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Electrical Properties of In_2O_3

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Conductivity data for In_2O_3 both from literature and from new measurements are critically compared. They are correlated with atmospheric conditions and temperature. The conductivity data and structural considerations lead to the conclusion that non-stoichiometric In_2O_3 is an *n*-type semiconductor. Interstitial indium ions are probably the predominant defects.

Introduction

The electrical conductivity of In_2O_3 has been the subject of many investigations (*1–5*, *8*). The measurements included dark- (*1*, *3*, *4*) and photoconductivity (*2*, *5*) of single crystals (*3*, *4*), thin layers (*2*, *5*, *8*) or pressed tablets (*1*).

The results scatter widely (Fig. 1), due to several reasons. Both single- and polycrystalline In_2O_3 reported in literature is non-stoichiometric, with an In/O ratio larger than the ratio 2/3. A result of this non-stoichiometry is a very good *n*-type semiconductivity, as was confirmed by Seebeck and Hall experiments (*1*, *3*). This semiconductivity depends on the conditions of preparation. This has been overlooked too often, which is one reason for the poor reproducibility of experimental data. Other reasons are grain-boundaries and impurity contents, which vary from sample to sample.

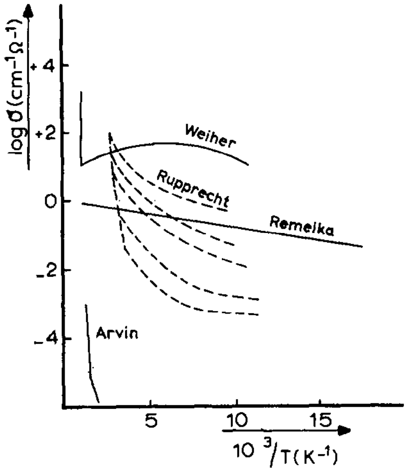

FIG. 1. A survey of experimental data concerning the temperature dependence of the conductivity from literature. Weiher: single crystal in air. Remeika: single crystal in air. Arvin: pressed tablet in air. Rupprecht: thin layers in vacuum.

Oxidation-rate measurements on In and InSb by Rosenberg and Lavine (*6*, *7*) have shown the presence of $In_i^{\cdot\cdot}$ interstitials in a remarkably high concentration ($In_i^{\cdot\cdot} = 10^{21}$ cm^{-3}, at 300°C).* The crystal structure of In_2O_3 supports the idea of $In_i^{\cdot\cdot}$ interstitials.

Data from optical measurements on In_2O_3 are rather poor. Therefore local energy-levels in the forbidden bandgap have not yet been assigned to any defect. The bandgap at room temperature is about 2.8 eV (*14*), with a temperature dependence of 1.10^{-3} eV deg^{-1}. This bandgap excludes intrinsic semiconductivity as an explanation for the conductivity data. In this paper data from recent electrical measurements are reported and an attempt is made to correlate the results with already known properties. Especially the ambient circumstances will be taken into consideration.

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* Here and throughout this paper the defect notation of Kröger is used (*18*), · denotes an effectively positive charge, an effectively negative and × an effectively zero charge.

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TABLE I

SPECTROCHEMICAL ANALYSIS WT %.

Element	Fluka no treatment	B.D.H. no treatment	Cerac no treatment	Prepared from In	Fluka I	Fluka II	Fluka III	Crystal vapour phase
Si	.001	.002	.002	.02	.005	.0009	.04	.2
Tl	.01	abs. (<.0003)	.0005	—	.009	.007	—	—
Pb	.0002	.0001	.0004	.003	.003	.0002	.00007	.001
Mg	.0007	.0003	.004	.001	.004	.0005	.002	.0005
Fe	.0008	.0002	abs. (<.0002)	.002	.0009	.001	.001	.0006
Al	.0004	abs. (<.00007)	abs.	.002	.0004	.0006	.002	.0002
Sn	.0005	.001	.0002	.0008	.0004	.0005	.0002	.001
Cu	.0005	.0001	abs. (<.00003)	abs.	.0006	.0005	abs.	.0001
Cd	.009	abs. (<.002)	abs.	—	.02	.008	—	—
Na	abs. (<.005)	abs. (<.005)	abs.	.04	.02	abs.	.02	.06
Ca	abs. (<.001)	abs.	abs.	.004	.02	abs.	.003	.02
B	abs. (<.0002)	abs.	abs.	.0003	.0005	abs.	abs.	.0001
Zr	abs. (<.0006)	—	abs.	abs.	.0006	abs.	.0004	abs.
V	abs. (<.0001)	abs.	abs.	.0002	abs.	.0003	.0002	abs.
Mn	abs. (<.0004)	abs.	abs.	.0004	.00004	abs.	.0002	.00004
Ag	abs. (<.00007)	abs.	.000007	abs.	.000008	abs.	abs.	.00004
Cr	abs. (<.0003)	abs.	abs.	abs.	abs.	abs.	.0002	.0003
Ni	abs. (<.0003)	abs.	abs.	abs.	abs.	abs.	abs.	abs.
Mo	abs. (<.0001)	abs.	abs.	abs.	abs.	abs.	abs.	.00005
Be	abs. (<.00001)	abs.	abs.	abs.	abs.	abs.	abs.	abs.
Pt	abs. (<.0001)	abs.	abs.	abs.	abs.	abs.	.003	abs.
Ga	—	—	—	.0001	—	—	abs.	abs.
Au	—	—	—	abs. (<.0001)	—	—	.0002	abs.
Ti	—	—	—	abs. (<.00009)	—	—	abs.	abs.
Ba	—	—	—	abs. (<.02)	—	—	—	abs.
Pd	—	—	—	abs. (<.0001)	—	—	—	abs.
W	—	abs. (<.01)	—	—	—	—	—	—

Fluka I: treated in glass vessel.
Fluka II: treated in polyethylene vessel.
Fluka III: powdered tablet after treatment in glass and sintering on Al_2O_3 in air at 1300°C.

Experimental

A. Preparation of Materials

Single crystals were prepared in two ways: (a) from the vapour phase, as described elsewhere (*9*), (b) growing from the flux ($PbO–B_2O_3$) as described by Remeika and Spencer (*4*).

Polycrystalline tablets were made of In_2O_3 powder from various origins.

The following materials were used: (1) B.D.H. reagent (98.5 %), (2) Fluka In_2O_3 (purissimum), (3) Cerac/Pure (99.999 %), (4) In_2O_3 powder prepared from In metal (α-Inorganics, 99.99 %) in our laboratory.†

The impurity content of these materials is reported in Table I.‡ Some preliminary experiments showed that the conductivity behaved analogously for the different materials. The rest of the experiments were carried out with the Fluka reagent. The powder was treated according to a standard procedure used in this laboratory. This includes: (a) One gram of the powder is stirred thoroughly in 100 ml of deionised water for 20 hr; this wetting procedure proved to be necessary to obtain a material with reasonable sintering properties. This improvement of sintering properties can be attributed to the formation

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† Thanks are due to Mr. A. J. van Dillen for providing this material ready for use.

‡ The spectrochemical analyses were carried out in the Philips Research Laboratories (Eindhoven, The Netherlands).

of hydroxyl groups at the surface of In_2O_3 (*11*). Hereafter the mixture was dried in air at 140°C. It proved necessary to use polyethylene vessels instead of glass to prevent contamination with Si, Na and Ca (Table I). (b) The powder was pressed into a tablet using a pressure of 3 ton cm^{-2}. (c) The tablets were sintered on Al_2O_3 plates at 1300°C in air for 8 hr; they were slowly cooled to 1000°C (100°C hr^{-1}), and then quenched to room temperature in one minute. Apparent densities of 50–65% of the theoretical value (7.12 g cm^{-3}) were obtained. These polycrystalline tablets as well as the single crystals were treated in various ways. Some were powdered for analysis (Table I). Polycrystalline tablets with the same density were chosen for annealing experiments under different ambient circumstances. For this purpose they were sealed in a quartz ampoule which was filled with a known amount of oxygen. The annealing was performed at 800°C, whereafter the ampoules were dropped into water for quenching.

B. Electrical Conductivity

The very high conductivities (>1 Ω^{-1} cm^{-1}) were measured with a Kelvin bridge arrangement (*15*). A Tektronix oscilloscope was used as a null detector. For lower conductivity values a General Radio Bridge (type 1608 A) arrangement was used. All measurements were carried out at a frequency of 1000 Hz. The tablet or crystal was mounted in a quartz cell as shown schematically in Fig. 2. This cell could be evacuated. Furthermore, a gas stream could be passed through it. The cell was designed in such a way that the electrode pressure on the sample remained constant at different temperatures even when the cell was evacuated. Temperatures up to 800°C could be reached. The temperature was controlled with an Eurotherm P.I.D. temperature control unit. Electrode contacts were provided by platinum paint (Degussa) or by vacuum deposited gold layers. Both types of contact proved to be ohmic. Nitrogen gas was passed through a BTS catalyst (BASF) for purification and then passed through a molecular sieve (A4, BDH) for drying. Oxygen gas was dried by passing it through a molecular sieve. Isobaric conductivity measurements were performed by heating or cooling with intervals of 50°C. Each measuring point was taken after the conductivity had remained constant for one hour. Isothermal measurements were performed by first equilibrating a sample at 1.0 atm of oxygen at a chosen temperature.

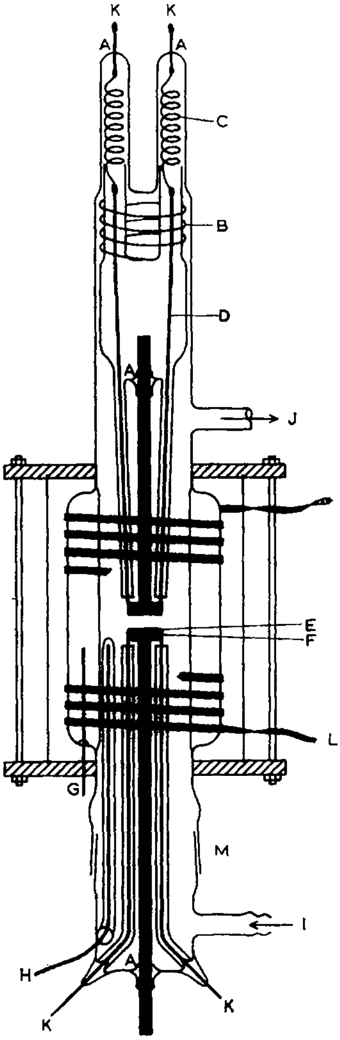

FIG. 2. Conductivity cell; the quartz cell can be used for measurements from 25°C to 800°C under various ambient conditions. The electrode pressure is regulated by means of a spring. Four electrode contacts are provided. A, Tungsten feed-through. B, Steel spring. C, Ni-electrode connection. D, Pt electrode wires. E, Pt-electrode surface. F, Ni-electrode support. G, Pt Rh 10% Pt thermocouple. H, Chr/Al thermocouple. I, Gas input. J, Gas output. K, Pt contact points. L, Kantal wound furnace. M, Ground glass joint.

Then lower oxygen pressures were obtained by pumping via a capillary for a short time. The pressure was read from a mercury manometer.

C. Hall Measurements

Hall measurements were performed with both dc and ac equipment.** The measurements were

** Thanks are due to Mr. Th. Pieters of this laboratory for performing these measurements.

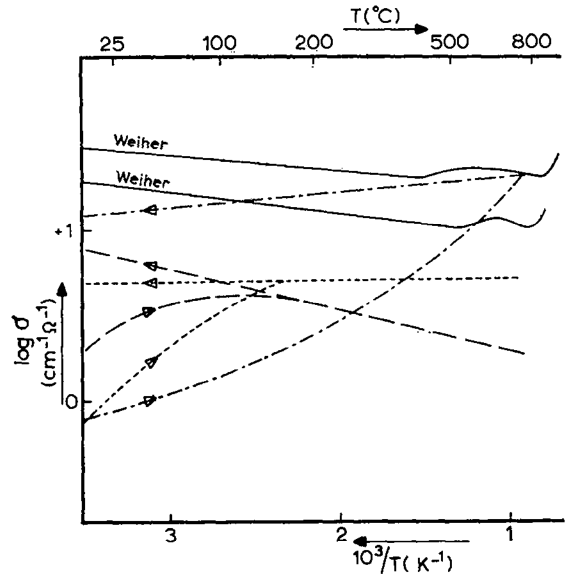

FIG. 3. Some conductivity isobars. All in nitrogen. —·— Flux crystal. ------- Vapour phase crystal. ——— Polycrystalline tablet.

performed in air. For measurements below 200°C this introduces no difference compared to measurements in a nitrogen atmosphere, as conductivity results showed. Experimental details will be published elsewhere (*12*).

Results

Figure 3 shows some isobaric log σ–$1/T$ plots. The measurements were performed in nitrogen.

The flux grown crystal and somewhat less the vapour phase grown crystal show an irreversible increase in conductivity when heating them. Cooling the crystals delivers a different curve, which is retained when heating and cooling are repeated.

The polycrystalline sample shows a similar behaviour; ultimately however the slope becomes negative.

The measurements of Weiher (*3*) of crystals in air are shown in Fig. 3 for comparison.

Figure 4 shows the conductivity measurements of a polycrystalline sample with a density of 46%. This lower density was obtained by using a lower pressure in the preparation of the tablets. The measurements were performed directly after quenching from 1300°C in air. One measurement was performed in oxygen, the other in nitrogen. The measurement in nitrogen gives similar results as were obtained for the polycrystalline sample in Fig. 3. However, the conductivity is lower throughout the whole temperature range, and it has a small positive slope. In an oxygen atmosphere, the conductivity initially decreases during heating, but a minimum is reached at 400°C. Cooling shows a strong decrease resulting in a low room-temperature conductivity far below the original room-temperature value.

Figure 5 shows the oxygen pressure dependence of the conductivity at 800°C for three different polycrystalline samples. The differences in conductivity at one pressure are the results of different temperature pretreatments of these samples, not mentioned in this paper.

In Figure 6 the results of Hall measurements on a polycrystalline sample are pictured in comparison with some literature data. The upper half of the figure shows the electron concentration as a function of the temperature.

Discussion of Conductivity and Mobility

Before discussing the results we want to sum up all the factors that influenced our results. Of these

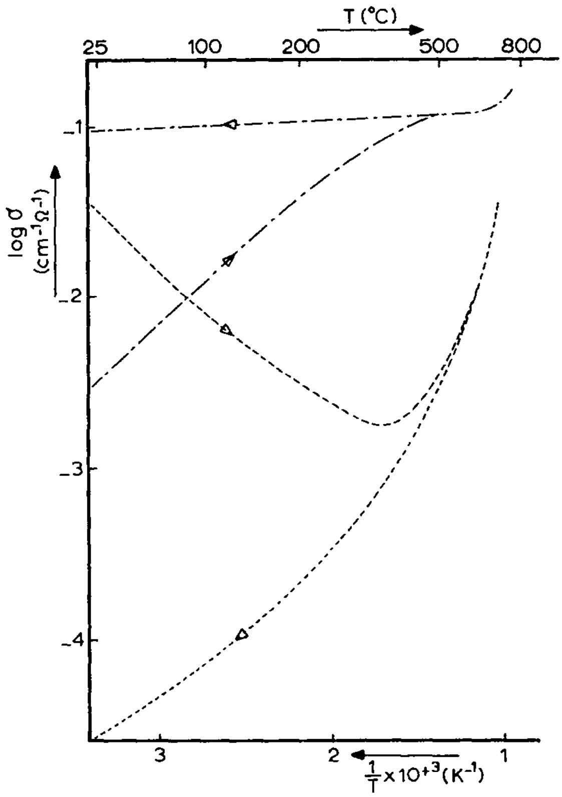

FIG. 4. Log σ vs $1/T$ for a low density (46%) polycrystalline sample. —·— N_2. ------- O_2.

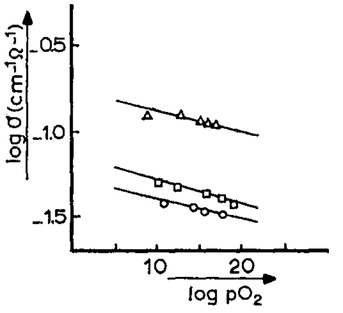

FIG. 5. Conductivity isotherms for three different polycrystalline tablets.

factors a different one predominates in every discussed case.

(a) Annealing at 1300°C and quenching results in a metastable situation.

(b) The impurity content fluctuates.

(c) The density of the sintered polycrystalline samples varies.

(d) After annealing at 800°C and cooling, the 1300°C equilibrium may be relaxed.

(e) The chemisorption of oxygen.

(f) The oxygen bulk interaction.

(g) The differences in grain boundary resistance even for samples with a similar density.

In Fig. 3 conductivity isobars are shown which are all measured in a nitrogen atmosphere. The high conductivity found for the flux-grown crystals is probably due to contamination with lead (*4*). The colour of these crystals is nearly black. The crystals grown from the vapour phase show a smaller but still high conductivity. The colour of these crystals is green.

The major contaminations are Si and Na and perhaps Cl (see Table I). The polycrystalline sample shows a similar behaviour. Here Si and Na are also the major contaminations. The very good conducting samples of Weiher (*3*) were probably contaminated. No analysis is available. Thus we are inclined to ascribe the differences in conductivity at one temperature and under the same ambient circumstances to contaminations. Because the available data don't permit to establish the incorporation mechanism of the impurities, no quantitative interpretation is possible.

The samples of Fig. 3 all show an irreversible increase in conductivity in a nitrogen atmosphere, when the temperature is raised. All three samples, the flux grown crystal, the vapour phase grown crystal and the polycrystalline tablet were prepared or pretreated at temperatures above 800°C (the highest measured temperature in

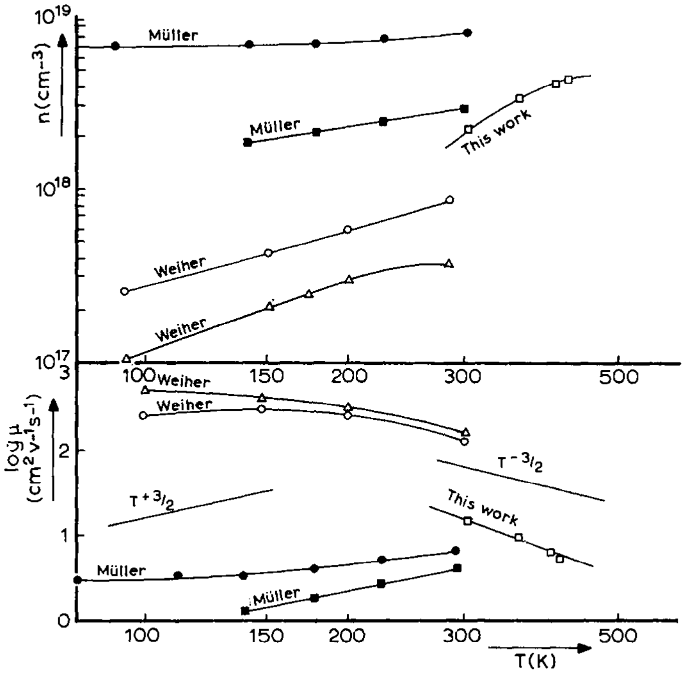

FIG. 6. Electron concentration and mobility as a function of the temperature in comparison with some literature data.

Fig. 3) whereafter a quenching procedure was performed in air. Therefore, this irreversible change might be influenced by the disappearance of the (partially) frozen-in situation created by quenching the sample. For the polycrystalline sample the desorption of oxygen might have some influence. This desorption phenomenon can be more pronounced for a polycrystalline sample with a smaller (46%) (54% for the sample of Fig. 3) density (Fig. 4). This sample has a lower conductivity than the polycrystalline sample in Fig. 3. Since no analyses are available for this sample, it remains difficult to decide whether this low value of the conductivity is due to contaminations or to the smaller density with a larger grain boundary resistance. When measuring the conductivity from room temperature to 800°C, the measurement in oxygen shows a minimum at 400°C. Cooling to room temperature shows a strong continuous decrease in conductivity. We believe that this behaviour is a result of a combined effect of the high temperature (1300°C) oxygen bulk interaction which has been frozen in and a chemisorption effect at temperatures especially below 400°C. The minimum in the conductivity after heating results from an increasing chemisorption of oxygen from room temperature to 400°C whereafter desorption starts up to 800°C. This kind of maximum in the chemisorption of oxygen on a semiconductor is not uncommon (*19*).

Cooling does not show the minimum since the material cannot return to the original situation in an oxygen atmosphere. This situation was the result of an air treatment at 1300°C, whereafter a quenching procedure was performed also in air. The measurement in nitrogen was performed after the oxygen measurement. In between the sample was treated in air at 800°C and cooled to room temperature in air. This explains the higher room temperature conductivity before warming up in nitrogen. The difference between the original room temperature conductivity (after quenching from 1300°C) and this new value must be ascribed to the quenching procedure at 1300°C. No quantitative interpretation is possible because quenching experiments performed in different oxygen pressures were not reproducible. Qualitatively, the results of the measurements in nitrogen show the same behaviour as reported in Fig. 3 for the denser sample.

The difference at 800°C between the oxygen and nitrogen measurement must be interpreted in terms of bulk atmosphere interaction according to Eqs. (4) or (5) as will be shown in the following section.

Figure 6 shows the temperature dependence of the mobility and the electron concentration for a polycrystalline sample (Fluka III) in comparison with literature values (*3*, *8*). These values were calculated from a combination of Hall and conductivity measurements, using the following equations:

$$V_H = 10^{-8} R_H \cdot I \cdot H/d \tag{1}$$

where H denotes the magnetic field strength in oersted, I the current (A), d the thickness of the sample (cm), V_H the Hall voltage (V) and R_H the Hall coefficient (cm^3 C^{-1}).

$$\sigma = n \cdot e \cdot \mu, \tag{2}$$

where n denotes the electron concentration (cm^{-3}), e the electron charge (C), and μ the mobility in cm^2 V^{-1} sec^{-1} and

$$R_H = 1/n \cdot e. \tag{3}$$

We assume that the Hall factor is equal to unity for our high conductivity samples. We suppose that the samples are fully degenerate.

Our sample showed that the electron concentration increases and the mobility decreases with increasing temperature. This behaviour is similar to that found by Weiher for his single crystals (Fig. 6). The mobility found by Müller did increase with increasing electron concentration.

According to Conwell and Weisskopf (*16*) the mobility for a non degenerate electron gas is $\mu_i = \text{const}\ T^{+3/2}$, when impurity scattering is the predominant mechanism. This is in accordance with the behaviour of Müller's thin layers. For the single crystals of Weiher another scattering mechanism seems appropriate especially at higher temperatures. According to Bardeen and Shockley (*17*) the mobility can be expressed by: $\mu_{ph} = \text{const}\ T^{-3/2}$ for phonon scattering. This mechanism seems to fit our polycrystalline samples too.

From Fig. 6 we read an electron concentration of 2.0×10^{18} cm^{-3} at room temperature. From Weiher's paper we can conclude that at this concentration the donor dissociation energy goes effectively to zero. Because of the probably high degeneracy of the donor states no dissociation energy can be read directly from Fig. 6. More detailed experiments of mobility and concentration phenomena for samples with various donor concentrations are necessary for a detailed interpretation.

Defect Chemistry

In_2O_3 is known as an *n*-type semiconductor, and our measurements confirm this result. The analyses showed that it is very difficult to obtain a material pure enough to expect a semiconductivity resulting from the host material. However, the samples in Fig. 5, of which no analyses are available, were very carefully prepared using only polyethylene vessels. They have a lower conductivity than the polycrystalline sample of Fig. 3 although the density is the same (55%). We ascribe the differences in conductivity between these three samples to fluctuations in grain boundary resistance.

Moreover only for these samples with a smaller conductivity, a clear oxygen pressure dependence of the conductivity at 800°C was observed. So we believe that the properties of these samples are intrinsic.

Two different types of defects can occur as donors: vacancies in the anion sublattice $V_i^{\cdot\cdot}$, $V_O^{\cdot}$, and $V_O^{\times}$) and interstitial cations ($In_i^{\cdot\cdot\cdot}$, $In_i^{\cdot\cdot}$, $In_i^{\cdot}$ and $In_i^{\times}$). In both cases the In/O ratio exceeds the ratio 2/3. Both types of defects can explain the conduction properties to a certain extent. Müller (*8*) observed an increase of the conductivity of thin layers of In_2O_3 after heating in vacuum and a decrease after an oxygen treatment. The conductivity increased by a factor 10^3 or more at temperatures above 150°C. The same phenomenon was observed by Rupprecht (*2*). Adsorption of oxygen gas as O^{2-}, O^- or O_2^- can decrease the concentration of free electrons resulting in a lower conductivity. This was the explanation Rupprecht used for his results. This seems to be acceptable for thin layers as well as for our polycrystalline samples with a relatively large specific area as has been discussed already. However, at temperatures above 500°C Rupprecht observed an equal oxygen pressure dependence as we found at 800°C, which can also be explained by an oxygen-bulk interaction. Rupprecht found an exponent of −0.19, whereas we observed $-(0.16 \pm 0.02)$. Now both an $In_i^{\cdot\cdot\cdot}$ and a $V_O^{\cdot\cdot}$ model can explain this exponent, using the following equations:

$$2In_{In}^{\times} + 3O_O^{\times} \rightleftarrows 2In_{In}^{\times} + 3V_O^{\cdot\cdot} + 1.5O_2 + 6e' \quad (4)$$

$$2In_{In}^{\times} + 3O_O^{\times} \rightleftarrows 2In_i^{\cdot\cdot\cdot} + 1.5O_2 + 6e'. \quad (5)$$

Using standard defect chemical equations and accepting $V_O^{\cdot\cdot}$ or $In_i^{\cdot\cdot\cdot}$ as the majority defect results in a pressure dependence exponent of −0.166 for the $V_O^{\cdot\cdot}$ model and −0.1875 for the $In_i^{\cdot\cdot\cdot}$ model. Both values are consistent with the experimental data within experimental error. It should be mentioned that the simple mass-action formalism used here [Eqs. (4 or 5)] is equivalent to a model which combines both the assumptions of a parabolic conduction band and of nondegeneracy of the carrier concentration.

This can only be true for the low carrier concentration samples. This may be the reason that no distinct oxygen pressure dependence could be measured for the high conductivity samples.

Quenching experiments performed on various samples after an annealing procedure at 800°C under various ambient circumstances resulted in an oxygen pressure dependence which could not be interpreted by using a bulk interaction as the only phenomenon. The exponent found was $-(0.50 \pm 0.10)$. Here adsorption of the oxygen after cooling and the resulting nonequilibrium situation after quenching make it impossible to give a quantitative interpretation.

It remains difficult to choose between the $In_i^{\cdot\cdot\cdot}$ and the $V_O^{\cdot\cdot}$ model. The existence of $In_i^{\cdot\cdot\cdot}$ has been made probable by the oxidation rate measurements of Rosenberg (*6*, *7*), performed on In metal. The concentration of these $In_i^{\cdot\cdot\cdot}$ interstitials was as high as 10^{21} cm^{-3} at room temperature. This shows the possibility of high electron concentrations resulting from a surplus of In in the lattice in interstitial positions. Structural considerations are not in contradiction with interstitial In, as we will show in another paper (*20*).

Conclusions

Hall and conductivity measurements did confirm the *n*-type character of In_2O_3 under various conditions. The influence of the oxygen pressure on the conductivity at 800°C can be given by Eqs. (4 or 5). We are inclined to accept the In interstitial model, because of the oxidation rate measurements of Rosenberg (*6*, *7*). From the coefficient (−0.16) follows that the majority of the In interstitials will be triply ionized at 800°C (or the majority of the oxygen vacancies doubly). This is sustained by Weiher's (*3*) finding on the ionisation energy of the donors in In_2O_3. This ionisation energy was very low (~0.01 eV). The dependence of the mobility on temperature and concentration does indicate an acoustical mode lattice scattering as the predominant scattering mechanism.

A quantitative interpretation of the atmospheric influence below 500°C seems not possible, because of the mixture of adsorption and bulk interaction phenomena plus the influence of impurities. Quenching experiments after annealing at 800°C do show the difficulties arising from a nonequilibrium situation after quenching. The expected exponent of -0.16 could not be reached. A much higher value $\simeq 0.50$ was obtained, which cannot be explained with simple defect models. There too the adsorption at room temperature could be of interest. The increasing conductivity during the heating of a polycrystalline sample in nitrogen does indicate the same phenomenon. Also here a nonequilibrium situation after quenching from 1300°C and a desorption of O_2 seem to be the reason for this increase. The minimum in the conductivity vs temperature plot for a polycrystalline sample with a small density in oxygen can be explained by oxygen adsorption and desorption as well.

Acknowledgments

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