

EFFECTS OF Sb AND B DOPING ON
CONDUCTIVE PROPERTIES OF SnO₂

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THE EFFECTS OF Sb AND B DOPING
ON THE
CONDUCTIVE PROPERTIES OF TIN DIOXIDE

by

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ABSTRACT

This report deals with the effects of various parameters on the resistance and the temperature coefficient of resistance (or the T.C.) of tin dioxide films doped with antimony and boron. The films were produced on cylindrical ceramic substrates by the hydrolysis of SnCl_4 and SbCl_5 in the presence of HCl and H_3BO_3 . The T.C. was measured over the range of 25 to 150°C and averaged.

Under normal conditions, the films were produced at 950°C with an antimony concentration of 0.457 molar % and a boron concentration of 2.73 molar %. Varying this firing temperature (from 800-1100°C) was found to have no effect on the resistance but increased the T.C. by 2 to 3 ppm/°C per degree change. Varying the antimony content from 0 to about 1 molar % was found to have little effect on resistance. The effect on T.C. was to increase it at lower Sb levels and then to decrease the T.C. as the level increased.

Varying the boron content (0 to 4.46 molar %) was also found to have little effect on resistance. A decrease in T.C. with boron content was noted when only the boron was varied, but an increase in T.C. was found when HCl and H_2O volumes were varied with the boron. The introduction of additional air into the system was found to have no effect.

Film thicknesses were varied by controlling the chemical flowrates. Thinner films were found to have dramatically higher resistances and reduced T.C. values. It was observed that below a certain flowrate resistive failure occurred in the films. It was found in this study that within the

statistical distribution of film values, those samples with above average resistance had below average T.C. values and vice-versa. Annealing in vacuum at 500°C was found to produce samples of reduced resistance and increased T.C. while the opposite was found with air annealed samples. Quickly cooled samples were found to be more stable.

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CHAPTER 1

INTRODUCTION

Tin dioxide is an unusual material that, being generally a transparent conductor, has many applications. The most wide-spread use of tin dioxide is in the manufacture of resistors, where the resistance is provided by either a thin or a thick film of SnO_2 on a non-conductive substrate. SnO_2 is a good choice of material for resistors because it is relatively thick (compared to other resistive film materials) and therefore robust, it can endure high temperatures and overloads with little danger of catastrophic failure, and the properties of the film can be varied over a wide range by altering the doping and preparation of the material.

In its purest form, SnO_2 is insulating⁽¹⁾ but under usual preparation conditions, (the hydrolysis of SnCl_4), the defect (oxygen deficiency) structure of the material results in a conducting n-type semiconductor. With proper doping, SnO_2 properties can approach those of either a metal or a good insulator. It has been found that SnO_2 doped with 5% (molar) indium has as surface resistivity 1000 times greater than that of undoped SnO_2 films, which in turn have a surface resistivity 100 times greater than that of SnO_2 films doped with 10% antimony.⁽²⁾

Antimony, which acts as a donor in SnO_2 , is the most commonly used doping agent in theoretically oriented studies^(2,3,4,5,10) and applications related studies^(14,15,16,17) to date. These studies have found that, be-

sides reducing the resistance of the SnO₂ films, antimony doping affects the temperature coefficient of resistance of the film (the relative change in resistance as the film's temperature is increased by one degree). This is usually expressed in parts per million per degree Centigrade, and will hereafter in this report be referred to as the T.C.

Boron is commonly used as a dopant in the production of SnO₂ resistors. Boron has a double effect on SnO₂ in that it acts as an acceptor and it also deforms the lattice structure of SnO₂. Except for empirical observations in reports concerned with the optimization of SnO₂ resistor production, (11,14,15,16,17) Boron has been ignored in SnO₂ studies to date.

SnO₂ films are most often formed by the hydrolysis of SnCl₄ at high temperatures (600-1100°C), although formation of the film by reactive sputtering gives much better control of results. (5) The temperature of the hydrolysis reaction was found to affect the film properties. Higher temperatures were shown to increase both grain size and oxygen deficiencies in the films (7), and to shift the T.C. of the material. (16,17)

Film thickness and its effects on the properties of SnO₂ have also been studied. For films thinner than 300 Å, it has been found that the bulk resistivity of the material is dependent on film thickness. (5) The T.C. is also affected by film thickness. (16,17)

Much attention has been focused on the effects of annealing on the film properties. (1,2,4,6,7,8,9,10) Annealing in an oxygen-rich atmosphere (air, pure O₂, etc.) results in oxidation of oxygen deficiencies and reduced conduction, while the opposite is true with films annealed in oxygen-poor atmospheres (N₂, vacuum, etc.).

This report is based on work done with Welwyn Canada Ltd. in London,

Ontario, an industrial firm producing resistors using tin dioxide and other compounds. The samples studied were standard resistor blanks prepared using normal the production procedures of the company and varying a number of parameters. The parameters studied were the film's antimony concentration (0-0.5 molar %), boron concentration (0-3 molar %), firing temperature (800-1100°C), the film's thickness (relative) and the amount of air entering the reactron area. The responses of some samples to annealing in vacuum and air were also studied. Statistical observations were made of the T.C. and resistance of a number of samples produced with identical parameters. Resistance values for production purposes are commonly measured as resistance grades where

$$\text{Grade} = 10 \log (\text{Resistance in ohms}) \quad (1.1)$$

Throughout this report, resistance values will be presented as grades. It can be assumed in most cases that resistivity is proportional to resistance. The samples which were measured were selected from an estimated 60,000 to 90,000 samples produced in the course of this study.

CHAPTER 2

RELEVANT CHARACTERISTICS OF SnO₂ THIN FILMS

2.1 Theoretical Characteristics

The SnO₂:B:Sb thin film system is a very complex one with many parameters (doping, defect structure, preparation effects, thickness, etc.) affecting the conductivity behavior. It is not possible at this time to develop a theoretical model of this system that explains the effects of these parameters, however, the general theory of conduction in semiconductors is useful in obtaining a qualitative idea of what happens in the SnO₂ system.

Conduction mechanisms in n-type semiconductors, in their simplest form, are represented by the formula

$$\sigma = n_0 e^2 \bar{\tau} / m^* \quad (2.1)$$

where σ is the conductivity, e and m^* are the charge and effective mass of the electron, n_0 is the free electron density, and τ is the relaxation time. ⁽¹²⁾

The relaxation time is the average time between randomizing collisions and is a function of energy and therefore temperature. The average relaxation time $\bar{\tau}$ is found from the equation

$$\bar{\tau} = \langle v^2 \tau \rangle / \langle v^2 \rangle = \lambda \langle v \rangle / \langle v^2 \rangle \quad (2.2)$$

where v is the electron velocity and λ is the mean free path between collisions. There are separate relaxation times associated with lattice scattering (τ_1) and impurity scattering (τ_2), which must be added:

$$1/\tau = 1/\tau_1 + 1/\tau_2 \quad \text{or} \quad 1/\lambda = 1/\lambda_1 + 1/\lambda_2 \quad (2.3)$$

The free electron density n_0 is a function of the energy of the band-gap, the temperature, the free hole density, and the electron and hole effective masses. Effective mass, in turn, is a function of the band-gap energy for SnO_2 . (For the effective mass to be a constant, the energy must be a parabolic function of k . This is not the case for $\text{SnO}_2^{(1)}$).

It can be seen from the above that the conduction of SnO_2 is a complex function of temperature, number and type of lattice defects, number and type of doping atoms, the band gap energy (which itself is affected by lattice defects and doping⁽²⁾), and other parameters not mentioned, as well as physical characteristics of the film (crystal size, film thickness, etc.).

In addition to the above, the free carrier scattering is not just limited to lattice and impurity scattering, as implied by Eq. (2.3), but has terms for scattering from film boundaries, imperfections (both chemical and physical), ionized impurities, and optical and acoustical phonon scattering. It has been found that for low resistance $\text{SnO}_2\text{:B:Sb}$ resistors, the T.C. follows the acoustic scattering ($T^{3/2}$) relation, while at higher resistances the T.C. is anomalous, reflecting some internal activation (possibly related to film thickness).⁽¹¹⁾ It is also postulated that high doping could dampen or distort thermally induced lattice vibrations and thus affect the acoustical and optical phonon scattering resulting in a reduction of the T.C.

2.2 Impurity Doping Characteristics

Intentional doping of the SnO_2 films in this study was confined to the addition of antimony and boron. However, the films were also being doped by oxygen deficiencies and chlorine impurities. In the case of an oxygen deficiency, an oxygen ion is missing resulting in the addition of two electrons

to the conduction band. As SnO_2 is an n-type semiconductor, conduction is increased and the deficiency is a donor.

The abundance of chlorine from the reactron makes its inclusion in the SnO_2 lattice a certainty. Chlorine may be included either interstitially or substitutionally⁽⁴⁾. If a chlorine substitutes for an oxygen ion, the result is the addition of an electron to the conduction band, increasing conduction, and the chlorine ions form a donor band close to or overlapping the conduction band.⁽²⁾ If a chlorine ion is inserted in the SnO_2 lattice in addition to the oxygen ions already there, it could act as an acceptor and reduce conduction, however, this is much less likely to happen.

2.3 Sb and B Doping Characteristics

Antimony has received more attention in studies of SnO_2 doping than any other substance. Antimony acts as a donor in SnO_2 by substituting for the tin. As the antimony has a +5 charge while the tin has a +4 charge, the main result is increased conduction, with little change to the lattice structure at moderate doping levels. SnO_2 is saturated with antimony at about one percent doping level.⁽⁵⁾ Antimony doping in one respect acts similar to oxygen deficiency doping, both increase conduction. However, antimony acts as a shallower donor than does the oxygen deficiency.⁽⁴⁾ This would result in a different T.C. effect for these two types of doping. Pure SnO_2 has a negative T.C., as expected for a semiconductor. Antimony doping has the effect of driving the T.C. more positive.

Little theoretical work has been done with boron doping to date. The boron ion substitutes for the tin ion, and due to its 3+ charge, acts as an acceptor, reducing conductivity. On the other hand, due to the fact that

boron is much smaller than tin, doping with boron should introduce severe deformities into the SnO_2 lattice structure. These deformities may increase conductivity.

Boron is known to promote the growth of SnO_2 crystals in the films at high deposition temperatures.⁽¹⁶⁾ The resistivity of the film is proportional to the degree of crystallinity. Without boron doping, the SnO_2 films are amorphous, resulting in high resistivity. Boron doped SnO_2 is deposited first as an amorphous, high resistivity layer on the substrate. This is followed by more crystalline layers with proportionately lower resistivity. The thickness of the higher resistivity layers is dependent on both the boron level and the preparation temperature. A lower boron level or a higher temperature results in thicker amorphous layers and therefore reduced resistivity.⁽¹⁶⁾

In addition to the above, a high resistivity layer is built up on the surface of the film due to either a heat treatment effect or possibly doping by constituents found in the ceramic material of the furnace.⁽⁴⁾ It can be seen that, due to these factors, any non-uniformity in film thickness does not just give a change of resistance proportional to thickness, but a larger change due to the variation of resistivity with thickness.

The effect of moderate boron doping on the T.C. has been found to vary with firing temperature. For films prepared at 950°C and below, an increase in boron content results in a decrease in T.C., while at temperatures of 1050°C and above, the opposite is true.⁽¹⁷⁾ At high boron doping levels (above 8%), the T.C. decreases with added boron regardless of the firing temperature.⁽¹⁶⁾ An increase in the boron doping level has also been found to reduce the thickness of the film.

Antimony doping from zero to one half percent results in an increase in the T.C. Further increase in the antimony doping level results in a decrease in the T.C. There is little overall change in T.C. between one and five percent doping (<200ppm negative), but above this level the T.C. goes steadily more negative.⁽¹⁶⁾ The firing temperature has no qualitative effect on this behavior. Lepic⁽¹¹⁾ has attempted to quantify the effects of antimony and boron doping on the T.C. in the form of an equation:

$$R = R_0 T^{F+G}, \text{ where } F = \frac{118}{[B]} \frac{[Sb]}{[Sb]} \quad (2.4)$$

G has a value between .015 and .038 in this equation, depending on the film thickness and R+T are resistance and temperature respectively. However, due to the non-linear doping behavior noted in the previous paragraphs, this equation can only apply over a limited doping range and with the preparation temperature and conditions of the original experiments. Therefore, the usefulness of this type of representation is very limited.

2.4 Film Preparation Characteristics

The film preparation characteristics of particular interest in this section are those related to the temperature at which the films were fired and the thickness of the deposited films. It has been found that both the grain size and the oxygen deficiency concentration of the films were increased with an increase in firing temperature while the concentration of chlorine was reduced.⁽⁷⁾ These factors would be expected to reduce the resistance of films with respect to films prepared at lower temperatures, although there is no experimental evidence for this. Other studies have shown that an increase in firing temperature results in films of increased thickness and a more positive T.C.⁽¹⁷⁾

The thickness of the film deposited has a dramatic effect on the resistance of the film. The variation of resistivity with thickness has already been described in section 2.3. The film is basically a sandwich of low resistivity bulk material surrounded by high resistivity material, although no boundary between the two types of material exists. One study has found bulk annealed resistivity (the resistivity of the inner material) to be a constant 0.006Ω for films over about 500 \AA thick, and dependent on the film thickness for thinner films.⁽⁶⁾ The thickness of the hydrated surface layer in such material is about 400 \AA or greater. The thickness also affects the stability of the films. Films less than one micron thick tend to be unstable.⁽¹⁴⁾ Variations in film thickness and its effects on the various resistivity layers are the main reasons for the large spread commonly found in the values of both resistance and T.C. of otherwise similar samples.

Experimentally, increasing the film thickness has been found to produce different effects depending on the antimony concentration of the film. This suggests an inter-relationship between antimony, surface and bulk resistivity, and/or the thickness of the surface and bulk layers that has not yet been explained. At low antimony levels (0-0.1%) an increase in film thickness decreases the film resistance while increasing the T.C. At higher levels (5% Sb) the increased thickness results in increased resistance and decreased T.C.⁽¹⁷⁾ In these instances it is predominantly the surface resistivity which determines the resistance and T.C. behavior. The same is true for this report.

2.5. Annealing Characteristics

Many studies have been made of the effects of annealing on SnO_2 resistance. There is evidence that irreversable changes may occur in SnO_2 films at

temperatures as low as 200°C when heated in vacuum.⁽⁹⁾ Samples annealed at 300°C generally show a reduction in resistance in a vacuum or inert atmosphere and an increase in resistance in an air atmosphere.⁽⁸⁾ However, very pure films produced by R.F. sputtering show a decrease in resistance with air annealing.⁽⁶⁾ As the change in resistance is mainly due to a change in the oxygen deficiency concentration, this suggests that both types of film are moving towards an equilibrium oxygen deficiency concentration at this temperature. In vacuum or inert atmosphere annealing, the oxygen tends to dissociate and evaporate from the film. The tin may also evaporate when heated for a long time.⁽⁸⁾ The changes noted above are larger for thin films. It has been found that the oxygen deficiency concentration increases with increased treatment temperature.⁽⁷⁾

Annealing at higher temperatures (above 600°C) produces changes similar to those at lower temperatures.⁽¹⁾ In addition to these, a small change in resistance is attributable not to chemical changes (oxidation or reduction of the film), but to an increase in the grain size of the film.⁽¹⁰⁾ It has been observed that when samples are annealed in air for long periods at these temperatures, a number of different steps are discernable.⁽⁵⁾ First, the resistance is reduced due to the effects of nucleation and crystalization on the surface. After that, the resistance is increased due to oxidation within the film, after which the resistance may again be reduced as in the first step. Finally, dopants such as antimony tend to be removed (exsolved) from the film and more oxidation takes place.

At annealing temperatures in excess of 900°C oxygen and chlorine are both decreased in concentration within the film, even in an O₂ atmosphere⁽⁷⁾

and the film may start to break up.⁽¹⁰⁾ At all temperatures the effects of furnace doping of the surface with ceramics or metals must be taken into account.⁽⁴⁾ Careful attention must be given to the processes of annealing (heating) and quenching (cooling) in order to obtain reproducible results.⁽⁵⁾

CHAPTER 3

SAMPLE PREPARATION

3.1 Sample Feeding and Temperature Control

The samples used in this experiment were ceramic rods measuring 9/16 inch long by just under 3/16 inch in diameter. The apparatus used to prepare the samples is shown in Figure 1. The rods were fed end to end by the feed mechanism into a 1/4 inch diameter quartz tube running the length of the horizontal oven. The rods were fed into the tube at a basic feed-rate of 60 rods per minute. The feed rate was varied, as one of the parameters under study, between approximately 30 and 120 rods per minute and the results were observed.

Once in the horizontal oven, the rods were pushed through it by the feeding of additional rods into the tube. At the end of the tube, the rods dropped under the force of gravity quickly through the vertical oven into the drop tube, where they were coated with SnO_2 , and then into a collector. The length of time the rods spent in the ovens was directly proportional to the feed-rate. At a feed-rate of 60 rods per minute, the rods spent approximately 78 seconds each in the ovens. The oven temperatures were controlled by two thermostat units connected to thermocouples and regulating the current supply to electrical heating elements in the two ovens. The basic temperature setting for both ovens was 950°C. Optical pyrometer measurements made on rods emerging from the horizontal oven showed rod temperature to be almost identical with that set for the oven at all feed-rates tested. As one of the parameters under study, oven temperature was varied from 800°C to 1050°C and the effects

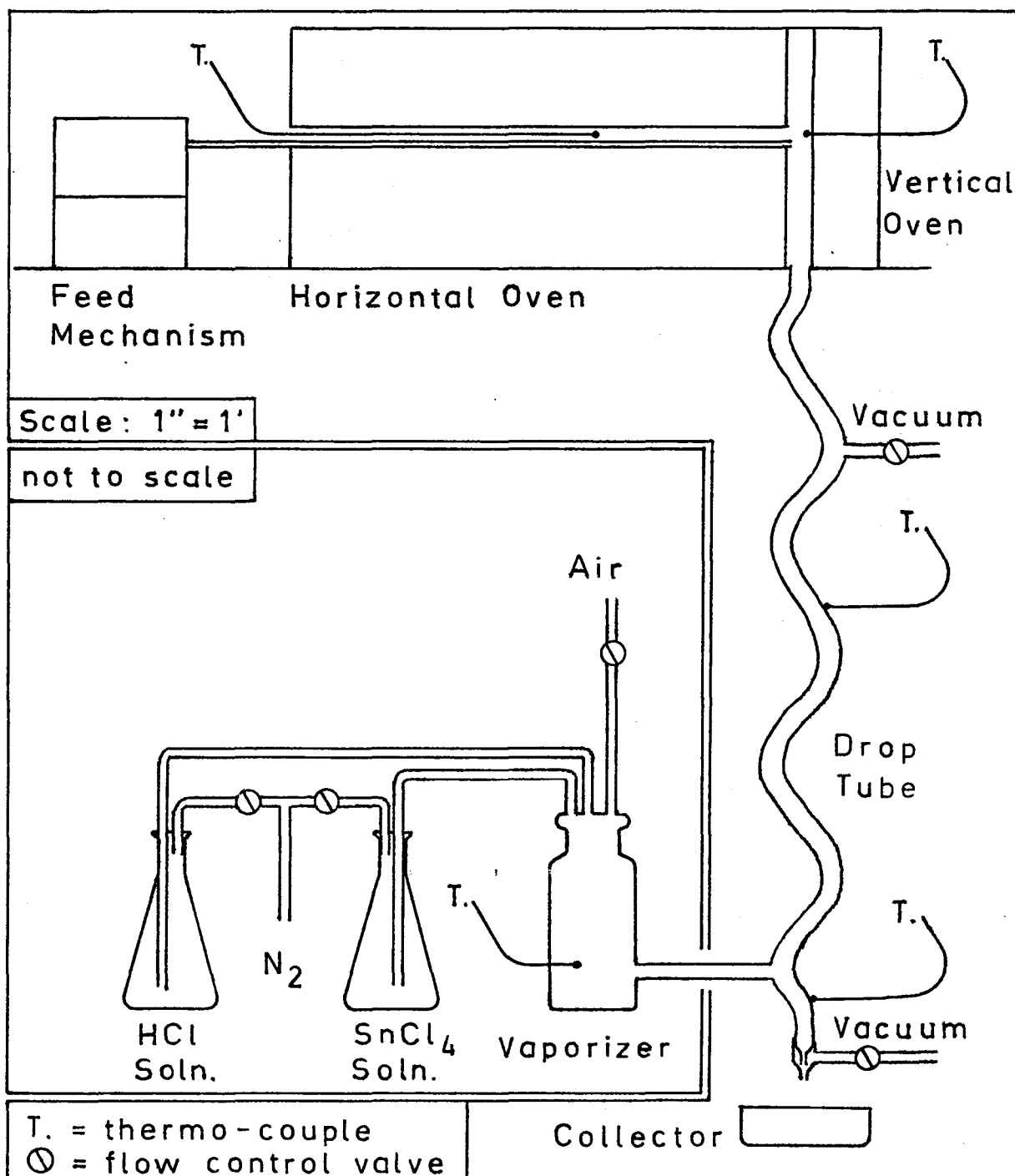


Figure 1.

Sample Preparation Schematic

(Welwyn Tin Oxide Furnace)

on the sample properties were observed.

No serious problems were encountered with this part of the operation. Minor problems included: 1. the jamming of the feed mechanism due to mechanical difficulties and variations in size between rod batches; 2. the jamming of rods in the horizontal oven when allowed to remain there for too long a period; 3. the burning out of oven elements due to caustic fumes from the drop tube entering the ovens occasionally; and 4. miscellaneous alignment problems.

3.2 Chemicals and Vaporizing

The rods were coated with SnO_2 by the hydrolysis of SnCl_4 on the rod surface. The chemicals used in this process were prepared as two solutions, the contents of which are listed in Table 1. The two solutions were put in air-tight beakers, as shown in Figure 1. Compressed nitrogen gas was used to force the two solutions out of the beakers through capillary tubes into the quartz-walled vaporizer. In the vaporizer, the solutions were turned to vapor by heating and air was added. The vaporizer was heated to 300°C by an electric element controlled by a thermostat and thermocouple. The flowrates of nitrogen into the two beakers (and therefore the flowrates of solution out) and air into the vaporizer were regulated and metered.

The flowrates for both solutions were 2.75 cc/min. normally and were varied between 0.5 and 4.0 cc/min. independently depending on the experimentation. The air flowrate was normally 800 cc/min. and was varied between 0 and 1200 cc/min. at different stages of testing. The vaporized chemicals and air flowed from the vaporizer into the droptube where the coating took place. In addition to the air, each cc. of HCl solution produced 1200 cc. of vapor and each cc. of SnCl_4 solution produced 190 cc. of vapor.

<u>SnCl₄ Standard Solution</u>	
SnCl ₄	1000 ml.
SbCl ₅	5 ml.
Molar content of Sb relative to Sn is 0.457%.	
<u>HCl Standard Solution</u>	
HCl	1000 ml.
H ₂ O	450 ml.
H ₃ BO ₃	20 g.
For 1:1 mixture of SnCl ₄ solution and HCl solution, molar content of B relative to Sn is 2.74%.	

Table 1.

Standard Solutions Used in SnO₂ Production

The chemicals were prepared as two solutions mainly so that the ratio of the two solutions could be varied while in use. The two solutions could have been mixed before being vaporized with no bad effects. SnCl_4 reacts according to the equation



at high temperatures (above 500°C). The SbCl_5 included in the SnCl_4 reacts similarly. At lower temperatures SnCl_4 and H_2O may react to form such compounds as SnCl_2 , SnO_3H_2 , which forms at a pH greater than 3.2,⁽¹³⁾ or $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, which is intermediate between SnCl_4 and SnO_3H_2 in water.⁽²⁾ All of these form precipitates which would interfere in the vaporizing and firing process. The large amount of HCl in the second solution prevents these reactions from occurring in any significant amount. The HCl may also slow down the reaction on the resistor rod surface and have an effect on the chlorine level in the film.

A number of serious (and repetitive) problems were encountered dealing with the chemicals and vaporizer. The anhydrous SnCl_4 solution fumed and reacted to form crystals whenever there was any moisture in the nitrogen gas, resulting in occasional plugging of both the capillary tube and the vaporizer. Once vaporized, the chemicals would etch any metal in sight, which resulted in corroded copper and stainless steel tubes between the vaporizer and the drop tube and burnt out heating elements in both. However, the most serious problem was the formation of a precipitate, mainly antimony and boron, at the bottom of the vaporizer. This throws some doubt on the actual doping levels of the films, especially those formed after changes in solution parameters, when the precipitate could not be considered at equilibrium.

3.3 Rod Coating, Collection, and Measurement

The coating of the rods with SnO_2 took place in the drop tube, as described earlier and shown in Figure 1. The zig-zag shape of the tube (as shown in the figure) was to slow the drop of the rods, thus resulting in a thicker SnO_2 coating than was otherwise possible with this system. The drop tube was maintained at 350°C by two thermostatically controlled (thermocouple) electric elements surrounding the tube. The flow of vapor through the system started from the vaporizer, up the drop tube, and out the upper vacuum tube, where the vapor was washed and exhausted. The upper vacuum tube was maintained at about two centimeters of negative pressure to draw the vapor out using a Venturi device. The amount of vacuum had a direct effect on the concentration of vapor in the drop tube and therefore on the thickness of the SnO_2 film. However, as this concentration could be more easily controlled by controlling the vaporizer flowrates, no study was made on the effects of vacuum variation.

The original collector system used was a closed collector sealed to the bottom of the drop tube with no lower vacuum tube. However, this resulted in a large resistance and T.C. spread, due to the heat treatment lower levels of rods in the collector were receiving from the rods dropping in. The closed collector also required frequent stopping of the process to empty the collector. These problems were solved by the use of an open collector system below and not connected to the drop tube. However, the opening of the bottom of the drop tube created a new problem. Due to the natural tendency of hot gasses to rise, air was drawn into the bottom of the drop tube forcing the vapor to rise into the oven area. To counter-act

this, a second (lower) vacuum tube was attached to the bottom of the drop tube as shown in Figure 1. Its action was to draw off the air flowing into the bottom of the drop tube and to create a back-pressure to counter-act the pressure caused by the vapor temperature differential. It was operated at about five centimeters negative pressure using a mechanical pump and under proper operation drew in no vapor.

After collection and cooling, the sample rods were capped at both ends with nickel caps to make good electrical contact and then measured. The resistance was measured using a V.T.V.M.-like device which read directly in resistance grades. The T.C. was measured by placing the sample in a resistance bridge which was zeroed at room temperature (25°C). The sample rod was then heated to approximately 150°C by a stream of hot air at that temperature directed on the sample. The change in resistance was then measured and the T.C. calculated. The samples were then cooled to check the return to zero (i.e. the film's stability). The measured T.C. value was obviously the average T.C. over the 25 to 150°C range. The instantaneous T.C. value is different at different temperatures. Some samples were annealed by heating to 500°C in air or vacuum and cooling over 48 hours. These samples were then capped and measured and the measurements were compared with control groups.

A summary of the normal settings of all system parameters is presented in Table 2.

<u>System Parameter</u>	<u>Normal Setting</u>
Feedrate	60 rods/min.
Horizontal Oven Temp.	950°C
Vertical Oven Temp.	950°C
Drop Tube Temp.	350°C
Vaporizer Temp.	350°C
SnCl ₄ Solution Flowrate	2.75 cc/min.
HCl Solution Flowrate	2.75 cc/min.
Air Flowrate	800 cc/min.
Upper Vacuum Pressure	-2 cm.
Lower Vacuum Pressure	-5 cm. (approx.)
Collector System	Open

Table 2.

Normal Firing Parameters for Furnace

CHAPTER 4

RESULTS AND OBSERVATIONS

4.1 Grade and T.C. Distributions

It can be expected in all studies involving multiple samples that more than one value will be recorded for the same measured parameter; i.e., samples prepared under identical conditions do not turn out identical. This is true of the experiments reported here.

Samples from the same batch (identical preparation conditions) in this study generally followed a normal Gaussian distribution with respect to both grade (resistance) and T.C. values. Using the open collector system, as described in the previous chapter, the standard deviation of the resistance was between .5 and 1.0 grades, and the standard deviation of the T.C. was between 50 and 110 ppm/°C. These values depended on the batch being tested. Much larger standard deviations were recorded using the closed collector system, which is why the open collector was developed early in the project. The larger spread was probably due to a heat-treatment effect, as previously noted.

One puzzling aspect of the grade and T.C. distributions is their relationship. It was found that, for any batch tested, samples with above average grades also had below average T.C. values. This is shown for one batch in Figure 2. This figure represents an early batch produced using a closed collector, and is presented here because of the wide spread. The slope of the graph is $-133 \text{ ppm-}^{\circ}\text{C}^{-1}$ per grade. All the other figures pre-

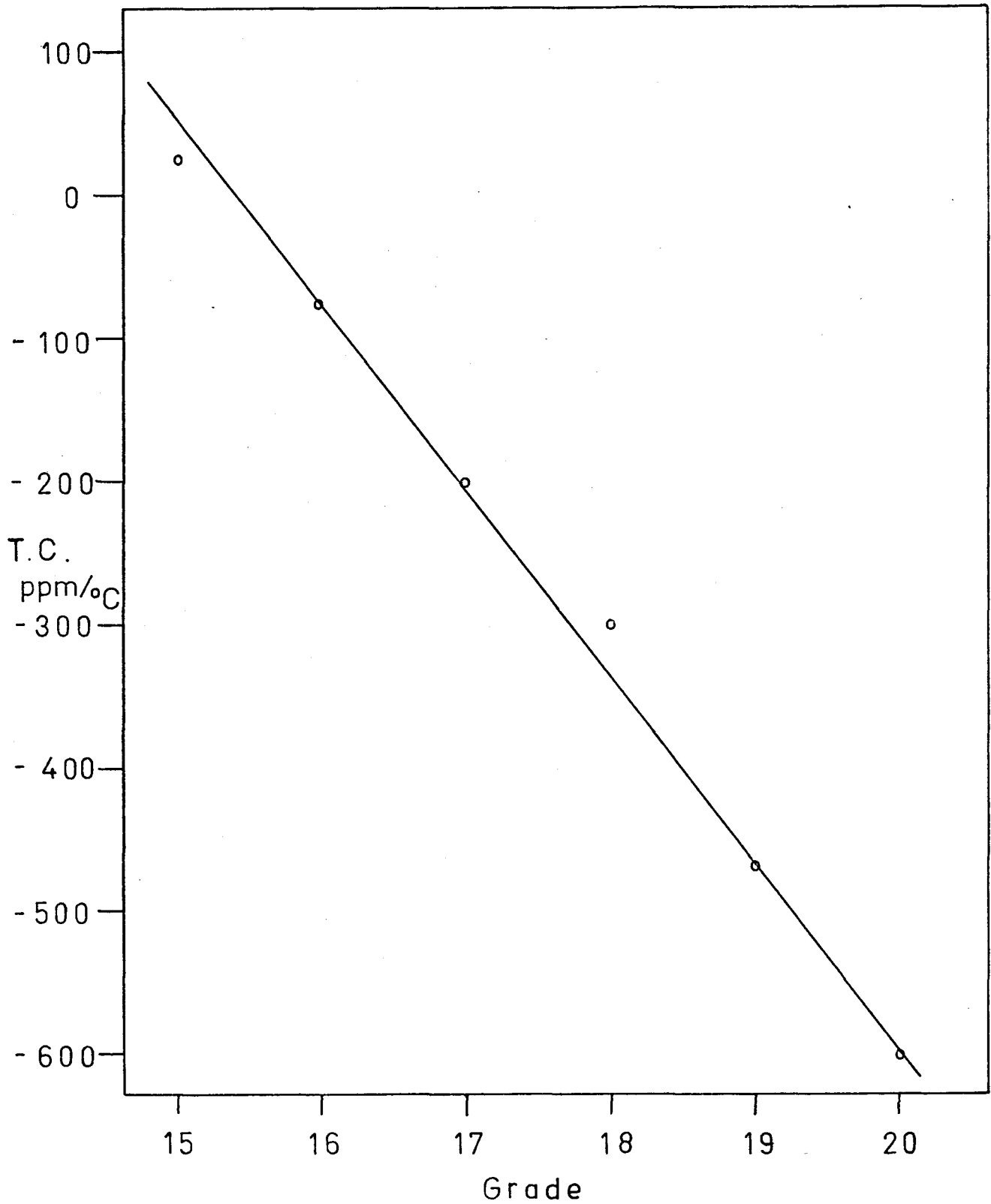


Figure 2.

Normal Distribution of T.C. vs. Grade
(Run 002)

sented in this report represent batches produced using open collector systems, however, the grade - T.C. relationships are all similar to that represented here. The slopes of the grade - T.C. curves of the other batches ranged from approximately -75 to -150 ppm- $^{\circ}\text{C}^{-1}$ per grade. The variation in slope of these curves was not identifiable to any system parameter, nor was the slope repeatable, except between the above limits, for batches prepared under identical firing conditions and parameters. Studies by other investigators^(15,16) have resulted in grade versus T.C. curves with slopes similar to those presented here.

Although the reason for this T.C. - grade relationship has not been determined, there are a number of possible causes. As noted in section 2.3, a small variation in film thickness can result in a much larger variation in the resistive properties of the film due to the dependence of resistivity on film thickness. Another factor could be the cooling rate of the film. The first samples in the collector cooled relatively quickly while following samples cooled more slowly due to the residual heat in the collector. This could have resulted in a heat treatment of the film, and would explain the larger spread found with the closed collector. Quick cooling (quenching) could also result in cracking of the film. Finally, a slim possibility exists that uneven vaporizer action could have resulted in uneven doping of the films. It is beyond the scope of this report to determine the actual mechanisms of the grade to T.C. relationship.

4.2 Feedrate and Airflow Dependence

It can be assumed that the feedrate of the samples through the furnace

would affect only the temperature of the samples, as the feedrate affects only the time the samples spend being heated and not the length of time the samples are being coated with SnO_2 . Readings were taken with an optical pyrometer of the sample temperatures leaving the horizontal oven at feedrates ranging from 30 to 120 rods per minute. It was found that the temperatures at the different feedrates were, within the accuracy limits of the pyrometer, identical both with each other and with the temperature setting for the ovens. It can then be safely assumed that the feedrate is not a parameter affecting the properties of the films, at the feedrates used in this project.

To observe the effect of vaporizer airflow, the flow rate of air entering the vaporizer was varied between 400 and 1200 cc/min. (Other system parameters were as listed in Table 2.) This had the effect of varying the vapor flow out of the vaporizer from 3700 to 4500 cc/min. The effects of the airflow on the grade and T.C. values of the sample films are shown in Figures 3 and 4, respectively. (Each small circle in these and all other figures in this report represents the average of at least 15 samples taken from one batch.) As can be seen from these figures, within the accuracy of the experiment, the airflow has no discernable affect on the properties of the sample SnO_2 films.

4.3 Antimony Doping Dependence

To study the effects of antimony doping on the resistive properties of SnO_2 films, batches of samples were prepared with Sb contents of 0.228, 0.457, 0.685, and 0.914 molar percent relative to Sn. This corresponds to 0.25%, 0.5%, 0.75%, and 1.0% by volume of SbCl_5 to SnCl_4 . The

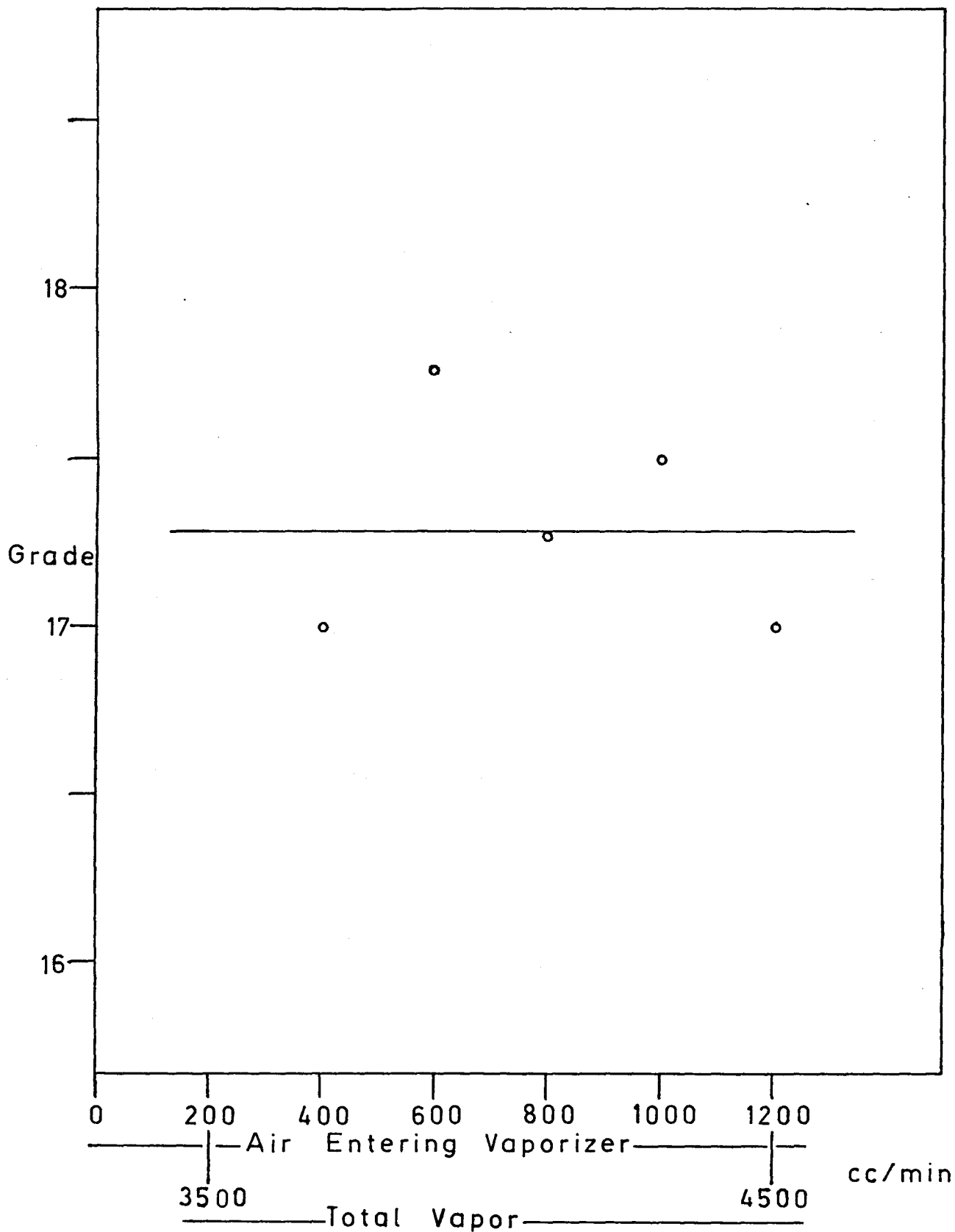


Figure 3.

Dependence of Grade on Airflow

(Runs 014,015)

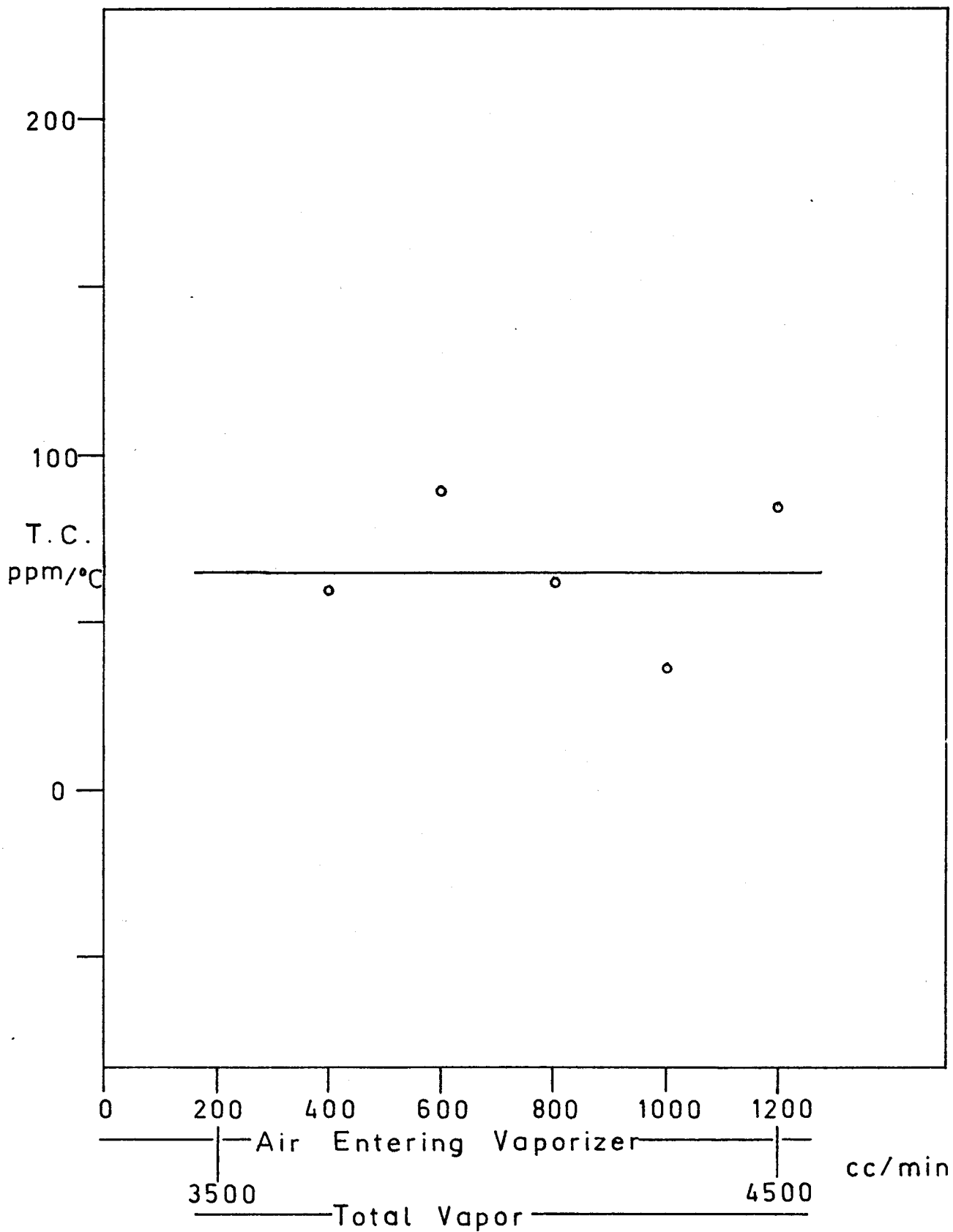


Figure 4.

Dependence of T.C. on Airflow

results of grade and T.C. measurements on these samples are shown in Figures 5 and 6. (Other system parameters were set as listed in Table 2.)

The measurements of resistance grade as a function of Sb doping shown in Figure 5 indicate that, within the limits of accuracy of the testing, the antimony content had no discernable effect on the grade. This is very surprising, as other studies⁽²⁾ have indicated a change in resistance of over an order of magnitude between zero and one molar % Sb. There are a number of possible explanations for this discrepancy. First of all, it was necessary to stop the furnace operation and change the solutions being used in order to achieve the different doping levels. Always associated with such an operation was a random change in the film properties. However, although this random factor could introduce some error into Figure 5, it could not account for anything near an order of magnitude discrepancy. Another possibility is that the majority of the resistance change between 0 and 1% actually takes place between 0 and 0.228%. Although this may be part of the answer, it will be seen in section 4.6 (Figure 19) that this does not account for any large change either. Perhaps the best explanation is that the intrinsic (oxygen deficiency) doping level in the films was so large that the contribution of antimony to the conduction of the films was not significant. Another possible cause would be the doping of the films with Sb from the sediment at the bottom of the vaporizer at nominally low doping levels.

The effect of antimony doping on the T.C. values of the films was found to be much more consistent with what was expected. The plot of T.C. versus antimony in Figure 6 has an approximate slope of $-400 \text{ ppm-}^\circ\text{C}^{-1}/\text{mole } \%$,

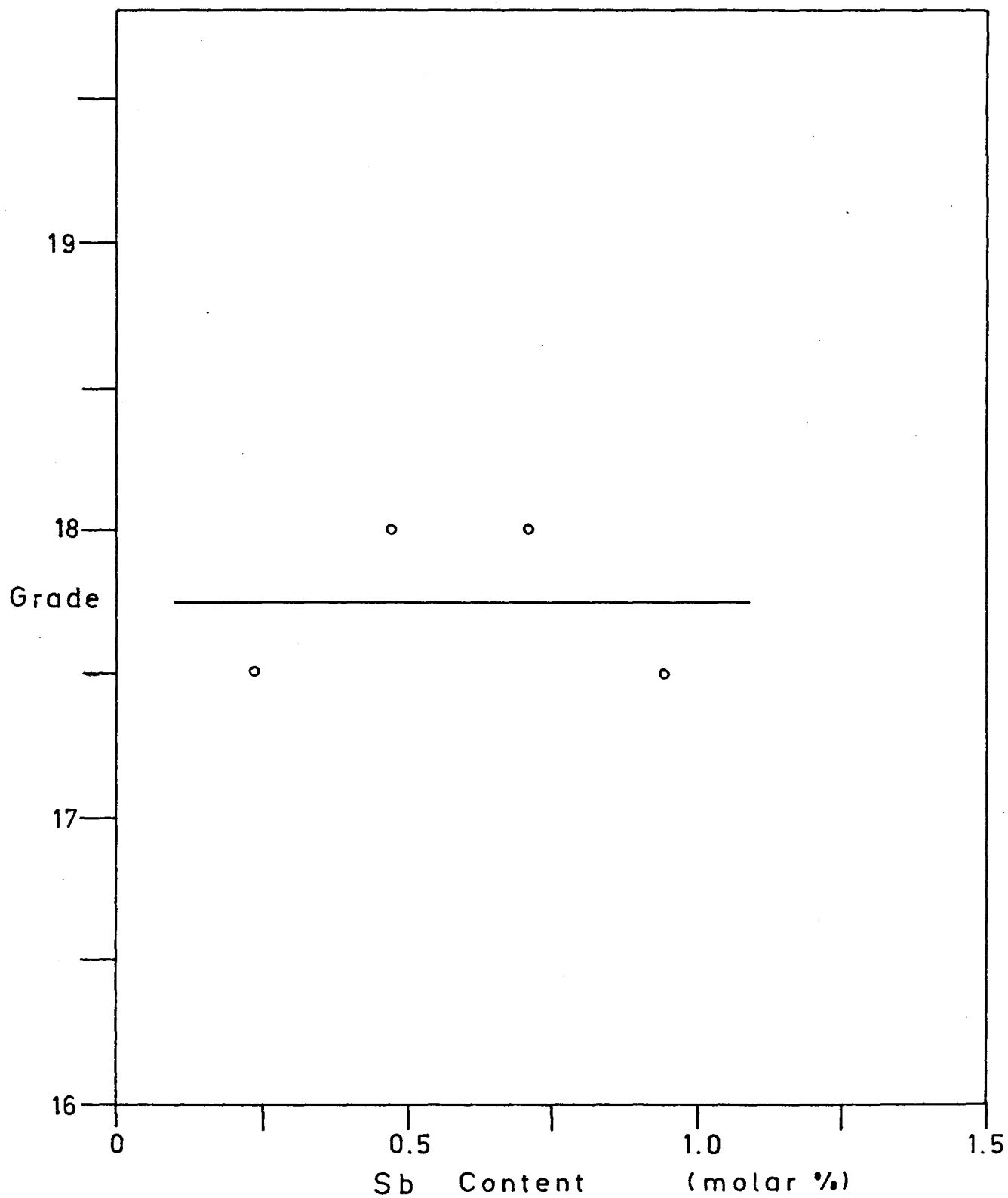


Figure 5.

Dependence of Grade on Sb Doping
(Run 019)

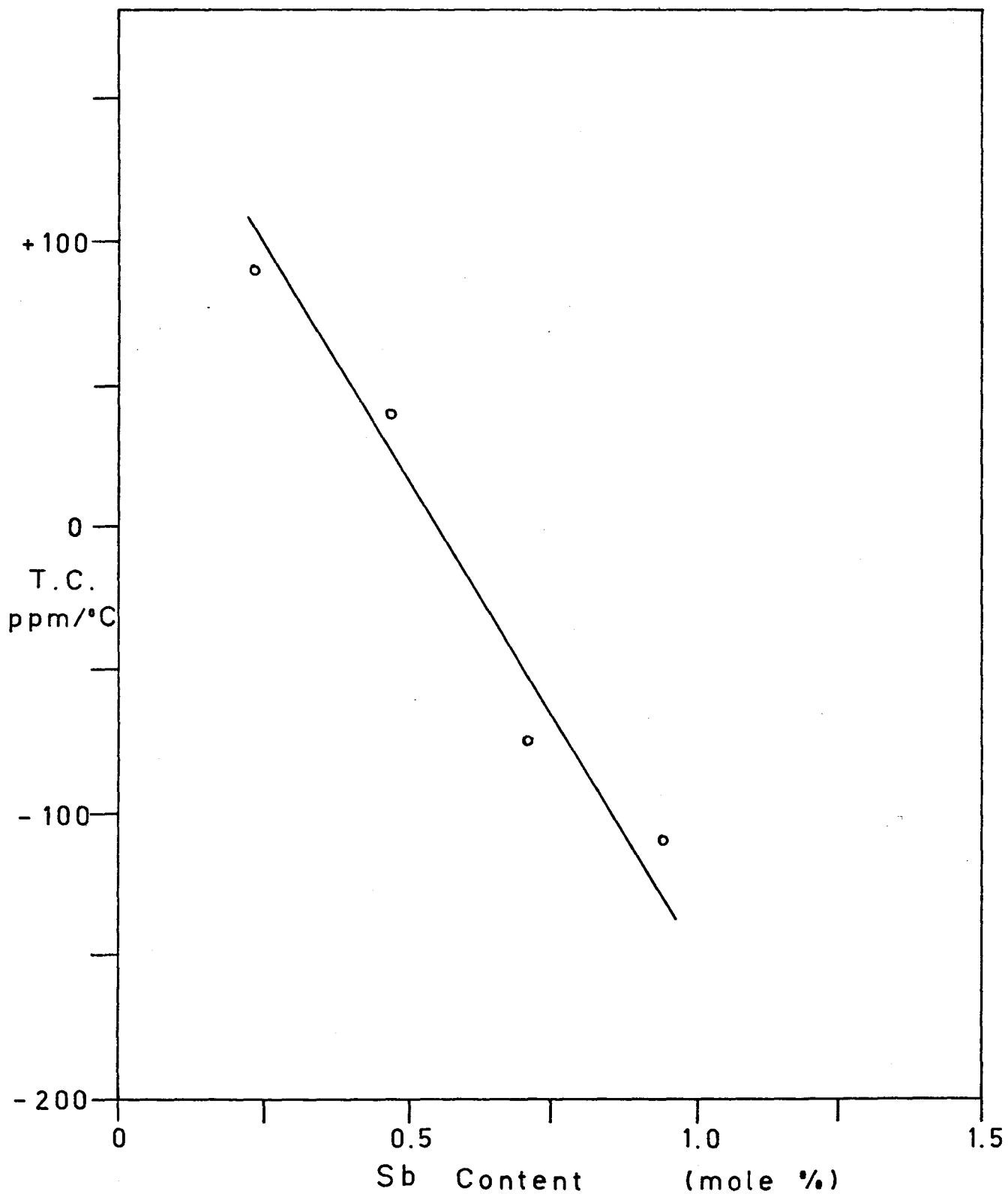


Figure 6.

Dependence of T.C. on Sb Doping

which over the range of 0.5 to 1.0% is close to the results of Welwyn (England) investigations⁽¹⁶⁾ at the same firing temperature (950°C). Below 0.5%, however, the other investigations indicate a reversal in T.C. behavior with doping which is not seen in Figure 6. That such a reversal exists is also confirmed by this report in section 4.6 (Figure 19) where it is noted that undoped films have T.C. values more negative than those of .5% Sb doped films. There are at least two possible causes for the low end discrepancy between Figure 6 and the Welwyn reports. First, it is possible that other parameters were different for the two studies. For instance, the Welwyn study⁽¹⁶⁾ found that increasing the firing temperature to 1050°C moved the inflection point of the T.C.-Sb graph to about 0.25% Sb. Another possible cause is again the effect of excess Sb in the vaporizer resulting in a shifting of the doping levels towards 0.5% regardless of the settings.

In addition to the experimenting described in this section where only the antimony content was varied, studies were also made of the effects of firing temperature (section 4.4), film thickness (section 4.5), and boron and HCl concentrations (section 4.6) on the film properties. These were all repeated using two different antimony concentrations to observe their inter-relation with Sb doping.

4.4 Firing Temperature Dependence

To study the effects of firing temperature on the resistive properties of SnO₂ thin films, oven temperatures ranging from 880 to 1100°C were used in the preparation of samples with all other parameters set as described in Table 2. The data recorded from these samples is presented in Figures 7 and 8, which deal with the effect of firing temperature on the

resistance grade and the T.C. respectively. As more than one run was involved, the secondary runs were normalized to the primary run. (One run represents one session or day with the furnace.) This was done because, although results are generally consistent within a run, they are not usually consistent from run to run. The T.C. versus grade profiles for some of these firing temperatures are presented in Figure 9.

The plot of the effect of firing temperature on resistance grade in Figure 7 requires some explanation. The small arrows on the figure represent the passage of time within the runs. It was found in these runs that when the lower temperature batches were produced first in a run, the grade increased with each subsequent batch. However, when the high temperature batches were produced first and subsequent runs were at lower temperatures, the grade still increased with each batch. It was concluded on this basis that the shift of grade with temperature was completely artificial, and that the temperature has no effect on the grade within this range. This conclusion is strengthened by the results of other runs where temperature was varied (including the results presented in Figure 10). The increase in grade was probably a result of a decrease in solution flow rates as the runs progressed, due to capillary or vaporizer blockage. This sort of problem was quite common in some runs. On this basis the data presentation of Figure 9 is also misleading. It can be assumed that in a correct representation the dotted lines in that figure would be approximately vertical.

The firing temperature has a definite effect on the T.C. values of the films, as shown in Figure 8. The change in T.C. with temperature was found in this study to be +2 ppm/°C per °C of firing temperature. This is

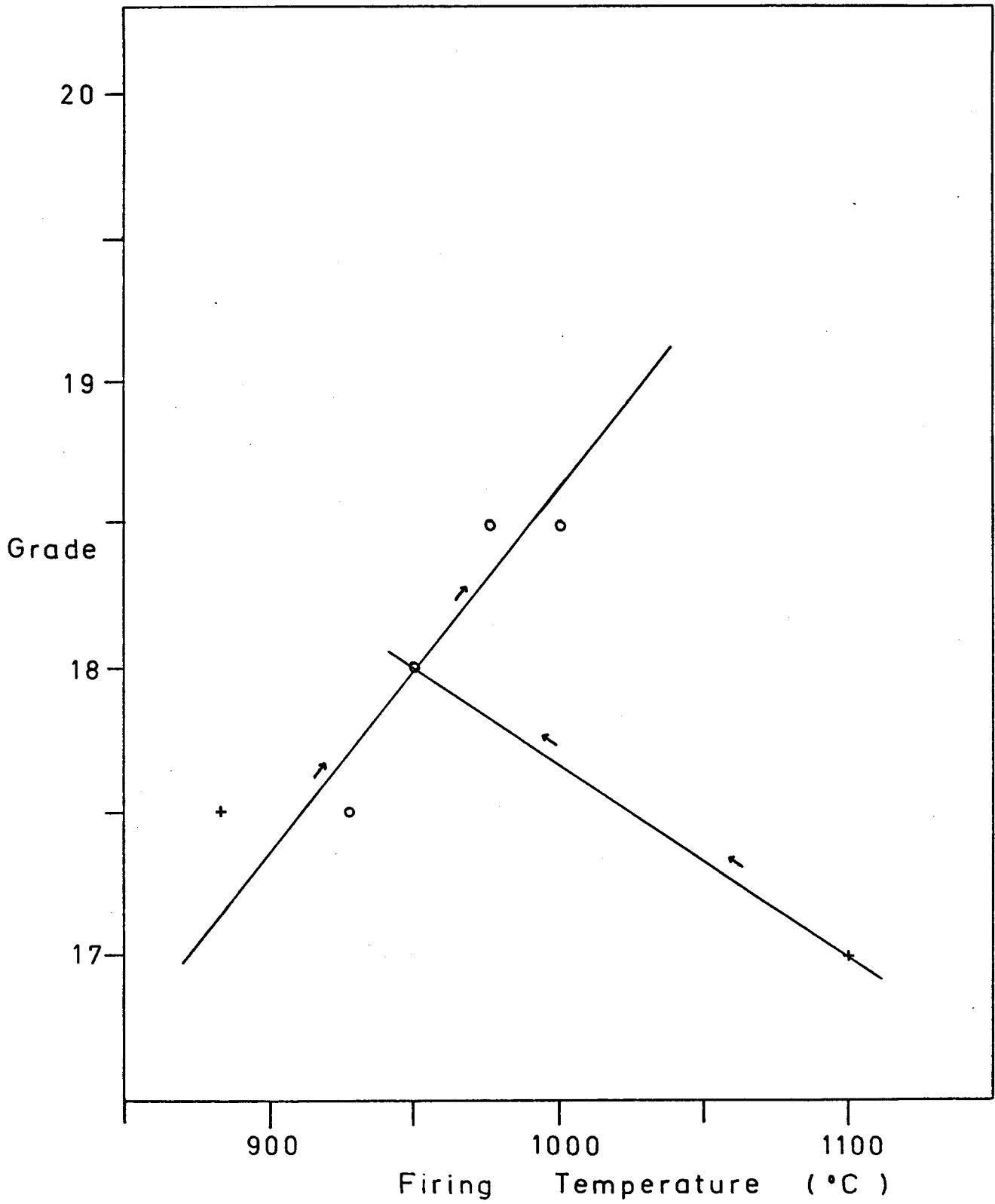


Figure 7.

Dependence of Grade on Temperature (o - Run 024;
+ - Run 016 normalized
to 024 at 950°C)

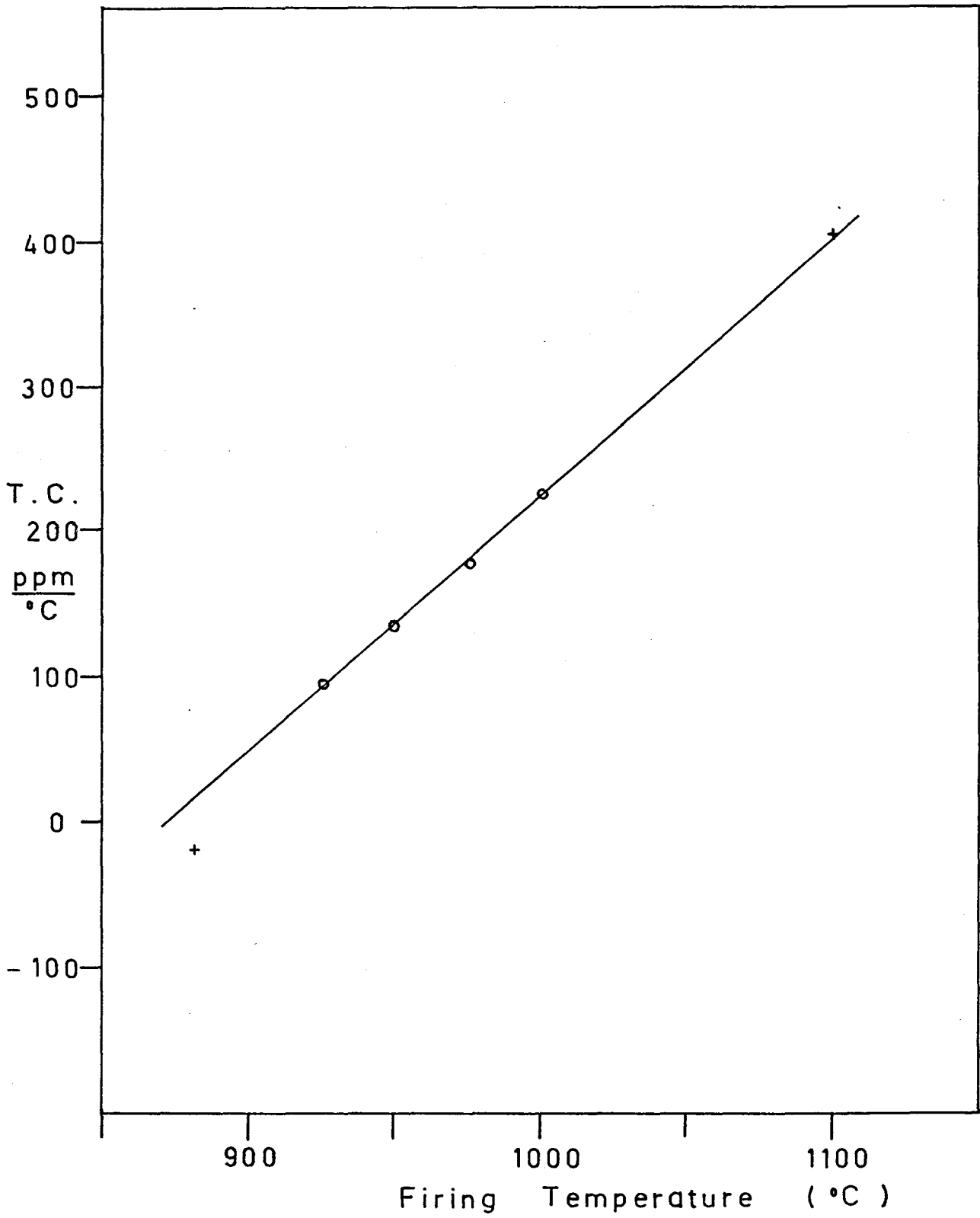


Figure 8.

Dependence of T.C. on Temperature

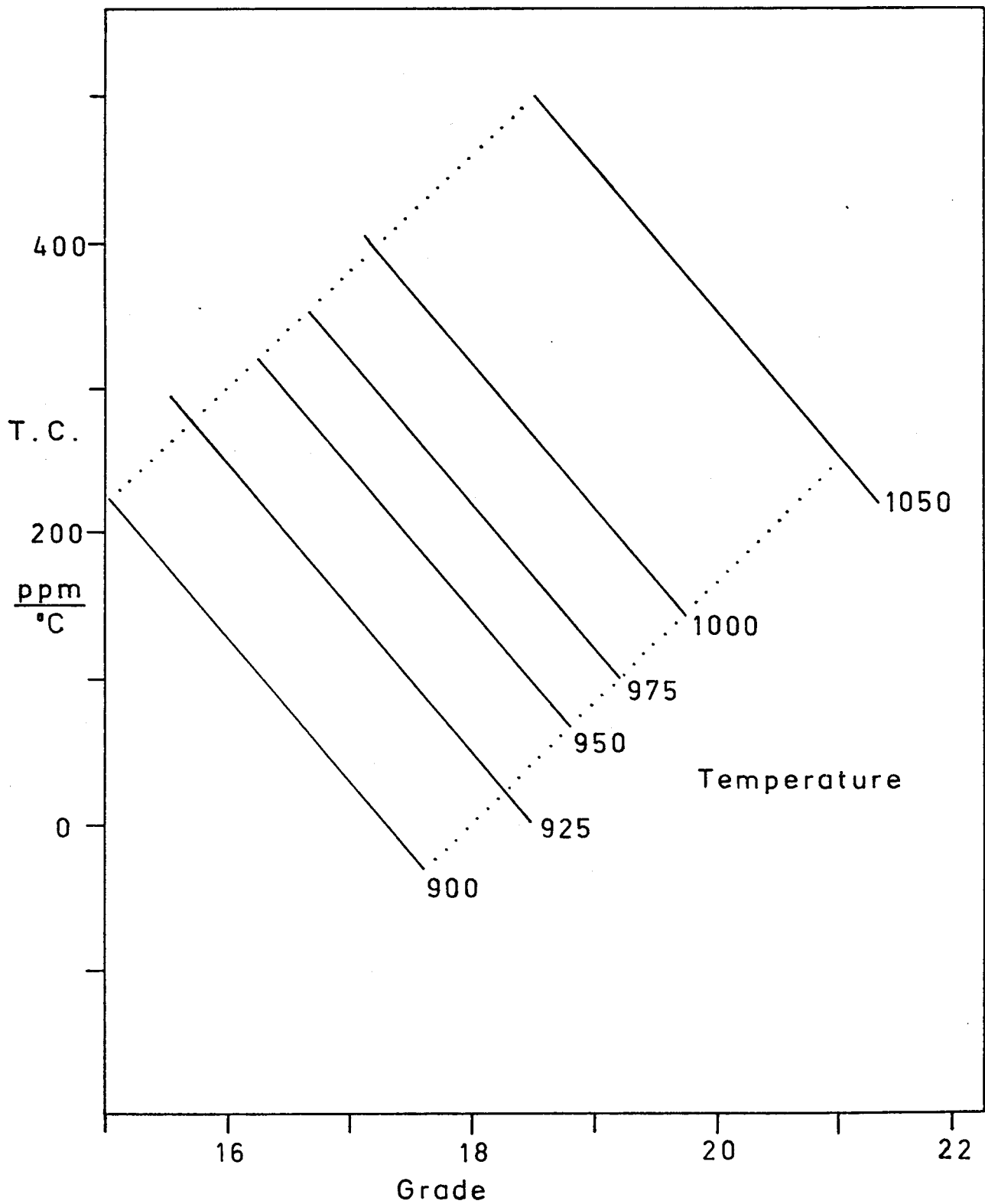


Figure 9.

T.C. - Grade Distribution at Various Temperatures
(Run 024)

consistent with the findings of other studies.^(16,17) The theoretical explanation of the increase in T.C. with temperature is probably related to an increase in grain size and/or film thickness effects as the firing temperature is increased. As can be seen in Figure 9, the slope of T.C. versus grade is invariant with temperature. (As noted previously, the T.C. - grade slope was invariant with all parameters in this report.

The effect of firing temperature on the grade and T.C. values of SnO₂ films was also studied using reduced antimony doping levels. The standard doping level was 0.457 molar %. The results using 0.228% Sb are presented in Figures 10 and 11 for grade and T.C. dependence respectively. As can be seen in Figure 10, the firing temperature has no discernable effect on the resistance grade, the same as was concluded at standard doping levels. The gradient of T.C. with temperature in Figure 11 is +2.75 ppm/°C per °C firing temperature. This is about 38% greater than the gradient in Figure 8 for normal Sb doping. The significance of this difference is not clear. It may be a genuine difference or it may be caused by the shift in grade in the 0.475% Sb case (see Figures 7 and 9). The difference could also be accounted for by the combined maximum errors in Figures 8 and 11.

4.5 Film Thickness Dependence

The effects of film thickness on the resistive properties of SnO₂ films were observed by varying the flow rates of the two chemical solutions between 0.5 and 3.0 cc/min. These two flow rates were kept equal to each other and the remaining system parameters were as listed in Table 2. It was assumed that the film thickness was directly proportional to the solution flow rates. The effect of film thickness on sample resistance is

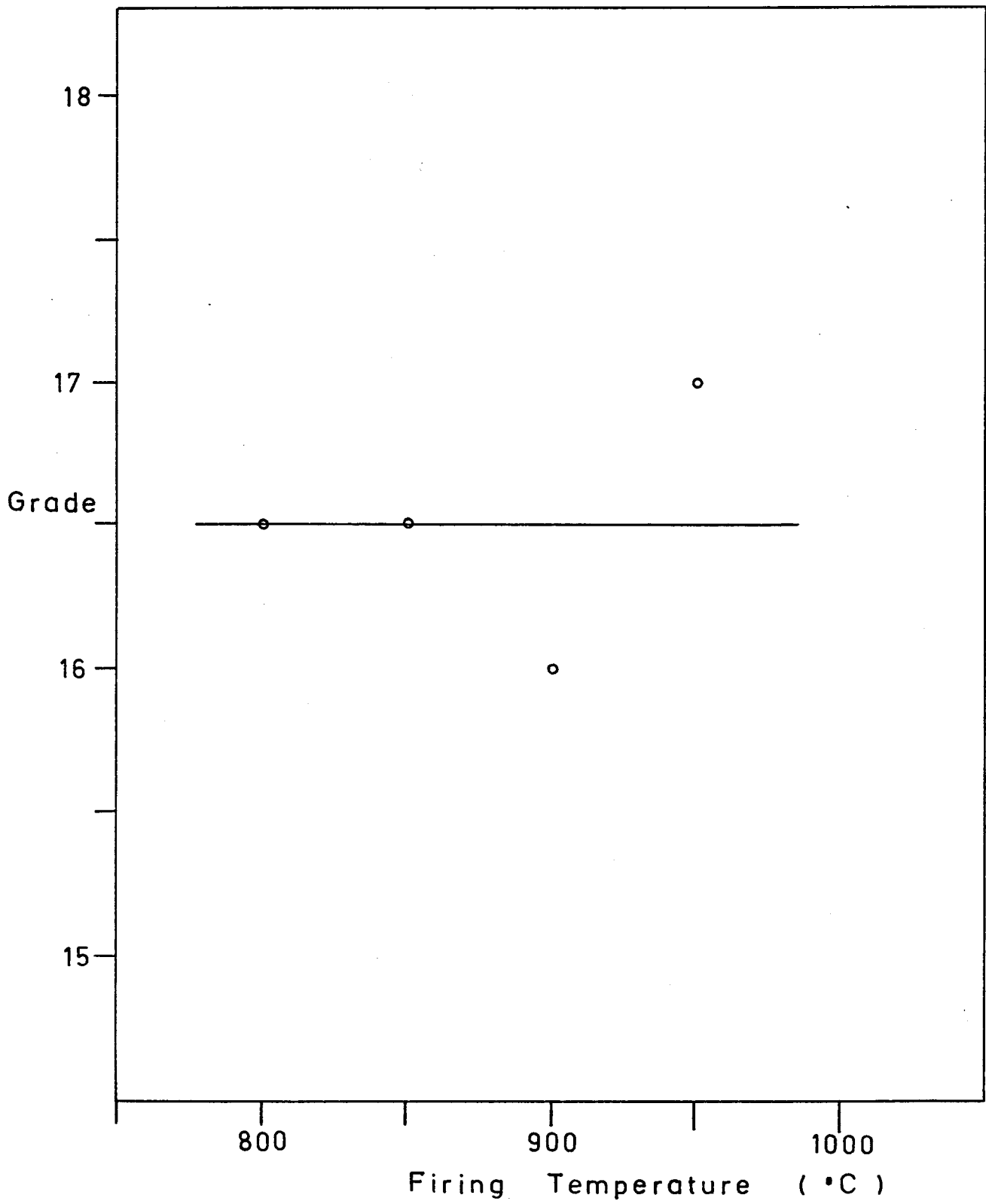


Figure 10.

Dependence of Grade on Temperature (Reduced Sb)
(Run 020)

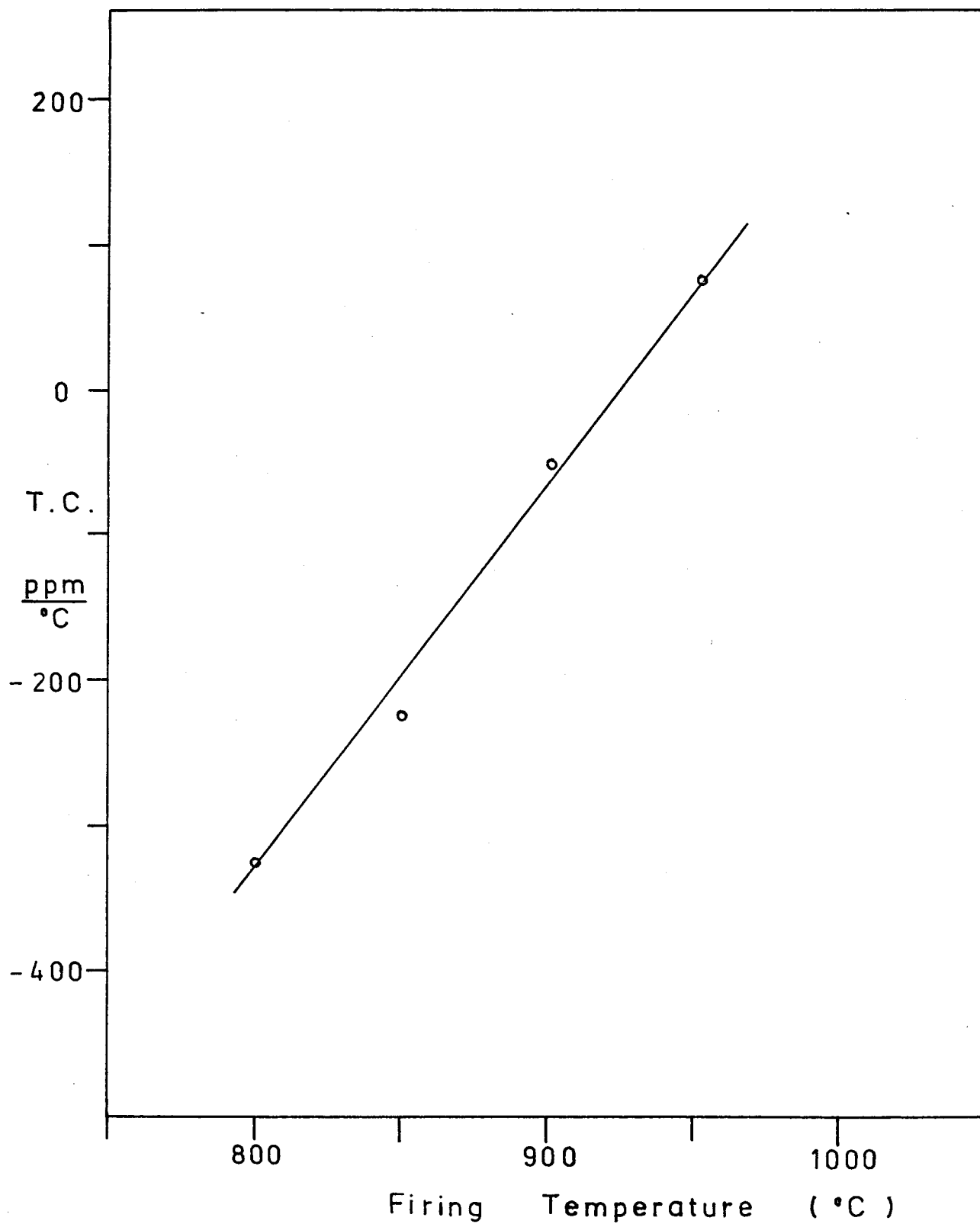


Figure 11.

Dependence of T.C. on Temperature (Reduced Sb)

shown in Figure 12 and the average spreads of the resistance values, around the mean values given in Figure 12, are presented in Figure 13. The effect of film thickness on film T.C. values is plotted in Figure 14.

Figure 12 shows that, as expected, thinner films have higher resistances. However, the rate of change of resistance is much higher than would be expected if film resistivity were constant with thickness. It would be expected that halving the thickness (reducing flowrates from 3.0 to 1.5) would double the resistance (add 3 grades). In fact, 7 1/2 grades are added in going from 3.0 to 1.5 cc/min. This is explained by the fact that film resistivity is a function of film thickness, as described in section 2.4. Figures 12 and 13 show a marked change in resistive behavior between SnO₂ films produced at flowrates above and below 1.5 cc/min. Above 1.5 cc/min., the change of grade with flowrates is -5 grades per cc/min. with an average spread of two grades. Below this flowrate the change in grade averages approximately -8 grades per cc/min. and the grade spread is much larger. To clarify the situation somewhat, extra points have been plotted on Figure 12 in the region of the transition. The two + signs are the average grades of those batches with the higher grades disregarded. The two dotted lines are the upper and lower limits of the grade values. These extra points and the grade spread lead to the conclusion that the samples at low flowrates were still being produced in line with those produced at higher rates but that something was happening to some of the thinner films to increase their resistance dramatically. It is probable that this something was in fact physical damage or blemishes in the thinner films. Thus it is assumed that the thicker films were not affected significantly

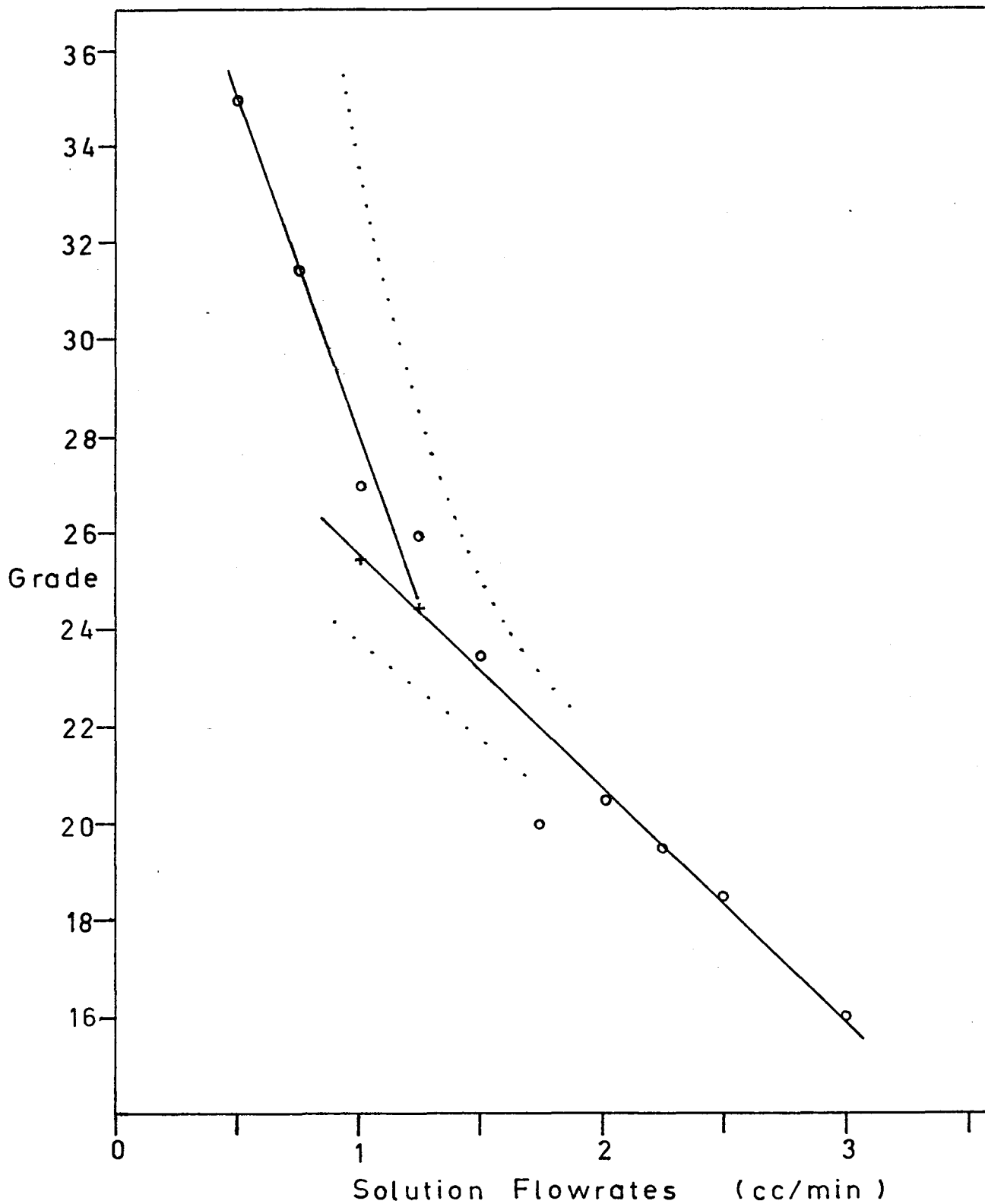


Figure 12.

Dependence of Grade on Film Thickness

(Run 017)

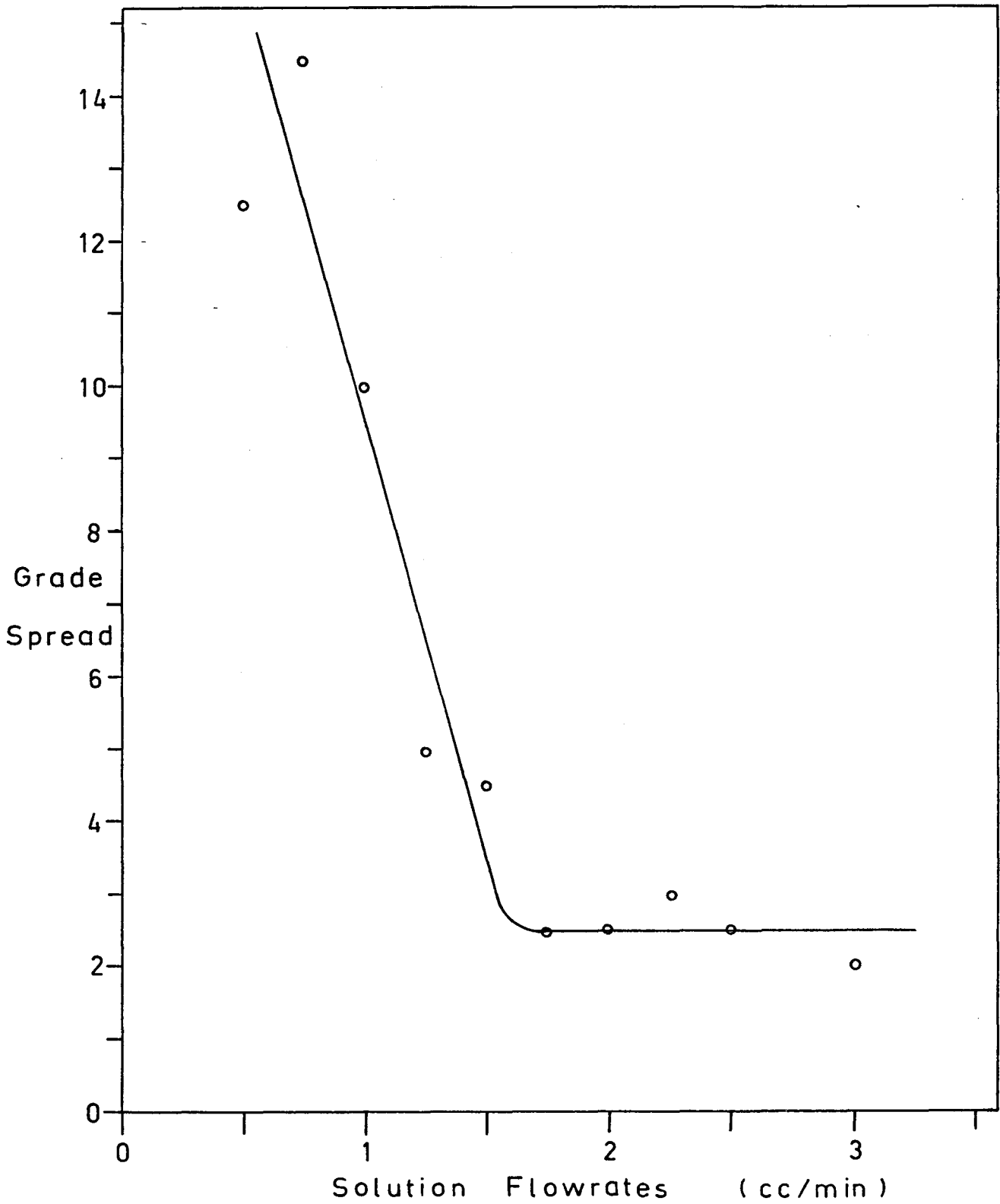


Figure 13.

Dependence of Grade Spread on Film Thickness

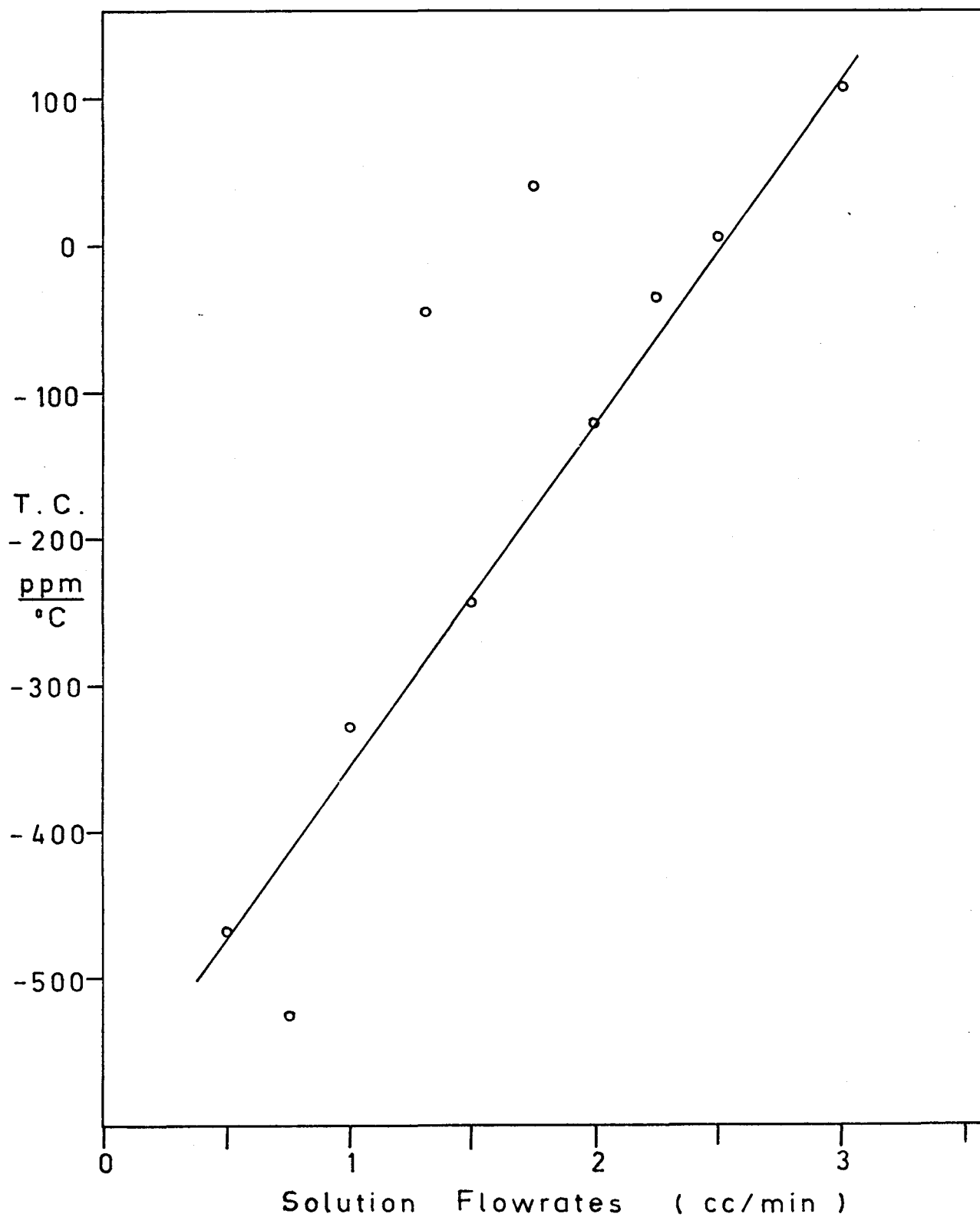


Figure 14.

Dependence of T.C. on Film Thickness

by such physical problems, while films produced at flowrates under 1.5 cc/min. were increasingly more likely to suffer failure due to the small thickness of the films.

The plot of T.C. versus film thickness (Figure 14) shows an increase in T.C. as the flowrates are increased which is consistent with the findings of other studies.⁽¹⁷⁾ The change of T.C. with flowrate in Figure 14 is +225 ppm/°C per cc/min. However, there is room for a large amount of variation in that slope as there is a fairly large statistical error associated with the data points and especially as the data points for flowrates of 1.5 cc/min. and below are under suspicion due to the grade behavior in that region and the known variance of T.C. with grade. These factors would contribute to a shallower slope. Also, the highest T.C. values for each batch showed very little variation with T.C. No theoretical mechanism has as of yet been postulated to explain the relationship of the T.C. of SnO₂ films to the film thickness.

A study was also made of the effect of film thickness on the resistive properties of films produced with half the normal amount of antimony (0.228 versus 0.457 molar %). The effects of film thickness on the grade and T.C. values of such films are shown in Figures 15 and 16 respectively. The plot of grade versus flow rate in Figure 15 matches Figure 12 so closely in the region where they overlap that the two figures form a straight line (above 2 cc/min.) when superimposed. This would indicate that Sb doping (from 1/4 to 1/2 %) has no significant effect on the film thickness dependence of resistive grade. In Figure 16, however, the dependence of T.C. values on the films thickness is found to be approximately +75 ppm/°C per

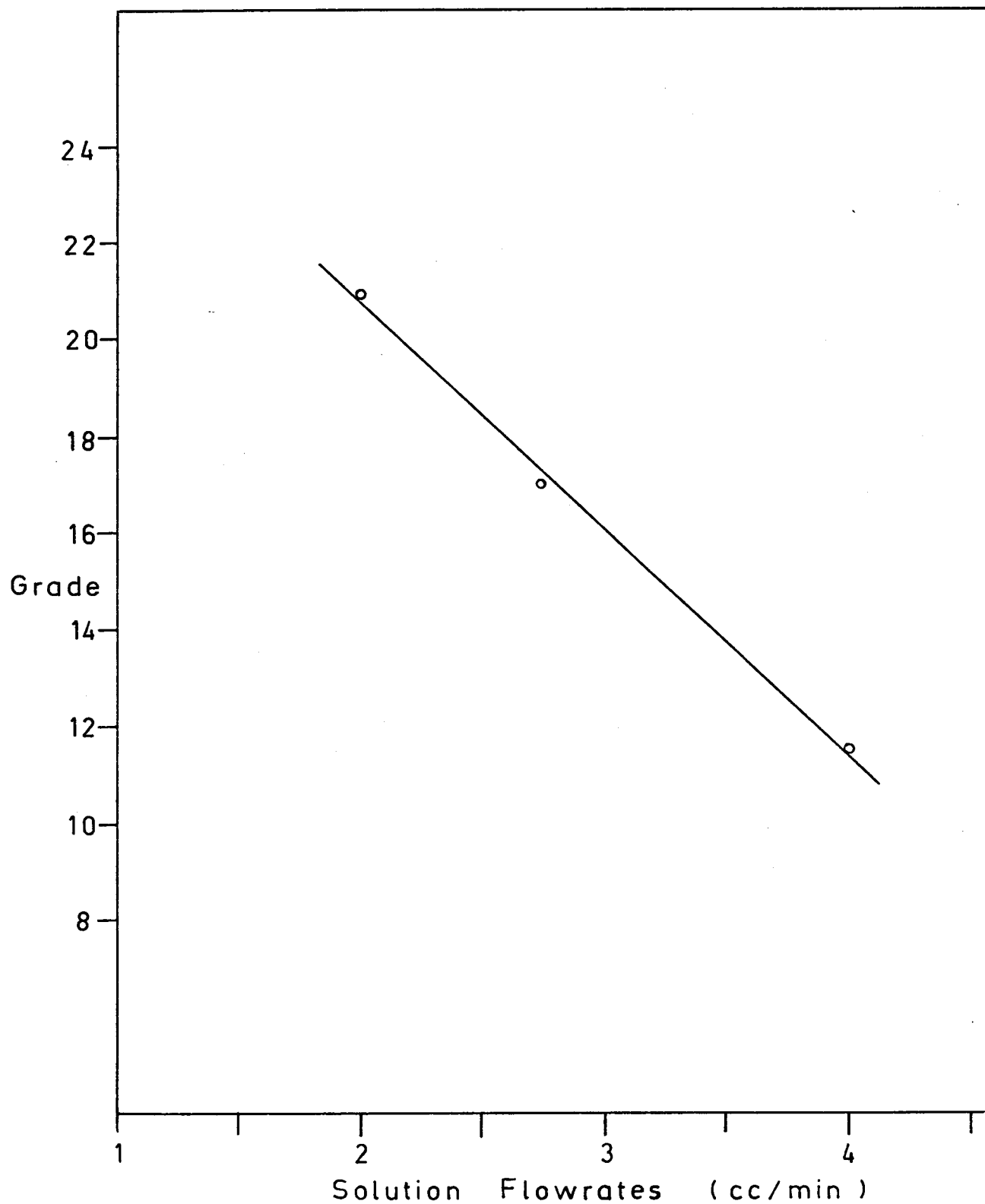


Figure 15.

Dependence of Grade on Film Thickness (Reduced Sb)
(Run 022)

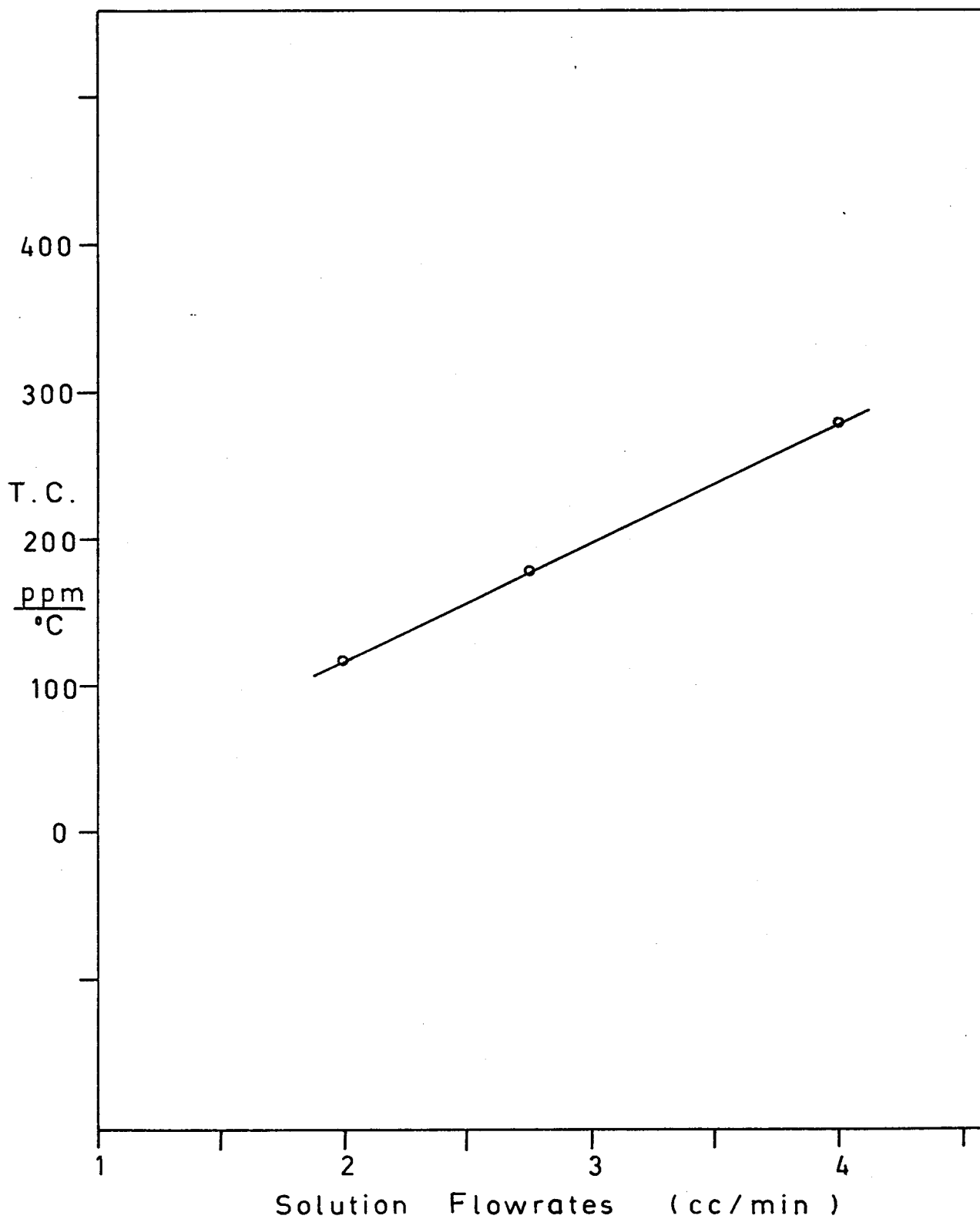


Figure 16.

Dependence of T.C. on Film Thickness (Reduced Sb)

cc/min. flowrate. This is significantly below the value of +225 found for the more heavily Sb doped films (Figure 14). This difference in slope could be a genuine effect of antimony doping, however, some variation in the grade-thickness behavior with doping would also be normally expected in such a case. The other possible explanation is that the difference is artificial and represents a large error, predominantly in Figure 14. Whether the difference in slope is a result of the first or the second of these reasons or a combination of both, cannot be determined with the data available for this report. This question must be left for future investigation.

4.6 Boron and HCl Solution Dependence

The dependence of SnO_2 film properties on the boron content was studied in two different ways. In the first examination of this dependence, the boron content was varied by varying the HCl solution flowrate while holding the SnCl_4 flowrate constant. The results on the film properties are shown in Figures 17 and 18 for grade and T.C. dependence respectively. It was assumed at the time that, as there was an excess of water in the HCl solution to take part in the reaction, and as the HCl in the solution did not undergo chemical reaction, the only effect on the film properties related to this change in flowrate would be the effect of varying the boron concentration. However, in retrospect, this assumption may have been invalid. The method of varying the boron content by varying the flowrate instead of by changing the boron content of the solution was chosen because there was more error associated with varying the solution's boron

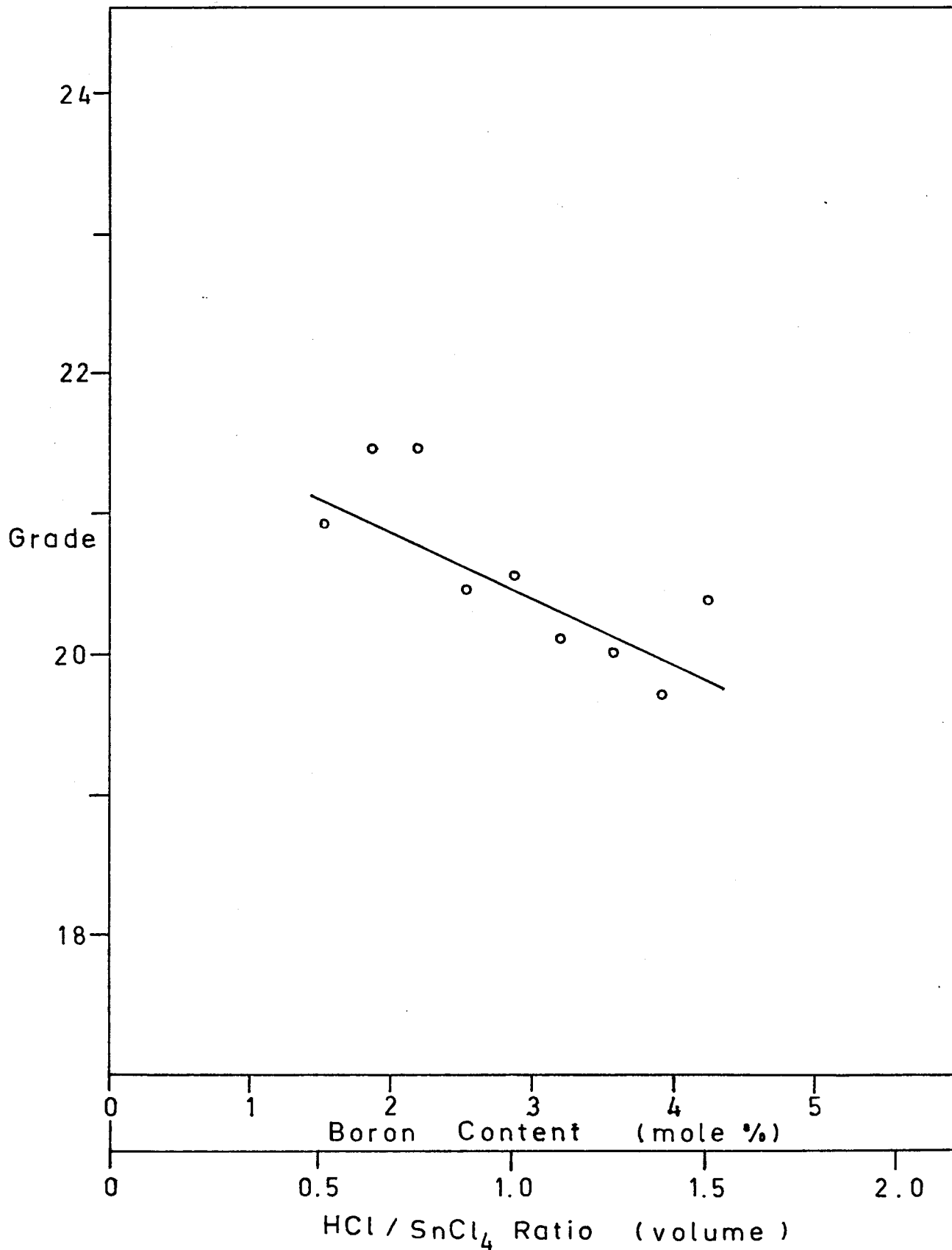


Figure 17.

Dependence of Grade on HCl Solution

(Run 023)

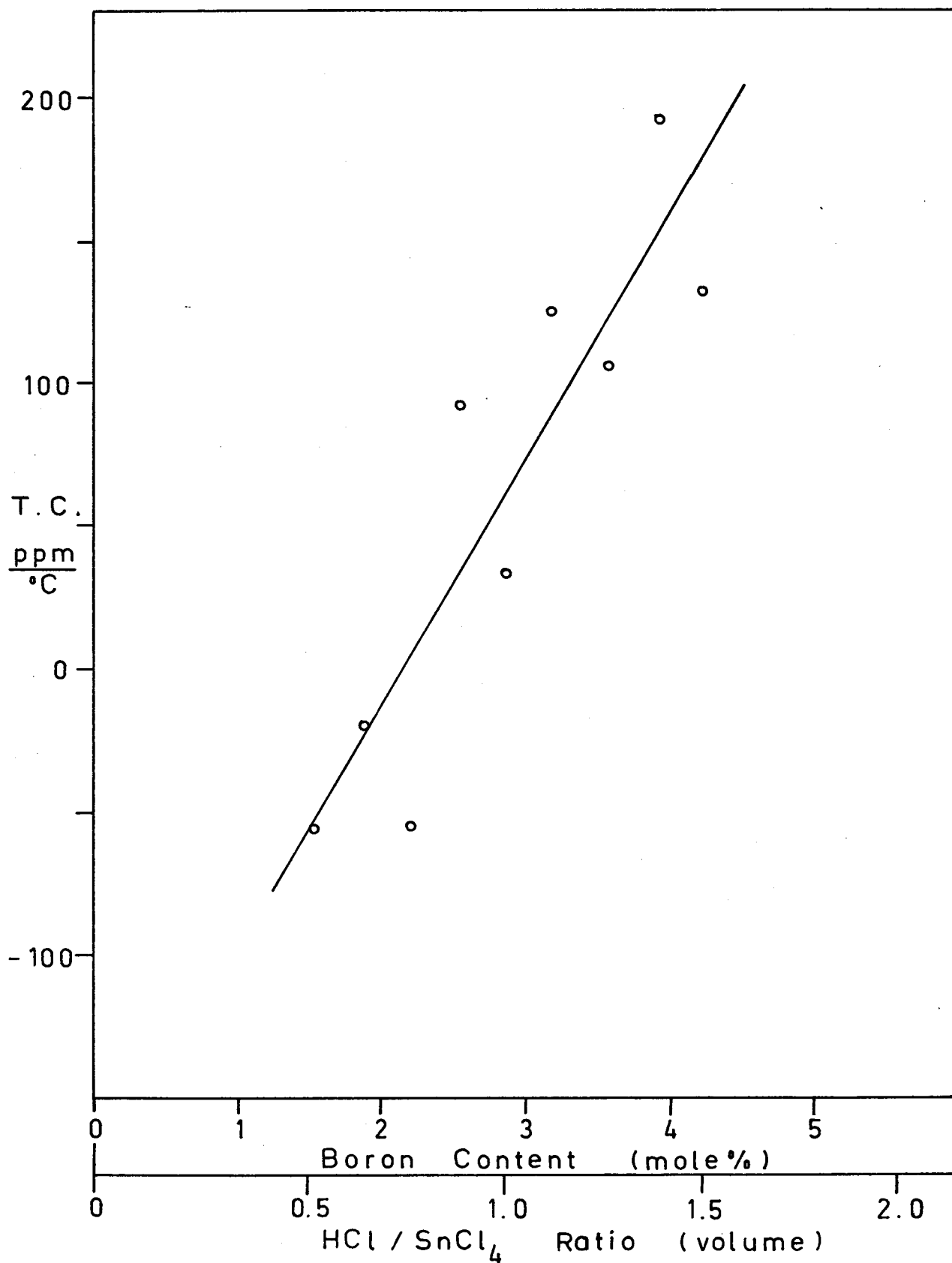


Figure 18.

Dependence of T.C. on HCl Solution

content due to the necessity of interrupting the furnace operation to change solutions. An additional study was made in which the solutions were changed to effect concentration changes. (Flowrates and all other parameters were set as described in Table 2.) Two HCl solutions were used with the boron content being either normal (2.74 molar %) or zero. In addition, two SnCl₄ solutions were used with either normal (0.457 molar %) or zero antimony content. The results of this study are presented in a graphical matrix form in Figure 19. It should be noted that the data presented in the left-hand column of this figure is identical to the data presented in the right-hand column; only the method of presentation is different.

The effect of boron content on the resistive grades of the films, as presented in Figures 17 and 19 is contradictory. In Figure 17 the resistance is reduced by about 1/2 grade per mole percent boron, while in Figure 19 the resistance is increased with boron at about the same rate. The discrepancy could be explained in three ways. First, the two slopes are so shallow that systematic error in the data points (for example, a shift in firing conditions during a run) could account for both slopes and the grade dependence on boron could be zero. Second, Figure 17 could be accurate and the discrepancy explained by a curvature in the boron dependence that does not show up in Figure 19. Lastly, Figure 19 could be the more accurate and the discrepancy would be explained by the effect of varying the HCl and/or H₂O on the plot in Figure 17. Theoretically, as explained in section 2.3, the effect of boron in SnO₂ is to reduce resistance in some ways and to increase it in others.

As with the grade dependence, the picture of the T.C. dependence on

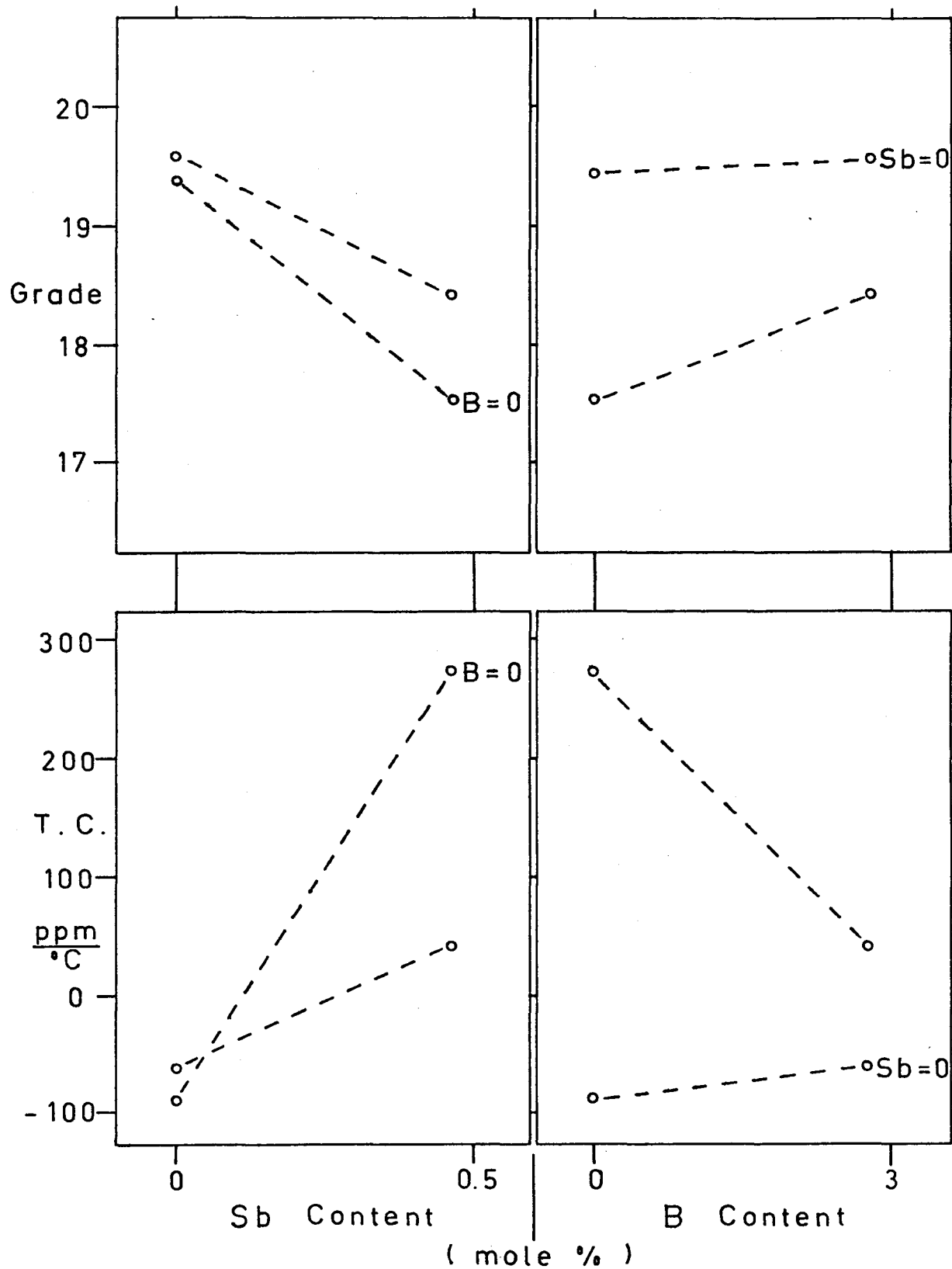


Figure 19.

Grade and T.C. Comparison for Sb and B Doping

boron presented by Figures 18 and 19 is contradictory. In Figure 18, the T.C. increases with boron content at the rate of +115 ppm/°C per mole % boron. In Figure 19 the T.C. decreases at a similar rate. The large values of these slopes rules out systematic error as a cause of the T.C. discrepancy. Other research^(16,17) has produced plots of T.C. versus boron doping similar to that in Figure 19 over the region covered. This rules out the possibility of a curvature in the T.C. - boron relationship being undetected in Figure 19 and leaves only the possibility that Figure 19 represents the effect of boron on the T.C. and the reversed slope of Figure 17 is due to some effect related to the change in HCl and/or H₂O as the flowrate was varied. This effect may have taken the form of an increase in chlorine included in the film as the HCl was increased.

The effect of antimony content on the films as shown in Figure 19 is consistent with the findings in section 4.3. As the antimony level goes to zero in this figure, the grade increases, while no grade change was found in section 4.3 at higher doping levels. However, the increase was expected theoretically, and the fact that a greater increase was not found indicates high intrinsic doping, as already noted. The slope of T.C. with antimony doping in Figure 19 is positive while in section 4.3 (Figure 6) it is negative. However, this is completely explained by other reports⁽¹⁶⁾ which indicate that this slope is positive for low Sb doping values and negative for higher values. The transition takes place between 0.25 and 0.5% Sb, where Figures 6 and 19 overlap. It can be seen from Figure 19 that the effect of boron on the grade and T.C. versus antimony content curves for SnO₂ films is to decrease the slopes of these two plots when boron is

present. Likewise, the effect of antimony on the grade and T.C. versus boron content curves is to increase the slopes when antimony is included.

4.7 Annealing

A brief study was made of the effects of annealing in vacuum and air on the properties of SnO₂ films produced in the study. Three lots of samples were selected from a uniform batch of samples fired at the normal conditions in Table 2 (Run 015, batch 1). One lot was kept as a control. Of the other two lots, one was heated to 500°C in vacuum. Air was bled in to approximately one atmosphere as the samples cooled slowly. The other lot was heated to 500°C in air before being cooled. The cooling cycle was spread over 48 hours.

The average resistance for the lot heated in vacuum was reduced by one grade relative to the control lot while the lot heated in air was increased by one grade relative to control. This is consistent with the expected results for oxidation and reduction of SnO₂ and has been found in other studies.^(2,8) The average T.C. increased by about 50 ppm/°C for the lot heated in vacuum while a reduction was noted for the lot heated in air. This could be attributed to the grade - T.C. relationship described in section 4.1. This, in turn, would support the contention that the grade - T.C. relationship found in all aspects of this study was at least partly due to a heat treatment effect. A rather surprising finding in these tests was that the samples annealed in air were less stable than the control group. This development could be attributed to the long cooling time employed. It appears that the optimum oxygen deficiency concentration for SnO₂ films is a function of both temperature and atmosphere at annealing temperatures.

This deficiency level is probably locked into the film by quenching (fast cooling). As T.C. measurements (and many high load situations) involve quenching, some instability would be found in slowly cooled films. As noted elsewhere,⁽⁵⁾ careful attention to the process of quenching is needed to ensure repeatability in subsequent measurements.

CHAPTER 5

CONCLUSIONS

Observations of the spread of resistance and temperature coefficient values for samples produced under identical conditions have indicated that these spreads are related. Samples with above average resistances had below average T.C. values. This was attributed to film thickness effects and/or heat treatment in the collector. This latter conclusion was strengthened by annealing tests which revealed that vacuum heat treatment resulted in reduced grade and increased T.C. while the opposite was true with heat treatment in air. Another finding of the annealing tests was that the process of quenching was important to film stability, probably due to a locking in of oxygen deficiencies.

The varying of the resistor rod feed rate and the air flowrate to the vaporizer were both found to have no effect on the film properties. Varying the temperature of the rods at which the SnO_2 forming reaction took place was found to vary the T.C. while having no effect on the grade. The T.C. values were increased with increased temperature at a rate of 2 to 3 ppm/ $^{\circ}\text{C}$ per degree, and the rate of increase was marginally higher at lower antimony concentrations. It was tentatively concluded that the increase was due to an increase in grain size and possibly related to film thickness. As expected, increasing the film thickness by increasing the flow rates, resulted in a decrease in resistance. An increase in T.C. also occurred. The decrease in grade was much larger than proportioning to film thickness

would suggest due to the variation of film resistivity with thickness. The findings suggest that the change in T.C. with thickness is much greater at higher Sb doping levels although this is not certain. It was also found that films prepared at low flowrates (below 1.5 cc/min.) were not dependable.

Both antimony and boron doping were found to have little effect on the resistance grade of the SnO₂ films prepared for this report. This is probably due to high intrinsic doping levels (oxygen deficiencies). The graph of grade versus antimony appear to have a slight negative slope while the opposite is true with boron. The slope of the T.C. versus Sb doping level has a positive value at very low levels and a negative value at higher levels. Between 0.25 and 1% Sb, the slope was -400 ppm/°C per mole %. The removal of boron from the film increased this slope. The slope of T.C. versus boron doping was also found to have a negative slope. However, varying the HCl and water components of the firing solutions along with the boron resulted in a positive T.C. slope. Thus it can be concluded that HCl and water concentrations, even when in excess, affect the resistive properties of SnO₂. It was found that the removal of Sb from the films resulted in a reduction in the slopes of T.C. and grade versus boron.

Some conclusions can be drawn from this report pertaining to the production of tin oxide resistors. The open collector system produces tighter resistor value spreads than the closed system, making the open system preferable. The most successful method of varying the resistor grade is to vary both flowrates equally, although flowrates below 1.5 cc/min. produce unreliable results. Good results are achieved by using the oven temperatures to vary the T.C. values. And finally, it appears that quick cooling is useful in ensuring film stability.

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