ELECTRICAL PROPERTIES AND DEFECT STRUCTURE OF STANNIC OXIDE SINGLE CRYSTALS

By

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ABSTRACT

A study of the defect structure of stannic oxide was undertaken by
measuring electrical conductivity over the temperature range 700°C-1350°C
and from 1 to 10⁻² atm of oxygen. This is the first reported attempt to
study the non-stoichiometric behaviour of stannic oxide. In the range
1100°C-1350°C it is believed that a single non-stoichiometric defect, which
has been tentatively identified as a doubly-ionised oxygen vacancy dominates
the conductivity, while below 850°C, the conductivity appears to be impurity-
controlled.

Undoped samples were heat-treated and quenched in a manner which would
'freeze' a large number of the above-mentioned defects. Hall measurements
indicate a shallow donor level 29±7 mev below the conduction band. With
similar heat-treatments, but without identifying the non-stoichiometric
defect, Marley et al reported a donor level consistently 4-6 times deeper.
An oxygen-vacancy two electron-trapped model has been tentatively proposed
to account for this discrepancy, and available spectrochemical and mass
spectrographic data has been used to identify what are believed to be
compensating impurities.

Hall studies on samples intentionally doped with antimony indicate a
shallow donor level at 40±5 mev which is in good agreement with values
reported in literature. Heat-treating these samples in a hydrogen-rich
ambient resulted in large and uniform increases in the carrier concentration
and a new, somewhat deeper level at 50± mev. Simplified models have been
proposed to explain this.

Thesis Supervisor: C.G. Fonstad
Title: Assistant Professor of Electrical Engineering
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CHAPTER I

1.1 INTRODUCTION

Stannic Oxide is a wide bandgap semiconductor with potential for use in active electronic devices. It was originally used for transparent conductive coatings on glass and for high temperature electrodes (mpt over 2000°C), but an early investigation by Kohnke\textsuperscript{1} revealed SnO\textsubscript{2} to be a wide-bandgap semiconductor.

Stannic Oxide occurs in nature as the mineral cassiterite; it crystallizes in the tetragonal system class 4/m 2/m 2/m. The space group is D\textsubscript{4h}; with two Sn atoms and four oxygen atoms per unit cell (see Fig. 1.1). The lattice constants are a\textsubscript{o} = 4.738Å and c\textsubscript{o} = 3.188Å.

Marley et al\textsuperscript{2} were the first group to successfully grow stannic oxide crystals at the Corning Glass Works Laboratory in 1961, by a vapor deposition technique at 1600°C. They used mullite and alumina tubes in their growing furnace, resulting in high concentrations of Al and Fe impurities in their crystals. They made extensive electrical\textsuperscript{3} and optical studies\textsuperscript{4} on their crystals. Reed et al grew crystals of stannic oxide soon after at Lincoln Laboratories, followed by Wright et al\textsuperscript{5} in Britain. The latter have reported electrical\textsuperscript{5,6} and optical\textsuperscript{6,7} measurements on their crystals. They were followed by Nagasawa\textsuperscript{8} et al in Japan, who grew crystals by the vapor reaction of SnCl\textsubscript{4} with H\textsubscript{2}O, and have reported fairly extensively on their electrical\textsuperscript{9,10,11} and optical\textsuperscript{9,10,11} measurements. More recently Fonstad\textsuperscript{12} has developed a low pressure, chlorine transport chemical vapor deposition system to grow high quality stannic oxide crystals under controlled conditions, and reported electrical\textsuperscript{13} measurements on them.

Stannic oxide is reported to be a direct bandgap semiconductor\textsuperscript{14,15} with two valence bands. The gap at room temperature is 3.45eV with a
Fig 1.1. Perspective view showing tin atoms arranged in a body-centered tetragonal lattice, each tin atom being surrounded by an octahedron of oxygen atoms.
valence band separation of 0.12 ev and 3.597 ev at 5°K with a valence band separation of 0.123 ev.\textsuperscript{14,15}

Marley\textsuperscript{3} et al have reported extensive electrical measurements on samples which were as-grown, annealed in an oxygen ambient, on degeneratively doped with antimony. A number of undoped samples were heat-treated between 1290°C-1390°C and quenched in liquid nitrogen. Analysis of the carrier concentration data placed the donor level at 150-8.7 \times 10^{-5} \text{Nd}^{1/3} \text{ mev} below the conduction band. This level was ascribed to a non-stoichiometric defect. Mobilities around 200 cm\textsuperscript{2}/v-sec at 300°K were measured, and the electron density of states effective mass was found to be 0.22m\textsubscript{0}.

Subsequently Nagasawa\textsuperscript{9,10} et al and Crabtree et al, have reported that the electrical properties of stannic oxide are sensitive to 'oxidation' and 'reduction' treatments, and this has been ascribed to non-stoichiometric defects. However so far no attempt has been made to directly identify possible non-stoichiometric defects. Shallow donor levels have been found by Fonstad\textsuperscript{13} at 37 mev (ascribed to antimony) and 140 mev; and Nagasawa\textsuperscript{11} et al have reported levels at 24, 13.7 and 3.4 mev. The identity of the levels however has not been determined. All results reported have been on n-type material. Attempts to grow p-type gallium-doped crystals\textsuperscript{16} resulted in heavily compensated crystals with n-type conductivity.

In the present study an attempt has been made to identify the non-stoichiometric defect structure by measuring the electrical conductivity as a function of the partial pressure of oxygen from 10\textsuperscript{0} to 10\textsuperscript{-2} atmospheres, and in the temperature range 700°C-1350°C. The theoretical pressure dependences for Sn interstials and oxygen-vacancies have been derived
using standard techniques.\textsuperscript{17} In the temperature range from $1100^\circ$C-1350$^\circ$C it is believed that a single non-stoichiometric defect dominates the conductivity and it has been tentatively identified as a doubly-ionised oxygen vacancy. Undoped samples have been heat-treated between 1275$^\circ$C-1450$^\circ$C in an oxygen ambient and quenched in liquid nitrogen. The large increases of carrier concentration are caused due to the 'freezing-in' of non-stoichiometric defects, identified above as oxygen vacancies. Analysis of the carrier concentration data at low temperatures, indicates a shallow level at 29$\pm$7 mev. Marley\textsuperscript{3} heat-treated and quenched his undoped samples in an identical manner (though he did not identify the defect), and his results indicate a level which is consistently 4-6 times deeper for samples with similar room temperature carrier concentrations. An oxygen vacancy two electron-trapped model has been tentatively proposed to account for this large discrepancy.

Antimony doped samples have also been analyzed, and a shallow donor level at 40$\pm$5 mev detected, which is in reasonably good agreement with values reported in literature.\textsuperscript{13} The effect of annealing $\text{SnO}_2$ samples in a hydrogen-rich ambient has also been investigated.

1.2 GROWTH OF STANNIC OXIDE CRYSTALS USED IN THIS STUDY

The crystals used in this study have been grown by Professor C.G. Fonstad\textsuperscript{12} by a chlorine transport, chemical vapor deposition method, which is briefly reviewed below.

Chlorine gas reacts with tin in an external reactor at 100$^\circ$C, where the following reaction takes place

$$\text{Sn(s)} + 2\text{Cl}_2(g) \xrightarrow{\Delta} \text{SnCl}_4(g)$$
The pressure in the entire system is about 10 torr so that stannic chloride is a gas. Stannic chloride is then injected into the growing furnace with hydrogen and oxygen forming SnO₂ which nucleates on the walls of the quartz tube.

\[ \text{SnCl}_4(g) + 2\text{H}_2(g) + \text{O}_2(g) \xrightarrow{\Delta} \text{SnO}_2(s) + 4\text{HCl}(g) \]

Growth occurs at around 1300°C. Hydrogen and SnCl₄ are fed into the furnace through concentric quartz and zirconia nozzles respectively. Antimony or gallium doping is performed by using another reactor in parallel with the pure SnCl₄ reactor.

This system gives high purity crystals, with good control over the crystal growth and electronic dopants. Crystals from most of the runs (except 207) contain 2 ppm or less of impurities like Al, Fe, Mg, Ca etc. The dominant crystal habit gives diamond cross-sectioned prisms attached at their base to the quartz liner, with a slight tilt upstream. The crystals are twinned and the twin plane is (011). The samples have been numbered according to the run from which they were taken, the first three digits representing the number of the run. (e.g. 015-1 or 015-2 etc)
CHAPTER II STUDY OF THE DEFECT STRUCTURE OF TIN OXIDE AT ELEVATED TEMPERATURES

2.1 THEORY

The method used, involved measuring the conductivity of stannic oxide single crystals as a function of partial pressure of oxygen at various fixed temperatures. This is a standard technique used to study the defect structure of a large number of oxides.\textsuperscript{17} Since SnO\textsubscript{2} is isomorphous with TiO\textsubscript{2}, the work reported\textsuperscript{18–22} on the latter was particularly useful in deciding on certain experimental aspects (like instrumentation, equilibration times and other details). The general expression for conductivity is

\[ \sigma = \sigma_0 + \sum_i A_i p_{o_2}/n_i \]  

(1)

where \( n_i \) can have a number of possible values. The contribution to conductivity from impurities is absorbed in the term \( \sigma_0 \). The second term depends on defect mechanisms and is diffusion controlled. It depends on the activation energy of the defect (which is a constant) and on the concentration of the defect species. At high enough temperatures the latter is determined intrinsically by Schottky or Frenkel type defect mechanisms\textsuperscript{17} (which is the case of oxides is dependent on the partial pressures of oxygen), and at lower temperatures by the presence of 'quenched in' defects. In samples which contain impurities, at lower temperatures the conductivity is independent of the partial pressures of oxygen, (the so-called 'impurity-controlled' range), and it is only at higher temperatures that the other terms start to dominate.

The laws of mass-action and electro-neutrality can be applied to defect
mechanisms,\textsuperscript{17} and in the case of oxides it has been found that the concentration of a particular non-stoichiometric defect depends on the partial pressure of oxygen in a definite way (e.g. 1).

Take the case of a singly-ionised oxygen vacancy in \( \text{SnO}_2 \). The governing equation is

\[ \text{O}^x \Rightarrow e + \frac{1}{2} \text{O}_2 + V_o^\circ, \]

where \( V_o \) represents an oxygen vacancy. Applying the law of mass action to the above equation

\[ n^2[pO_2]^{1/2} = k \]

where \( k \) is a constant and \( V_o^\circ = n \)

therefore \( n \propto pO_2^{-1/4} \)

where \( n \) represents the number of charge carriers.

For a doubly-ionised oxygen vacancy the governing equation is

\[ \text{O}^x \Rightarrow 2e + 1/2 \text{O}_2 + V_o^{\circ\circ} \]

and \( n^3[pO_2]^{1/2} = k \)

or \( n \propto pO_2^{-1/6} \)

Now take the case of a singly-ionised tin-interstitial. The governing equation is

\[ \text{Sn} + 20 \Rightarrow e + 0_2 + \text{Sn}_1^\circ \]

and \( n^2[pO_2] = k \)

or \( n \propto pO_2^{-1/2} \)

For doubly, triply and quadruply ionised interstitials the equations and corresponding pressure dependences are
2.2 APPARATUS

The apparatus used for this study is illustrated in Fig. 2.1. It has been originally set up by Dr. K. Kitazawa for making similar studies on $\text{Al}_2\text{O}_3$. A molybdenum–hydrogen furnace was used, to achieve temperatures up to $1450^\circ\text{C}$, and the hydrogen was burnt at an outlet in the presence of a catalyst (platinum). A mixture of oxygen–argon was used to achieve dynamic oxygen pressures in the range of $10^0$ to $10^{-2}$ atmospheres. The ratio of the two gases was controlled by adjusting the needle-valves of the flow-meters. After passing through the furnace the gases were passed through a stabilized zirconia galvanic cell, a bubbler and finally through a vent. The impurities in the two gases are listed in Appendix C. The partial pressure of oxygen was determined using the standard Nernst equation

$$E = \frac{2.303RT}{nF_1} \log \frac{pO_{21}}{pO_{2II}}$$

$n = 4$ for an oxygen concentration cell

$R = 1.987 \text{ cal/mole} \times 4.184 \text{ joules/cal}$

$F_1 = 98700 \text{ coul/mole} \text{ (Nernst potential)}$
Fig 2.1 Apparatus used for studying the non-stoichiometric structure of Stannic Oxide.
p_{O_2} = 0.21 \text{ atm (in air)}

p_{O_2} = \text{partial pressure of oxygen inside the system}

E = \text{measured emf in volts.}

Mixing of the gases in the furnace was enhanced using a sapphire rod. Temperature was initially measured using a Pt-Pt10% Rh thermocouple, but after it got damaged, a portable Leeds Northrup optical pyrometer was used. Conductivity measurements were made using a Keithley Model 225 d.c. current source and high-impedance milli-voltmeter. No appreciable d.c. polarization effects were observed, though the d.c. field was normally not left on for more than 15-20 seconds.

**Sample Preparation**

Bar-shaped samples about 4-5 mm. long were cut from crystals from runs 015 and 017. In the former run an attempt was made to lightly dope with antimony and Hall-effect studies on crystals from this run indicated room-temperature carrier concentrations of about $10^{17}$ cm$^{-3}$. The presence of these impurities is not serious, because in the region of interest, the conductivity is controlled by non-stoichiometric defects. In the latter run, an attempt was made to dope with gallium, a p-type dopant. Spectrochemical analysis shows no gallium in these crystals, and the as-grown room temperature carrier concentrations are around $10^{16}$ cm$^{-3}$.

The samples were lapped to give well-shaped rectangular bars, then etched in boiling NaOH, washed in methyl alcohol and dried. The samples were then annealed$^{17}$ in a quartz boat in an inert argon atmosphere at 900°C for about 14 hours, and allowed to cool slowly during withdrawal.
Experimental Technique

A four probe technique was used for measuring the conductivity, as shown in Fig. 2.2. Since the current and voltage probes were different the effect of contact resistances is eliminated. Furthermore it appears from the modified phase diagram of Spandau et al, that even for the highest temperature at which measurements were made, there is no gaseous species of stannic oxide present, and hence the problem of gas-phase conduction is not expected to be troublesome. The problem of surface resistance is more real. The surface 'oxidizes' and 'reduces' faster than the bulk, and it is conceivable that for inadequate equilibration times, the surface resistance could be different from the bulk resistance and this could give erroneous results. Two mil platinum wires were used for the current and voltage probes. Wires of this dia are very flexible and contacts were made by tying a single knot around the sample using tweezers. These wires were then attached to 20 mil platinum wires which were fed through an alumina tube to the measuring electronics. The sample was mounted on an alumina base which was fixed to the alumina tube. The inlets for the thermocouple and sample holder were sealed with silicone seal, which was allowed to dry overnight. This is essential to prevent the creation of air-pockets and leakages. The system was checked for leaks using a leak detector (Snoop). Before making measurements, the furnace was allowed to stabilize for at least 12 hours at each new temperature. As mentioned earlier, a Keithley model 225 d.c. source, and high impedance milli-voltmeter were used. D.C. polarization effects were not observed, though the d.c. field was not left on for more than
\( R_b \) = bulk resistance. \( R_{s1,2,3} \) = surface resistance. 
\( R_{g1,2,3} \) = resistance due to gas phase conduction.

Fig. 2·2. Sample contacting technique.
15-20 seconds. Observations at any particular temperature were taken at fixed time intervals for both forward and reverse currents to insure a fixed sample resistance, and to eliminate the effect of thermal e.m.f.s. Equilibration times for temperatures greater than 1100°C were found to be about 5-10 minutes after the zirconia cell reading stabilized at each partial pressure (which takes about 10 minutes). Normally, however, about 30-35 minutes was allowed, to ensure a constant sample resistance.

At temperatures less than 1100°C, the data points represent equilibration times of several hours each. Readings were taken while increasing and decreasing the partial pressure of oxygen. For temperatures greater than 1100°C, the reproducibility was found to be very good.

2.3 RESULTS AND DISCUSSION

The results obtained on samples from run 015 and run 017 are presented in Figures 2.3 and 2.4 respectively. It appears in both the samples studied that in the temperature range from 1150°C-1350°C, the electrical conductivity is entirely dependent on the partial pressure of oxygen, and is controlled by the presence of non-stoichiometric defects induced via a reduction process. The negative slopes of $\ln\sigma$ vs $\ln p_0$ plots are in agreement with the 'metal excess nature' of stannic oxide, and the theoretically calculated oxygen pressure dependences.

In accordance with equation 1, it was found that a line with a slope of approximately $-1/6.5$ could be passed through all the data points at a particular temperature. It would therefore seem that the conductivity of the samples between 1150°C-1350°C is probably dominated by the presence of oxygen vacancies, with both electrons excited to
Fig. 2.3 Log conductivity vs Log $\text{PO}_2$ from 700°C - 1310°C for sample from run 015.
Fig. 2.4 Log conductivity vs Log PO₂ from 1090 C - 1330 C for sample from run 017.
conducting states. This evidence is strong but not unambiguous, and the possibility of defect complexes with very similar \( p_{O_2} \) dependence cannot be ruled out. For example a defect complex consisting of two doubly-ionised oxygen vacancies and one singly ionised tin interstitial would have a \( p_{O_2}^{-1/8} \) dependence.

At temperatures less than 850°C, the conductivity appears to have remained essentially constant (sample 015) with respect to \( p_{O_2} \), and the major contribution to the conductivity would be from the ionised impurities like antimony. There might be some intrinsic semi-conduction, but it is not very likely because of the wide bandgap of stannic oxide between 850°C-1100°C, the data points obtained for both samples were not satisfactory. The reproducibility was not very good, and since equilibration times were much longer, it was sometimes difficult to decide whether the change in conductivity between any two partial pressures was a real change, or was due to a shift in the contacts. The results in this range would be interesting, because it should be possible to see the effect of singly-ionised oxygen vacancies resulting in a slope of \(-1/4\). The availability of larger samples and better contacting techniques would make measurements in this range more reliable. The energy of formation of the non-stoichiometric defect is found by plotting \( \log \sigma \) vs \( 1/T \) (\( p_{O_2} = 1 \) atm) and measuring the slope. (Figure 2.5). It was found to be about l.e.v., (it appears a little low, but the order of magnitude is reasonable), for temperatures above 1000°C. Sample 015 seems to have two-slope behaviour at lower temperatures, but there are not enough data points to be really sure of this. Also the estimate made of the energy of formation is rough because:
Fig. 2.5 Log conductivity vs $1/T$
(a) We would have to be sure that the contacts do not move at all while raising the temperature since we are interested in the actual value of conductivity at each temperature.

This was not so important for the identification of the defect, because then we were only interested in the way the conductivity varied with $p_{O_2}$ at a particular temperature.

(b) The samples were not oriented. Once again this is not important for defect-identification for the same reason as above, but is significant if we were interested in the actual value of the conductivity. This is because conductivity depends on the mobility which depends on crystal orientation for non-cubic crystals.

In conclusion, it seems that in the temperature range $1100^\circ$C-$1300^\circ$C and oxygen partial pressure range of $10^0$ to $10^{-2}$ atmospheres, the conductivity is controlled by a single non-stoichiometric defect, which has been tentatively identified as a doubly-ionised oxygen vacancy. Below $850^\circ$C the conductivity is largely independent of $p_{O_2}$ and is probably due to the presence of impurities.
CHAPTER III BULK ELECTRICAL PROPERTIES

3.1 REVIEW OF CRYSTAL ANISOTROPY AND SAMPLE PREPARATION

Stannic oxide crystallizes in the tetragonal system with $D_{4h}$ symmetry and an axial ratio $\frac{c}{a} = 0.672$. The resistivity tensor $\rho$ in the rutile structure for a rectangular co-ordinate system is:

$$
\rho = \begin{bmatrix}
\rho_1 & 0 & 0 \\
0 & \rho_2 & 0 \\
0 & 0 & \rho_3
\end{bmatrix}
$$

where $\rho_1 = \rho_2$

there being only diagonal elements, two of which are equal. (Corresponding to the 'a' axes). The mobility tensor has the same form as the resistivity tensor above. The Hall coefficient tensor $R$ has two independent elements corresponding to when the magnetic field is applied parallel to either the $a$-axis or the $c$-axis. These are related to the carrier concentrations by the relations

$$R_a = \frac{r_a^H}{ne}$$

and

$$R_c = \frac{r_c^H}{ne}$$

where $r_a^H$ and $r_c^H$ are the Hall scattering coefficients. It is thought that the ratio $\frac{r_c^H}{r_a^H}$ is approximately constant with temperature and equal to unity. Furthermore the resistivity anisotropy ratio $\frac{\rho_c}{\rho_a}$ is reported to be small ($\frac{\rho_c}{\rho_a} < 1.2$ at 77°K and 300°K). It was therefore felt that in view of size considerations it would be impractical to try to orient the crystals. Samples were prepared by cutting thin
platelets from crystals with a string saw. The platelets were then mounted on a polishing block and lapped flat with 200 grit paper on a polishing flat. They were then boiled in a 0.1 M NaOH etch for a few minutes, washed with methyl alcohol and dried.

3.2 MEASUREMENT TECHNIQUE

All measurements were made using the conventional four-probe Vanderpauw\textsuperscript{30} technique. Ohmic contact to the samples was made using sharpened tungsten probes. As previously reported tungsten\textsuperscript{4} was found to give a very satisfactory low resistance ohmic contact. Occasionedally a contact turned out to be rectifying, but was found to become ohmic on applying a capacitive discharge between any two probes. A capacitance of 80uf and voltages from 65-135 volts sufficed for all the samples studied. Contacts were made near the periphery of the samples, and the samples were made as thin as possible to get better sensitivity. The Hall voltage was measured for all four combinations of field and current, and the resistivity was measured without the field. Only dc. measurements were made throughout. The equipment used was set up by Dr. M. Lichtensteiger as a central facility for the Centre for Materials Science and Engineering. It consisted of a Varian 9-inch Fieldial Mark II magnet, a Keithley model 225 current source and a Keithley model 602 electrometer. From 300°K down to 77°K, a copper-constantan thermocouple was used to monitor the temperature. The thermocouple junction was fixed in a hole very near the sample, and measurements were made as the samples warmed slowly in a simple liquid nitrogen dewar. The top of the dewar was sealed with felt—it was found that this reduced the warming-up rate considerably. All connections were shielded to eliminate the effect
of static charges. Hall measurements were made on one of the samples (015-1) up to 700°C. For this purpose a specially manufactured commercial Hall probe, cold-wall furnace was used, and a probe holder was designed to fit it, (for details see Appendix B). The vander-pauw probes were screwed to a ceramic base at the end of a 7-bore tube, which was held by the probe-holder.

In all the measurements, currents between 500 A and 5mA and a magnetic field of 10kG were used. The carrier concentration $n$ was calculated from the measured Hall voltage and sample thickness, and the known current and magnetic field. The resistivity $\rho$, was obtained from the resistivity voltages (zero magnetic field), current and sample thickness. The Hall mobility $\mu_H$ was calculated directly from the carrier concentration and resistivity.

Sample thickness was measured using a No 230 Starrett micrometer.

3.3.1 UNDOPED SAMPLES (017)

In run 017 an attempt was made to dope with gallium. Spectrochemical analysis show no trace of gallium and the samples were high resistivity. Three samples labelled 017-8-1, 017-8-2 and 017-8-10 have been studied. Samples 017-8-1 and 017-8-2 were cut from the same crystal, but 017-8-10 was from another crystal. The as-grown samples had room temperature carrier concentrations of $1.44 \times 10^{16} \text{ cm}^{-3}$ (017-8-1) and $9.05 \times 10^{15} \text{ cm}^{-3}$ (017-8-2). These samples were then heat treated in a quartz boat at about 1450°C and 1350°C respectively in an oxygen ambient (1 atmosphere) for 12-14 hours, in the same furnace used for studying the defect structure. Under these conditions the conductivity is controlled
Fig. 3.1 Carrier concentration vs $1/T$ for 017 samples.
by what seems to be a single electronically active non-stoichiometric
defect (possibly oxygen vacancies) as determined earlier. The samples
were pulled out of the furnace and quenched in liquid nitrogen. In
this way it is expected that a large number of the non-stoichiometric
defects mentioned above are trapped. The room temperature carrier
concentrations after this heat treatment were significantly higher;
for sample 017-8-1 it was $4.48 \times 10^{17} \text{ cm}^{-3}$, and for sample 017-8-2
it was $3.3 \times 10^{17} \text{ cm}^{-3}$. Sample 017-10 was heated treated at 1400°C
in air ($p_{O_2}=0.21 \text{ atm}$), for about 14 hours, and quenched. The room
temperature carrier concentration was $3.06 \times 10^{17} \text{ cm}^{-3}$ after
heat-treatment.

The heat-treated samples were found to have high resistive surface
layers ($10^5 \ \Omega\cdot \text{cm or more}$). The resistivity of the bulk was much lower
and uniform (about 0.1 $\Omega\cdot \text{cm}$ in all three samples). It was therefore
necessary to lap about 20$\mu$ from the surfaces of heat-treated samples.
This high resistive surface layer may be due to the compensation of the
surface by acceptor-type impurities like iron and aluminium which could
come from the inside of the furnace tube; most of the high temperature
ceramics commonly used have a lot of iron and aluminium in them. Hall
measurements were then made on these samples as a function of temperature
from 77$^\circ \text{K}$ (liquid nitrogen) to 300$^\circ \text{K}$ (room temperature.), and the results
are shown in Figure 3.1.
3.3.2 UNDOPED SAMPLES (207)

The crystals produced in run 207 were undoped and very high resistivity. Two samples labelled 207-1 and 207-2 have been studied. Attempts at making Hall measurements on the as-grown samples were unsuccessful, because of their high resistivity. The samples were then heat-treated in a quartz boat at 1275°C for about 20 hours, and then quenched in liquid nitrogen. The heat treatment was done in an oxygen ambient, in a new furnace which was set up and was capable of going up to 1300°C. (The furnace used for 017 samples, could not be used again because it had been dismantled.) As usual the quartz liner and boat were well-etched and cleaned with 'aqua-regia' before used to avoid contamination. It was found that the heat-treated samples had much lower resistivity. The room temperature carrier concentrations were about \(10^{17} \text{cm}^{-3}\), with resistivities in the range of 0.4 - 0.8 \(\Omega\text{-cm}\). The results are shown in Figure 3.2.

3.3.3 GALLIUM-DOPED SAMPLES (018)

In run 016 gallium doping had been tried in an attempt to get p-type material. All the crystals obtained were compensated n-type. The as-grown crystals were highly resistive and it was not possible to pass any current through the samples, even with the voltage compliance as high as 100 volts. Measurements were tried on three different samples, but they were unsuccessful. The samples were then heat-treated in a quartz boat at 1275°C for 18-20 hours, and quenched in liquid nitrogen. The heat-treatment was done in an oxygen ambient (1 atmosphere). The
Fig. 3.2  $n$ vs $1/T$ for 207 samples.
heat-treated samples were still highly resistive, inspite of a large
defect concentration. It was barely possible to pass a current of 10\textmu a
through one of the samples. The reading was unreliable and no further
measurements were made. The high resistivity is possibly due to the fact
that there are still no carriers because of the large number of compensating
states.

3.3.4 ANTIMONY-DOPED SAMPLES (015)

In run 015 an attempt had been made to dope lightly with antimony.
Most samples from this run have room temperature carrier concentrations
of about $10^{17} \text{cm}^{-3}$. Three samples labelled 015-1, 015-2 and 015-3 have
been studied. The studies made on these samples had a two-fold objective.
a) To determine the location of the shallow donor level due to antimony
atoms in the bandgap. b) To examine the effect on the carrier con-
centration of annealing the samples in a hydrogen-rich ambient. This
is of interest because in the chemical vapor deposition growth technique
developed by Fonstad\textsuperscript{12}, there is hydrogen in the growing system.
Furthermore semi-quantitative analyses on some of the crystals grown by
this technique, indicate the presence of fairly large amounts of hydrogen.

Hall effect measurements were made on sample 015-1 from room-
temperature up to 700°C, in the Hall probe cold wall furnace mentioned
earlier. Measurements were made while raising the temperature up slowly.
The furnace was evacuated with a mechanical pump. It was noticed that
there was a slow but perceptible drift in the readings above about 300°C.
The system was then allowed to cool slowly overnight. It was found that
the room temperature carrier concentration had increased a little but not
significantly (about 5%). The Hall furnace was then removed, the sample was mounted on a separate holder, and Hall effect measurements were made as a function of temperature from 300°K to 77°K. The high and low temperature portions of the carrier concentration curve were matched up as shown in Figure 3.3.

Finally the sample was put in a quartz boat and placed in a furnace at 900°C in a 15%H₂-85%Ar ambient for 1 \( \frac{1}{2} \) hrs. The quartz liner and boat were well-etched with 'aqua regia' to eliminate the possibly of contamination. (Appendix A). On withdrawing the sample, it was found that the surface was badly damaged. The sample was lapped and a Hall measurement made. The room temperature carrier concentration was found to have increased drastically to about 8 \( \times 10^{18} \) cm⁻³ (degenerate) from an original value of \( 10^{17} \) cm⁻³. The sample was then lapped in steps of about 50 microns, and at each stage a Hall measurement was made. There was almost no change in the carrier concentration, indicating that what was seen originally was not just a surface effect. Measurements were not made down to 77°K, because for degenerate samples the carrier concentration is expected to remain approximately constant.

Sample 015-2 was annealed at 900°C for almost 24 hours in an inert argon ambient. The sample was allowed to cool slowly by withdrawing it gradually from the furnace. In this way dislocations are annealed out. Hall measurements were then made as before from 300°K to 77°K. The room temperature carrier concentration was 1.38 \( \times 10^{17} \) cm⁻³. The sample was then heat-treated at 900°C for 40 minutes in a 15%H₂-85%Ar ambient. After lapping off the surface Hall measurements were made from 300°K to 77°K. The new room temperature carrier concentration was 9.6 \( \times 10^{17} \) cm⁻³. A further 100
Fig. 3.3 Carrier concentration vs $1/T$ for 015 samples.
microns was lapped off (about half the sample thickness) and a room
temperature Hall measurement made. The carrier concentration was just
a little lower (8 x 10^{17} \text{ cm}^{-3}).

Finally sample 015-3 was studied. The as-grown room-temperature
carrier concentration was 8.5 \times 10^{16} \text{ cm}^{-3}. In this sample no attempt was
made to detect the antimony level. Instead it was directly heat-treated at
900\degree C in a 15\%H_2-85\%A_r\text{ ambient for about an hour. The new room temperature}
carrier concentration was 10^{18} \text{ cm}^{-3}. Hall measurements were then made
as usual from 300\degree K to 77\degree K.

3.4 ANALYSIS OF CARRIER CONCENTRATION VERSUS TEMPERATURE DATA

The conductivity tensor has two independent elements $\sigma_a$ and $\sigma_c$,
and the Hall effect tensor also has two independent elements $r_a^H$ and
$r_c^H$ for the rutile structure. It has been shown that the conductivity
anisotropy ($\sigma_a / \sigma_c$) and Hall-effect anisotropies ($r_a^H / r_c^H$) are small.\textsuperscript{13}
The conductivity anisotropy $\sigma_a / \sigma_c$ lies in the range 1.0-1.2 between 77\degree K
and 300\degree K, and the Hall effect anisotropy is between 1.00-1.01 in the same
temperature range. These facts are useful because the crystals were not
oriented. In all the samples studied we took $r_a^H = r_c^H = r^H = \frac{3\pi}{8} (1.18)$.

At all temperatures $r^H$ is theoretically $\frac{3\pi}{8} (1.18)$ for acoustic deformation
potential scattering,\textsuperscript{23} and it has been shown that above 250\degree K it is in the
range $1.18 \pm 0.05$ for polar optical mode scattering.\textsuperscript{13} The above assumptions
therefore seem justified.

The donor levels and effective mass $m^*$ were calculated using Hutson's
technique\textsuperscript{24}. For a non-degenerate semi-conductor with a single parabolic
conduction band minimum\textsuperscript{25}
\[ n = 2 (2\pi k T m^*/h) ^{3/2} \exp(-(E_C - E_F)/kT) \quad ; \quad (E_C - E_F) >> kT \]

and
\[ n = \frac{N_d}{[1 + \beta \exp(E_d - E_F)/kT]} \quad - \quad N_a \]

where \( N_d \) and \( N_a \) are the donor and acceptor concentrations respectively. \( E_d \) is the donor level, assuming a single donor, and \( m^* \) is the density of states effective mass. It is equal to \( (m_{||} m_{\perp})^{1/3} \) where \( m_{||} \) and \( m_{\perp} \) are the effective masses parallel and perpendicular to the \( c \)-axis respectively.

If \( \frac{E_F}{kT} \) is eliminated between the two above equations, the resulting expression is

\[ \frac{n(n+N_a)}{(N_d-N_a-n)T^{3/2}} = \beta^{-1/2} \left( \frac{2\pi km^*}{h^2} \right)^{3/2} \exp(-E_d/kT) \]

\( \beta \) was taken as 2 for a single donor and 1/2 for the first ionised state of a double donor. Choosing appropriate values of \( N_d \) and \( N_a \) and plotting \( \log E \frac{n(n+N_a)}{(N_d-N_a-n)T^{3/2}} \) versus \( \frac{1}{T} \), it is possible to get a straight line, the slope of which is equal to \(-E_d/k\), and the intercept on the vertical axis is given by \( \beta^{-1/2} \left( \frac{2\pi km^*k}{h^2} \right)^{3/2} \).

As will be noted from what follows, this technique is good for determining \( E_d \), but of less value in determining \( m^* \).

3.4.1. UNDOPED SAMPLES (RUNS 017, 207)

Samples from run 017 and run 207 were heat-treated in an oxygen ambient (1 atm) at temperatures of 1275°C–1450°C for 12–20 hours, and then quenched in liquid nitrogen, thus 'freezing in' a large number of
non-stoichiometric defects. This is clear from the large increases of carrier concentration seen over the as-grown specimens. In the range of temperature and partial pressure in which the samples were heat-treated, the main non-stoichiometric defect was tentatively identified in Chapter 2 as doubly-ionised oxygen vacancies. It is therefore felt that most of the defects 'frozen in' are oxygen vacancies.

Applying Hutson's technique\textsuperscript{24} to the carrier concentration from 300°K to 77°K, a shallow donor level at 29±7 mev was found for all the samples. Assuming this to be the first ionised state of a double donor, the density of states effective mass \( m^* \) was calculated from the intercept at \( \frac{1}{T} = 0 \), with \( B = 1/2 \) and was found to be 0.26\( m_o \). This is fairly close to the value of 0.275\( m_o \) found by cyclotron resonance studies. Marley et al\textsuperscript{3} and Wright et al\textsuperscript{3} have respectively reported lower values of 0.22\( m_o \) and 0.17\( m_o \) on the basis of their electrical studies. The samples used by Wright et al were however not thermally characterised. Subsequently Fonstad\textsuperscript{13} has reported an effective mass of 0.39\( m_o \). At this point it should be mentioned that when plotting \( \log_{10} \frac{n(n+Na)}{(Nd-Na-n)T^{3/2}} \) versus \( \frac{1}{T} \) it was found that the intercept at \( \frac{1}{T} = 0 \) was more sensitive to the choice of donor-acceptor parameters than the slope \(-E_D/k\). It is therefore felt that Hutson's technique\textsuperscript{24} gives a good measure of the donor level, but a rather rough estimate of the effective mass. Nagasawa et al\textsuperscript{11} have reported levels at 24±4 mev, 13.7 mev and 3.4 mev on what appears to be an undoped sample, they studied down to 4°K. The donor level at 24±4 mev seems fairly close to the level detected in this study, but since their sample was not thermally characterised, any positive identification is not possible.

Marley et al\textsuperscript{3} have made fairly extensive measurements on a number of
Fig. 3.4 Log \[ \frac{\frac{2}{n}}{(N_d-n)T^{3/2}} \] vs 1/T for 017 samples.
Fig 3.5 Log $\frac{n^2}{(Nd-n)^{3/2}}$ vs $1/T$ for 207 samples.
undoped samples which they heat-treated (in the range 1290°C-1400°C, 
p_{02}=1 atm) and quenched in an identical fashion. Therefore, there is 
every reason to believe that they were creating the sar- type of non-
stoichiometric defect (i.e. oxygen vacancies). However the donor levels 
reported by them are consistently 4-6 times deeper than those reported 
in this study for samples with similar room temperature carrier concentrations.

A two electron-trapped oxygen vacancy model has been tentatively 
proposed to account for this gross discrepancy. It has already been 
determined that heat-treating samples in the specified range of temperature 
and partial pressure and rapidly quenching results in a large non-stoichio-
metric defect concentration identified as oxygen vacancies. This would 
result in two relatively shallow donor levels \( E_1 \) and \( E_2 \) in the bandgap 
(Figures 3.6 and 3.7) corresponding to the singly-ionised and doubly 
ionised conditions respectively.

Suppose that a particular heat-treatment, results in the creation 
of \( N \) oxygen vacancies. The extent of compensation will determine which 
of the two levels \( E_1 \) or \( E_2 \) will house the Fermi level at low temperatures. 
If the compensation is small, the Fermi-level will lock on to \( (E_c - E_1) \) at 
low temperatures and

\[
n \propto b_1 N_c \left( \frac{N-Na}{Na} \right) \exp \frac{E_1}{kT} \quad \text{low temp} \\ Na<N
\]

As the temperature rises, the first stage of ionisation becomes 
complete and \( n \propto (N-Na) \). Further heating should drive the Fermi level 
down towards and beyond the second ionisation energy \( E_2 \), and an additional 
\( N \) electrons should be added to the conduction band in the course of this process.
Fig. 3.6. Conventional way of indicating the energy states for a divalent donor, (a) the neutral condition, (b) the singly ionized condition, (c) the doubly ionized condition.
Fig. 3.7. Proposed oxygen-vacancy two-electron trapped model.
On the other hand if N<Na<2N, the saturation free electron density is (2N−Na) which is smaller than Na. A drop of n should occur as soon as the temperature is low enough for Φ to approach (E_c−E_2), and on further cooling the Fermi level should lock on to this energy and provide an \( \exp(-E_2/kT) \) temperature dependence for n.

The vapor-grown single crystals used in this study were very pure and in most cases have less than 2 ppm of compensating impurities like Al and Fe. It is believed that because of the presence of a low acceptor concentration, the upper level E_1, corresponding to the singly-ionised state has been detected. Some of the samples from run 207 have higher acceptor impurity concentrations (10−15 ppm of Al and Fe). and it was hoped that the upper level E_1 would be compensated, allowing us to see the second level E_2. However, the deeper level was never seen, and the shallow level observed by us at 29±7 mev probably corresponds to the singly ionised state. Samples from run 018 have a high gallium acceptor concentration, but as mentioned earlier these samples had very high resistivity and no electrical measurements could be made.

The crystals used by Marley et al \(^3\) were grown at 1600°C in mullite and alumina tubes, and have very high acceptor-impurity concentrations. Spectrochemical analysis of these crystals indicate Al and Fe concentrations from 40−110 ppm \(^4,26\). It is believed that these impurities are responsible for completely compensating the upper level E_1 and the deeper level seen by Marley et al \(^3\) probably corresponds to E_2 or the doubly-ionised condition. Furthermore there is little correlation between the carrier concentrations and temperatures at which his samples were heat-treated. This could be explained by the presence of a large and variable concentration of compensating
impurities, which besides completely compensating the upper level $E_1$ could also be responsible for partial compensation of the deeper level $E_2$.

The deeper level was not conclusively seen by us. Driving the Fermi-level down several $kT$ below this level, by raising the temperature does not seem feasible, because to do this successfully would require making Hall measurements at least up to about 500°C. This could affect the stoichiometry of the crystal. Measurements up to 280°C were made on sample 207-1, and an increase in carrier concentration of about 25% was observed. However, it is difficult at this stage to unambiguously ascribe this the partial ionisation of the second level. A method recently suggested by Glover\textsuperscript{31} of studying deep levels from C-V measurements on Schottky barriers, appears to be a good technique to use without affecting the crystal stoichiometry.

3.4.2 ANTIMONY-DOPED SAMPLES (RUN 015)

As mentioned earlier, in this run an attempt was made to dope lightly with antimony. Analysis of the carrier concentration data for samples 015-1 and 015-2 yielded a single shallow donor level at 40±5 mev, which was ascribed to antimony atoms. This is in reasonable agreement with values reported in reference 13. Hall measurements on sample 015-1 above 300°C did not yield any new information.

The results of subsequently heat-treating the 015 samples in a hydrogen-rich ambient for short periods of time were drastic. The large, almost uniform increases in carrier concentration seen in relatively short times seems to suggest that hydrogen diffuses very rapidly through the samples.
Analysis of the carrier concentration data for samples which did not become
degenerate, indicates a new, shallow donor level at 50±5 mev. Sample
015-3 which had been treated, was then studied by another member of this
group making optical measurements on SnO$_2$. Luminescence spectra involving
shallow donor states was found to have shifted a little, to longer wave-
length compared to an antimony doped sample which had not been treated$^{27}$. This
seems to indicate a new donor level which is a little deeper than that due
to antimony atoms, with respect to the conduction band. The agreement with
the results of our electrical studies seems to be rather good. The
nature of this level however is open to conjecture. Two possibilities
are suggested. The shallow level may be due to hydrogen atoms in interstitial
locations, or could be due to the formation of hydroxyl ions.

$$0 = S = 0 \to 0 = \cdot \cdot \cdot + _\downarrow \cdot - _\uparrow \cdot \cdot \cdot + e^-$$

Kohnke$^1$ and Katiyar et al$^{28}$ have reported an infra-red absorption peak
in the 2-3 μm range, attributed to the existence of hydroxyl ions in a
plane perpendicular to the c-axis.

This would seem to suggest the existence of the latter mechanism,
though the possibility of both mechanisms occurring simultaneously cannot
be ruled out. There is a lot of hydrogen in the growing system, and semi-
quantitative analyses of some of these crystals indicates its presence in
varying degrees.$^{32}$

No further work was done on this aspect, but in view of the drastic
changes seen, further investigation of this effect would be meaningful.
3.5 MOBILITY DATA

A detailed study of the mobility data was not undertaken, but the results obtained in the course of the bulk measurements have been presented. The mobility has been plotted versus temperature on a log-log scale. It has previously been shown that above 250°C the main scattering mechanism is due to polar optical mode scattering,\(^{13,3}\) and below 250°C acoustic deformation potential scattering dominates.\(^{13,3}\) At still lower temperatures, the effects of ionised impurity scattering are important.\(^{13,3}\)

Piezoelectric scattering is not important because SnO\(_2\) is centro-symmetric.

The mobility curves of the 015 samples have been presented in Fig. 3.10. The curves moved down with increasing carrier concentration. Sample 015-1 had the lowest room temperature carrier concentration (about \(10^{17} \text{cm}^{-3}\)) and a Hall mobility of 2100cm\(^2\)/v-sec at 80°C was measured, which is probably the second highest value reported so far. Fonstad\(^{13}\) has reported a Hall mobility of 8800cm\(^2\)/(v-sec\(^{-1}\)) at 80°C. Sample 015-2 after heat-treatment had a room temperature carrier concentration of about \(9 \times 10^{17} \text{cm}^{-3}\) and the mobilities were correspondingly much lower. The effect of ionised impurity scattering which manifests itself as a fall off in mobility with decreasing temperature, was observed in all the 015 samples, and it became significant at higher temperatures for samples with higher carrier concentration. Sample 015-3 (H\(_2\)-treated), has a room temperature carrier concentration which is a little larger than that of sample 015-2 (H\(_2\)-treated), yet the mobility curve is higher up. At higher temperatures, the qualitative agreement with the other curves is not very good. At present no satisfactory explanation can be offered for this, particularly as the mobility curve of sample 015-2 (similarly H\(_2\) treated) appears well-behaved.
Fig. 3.10 Log Hall mobility vs Log Temp for 015 samples.
Fig. 3.8 Log Hall mobility vs Log Temp for 017 samples.
Fig 3.9 Log Hall mobility vs Log Temp for 207 samples.
The results of samples from runs 207 and 017 are shown in Figures 3.9 and 3.8 respectively. The mobility curves of samples 207-1, 207-2, 017-8-2 and 017-10 which have fairly large non-stoichiometric defect concentrations, conform to the expected pattern. Ionised impurity scattering was not seen in sample 207-2, but it is expected that this effect would become apparent at lower temperatures.

In summary, good qualitative agreement has been found between the results of this study and those of Fonstad$^{13}$ and Marley$^3$ et al.
CHAPTER IV SUMMARY OF RESULTS AND PROPOSALS FOR FUTURE WORK

In this study the defect structure of Stannic oxide single crystals was examined in the range 700°C-1350°C, and oxygen partial pressures of 10^0 to 10^-2 atmospheres. The main motivation for this preliminary study was the fact that several earlier workers had reported that the electrical properties of stannic oxide were sensitive to 'oxidation' and 'reduction' treatments, which pointed to the effect of non-stoichiometric defects. In the temperature range from 1100°C-1350°C, the predominant non-stoichiometric defect has been tentatively identified as a doubly-ionised oxygen vacancy. Below 850°C, the conductivity is believed to be 'impurity-controlled.' The results between 850°C-1100°C were not satisfactory. With larger-sized samples and better contacting techniques, measurements in this range would be interesting. It would also be worthwhile to extend this study to the lower ranges of oxygen partial pressure, to see if other possible non-stoichiometric defects dominate in those ranges.

Undoped samples annealed in an oxygen ambient between 1275°C-1450°C and quenched, showed large increases of carrier concentration, due to the 'freezing-in' of a large number of oxygen vacancies. Hall measurements at low temperatures indicate a shallow donor level at 29±7 mev below the conduction band. Marley^3 et al have a level consistently 4-6 times deeper with identical heat-treatments and with similar room-temperature carrier-concentrations. An oxygen vacancy two electron-trapped model has been proposed to account for this discrepancy, and available spectrochemical and mass spectrographic data has been used to identify the compensating centers in this model. The deeper donor level reported by Marley^3 et al has so far not been detected by us. Raising the temperature above 300°C to drive the
Fermi level down does not seem very promising, because this could affect the stoichiometry of the samples. Glover has recently reported a technique of determining deep levels in semiconductors from C-V measurements of Schottky barriers, and used it to measure a level at 0.83 ev on epitaxial n-GaAs. Since Fonstad has developed fairly good gold Schottky barriers on SnO$_2$, such a study seems well within reason.

Studies on antimony-doped samples have yielded a donor level at 40±5 mev, which is in good agreement with values reported in literature.

The effect of annealing SnO$_2$ in a hydrogen-rich ambient was investigated, and models suggested to explain the large increases of carrier concentration. Further studies to shed more light on the nature of this effect would be useful.

A Hall mobility of 2100 cm$^2$-(v-sec)$^{-1}$ at 80°K, was measured on one of the antimony-doped samples, which is possibly the second highest value reported so far.
APPENDIX A

FURNACES USED FOR HEAT-TREATING SAMPLES

(a) 015 samples were heat-treated in the furnace shown in Figure A-1. The quartz liner and boat in which the samples were placed were etched with 'aqua-regia' for 24 hours to minimize the possibility of contamination. The furnace had a good flat temperature profile, but the maximum operating temperature was only 1000°C.

(b) 207 samples were heat-treated in a similar furnace which was set-up and could go up to 1300°C. The temperature profile however was peaked with the peak occurring 5 inches from one end. The samples were heat-treated near this peak, and the corresponding temperature measured with a thermocouple.

(c) 017 samples were heat-treated in the same hydrogen-molybdenum furnace, which was used for the study of the defect structure (Figure A-2). Since the furnace tube was made of mullite, there is a possibility of some contamination.
Fig. A-1. Furnace used for heat-treating 015 samples.
Fig. A-2. Hydrogen-molybdenum furnace used for heat-treating 017 samples.
APPENDIX B

HALL PROBE COLD WALL FURNACE

The Hall probe, cold wall furnace (Figure B-1) has been specially designed by Advanced Vacuum Systems Inc., to permit the study of Hall Effect devices at elevated temperatures in vacuum and in inert atmospheres. The furnace is supplied with a nichrome heating element for operation at temperatures up to 925°C in vacuum. The heating element produces a thermal flat at 900°C approximately three inches long within ±5°C. The shield assembly and finned aluminum body limits the outside temperature to less than 150°C.

A probe holder (Figure B-3) was designed to fit the above furnace, and to allow for connections to the external measuring electronics.
Fig. B-1. Hall-probe cold wall furnace.
Fig. B-2. Temperature profile of Hall-probe cold-wall furnace.
Fig. B-3. Probe-holder designed for Hall-probe cold wall furnace.
Appendix C

Impurity Composition of Gases Used

The major impurities in the AIRCO gases used for obtaining dynamic oxygen partial pressures, while studying the defect structure are listed below.

**Argon**

<table>
<thead>
<tr>
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<tr>
<td>$O_2$</td>
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</tr>
<tr>
<td>$N_2$</td>
<td></td>
<td>20 ppm</td>
</tr>
<tr>
<td>Other</td>
<td></td>
<td>5 ppm</td>
</tr>
</tbody>
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**Oxygen**

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<tbody>
<tr>
<td>$A_r$</td>
<td>0.15 - 0.3%</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.2 ppm</td>
</tr>
<tr>
<td>$C_2H_2$</td>
<td>0.2 ppm</td>
</tr>
<tr>
<td>$N_2$</td>
<td>0.1 - 0.25%</td>
</tr>
</tbody>
</table>


   Contract No. AF19(604)8447, Corning Glass Works.


17. 'Chemistry of Defect Species', Kroger, Ch 13, pg 406-477.


27. D. Hubert, personal communication.


