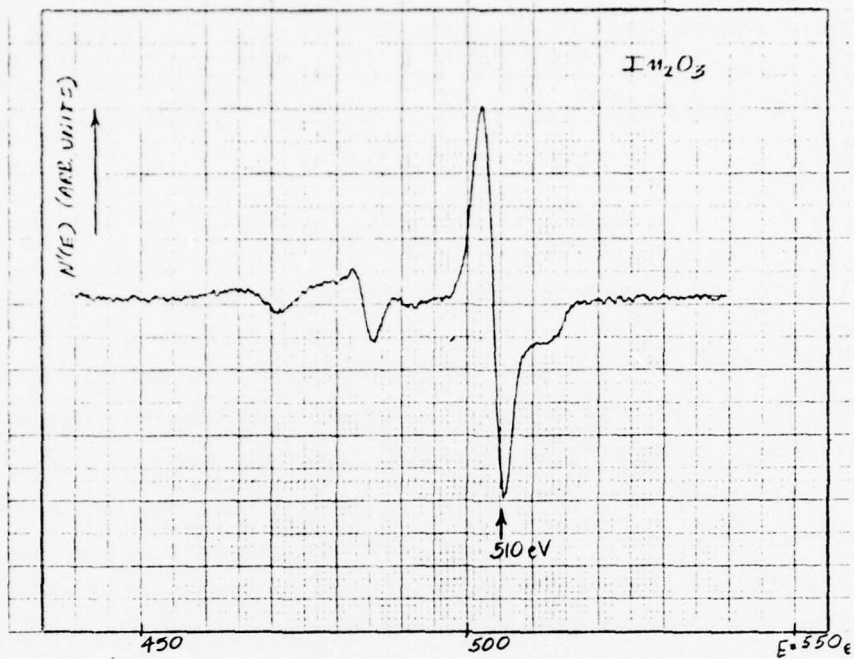


Fig. 4. AES DERIVATIVE SPECTRA OF HIGH-PURITY, POWDERED In_2O_3 .

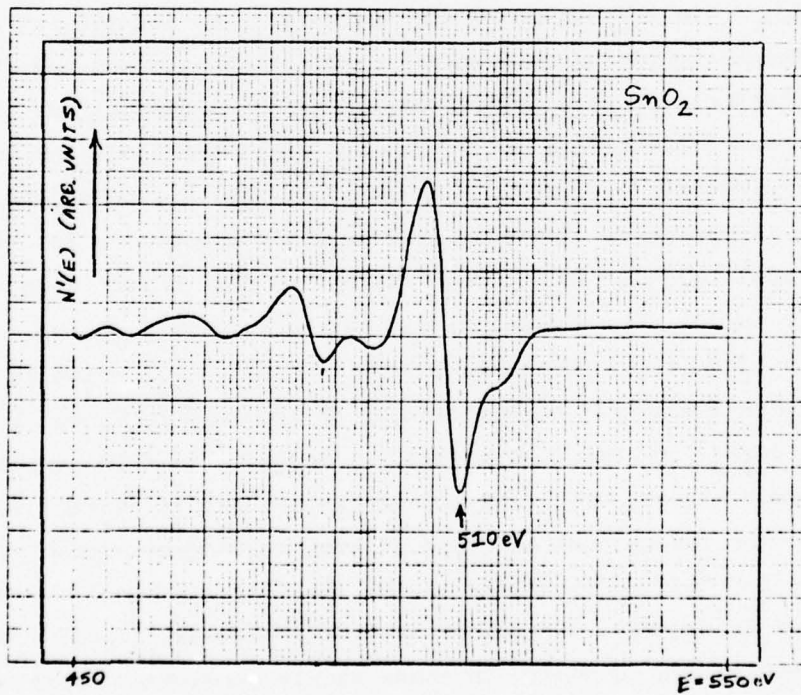
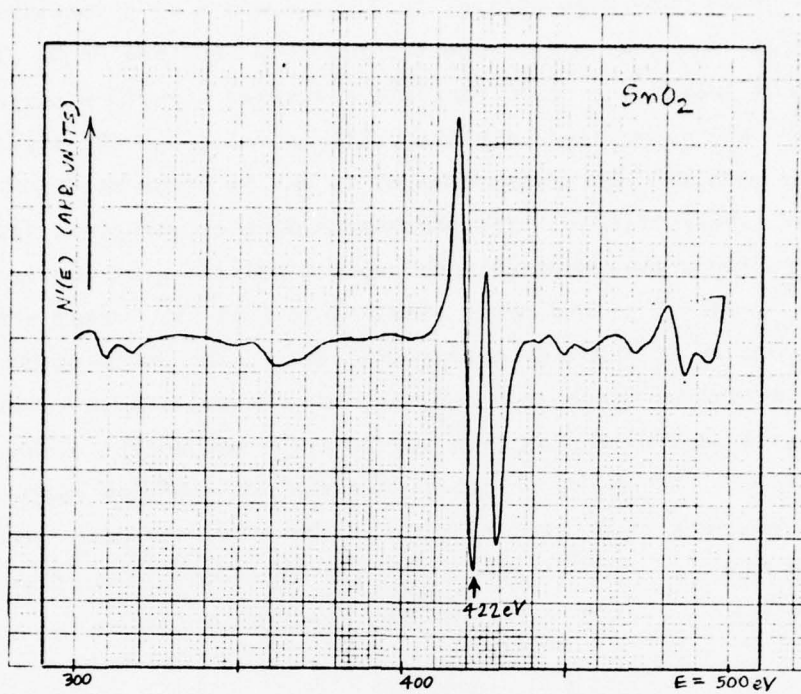


Fig. 5. AES DERIVATIVE SPECTRA OF HIGH-PURITY, POWDERED SnO_2 .

electrons $N(E)$ has been plotted in Figs. 4 and 5 as a function of their energy E . The $N'(E)$ spectra for both SnO_2 and In_2O_3 are seen to be almost identical. Each displays a triplet structure peaked at $E \sim 510$ eV and associated with the O KLL transition. The structures associated with the MNN transitions of In and Sn occur at $E \sim 396$ eV and $E \sim 422$ eV, respectively. The pronounced doublet structure (separation ~ 7.0 eV) reflects the comparable spin-orbit splitting of the initial M level ($3d_{5/2}-3d_{3/2}$) of the metal atom. Note that the weaker structure for In_2O_3 occurs at the same energy (422 eV) as the dominant Sn peak in SnO_2 . This must be taken into account when determining the strength of the Sn signal in ITO samples from the peak-to-peak height of Sn structure at 422 eV. We see from Fig. 5 that the peak-to-peak height ratio (PPHR) of the weak structure in In_2O_3 at 422 eV to the main peak at 396 eV is only about 2×10^{-2} . For In_2O_3 , the metal-to-oxygen PPHR determined from Fig. 5 is 1.2 while for SnO_2 the PPHR = 1.5.

B. ITO

In Fig. 6, we present an $N'(E)$ spectrum from a typical ITO film (~ 2000 Å thick) sputtered onto quartz. The sample was sputter-cleaned by Ar^+ bombardment in situ before AES analysis. Contributions from SnO_2 and In_2O_3 can be identified in $N'(E)$. If we subtract out the contribution from In_2O_3 to the structure at 422 eV, a PPHR of $\text{In}(396 \text{ eV})/\text{Sn}(422 \text{ eV}) = 47.5$ is obtained. Assuming each metal is present as its stoichiometric oxide, SnO_2 and In_2O_3 , comparison with the $N'(E)$ data for the pure powder oxides (Figs. 4 and 5) yields the following surface composition for the ITO film: 85 atomic % In_2O_3 and 15% SnO_2 , which is in close agreement with the target composition of 83 atomic % In_2O_3 and 17% SnO_2 (i.e., 90% In_2O_3 , 10% SnO_2 by weight). However, this film composition does not yield the measured oxygen peak-to-peak height in Fig. 6, which is $\sim 8\%$ smaller than expected. This discrepancy suggests that an 8 atomic % oxygen deficiency exists in the ITO films (or equivalently an 8% In and/or Sn excess). Deviation from stoichiometry is not unexpected since the conduction mechanism in these highly conducting metal oxides is believed to arise from donor electronic levels associated with excess interstitial metal and/or oxygen vacancies.¹⁰

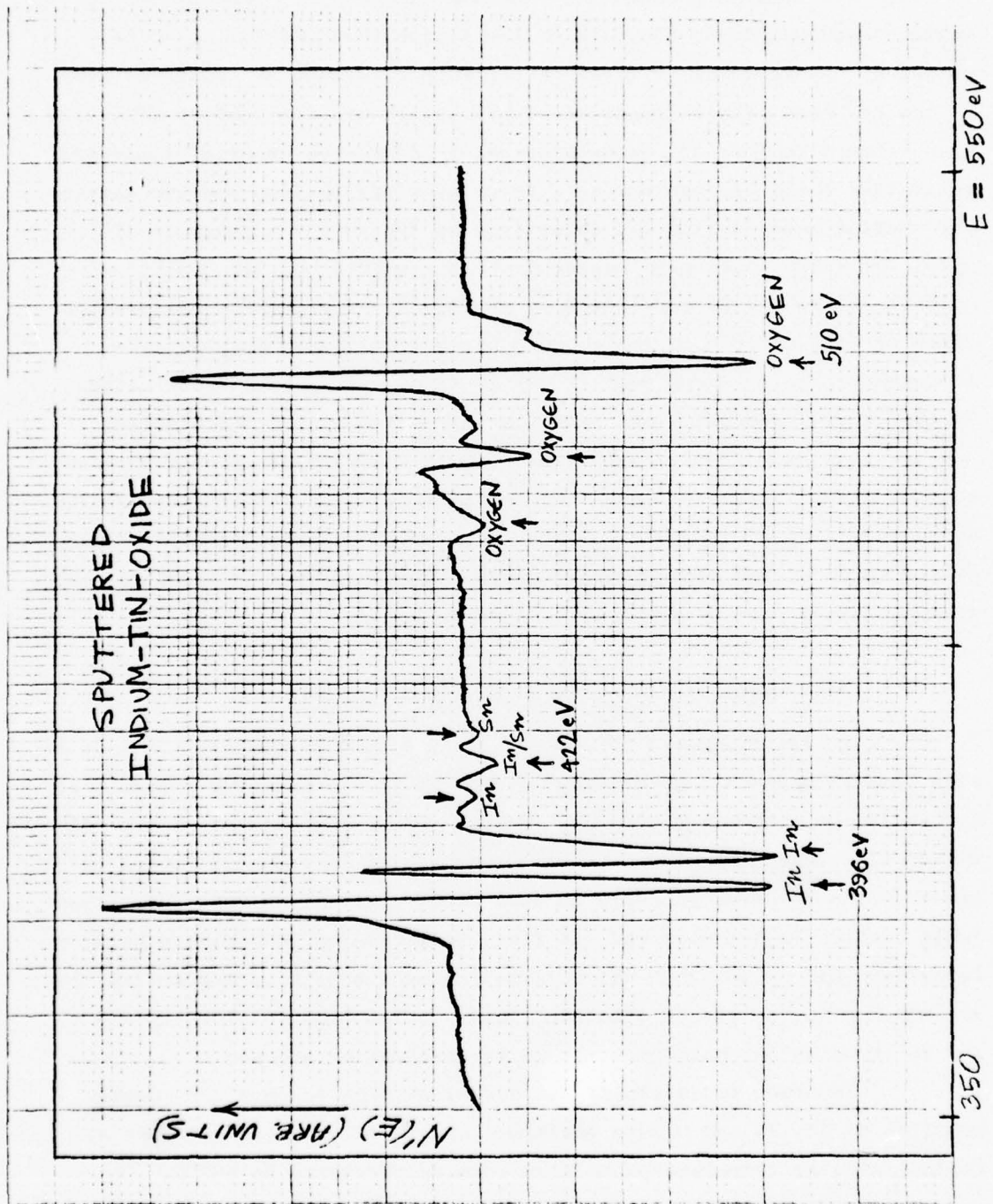


Fig. 6. AES DERIVATIVE SPECTRUM OF A SPUTTERED ITO FILM.

C. Depth Profiles

AES was used in conjunction with simultaneous Ar^+ ion sputtering so that chemical depth profiles of the activated ITO films could be obtained. As layer after layer of the sample surface is sputtered away by the Ar^+ beam, the composition of the layers are analyzed by AES. In this manner, changes in composition which might have observed following activation could be observed as a function of depth into the ITO sample. The sputter rate for ITO was determined by sputtering through an ITO sample of known thickness (measured using a quartz crystal thickness monitor during sample deposition). In Fig. 7, we present a calibration depth profile curve made for a 690 Å thick ITO film on quartz. The strength of the In Auger peak at 396 eV (i.e., its peak-to-peak height in the $N'(E)$ spectrum) has been plotted versus sputtering time for 1 KeV Ar^+ ions, $25 \mu\text{A}/\text{cm}^2$. Initially, the In signal increases as surface contamination is removed, then levels off and, after ~25 minutes, sharply decreases when the ITO/ SiO_2 interface region has been reached. Based on the width of the depth profile curve, we calculate that for 1 KeV Ar^+ the sputtering rate of ITO is $\sim 1.1 \text{ \AA}/\text{min}-\mu\text{A}/\text{cm}^2$.

1. The Effect of Temperature and Electric Field

It is reasonable to suppose, as has been suggested,¹ that both high temperature and high electric fields in the necked-down region play a role in the activation process. Since typical currents drawn are ~150 mA and film thickness ~1500 Å, current densities in excess of $10^6 \text{ A}/\text{cm}^2$ are expected to occur in a 0.1 mm wide neck. This gives rise to extreme joule heating in the neck and, in fact, temperatures $\gtrsim 800^\circ\text{C}$ have been reported. Since the break which forms across the neck during activation has width $\sim 5 \mu$, we expect electric fields on the order of $100 \text{ V}/5 \mu = 2 \times 10^5 \text{ V}/\text{cm}$ to be characteristic of the activation process.

In order to determine the effect of high temperature, depth profiles of Sn, In and O were performed on ITO films which had been annealed in N_2 at temperatures between room temperature and 600°C . No change in composition could be detected in the region probed--from the surface to $\sim 300 \text{ \AA}$ into the bulk.

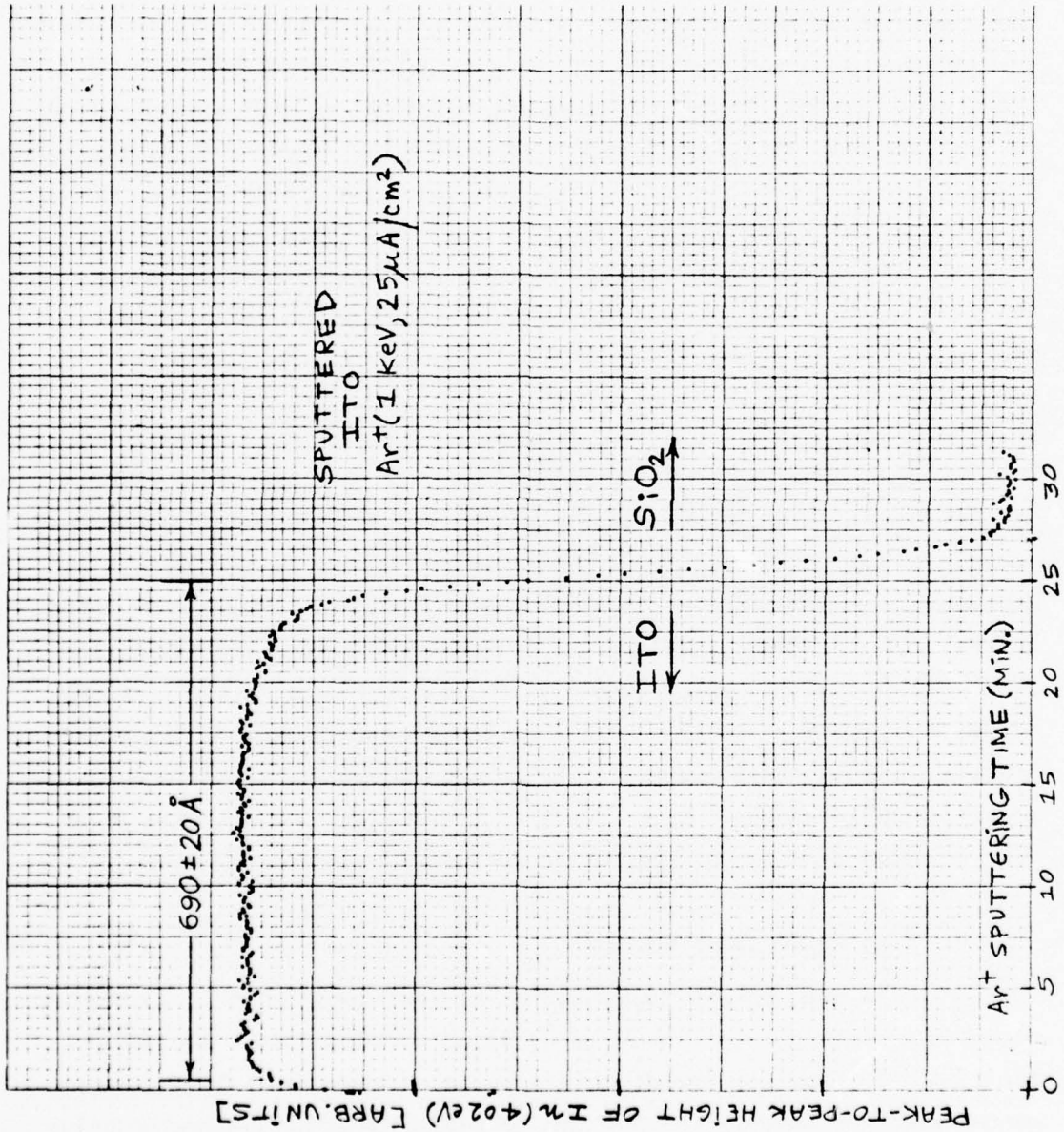


Fig. 7. CHEMICAL DEPTH PROFILE OF In IN A 690 Å SPUTTERED ITO FILM ON SiO₂.

We have some evidence, however, that the effect of temperature and electric field results in a surface composition different from the bulk. In Fig. 8 is shown the chemical depth profile of an ITO film which had been annealed at $\sim 200^\circ\text{C}$ in the presence of an \vec{E} field of 15 kV/cm normal to and directed away from the surface. If there are mobile positive ions in the sample, these ions could undergo a field-assisted diffusion to the surface. From Fig. 8, we see that the depth profiles of In and O are constant, while the Sn signal decreases by $\sim 10\%$ within $\sim 40 \text{ \AA}$ of the surface. This effect cannot be due to the removal of surface contamination which is expected to increase the signal from the underlying, clean layers. Unfortunately, time did not permit this experiment to be repeated or tried at higher annealing temperatures ($\sim 800^\circ\text{C}$) characteristic of the activation conditions. Therefore, we choose to regard the observed surface enrichment of Sn as a tentative result. Although not known for sure, the mechanism of electrical conduction in ITO films is believed to result from electronic donor levels associated with interstitial metal ions and/or oxygen vacancies.¹⁰ (In SnO_2 emitters the levels of donor impurities such as Sb must be considered as well.) Since the diffusion coefficient of interstitial Sn^+ in ITO is not known, we were unable to determine whether the magnitude of the observed Sn segregation seen in Fig. 8 is consistent with field-assisted diffusion at 200°C and 15 KV/cm. In any event, if the surface segregation is a real effect, we expect it to be even more pronounced during the activation process in which temperatures ($\sim 800^\circ\text{C}$) and \vec{E} fields ($> 200 \text{ KV/cm}$) are significantly larger. This assumes, of course, that some component of the \vec{E} field is directed toward the surface.

2. The Necked-Down Region

The strength of the Sn signal at the center of the necked-down region was monitored as a function of depth sputtered into the sample for five ITO films fabricated and activated at Stanford. The spot size of the electron beam used in AES was probably $\sim 20 \mu$ so that the 5μ wide break in the neck as well as the immediate surrounding area has been probed. As can be seen from Fig. 9, the Sn concentration for this sample decreases exponentially with depth. In fact, the Sn concentration

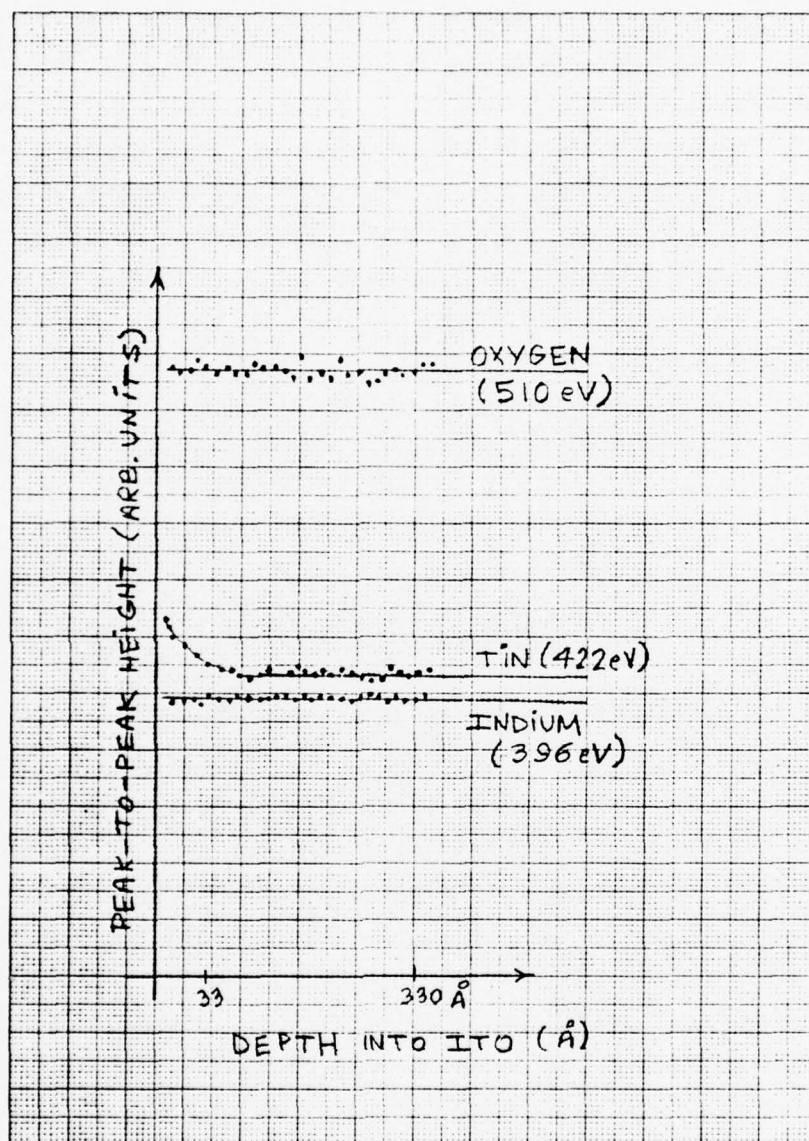


Fig. 8. CHEMICAL DEPTH PROFILES OF In, Sn, AND O FOR AN ITO FILM WHICH WAS ANNEALED AT 200°C IN A 15 KV/cm ELECTRIC FIELD NORMAL TO THE SURFACE. The vertical scales are not the same for each element.

for each of the five samples was found to fall off as $e^{-x/\lambda}$. For comparison, the Sn signal from the extremities of the neck (where the composition was the same as before activation) has been shown. We see that after activation the Sn is more highly concentrated at the surface; however, this concentration drops quickly with distance into the sample. It is instructive to plot the value of λ appropriate to each sample against the resistance R_f of the sample after activation. The sample resistance is determined by the resistance of the necked-down region since the remainder of the film is highly conducting and in series with the highly resistive neck. The resistance of each sample was approximately the same before activation. We see from Fig. 10 that $\ln R_f$ vs λ is a straight line. Hence, there appears to be a strong correlation between the distribution of Sn and the high resistance of the necked-down region, this high resistance being a characteristic feature of all SnO_2 and ITO cold-cathode emitters.

V. THE SnO_2 /ITO DATA BASE

From the published literature, it is difficult to evaluate the performance or potential of cold-cathodes based on SnO_2 or ITO. There are several reasons for this. In the first place, the literature is quite limited in the number of articles. In addition, reports are sometimes contradictory. For example, the Russian workers who first reported emission from SnO_2 later published emission currents over two orders of magnitude lower but made no mention of this discrepancy with the earlier dramatic results.^{1,2} Critical information is sometimes left out. For example, the report of high emission from ITO films⁵ did not mention that emitter lifetimes were brief, on the order of hours.¹² It is often difficult to compare the results of different workers when the methods used to fabricate the emitters (CVD, evaporation, sputtering) and the conditions under which activation occurred differ. Most distressing, private correspondence has revealed that the strong electron emission first reported could not, in some cases, be reproduced in later experiments. One example is the work of John Mize, Beta Industries, on SnO_2 cathodes and cathode arrays.⁸ The best cathodes made (so-called "high

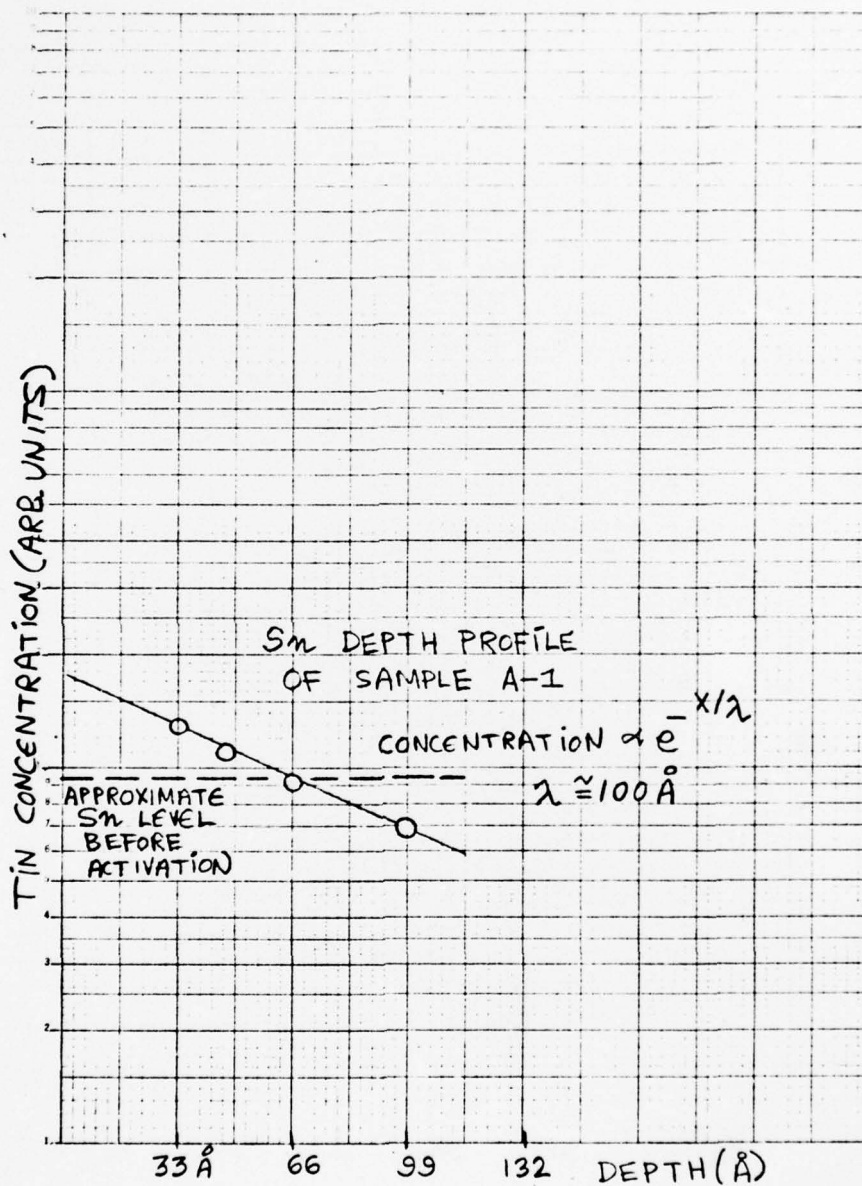


Fig. 9. CHEMICAL DEPTH PROFILE OF Sn IN THE NECKED-DOWN REGION OF AN ACTIVATED ITO FILM. There is an enrichment of Sn at the surface compared with the Sn level before activation. The concentration falls off exponentially with distance into the film.

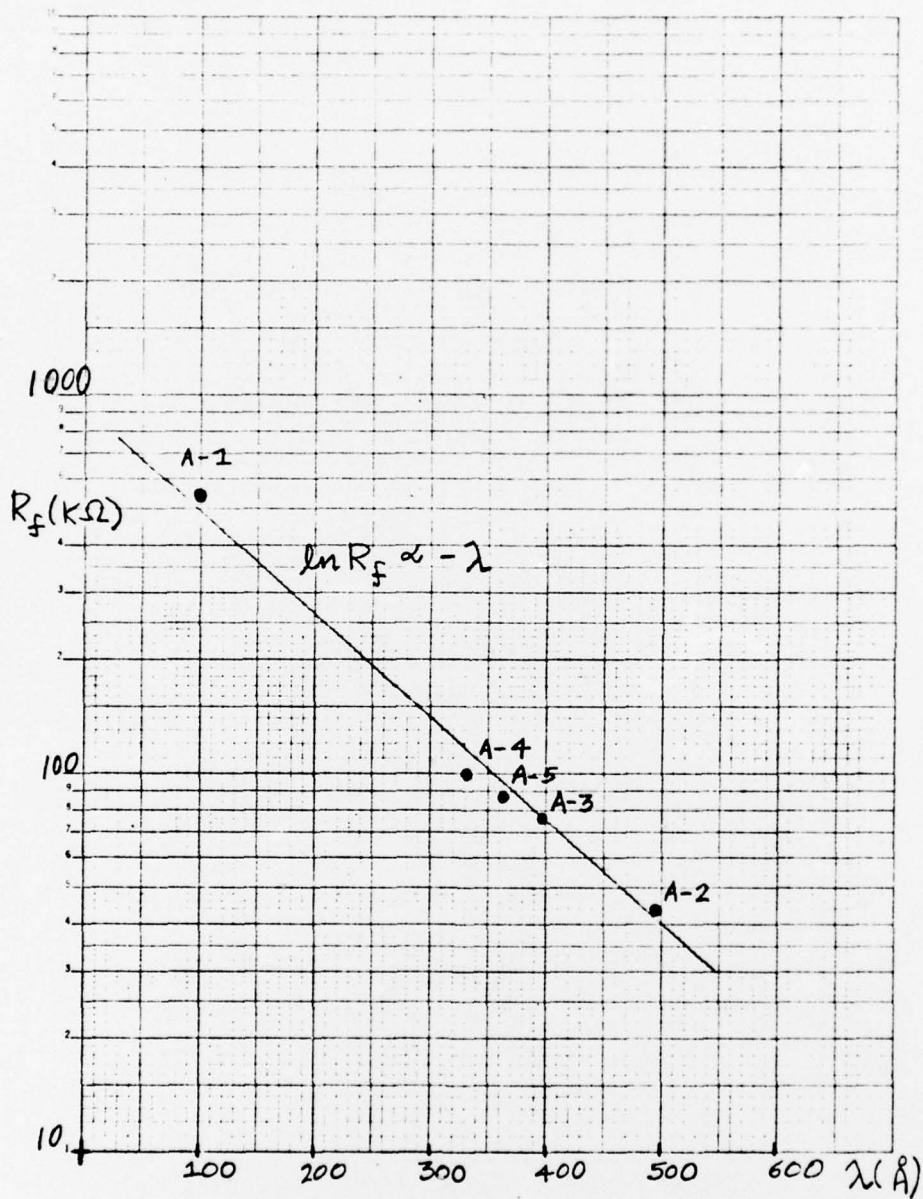


Fig. 10. THE FINAL RESISTANCE R_f OF SEVERAL ACTIVATED ITO CATHODES IS PLOTTED AGAINST THE PARAMETER λ , DETERMINED FOR EACH CATHODE FROM A CHEMICAL DEPTH PROFILE PLOT AS IN FIG. 9 FOR CATHODE A-1.

voltage" cathodes because of the high activation voltages >100 V) had $I_E \gtrsim 600$ μ A and efficiencies of $I_E/I_F \sim 60\%$. As we understand it, these encouraging results were the exception rather than the rule and could not be duplicated after 1974. More typical emission parameters would be $I_E \sim 20$ μ A, and $I_E/I_F < 1\%$. At MIT, Leslie Wong (a graduate student under Prof. C. G. Fonstad) has been unable to reproduce the earlier dramatic results of Mike Hartwell although she is using essentially the same equipment and techniques for fabrication, patterning, and activating the ITO films. Peak emission currents of only ~ 10 μ A were obtained.¹³ At Stanford, we have also activated and measured emission from ITO films prepared and supplied to us by Leslie Wong with similar results. Unfortunately, none of the earlier ITO films which exhibited such large emission could be obtained from MIT for Auger analysis at Stanford.

It is clear that without a reliable data base, decisions on the future support and/or direction of cold-cathode research cannot be made. Based on a consideration of all the information available to us, we feel the following statements are realistic.

- (1) Cold-cathodes can be formed from SnO_2 (either CVD or evaporated) and from sputtered ITO films.
- (2) Large emission currents (500 μ A-1 mA) and/or efficiencies $\gtrsim 50\%$ are the exception rather than the rule and have not been reproduced by the workers who have reported them. This is not to say that these results cannot be obtained again.
- (3) Emission currents of 10-100 μ A and efficiencies of 1-10% are representative at film voltages $V_F \sim 100$ V.
- (4) Activation and the subsequent emission is associated with the formation of a high-resistance region (in H-shaped samples, a 2-25 μ wide break across the neck) probably through the combined action of high temperature and electric fields.

VI. DISCUSSION

The increased concentration of Sn found at the sample surface following activation and the exponential fall-off ($\sim e^{-x/\lambda}$) into the bulk

is strongly suggestive of thermal diffusion. The different depth-profiles of Sn measured after activation would then be associated with different time-temperature profiles during activation. It is difficult to pursue this argument in a quantitative way since the diffusion coefficient of Sn in SnO₂ or ITO is not known and because the time-temperature profile during activation were not measured. It may, however, be possible to relate time and temperature during activation. Consider the following model for the activation process. The resistivity of SnO₂ and ITO films $\sim e^{\Delta E/kT}$, where ΔE is the activation energy for electronic conduction. In the case of SnO₂ doped with Sb, ΔE would represent the energy to raise an electron from an Sb donor level to the conduction band. In ITO, the donor levels would probably be associated with oxygen vacancies and/or interstitial metal cations. As current flows through the neck at a fixed voltage, I^2R losses increase the temperature and hence decrease R as $e^{\Delta E/kT}$. This increases I which leads in turn to even more carriers being thermally generated. This thermal runaway would explain the rapid exponential rise in current and temperature with time which is observed when the activation voltage has been reached. When sufficient energy has been dumped into the necked-down region, the break occurs and R drops to a value associated with the conduction mechanism appropriate in the break. If this explanation is basically correct, the dependence of temperature on time would be determined primarily by the conduction mechanism in the film and material parameters such as the thermal conductivity, melting point, etc.

The observation of surface enrichment of Sn in the Sn-O₂ system is not without precedent. As mentioned earlier (Part II), our previous photoemission measurements of O₂ chemisorption on evaporated Sn strongly suggest that the surface remained metallic even after saturation exposures to O₂ (>4000 L). It is well known that SnO₂, In₂O₃, and related oxides such as ZnO are almost never found to have perfect stoichiometry but instead contain an excess of metal. Under the extreme nonequilibrium conditions of activation, some of this metal could have diffused to the surface and remained. As the photoemission results indicate, there can exist conditions under which the surface segregation of Sn in SnO₂ is the energetically favored configuration.

Our preliminary results on the combined effect of temperature and electric field indicate that migration of Sn in ITO films is facilitated by the application of an \vec{E} field along the direction of migration. If this effect contributes to the build-up of Sn at the sample surface observed following activation, then the geometry of the break as it forms is probably such that \vec{E} fields exist which on the average are directed toward the surface. If the net \vec{E} field were directed toward the surface, a preferential diffusion of Sn along the net field and toward the surface would occur.

In Fig. 10, we showed that the resistance R_f of the high-resistance region correlated with the depth profile of Sn, viz, $\ln R_f \propto -\lambda$. This is difficult to understand. The dc conductivity $\propto N$, the total number of electronic carriers, so that $R_f \propto 1/N$. Now the amount of Sn, and therefore the number of carriers associated with the presence of Sn in ITO, $\propto \int e^{-x/\lambda} \propto 1/\lambda$. We then expect $R_f \propto 1/\lambda$ or $\ln R_f \propto -\ln \lambda$, instead of $\ln R_f \propto -\lambda$, as found. It should also be kept in mind when considering the possible effect of Sn on the final resistance of the sample that the surface regions are far from rich in Sn. We estimate that the surface of the necked-down region could have been enriched to only about 20% Sn over the preactivation value of 10%.

Regardless of the details of Sn migration, it is difficult to see how this could have increased the resistance of the film after activation--and by as much as three orders of magnitude! If the films were continuous, one expects that the surface region after activation, now richer in Sn, would be more conducting than before, even if the bulk of the sample were driven highly resistive by the activation process. What then is the origin of the high-resistivity region which is a characteristic of all reported emitting samples, either SnO_2 or ITO?

In order to arrive at a plausible explanation of the phenomenon, we have tried to take into account all the available data--not just our own for which information on emitting samples is limited.

In order to investigate the conductivity mechanism following activation, we have replotted I_F vs V_F data obtained by John Mize for CVD- SnO_2 emitters^{8a} as Fowler-Nordheim (FN) plots, i.e., as I_F/V_F^2 vs $1/V_F$. In Fig. 11, data from Ref. 8a, p. 42, has been replotted in this

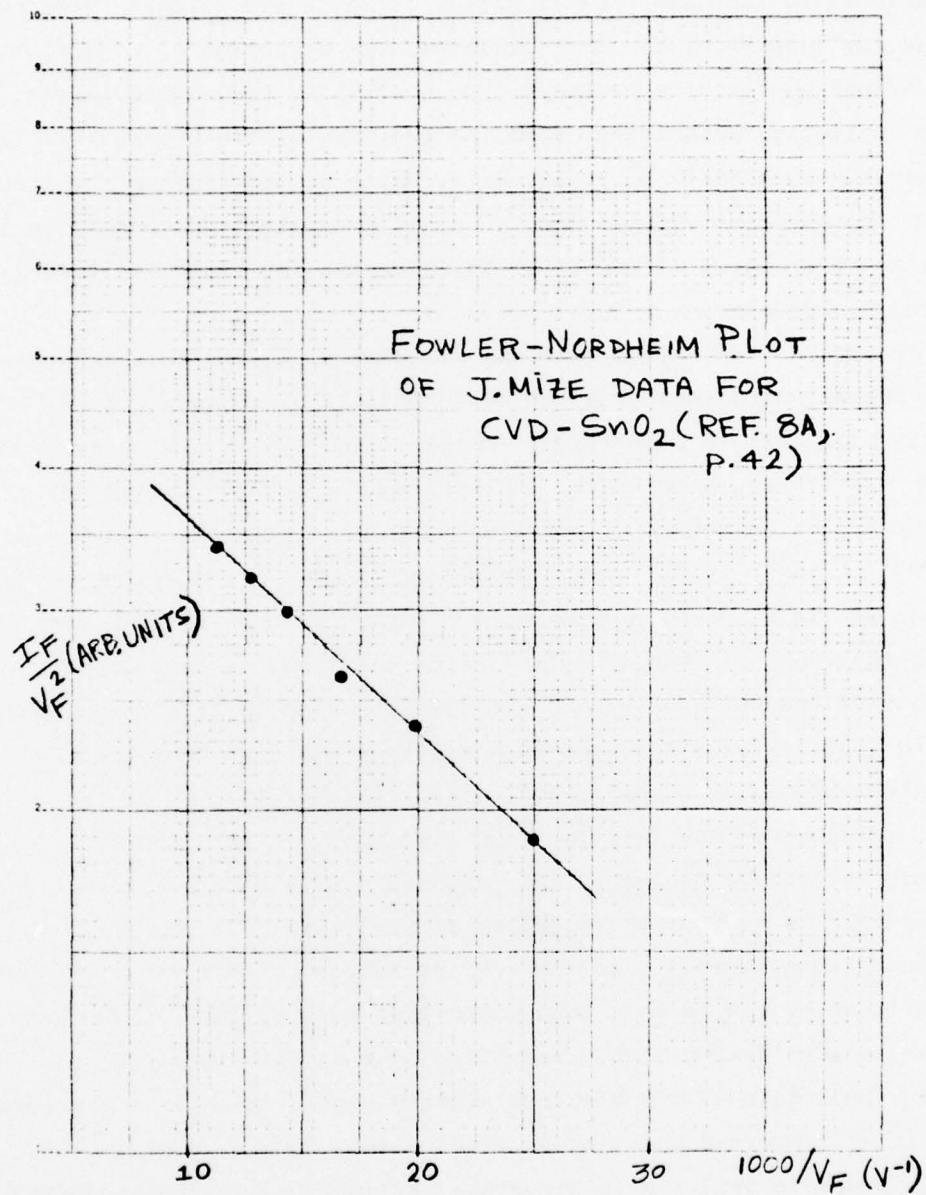


Fig. 11. FOWLER-NORDHEIM PLOT OF FILM CURRENT, I_F , AND FILM VOLTAGE, V_F , FROM THE DATA OF J. MIZE. The linear plot suggests that the conduction mechanism in SnO₂ after activation is field-assisted tunneling.

way and is seen to be linear. FN plots of other emitters (Ref. 8a, pp. 39-44) were also linear. This is in agreement with results obtained by Russian workers for CVD-SnO₂ emitters.² When a metal is placed in a strong external electric field, E, the potential outside the metal is altered so that quantum mechanical tunneling of electrons outside the metal becomes possible. The resulting electron current in the presence of the field E obeys the FN relation, i.e., $I \propto E^2 e^{-B/E}$, where $B = 4/3 \sqrt{2m/e} \frac{2}{\hbar} \phi^{3/2}$ and ϕ is the metal work function.¹⁴ We think it likely then that the break is not a continuous film but is instead composed of islands of the starting material (either ITO or SnO₂) that are isolated from one another by the SiO₂ substrate. This could have resulted from localized melting of the film during activation which reformed as the film cooled. Conduction in the film would then occur from island to island in the presence of the strong \vec{E} field set up across the break (10^{5-6} V/cm). This view has also been presented by Russian workers.² The increase in Sn at the surface of the islands could lower the work function at the surface and thus enhance the tunneling current and/or concentrate current flow at the surface, increasing emission probability.

Indirect support for this model comes from the observation by Japanese workers of self-sustained emission (SSE) from the necked-down region of SnO₂ emitters.⁷ That is, once an emission current was established, it continued even in the absence of a voltage applied across the film. This effect has also been reported in Al₂O₃ and MgO films under electron bombardment.^{15,16} The explanation was that the insulating film surface charged up positively as emission current was drawn off the sample to the anode. A strong \vec{E} field was then established at the film surface which could accelerate electrons from the bulk, subsequently creating an avalanche of secondary electrons. Critical to the occurrence of SSE was that the film be rough so that electrons could come from deep within the film and suffer sufficient secondary-producing collisions in transit to the surface. The rough, island-nature of the break which we have proposed satisfies this criterion for SSE.

The flow of field-emission current (tunneling current) is along the film and is expected to be greater along the surface because of the

metallic enrichment there. In the presence of a strong collecting field, however, some electrons could follow field lines to the anode and be collected (see Fig. 12). Hence, for a fixed collector voltage, the shape of the $I-V_F$ curves for I_E and I_F should be nearly identical. A rise in current along the film should give rise to a proportional increase in the number of electrons which can be diverted to the anode. The assumption is that the collector is biased sufficiently positive so that the energy of the electrons does not play a significant role in their collection probability. In fact, I_E and I_F do track one another at low voltages ($V_F \lesssim 60$ V), as can be seen in either the work of John Mize (Ref. 8a, pp. 34-44, 54-58) or of Russian workers.² However, as voltage V_F is increased above ~ 80 V, I_E increases far more rapidly than I_F . It has been suggested that secondary electrons, produced when field-emitted electrons collide with the edge of the gap, could also contribute significantly to the emission current at higher voltages.² This, of course, would be true only when the secondary yield is large. Without a knowledge of the secondary yield of SnO_2 or ITO as a function of electron energy, this possibility cannot be ruled out.

Such a mechanism could explain in part the short lifetimes of many SnO_2 cold-cathodes when operated at higher voltages. Since SnO_2 is not refractory, prolonged primary electron bombardment could result in the chemical and/or physical deterioration of the edge of the gap. This would result in a reduction of the secondary emission current with time.

VII. SUMMARY

Based on our present work and all other research on SnO_2 and ITO cold-cathode emission of which we are aware, the following model for the activation and emission process is put forth.

Activation is initiated by producing a thermal runaway condition in a localized area of the film. As the temperature increases from joule heating, the number of current carriers increases exponentially, further raising the temperature. When sufficient energy has been dumped into this small area, the film (through melting?) ruptures, producing a break of width $\sim 2-20$ μ composed of islands whose surface is slightly enriched

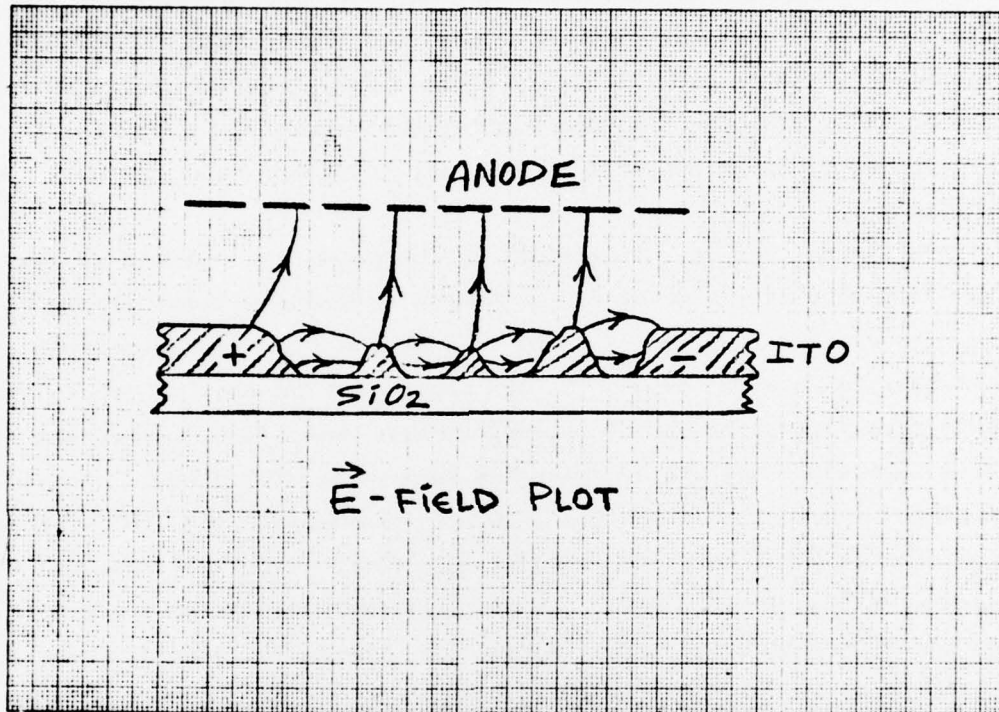


Fig. 12. ELECTRIC FIELD PLOT FOR AN ACTIVATED ITO OR SnO_2 FILM AFTER ACTIVATION BASED ON THE MODEL WE HAVE PROPOSED. The necked-down region consists of islands of ITO or SnO_2 , separated by the insulating SiO_2 substrate, and whose surface has been enriched in Sn. A similar model has been proposed by the workers of Ref. 2.

in Sn. Conduction across the break is by field-emission, i.e., by inter-island tunneling made probable in the strong electric fields which are set up across the break ($\sim 10^{5-6}$ V/cm). The lower work function of the Sn-enriched surface increases field-emission probability and concentrates current flow near the surface of the film. Emission then consists in diverting a fraction of this tunneling current which flows along the film surface to the positive anode. At high film voltages ($V_F \gtrsim 100$ V) we cannot rule out the possibility of secondary emission from electrons which collide with the positive edge of the break. This may explain in part the short lifetimes of many SnO₂ cold-cathodes at higher operating voltages.

We stress that the above model is tentative; however, it is consistent with much of the data--e.g., the Fowler-Nordheim behavior of I_F vs V_F , the similar shape of I_E and I_F at low V_F , the phenomenon of SSE observed from the break, the AES depth profiles we have taken, SEM photographs of the break, etc. Support also comes from independent studies done at Ft. Monmouth in which the neck of activated SnO₂ cathodes displayed a web-like structure in a SnO₂ matrix (see Fig. 13). The web consisted of channels which extended down to the SiO₂ substrate and whose edges were rich in Sn.¹⁷ This is in addition to the usual break which formed after activation. Put another way, the webbed region of the films consisted of islands of SnO₂ whose edges were enriched with Sn. These islands could contribute to the emission current.

An important question which remains unanswered regarding the phenomenon of cold-cathode emission is: what is so special about SnO₂ and ITO? In view of the proposed model, their most important characteristic is probably that they are both metal-excess semiconductors. This leads not only to the exponential thermal runaway during activation but to the metallic enhancement of the surface following activation. Likely candidates for cold-cathode emitters would then be thin films of metal-excess semiconductors (which tend to be metal oxides) such as ZnO and TiO₂.

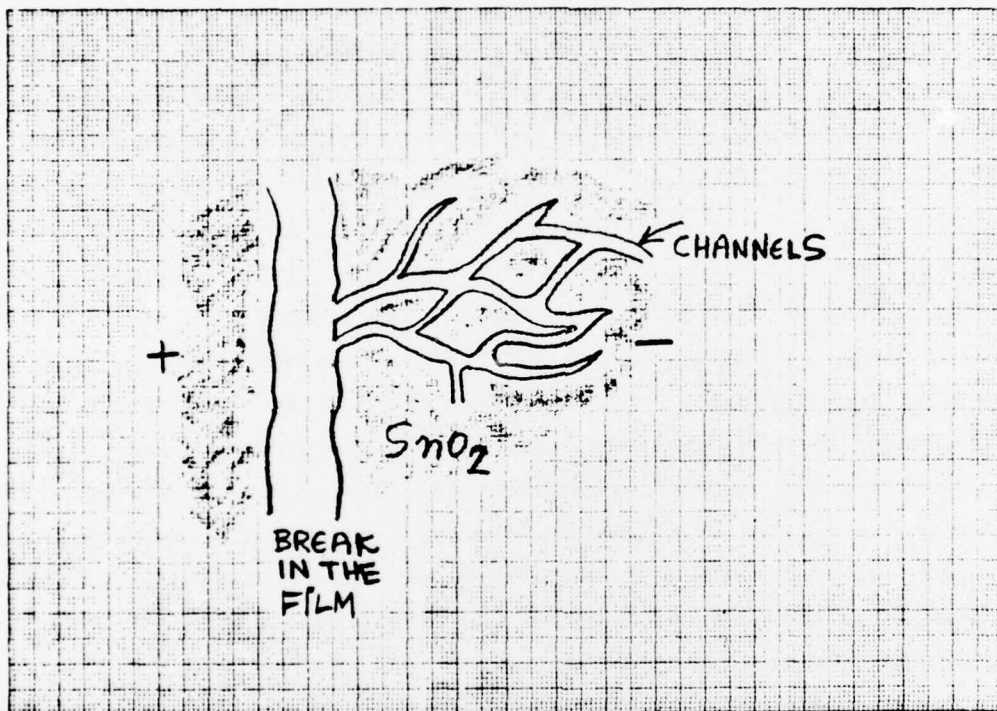


Fig. 13. THE PRESENCE OF WEB-LIKE STRUCTURES EXTENDING FROM THE BREAK IN THE NECKED-DOWN REGION TOWARD THE NEGATIVE ELECTRODE HAS BEEN FOUND BY WORKERS AT FT. MONMOUTH (REF. 17) IN ACTIVATED SnO₂ FILMS. The web consisted of channels which extended down to the SiO₂ substrate but whose edges were rich in Sn.

VIII. RECOMMENDATIONS

A characteristic feature of research into the cold-cathode emission properties of SnO_2 and ITO has been the failure to obtain consistent results. Optimistic reports of quality cathode performance have turned out in at least three cases not to be reproducible.^{2,5,8} In our own efforts, this was particularly distressing. We had invested over a year laying the experimental groundwork and building appropriate equipment to analyze SnO_2 emitters only to find out that the attractive emission, on which our involvement in the project was based, could not be reproduced. As discussed earlier, we next directed our efforts at ITO since such strong emission had been reported.⁵ It had never been our intention in proposing this work to fabricate cold-cathode emitters, and quite a bit of effort was used up in acquiring the necessary skills--how to sputter conductive ITO films, how to pattern and metallize the films, etc. To our disappointment, we never were able to get satisfactory emission from the ITO films we fabricated. Shortly before our contract terminated, we learned that we were not alone. The workers who first reported strong emission from ITO could not reproduce their own results. This is not to say that the earlier reports were in error. Whether a satisfactory emitting region can be formed in the cathode may depend critically on some film property that was not measured and therefore was not controlled during sample fabrication and activation.

Based on our experiences in this program, the following recommendations are made.

- (1) There seems little doubt that cold-cathode emission (~ 10 μA) can be obtained from activated SnO_2 and ITO. We also feel that reasonable progress may have been made toward a theoretical model for the activation and emission process. However, a major technical effort will be required if strong, reproducible emission is to be obtained.
- (2) Emphasis in such a program should be on (a) controlling the activation process--That is, assuming our model is correct, controlling the distribution, size, and properties of the islands in the break to optimize emission and emitter lifetime. The present activation technique is totally hit-or-miss and unacceptable--(b) gaining an understanding and control of the factors which influence

the physical and electrical properties of the materials employed as cathodes and which ultimately influence the performance of the cathodes. Unfortunately, we cannot rule out fundamental physical reasons why results have not been reproducible, so that such a program has no guarantee of success.

- (3) Since many of our own problems were caused by the failure of others to communicate their results to us, this program might best be conducted at one research facility. A 3-year program with a total budget of $\sim \$10^6$ is probably the minimum investment needed to do any meaningful work in this area.
- (4) Whether or not such a program should be undertaken can not be decided until some essential groundwork is done to determine if these cathodes can be economically incorporated into existing devices. Measurements of the spatial and energy spread of emitted electrons (even from poor emitters) should have a high priority before a decision is reached.

REFERENCES

1. M. I. Elinson, A. G. Zhdan, G. H. Kudintseva, and M. E. Chugunova, Radio Eng. and Elec. Phys. 8, 1290 (1965).
2. V. V. Nikulov, G. A. Kudintseva, M. I. Yelinson, and L. A. Kosul' Nikova, Radio Eng. and Elec. Phys. 8, 1153 (1971).
3. R. A. Powell and W. E. Spicer, "Investigations of Tin Oxide and Related Oxides with Regard to Cold Cathodes," DAHC-04-74-0022, U. S. Army Research Office (Semi-Annual Report, March 1975).
4. R. A. Powell and W. E. Spicer, Surf. Sci. 55, 681 (1976).
5. M. Hartwell and C. G. Fonstad, Technical Digest 1975 Int. Electron Devices Meeting, Washington, D.C. (1975), p. 519.
6. D. B. Fraser and H. D. Cook, J. Electrochem. Soc. 119, 1368 (1972).
7. T. Hanasaka, T. Satake, M. Hashiba, and T. Yamashina, Proc. 6th Int. Vacuum Congr. 1974 (Japan. J. Appl. Phys. Suppl. 2, Pt. 1, 277 (1974)).
8. John L. Mize (a) "Research and Development of Non-Active Surface NEA Emitter," ECOM-73-0225-2 (Final Report, May 1974); (b) "Research and Development of Non-Active NEA Emitter," ECOM-74-0225-1 (Semi-Annual Report, May 1974); (c) "Research and Fabrication of Solid State Emitter Arrays," ECOM-0195-F (Semi-Annual Report, August 1974); (d) "Development of Variable Barrier Photoemitter," DAAK02-72-C-0422 (Final Technical Report, November 1972); (e) "Solid State Emitting Device Based on SnO₂," U.S. Patent #3,821,773 (June 28, 1974).
9. Bernard Smith, Advanced Concepts and Technical Devices Team, U.S. Army Electronics Technology and Devices Laboratory, Ft. Monmouth, N.J.
10. J. L. Vossen, RCA Review 22, 289 (1971).
11. A literature search we have made reveals that, for whatever reasons, these Russian workers have not published in this field over the last five years.
12. Private communication with Prof. C. G. Fonstad, Center for Materials Science and Engineering, MIT.
13. Leslie Wong, "Electronic Thin Film Emitter In₂O₃/SnO₂," unpublished report for E.E. Course #6.991, MIT (May 1976).
14. See, e.g., "Introduction to the Theory of Solid State Physics," J. D. Patterson (Addison-Wesley, 1971).

15. L. Malter, Phys. Rev. 50, 48 (1936).
16. H. Jacobs, J. Freely, and F. A. Brand, Phys. Rev. 91, 804 (1953).
17. Private communication with Dr. H. H. Kedesdy, Electronics Technology and Devices Laboratory, Ft. Monmouth, N.J.