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THIN FILM TECHNIQUES IN THERMOELECTRICITY

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PERIOD: OCTOBER 20, 1961 to March 31, 1962

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I. INTRODUCTION

During the first six months of this investigation into the properties of thin film evaporated thermoelectric materials, the broad features of the problem have been explored. It is already clear that layers of either n or p-type can be formed with electrical characteristics approaching those of bulk materials. Variations in the properties can be made through controlled evaporation rate and substrate temperature. In spite of the complexity of the starting thermoelectric materials many of the results attained so far can be fitted into a simple unified description of the evaporation process. Detailed studies are now in progress to confirm these deductions and to obtain precise control over evaporation parameters in order to investigate the effects of such variables as crystal size, orientation, and chemical gradation in the films.

X-ray studies of the deposited films have been undertaken as well as preliminary Hall measurements made on some films. Diffraction patterns both of bulk materials and films are highly complex and although certain correlations of electrical properties and structure have been observed, detailed interpretations of the patterns have not been possible up to this time.

Annealing studies have shown that marked changes can be made in film properties principally in the direction of improvement. This appears to be an important area for future investigation and a study of the kinetics of the process is

being undertaken to aid in the interpretation of the effects.

With these investigations it is likely that a fundamental understanding of the nature of these evaporated thermoelectric films will be obtained which will enable us to make a meaningful evaluation of the applicability of film thermoelectrics to devices.

II. EXPERIMENTAL PROCEDURE

Thermoelectric alloys for use in this program have been prepared by melting the elemental components of 99.999% purity together in evacuated (10^{-5} mm.Hg) quartz tubes. The ampoules were manually agitated to insure proper mixing. Among the alloys of interest are those whose properties are recorded in Table I.

Films of these materials were deposited on 3 inch X 1-1/2 inch pyrex plates, which had been washed in detergent, rinsed in distilled water and oven dried. Substrate temperature was maintained during evaporation by holding the substrate in contact with a heated copper block.

Evaporation geometry was maintained constant with a 6" source-substrate spacing. A standard 1/2 gm sample (for 5 minute deposition time) of the required alloy was evaporated from a directly heated dimpled tantalum strip in a vacuum of 10^{-5} - 10^{-6} mm.Hg. After each run the residue was removed and a new strip heater inserted to avoid contamination. The deposited films were masked during the evaporation process to produce several parallel regions which were later contacted with strips

of silver paint. The samples were stored in a dessicator when not being examined.

Film electrical resistance could be measured with an ohmmeter on the various film regions and an average ohm/sq. resistance was computed. Seebeck voltages were determined using a copper block heated to 120°C as the hot junction and room temperature as the cold sink. The voltages developed were measured with a type K-2 Leeds and Northrup potentiometer.

Film thickness was determined microscopically by forming the layer on a polished "Koldmount" substrate and encapsulating it in a second "Koldmount" layer. After sectioning and polishing perpendicular to the plane of the film, thickness was measured microscopically at 1000X with a micrometer eyepiece with which films as thin as 1/4 μ could be resolved.

X-ray diffraction patterns to compare the structure of bulk alloys and films deposited under varying process parameters were obtained using Cu K α radiation with a Norelco recording wide-range goniometer.

III. EXPERIMENTAL RESULTS

Measurements of the thickness of p -type Bi-Sb-Te alloy films indicated that the average deposition rate, Figure 1, approximated a linear function of evaporator temperature; varying from 233 to 1100 $\text{\AA}/\text{min.}$ over the range of 560°C to 700°C studied. It should be noted that these measurements are averages from films deposited during a 20-30 minute interval.

The two gram alloy samples evaporated were larger than usual to avoid exhaustion of source material.

The process parameters varied, substrate and evaporator temperatures, were found to have a strong and complex influence on film Seebeck voltage. These are shown in Figure 2 and it may be seen that optimum Seebeck values for the p-type Bi-Sb-Te alloys are developed for deposition conditions near 580°C evaporator temperature and 100°C substrate temperature. The $210 \frac{\mu V}{^{\circ}C}$ exhibited by these films matches the Seebeck voltage for this material in bulk state.

Changes in film resistivity also occur with variation of the deposition parameters. Figure 3 illustrates these effects for films deposited in 30 minutes onto 23°C glass substrates. Confining our attention to as-deposited conditions for the present, the large dependence of resistivity on evaporation temperature is evident. In particular note the low resistivities of films formed with high source temperatures. These films also exhibited low Seebeck voltages opposite in polarity to that of the starting materials.

Figure 4 shows the continuous change in resistivity of a Bi-Sb-Te film during deposition from a 600°C source onto a 23°C pyrex substrate. On the assumption that film deposition rate is constant with time for the experimental conditions employed, resistivity will be proportional to the product of film resistance (ohm/sq.) and time. The changing nature of the film as deposition proceeds is evidenced both by the complex nature of the resistivity-

time function of Figure 4 and the contrast between the Seebeck voltage of $+135 \frac{\mu V}{^{\circ}C}$ noted at 30 minutes in the high resistance film and $-4 \frac{\mu V}{^{\circ}C}$ after 60 minutes.

Thus it can be seen that a low resistivity, slightly n-type low Seebeck voltage film is produced from a p-type bulk Bi-Sb-Te alloy by either high evaporation temperature or long deposition time with evidence that high substrate temperatures also favor such films. Samples of these films are now being analyzed to determine if a common chemical or structural alteration occurs.

The marked change in resistivity produced by heat treatment in air can be seen in Figure 3. Though the low resistivity films are relatively stable, mild heating produced a 200-fold reduction in resistivity of the high Seebeck voltage films with small accompanying reduction in thermoelectric power. It should be noted that after this aging resistivities are 5-100 times greater than that of the bulk starting alloy.

To pair with such p-type films, n-type films of comparable Seebeck voltages were formed from a 75% Bi_2Te_3 + 25% Bi_2Se_3 alloy doped n-type with 6 wt.% CuBr. The effect of dopant content on Seebeck voltage is plotted in Figure 5 for AgI and CuBr doped bulk materials. Though lower dopant contents result in increased E_s , high initial dopant was required to produce an n-type film for apparently a loss in dopant occurs during evaporation.

As in the p-type films, the Seebeck voltage of this set of films was dependent on deposition time, with the added feature that for short deposition time strongly p-type films were obtained, see Figure 6. After this initial anomalous period, E_S rose to a maximum and then decreased for longer evaporation times in a manner similar to that observed for p-type alloy films. It should be noted that these films were deposited during selected time intervals, by manipulation of shutters, over the 30 minute evaporation of the source alloy.

Because of the reversal in sign of E_S , exploration of the effect of process parameters on the properties of this n-type film was conducted using a ten minute evaporation period. The preliminary results of this study are tabulated in Table II.

Since the cations in CuBr and AgI have relatively low vapor pressures, it would be expected that severe fractionation of the dopant might occur during evaporation. Though doping is believed to be due solely to the halogen anion, the role, if any, of specific cation elements has not been established. Several BiI doped alloys exhibited resistivities approximately equal to AgI doped alloys of similar iodine content but their Seebeck voltages were systematically lower than those of the AgI alloys at the same iodine level as shown in Table III.

X-ray diffraction analyses of the Bi-Sb-Te p-type alloy films have so far revealed only one systematic correlation of thermoelectric properties with structure. As can be seen in Table IV, a diffraction peak at a 2θ value of 5.8° corresponding

to a lattice spacing of 15.2 \AA was noted for all films with Seebeck voltage above $37 \frac{\mu\text{V}}{\text{C}}$ and was absent in other films produced from the same alloy. Significantly, this line is also present in the bulk alloy for which, as noted previously, a Seebeck voltage of $210 \frac{\mu\text{V}}{\text{C}}$ was observed.

Changes in the X-ray diffraction patterns of 6% CuBr doped films were observed with annealing in air, and these are reproduced in Figure 7. Radiation was $\text{Cu, K } \alpha$, and intensity was recorded on a Norelco goniometer. A summary of the important features of these patterns is shown in Table V.

Large changes in film resistance also occurred on aging these films. However, the as-deposited characteristics of the film played a significant role in determining the direction of the resistance change. These variations are shown in Table VI.

The only simultaneous changes in the two sets of data are the large drop in resistance on aging 19b and the appearance of the 10.8° (diffraction) peak. Such a peak would be produced by diffraction from crystallographic planes spaced approximately 8.2 \AA apart. No lattice spacing of this amount has been reported in diffraction data for the various elements and intermetallic compounds possible in this alloy. Further data are being obtained on aging effects to provide a better understanding of these effects.

The effects of evaporator and substrate temperature indicate that the Bi-Te-Se thermoelectric materials undergo some decomposition during evaporation. Resistivity and Seebeck voltage data of the final films as well as the variation in film resistance during

evaporation support this point of view. The higher the evaporator temperature, the greater does this decomposition appear to be, so that for the highest temperatures used the films are probably degenerate having both low Seebeck voltages and resistivity. Elevated substrate temperatures seem to assist this process. It can be seen from Figure 2 that film properties are highly sensitive to temperature with Seebeck voltage changing rapidly over relatively small spans in evaporator or substrate temperature. These latest data were obtained with more precise temperature measurements and are a better determination of optimum conditions than given in an earlier report.

The variation in film resistance during evaporation shown in Figure 4 is particularly interesting, for it may document the actual fractionation of the materials. As evaporation temperature is altered it is expected that the curve of Figure 4 will be shifted and expanded or contracted along the time axis. We are now in the process of selecting out the "fractions" defined and separated by the plateau regions for auxiliary quantitative analysis. Figure 4 also furnished an indication of the range in properties attainable through evaporation.

Fractionation effects, especially with respect to dopant, have been more evident and straightforward with n-type materials. To achieve best properties in n-type films, overdoped starting materials were required. Crucible residue was always found to have a higher dopant content than the original charge.

The two most interesting observations in our recent work have been the discovery of the very low angle (5.8°) X-ray diffraction peak in only the higher Seebeck voltage laid down from p-type Bi-Sb-Te alloys. The d-spacing for this peak corresponds to about 15A and suggests an ordering effect in these layers. The second observation of large changes in film resistivity with mild heat treating is also expected to provide important information about the structure of the evaporated films. For example, we are examining the possibility that the films consist of islands of thermoelectric material separated by thin high resistance regions which are converted to low resistivity regions through the mild heat treatment.

IV. FUTURE PLANS

The changes in film resistivity and Seebeck voltage which take place during deposition are to be investigated in greater detail in an attempt to correlate them with chemical changes of the evaporant or structural changes in the films. Aging characteristics will be examined further through continuous X-ray diffraction studies during the heat treating cycle. Hall measurements are now being made and will be a valuable aid in the interpretation of the effects of aging as well as deposition parameters.

Bomb type crucibles are being built which will permit the evaporation of materials under conditions approaching equilibrium

between vapor and melt. Evaporation rate will be controllable separately from vapor temperature through alteration in the size of the crucible orifice.

A multi-layered p and n structure is to be fabricated using present optimum materials and conditions.

TABLE I
Composition and Properties of Bulk Materials

Alloy	E_s mV/°C	Conductivity Type	ohm-cm X 10 ⁴
Bi ₂ Te ₃	47	p	4.6
PbTe	220	p	20
Bi-Sb-Te	-230	n	1.88
Bi-Sb-Te	210	p	1.37
75% Bi ₂ Te ₃ 25% Bi ₂ Se ₃ with:			
6% CuBr	- 35	n	8.5
1% CuBr	- 60	n	4.5
0.1% CuBr	-168	n	15
6% AgI	- 53	n	11.8
1% AgI	-105	n	10.3
0.1% AgI	-215	n	33
25% Bi ₂ Te ₃ + 75% Sb ₂ Te ₃			
2.3% Te (excess)	168	p	11.2
20% Bi ₂ Te ₃ + 80% Sb ₂ Te ₃			
6% Te (excess)	163	p	11.5

TABLE II

Properties-Films from 75% Bi_2Te_3 - 25% Bi_2Se_3

6% CuBr Bulk Material

10-15 Min. Deposition Time

10^{-6} mm Hg. Vac.

Pyrex Substrate

Evaporation Temperature (°C)	23		100	
	$\mu\text{V}/^\circ\text{C}$	Ohms/Sq.	$\mu\text{V}/^\circ\text{C}$	Ohms/Sq.
600	-167	2500		
650	-77	1300	-130	2500
700	-28	350		

TABLE III

Characteristics of Bi-Te-Se Alloys
With Different N-Type Dopants

%I*	%AgI	%BiI	$E_s \left(\frac{mV}{^\circ C} \right)$	ρ (ohm-cm)
0.054	0.10	0.14	215 180	33.0×10^{-4} 34.7×10^{-4}
0.27	0.50	0.72	170** 106	9.35×10^{-4}
0.54	1.00	1.43	105 75	10.3×10^{-4} 7.28×10^{-4}
3.24	6.0		53	11.8×10^{-4}

* Calculated for AgI and BiI additions.

** By interpolation

TABLE IV

X-Ray Diffraction Analyses of
Bi-Sb-Te, P-Type, Alloy

Film E _S	2θ Values of Strong Diffraction Peaks				
	$\frac{eV}{^{\circ}C}$				
200	5.8°	-	27.8°	29.5°	38.5
103	5.8°	-	27.9°	-	39.0
37	5.7°	23.1°	27.8°	28.5°	-
15	-	-	27.8°	-	-
-3	-	23.2°	27.8°	28.3°	39.0
-3.5	-	-	27.8°	28.4°	38.8
Bulk					
210	5.7	-	-	28.3°	38.6

TABLE V

Important Features of X-Ray Diffraction Patterns

Film and Treatment	5.8° Peak	10.8°	29.2°
19b deposited	-	-	very weak
19b aged	-	present	stronger
19c deposited	sharp	-	very weak
19c aged	sharp	-	stronger

TABLE VI

Effects of Aging in Air of 75% Bi_2Te_3 ,
25% Bi_2Se_3 6% CuBr Films

	19 b Deposited during period from 5 to 10 minutes from start of evaporation		19 c Deposited from 15 to 20 minutes from start of evaporation	
	R ohm/Sq.	$E_s \frac{\mu V}{^\circ C}$	R ohm/Sq.	$\frac{\mu V}{^\circ C}$
As deposited	45,000	-167	6000	-104
1 hr. 90°C	32,000	-133	9000	-77
1/2 hr. 120°C	3,500	-65	10,000	-110
1/2 hr. 105°C	3,500	-	10,000	-
1/2 hr. 90°C	3,500	-	10,000	-
15 Min. 140°C	2,400	-49	13,000	-90
15 Min. 170°C	2,100	-	11,000	-
1 hr. 170°C	1,400	-51	15,000	-90

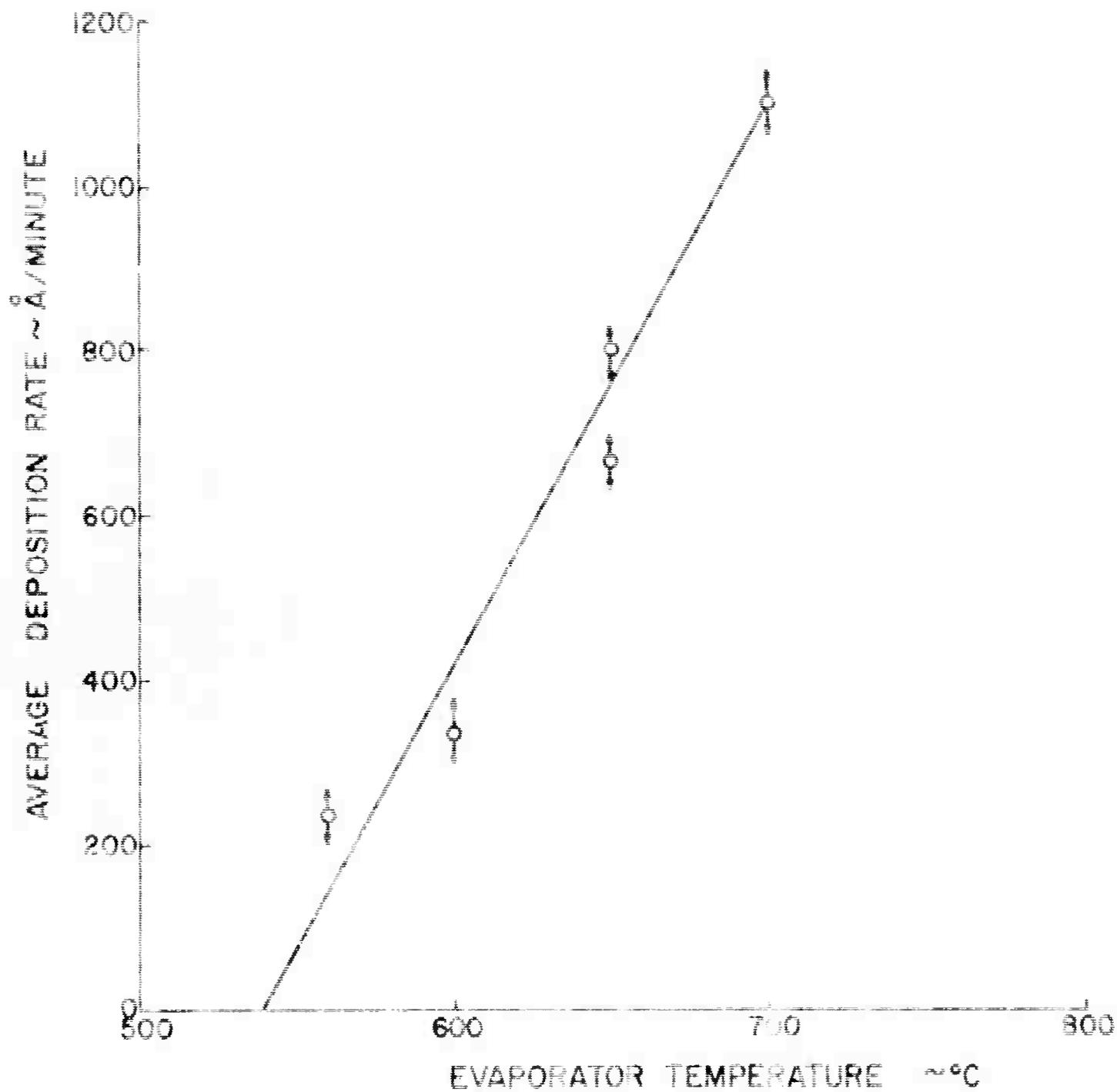


FIG. 1. RATE OF DEPOSITION OF p-TYPE Bi-Sb-Te ALLOY ONTO GLASS SUBSTRATE AT 23° C.

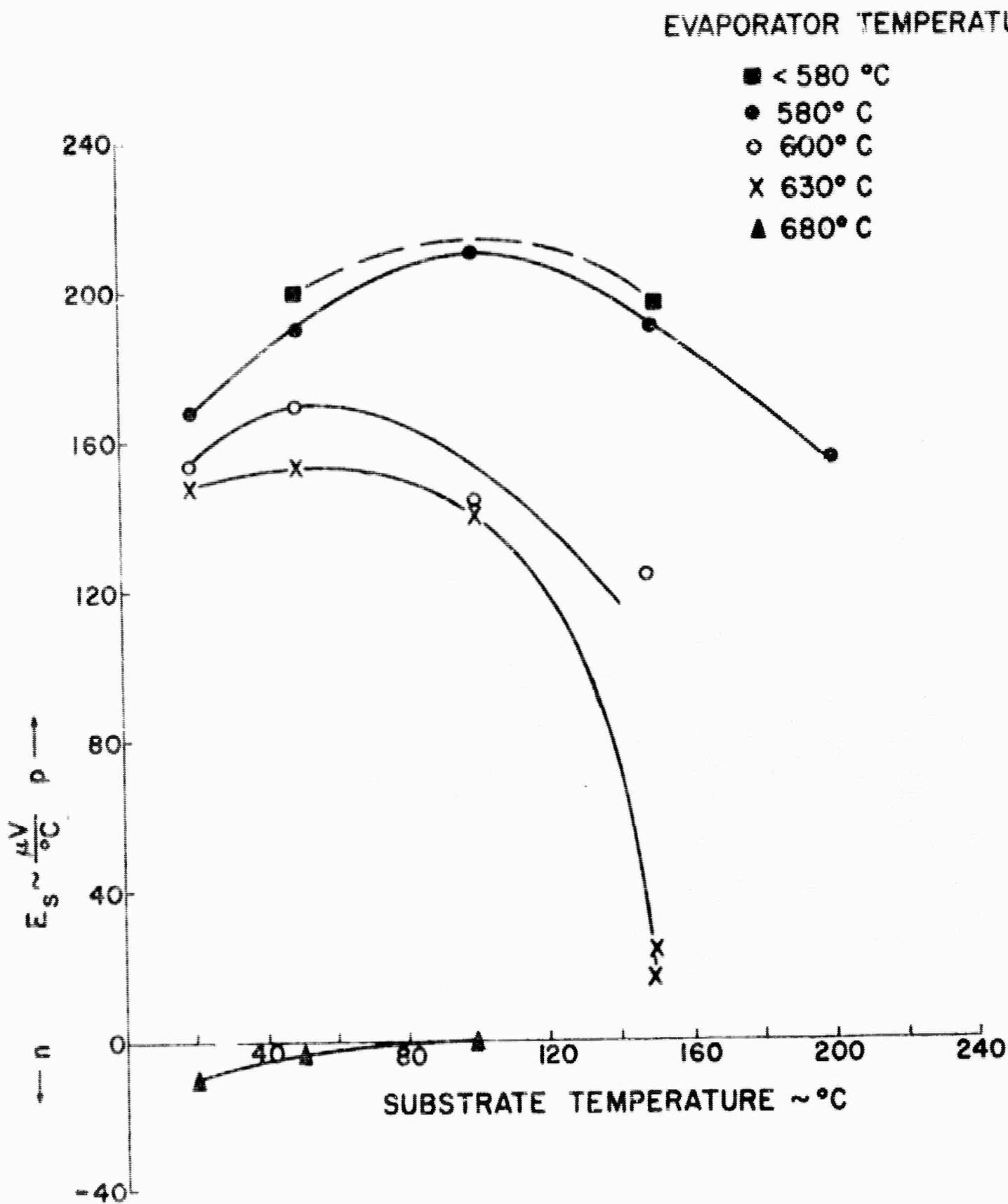


FIG. 2. SEEBECK VOLTAGES OF THIN FILMS DEPOSITED FROM A p TYPE Bi-Sb-Te ALLOY.

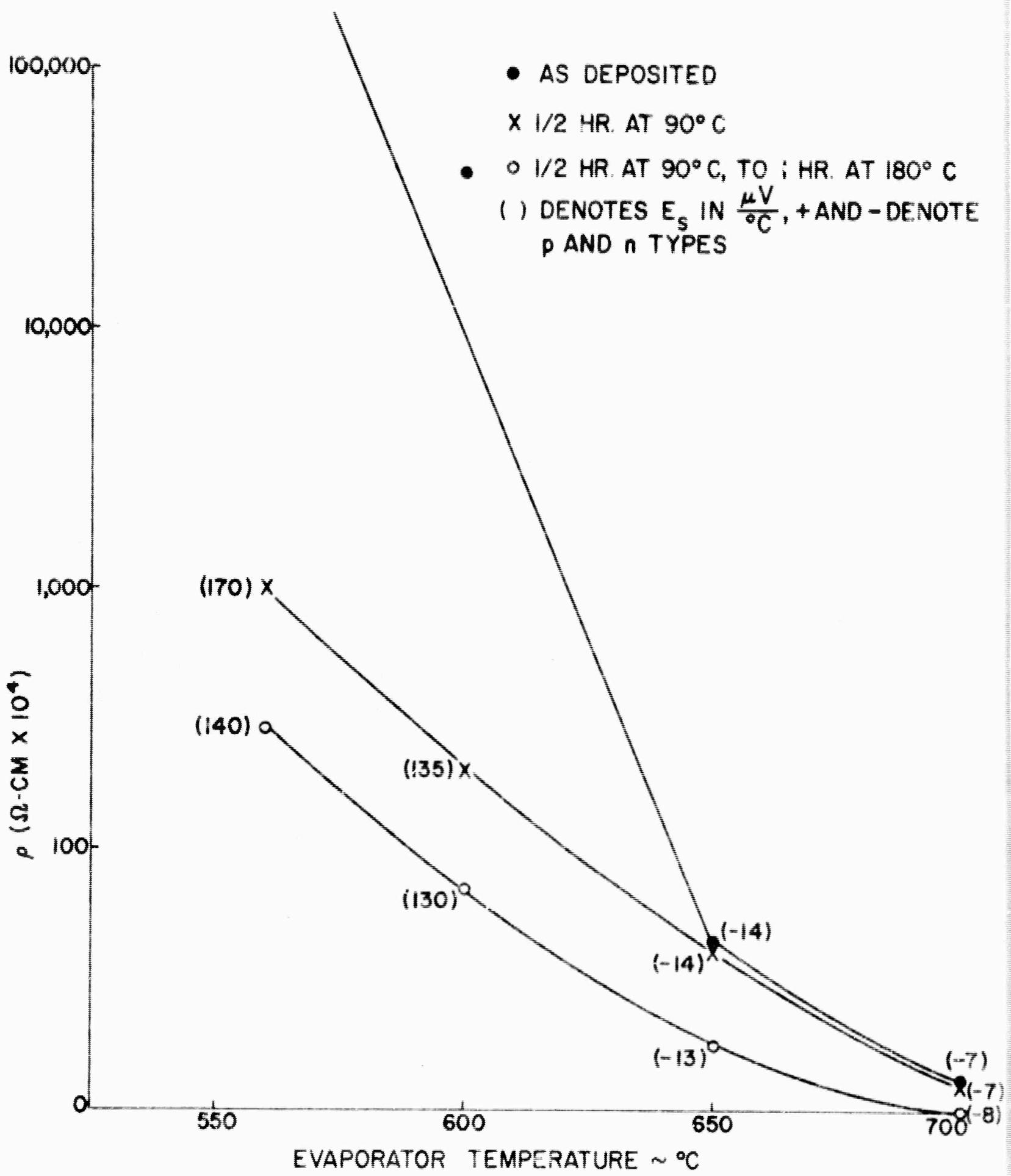


FIG. 3. RESISTIVITY OF Bi-Sb-Te FILMS DEPOSITED ON 23° C GLASS.

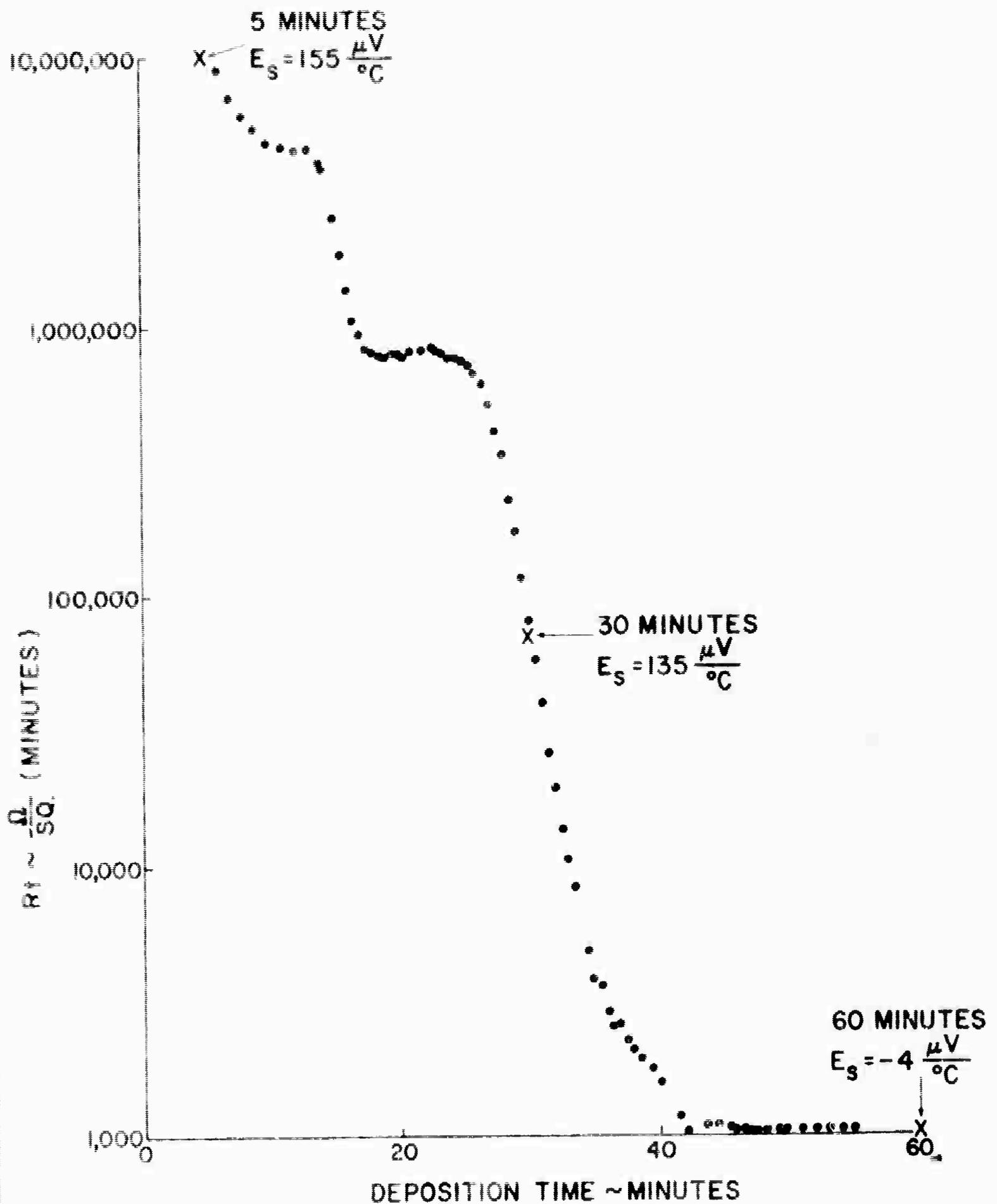


FIG. 4. RESISTANCE MEASUREMENTS OF Bi-Sb-Te FILM DEPOSITED FROM 600° C EVAPORATOR ONTO 23° C PYREX AS A FUNCTION OF TIME.

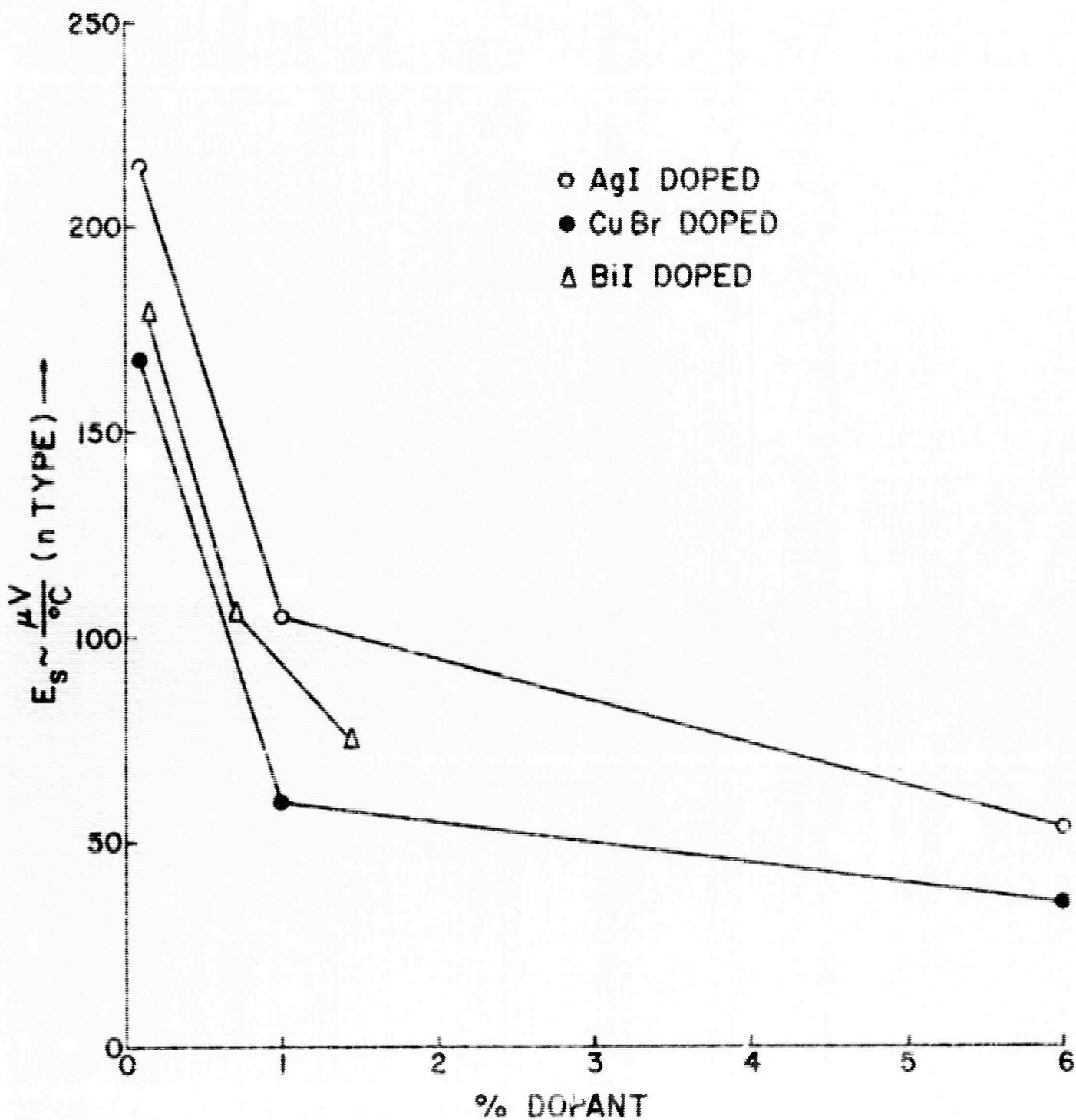


FIG. 5. EFFECT OF DOPING ON 75% Bi_2Te_3 + 25% Bi_2Se_3 ALLOY.

6% CuBr n-TYPE DOPED Bi-Te-Se EVAPORATED
 AT 600° C ONTO PYREX SUBSTRATE AT 23° C.

ARROWS INDICATE THE DEPOSITION INTERVAL.

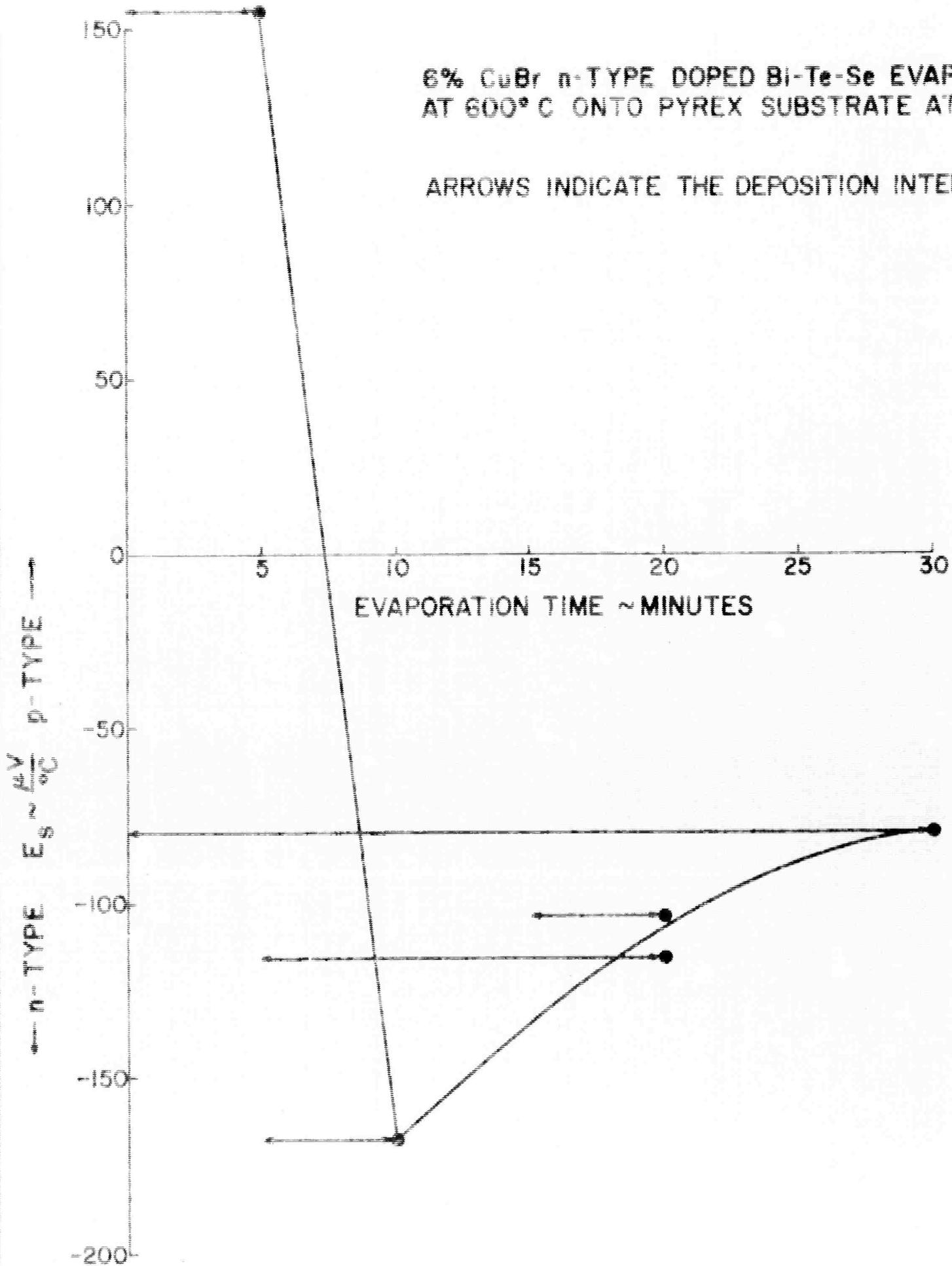


FIG. 6. SEEBECK VOLTAGES OF n-TYPE FILMS AS A FUNCTION OF RELATIVE DEPOSITION SEQUENCE.

FIG. 7 X-RAY DIFFRACTION PATTERNS FOR BI-Sb-Te (6% CUBI DOPED) FILMS

