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Electrical Properties of Pure In_2O_3 and Sn-Doped In_2O_3 Single Crystals and Ceramics

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The transport properties of undoped and Sn-doped In_2O_3 (ITO) single crystals prepared by a flux method are reported. Hall measurements are detailed: they show that the mobility increases as the Sn dopant concentration increases. A maximum value of 100 $cm^2V^{-1}s^{-1}$ is measured with an electron concentration of about 1.6×10^{20} cm^{-3}. However, at high dopant concentration the mobility decreases again and the presence of neutral entities such as $(SnO)_x$ is expected to be responsible for this behavior. Some results dealing with undoped and Sn- or Pb-doped In_2O_3 ceramics are also presented and discussed. © 1992 Academic Press, Inc.

I. Introduction

Simultaneous high electrical conductivity and transparency in the visible region of SnO_2-doped In_2O_3 (ITO) lead to interesting applications as transparent electrodes and heat mirrors. Hence much research has been devoted to characterization of the electrical and optical parameters of thin films (*1–4*) or single crystals (*5–8*). We report in this paper conductivity, carrier concentration and mobility measurements on pure In_2O_3 single crystals and SnO_2-doped In_2O_3 crystals. Various concentrations of SnO_2 have been tested; the solubility limit in our conditions has been determined and compared with previous results. The carrier mobility has been investigated in relation to the Sn/In ratio within the ternary oxide crystal.

As the crystals were grown in a PbO flux; traces of Pb were observed in the single crystals. Investigations have been carried out to determine a possible correlation between the lead traces and the electronic conductivity. This research was achieved by conductivity measurements on In_2O_3 ceramics doped with PbO. The transport properties of SnO_2-doped In_2O_3 ceramics were also examined and the results compared with those obtained with single crystals.

II. Preparation and Characterization of Samples

II.1. Single Crystals

Pure In_2O_3 and In_2O_3 doped with SnO_2 single crystals were grown by the flux method nearly as described by Remeika and Spencer (*9*). The starting materials were "99.999% purified" In_2O_3 and SnO_2, as well as "reagent-grade" PbO and "purified-grade" B_2O_3.

The procedure for a typical growth was as follows: reaction components and flux (total amount, 43.5 g) were intimately mixed and then put into a Pt crucible. Once the

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TABLE I

THE DOPING CONCENTRATION OF Sn-DOPED In_2O_3 SINGLE CRYSTALS WITH THEIR CORRESPONDING ELECTRICAL PROPERTIES

Sn/In ratio in starting materials	Sample	Sn/In ratio in the crystal	ρ ($\Omega \cdot$ cm)	n (cm^{-3})	μ ($cm^2\ v^{-1}\ s^{-1}$)
Pure In_2O_3 6 hr, 1250°C	S_1	0	10^{-2}	10^{19}	65
Pure In_2O_3 12 hr, 1250°C	S_2	0	10^{-2}	1.4×10^{19}	58
Pure In_2O_3 6 hr, 1300°C	S_3	0	10^{-2}	1.8×10^{19}	45
Sn/In = 0.25	S_4	0.25	3×10^{-3}	3.8×10^{19}	48
Sn/In = 1	S_5	0.5	1.2×10^{-3}	7.8×10^{19}	62
Sn/In = 2.5	S_6	0.8	3.9×10^{-4}	1.6×10^{20}	100
Sn/In = 10	S_7	1	3×10^{-4}	2.8×10^{20}	81
Sn/In = 20	S_8	1	3×10^{-4}	8.8×10^{20}	75

crucible with a closely adapted lid limiting evaporation of the solvent was introduced into the furnace, the thermal program was initiated: the temperature was raised up to 1320°C at a rate of 60°C/hr and held for 6 hr to ensure a complete interaction of In_2O_3 and SnO_2. Then the temperature was lowered at a rate of 5°C/hr down to 850°C and the crucible removed from the furnace. Results reported in this paper were obtained with crystals grown in ambient atmosphere.

By soaking the platinum crucible in an aqueous HNO_3 solution the flux was dissolved and In_2O_3 or ITO single crystals were separated. Traces of Pb have been sometimes observed on the crystal surface by Auger electron spectroscopy or Rutherford backscattering (*10*). Those traces are completely removed by dipping in a normal aqueous HNO_3 solution or by polishing the crystals. No traces of other elements were detected.

We have prepared several crystals with various starting powders, the SnO_2/In_2O_3 molar fraction ranging from 0.1 to 20%. The Sn/In ratio within the crystals was determined by spectrochemical analysis (Table I).

This ratio actually never exceeded 1% (i.e., SnO_2/In_2O_3 = 2%) and it is independent of the lead amount in the starting materials. The structure was checked by X-ray diffraction: ITO exhibits the cubic symmetry bixbyite-type structure of In_2O_3 (*11*).

II.2. Ceramics

Pure In_2O_3 and Sn (Pb)-doped ceramics were prepared by mixing In_2O_3 and SnO_2 (PbO) powders (99.999%). The mixed powders were cold-pressed in a steel die and then submitted to an isostatic pressure of 5 bar. The obtained pellets were sintered in air at high temperature, different attempts being made between 1150 and 1350°C.

Samples with various Sn/In (Pb/In) atomic ratios, between 0.02 and 11%, were prepared. X-ray diffraction showed that no structure change is observed as long as the Sn/In (Pb/In) atomic ratio does not exceed about 10%; above this limit traces of SnO_2(PbO) are detected. This characterization seems to imply an Sn/In ratio about 10 times larger in the ceramics than in the crystals. Scanning electron microscopy showed that the size of the grains is about 1 μm. The density measured has an average value of about 5. As for single crystals, the

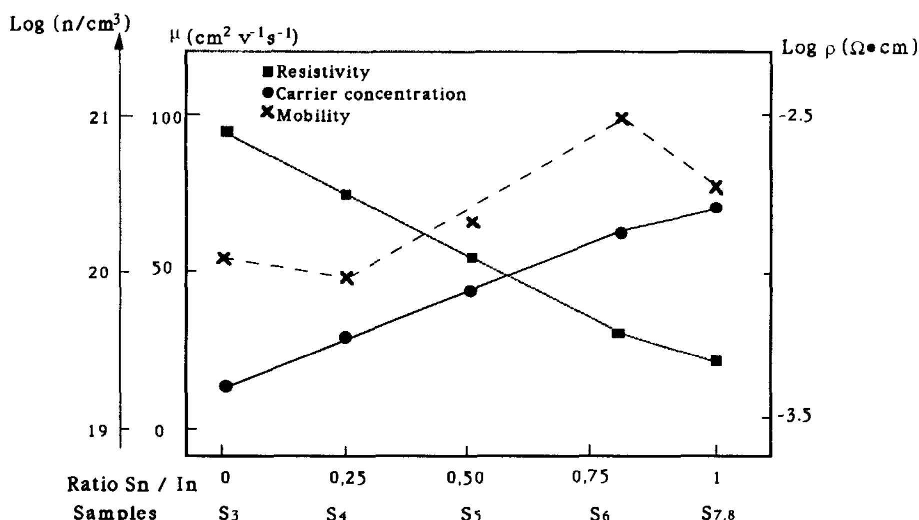

FIG. 1. Carrier concentration, mobility, and resistivity vs SnO_2/In_2O_3 molar fraction for pure and Sn-doped single crystals.

composition of ceramics has been determined by spectrochemical analysis.

III. Transport Properties

III.1. Single Crystals

Conductivity, carrier concentration, and mobility were measured using an ac Van der Pauw method in a field strength of 1.2 T. Dimensions of crystals are typically 2 × 2 mm with a thickness of about 1 mm. Ohmic contacts were realized with silver paste.

In order to evaluate the influence of the inhomogeneity in the lead content, we have performed Hall measurements after successive polishing of the crystals. The resistivity, the carrier concentration, and the mobility do not vary significantly from the surface to the inside of the crystal.

Figure 1 shows the variation in several single crystals of the resistivity, the carrier concentration detected by Hall effect measurements, and the mobility vs the Sn/In ratio at 300 K. In Fig. 2 the mobility is plotted as a function of carrier concentration.

III.1.1. Undoped crystals. Three undoped crystals, S1, S2, and S3, corresponding to slightly different thermal treatment of the crystals have been investigated. In these samples the carrier concentration varies with the elaboration conditions. As a consequence we may assume that the temperature induces in the crystal oxygen vacancies and that the electrons associated with the presence of those vacancies are responsible for the conduction mechanism.

The results are in good agreement with those obtained by Kanai, who utilized a similar crystal growth method (*6*). However, they slightly differ from those of Weiher, who used a vapor phase technique (*5*). In his paper the resistivity is about 10^{-1} Ω cm, the carrier concentration less than 10^{18} cm^{-3}, and the mobility approximately 160 cm^2 V^{-1} s^{-1}. The difference can be correlated to the crystal growth techniques; the flux method used here requires a higher tem-

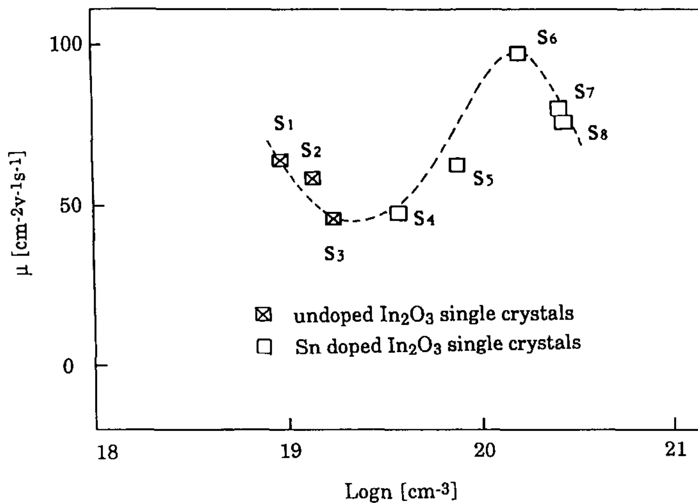

FIG. 2. Mobility vs the carrier concentration in pure and Sn-doped single crystals.

perature than the vapor phase one and it leads actually to a carrier concentration larger by one order of magnitude than that observed after vapor phase deposition. The number of oxygen vacancies is then large enough to allow that the wave functions associated with the vacancies overlap and form a narrow band which is more or less mixed with the conduction band of In_2O_3. Taking into account Weiher's model, we may assume that the mobility at room temperature in our samples may be a combination of acoustical mode lattice scattering and ionized impurity scattering, as the mobility seems to decrease as the carrier concentration increases.

III.1.2. Doped samples. In Sn-doped samples the conductivity and the Hall effect carrier concentration are enhanced (Fig. 1). The latter reaches a maximum of about 2.8 $\times$ 10^{20} cm^{-3}. We may notice that this value corresponds to an Sn/In ratio within the crystal of about 0.9% while the spectrochemical analysis performed on the same sample (S8) reveals an Sn/In ratio close to 1%. We can deduce that: (i) the solubility of Sn within the In_2O_3 lattice is limited to 1%; (ii) apparently a part of Sn introduced in the crystal lattice does not play a role in the conduction mechanism. At rather low doping rates (S4), the carrier concentration measured by Hall effect is roughly the same as the Sn concentration in the starting mixture. It confirms that Sn enters fully and as Sn(IV) in the lattice; i.e., Sn(IV) is substituted for In(III) ($In^{3+} \leftrightarrow Sn^{4+} + e$).

Let us now discuss the mobility in doped single crystals. As shown in Fig. 2, the mobility in the Sn-doped crystals begins to increase as the carrier concentration increases; it reaches a maximum at about 100 $cm^2\ V^{-1}\ s^{-1}$ for a carrier concentration of about 1.6×10^{20} cm^{-3} and then decreases for higher concentrations.

In degenerate semiconductors the mobility is expressed usually by $\mu = q\tau(E_F)/m^*$, where $\tau(E_F)$ is the relaxation time at the Fermi level and m^* the effective mass. Applying an addition rule to reciprocal $1/\tau_m$ values, where τ_m is the relaxation time for each particular scattering mechanism, we may write

$$1/\tau(E_F) = \sum \frac{1}{\tau_m(E_F^*)}.$$

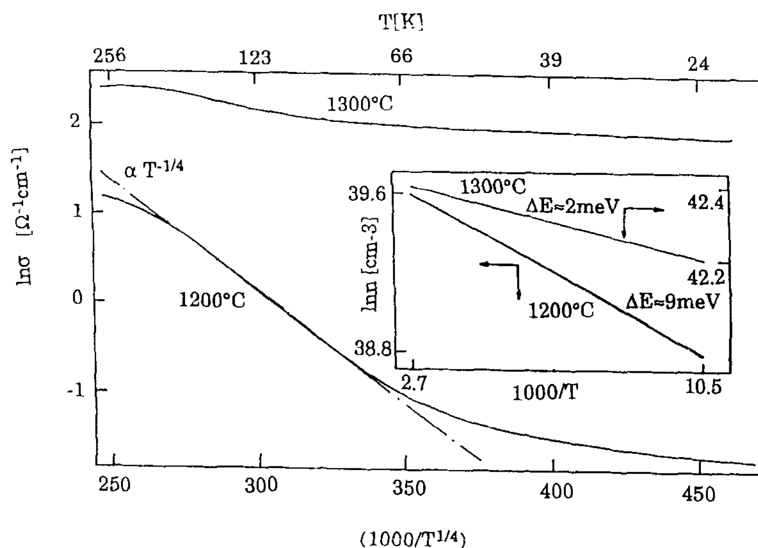

FIG. 3. Conductivity vs temperature for two In_2O_3 ceramics elaborated at, respectively, 1200°C (C1) and 1300°C (C2). Insert shows the carrier concentration vs reciprocal temperature variation.

The relaxation times τ_m are obtained under the form $\tau_m = \tau_0 E_F^{*r}$, where the exponent $r = -\frac{1}{2}$ corresponds to scattering by acoustical phonons, $r = \frac{3}{2}$ to scattering by ionized impurities, and $r = 0$ by neutral impurities. E_F^* is given in kT units. τ_0 is a function of the effective mass m^* and also of the impurity concentrations (*13*).

In the very simple approximation of a parabolic band bending, i.e., of the m^* constant, the scattering mechanism by acoustical phonons or ionized impurities (as Sn) should be correlated with a carrier concentration high enough to lead to decrease of the mobility as the carrier concentration increases. This behavior is not consistent with our results, so the hypothesis of a constant effective mass cannot be considered valid, and a modification of m^* with the Sn concentration has to be involved. In any case, in order to satisfy the mobility variation law, m^* must decrease as the Sn concentration increases, whatever the scattering mechanism. This point is consistent with the fact that the higher the Sn concentration, the larger the delocalization of the electrons in the conduction band.

On the other hand the mobility decrease observed, e.g., in samples S_7 and S_8, may be associated with the variation of the effective mass but a rather more plausible explanation can be suggested. As previously mentioned, it has been noticed by spectrochemical analysis that the electron concentration is slightly smaller (0.9%) than the Sn concentration in the crystal (1%). As a consequence one may expect the formation of some neutral clusters of the $(SnO)_n$ type. The occurence of nonionizable tin–oxygen $(SnO)_n$ clusters, where n is likely an integer, was in fact proposed before by various authors (*14*). The formation of such entities may strongly reduce the mobility. The relaxation time of neutral impurity scattering should vary, in this eventuality, according to a $\tau \alpha 1/N$ *law, where* N is the concentration of neutral impurities. SnO_2 microdomains are indeed not occluded at the phase limit composition.

TABLE II
THE DOPING CONCENTRATION OF Sn-DOPED In_2O_3 CERAMICS WITH THEIR CORRESPONDING MOBILITIES

SnO_2/In_2O_3 ratio in starting materials	Ceramics	n (cm^{-3})	μ ($cm^2\ V^{-1}\ s^{-1}$)
Pure In_2O_3, 1200°C	C_1	1.5×10^{17}	40
Pure In_2O_3, 1300°C	C_2	2.5×10^{18}	26
SnO_2/In_2O_3 = 0.1	C_3	4.5×10^{19}	33
SnO_2/In_2O_3 = 0.3	C_4	1.1×10^{20}	30
SnO_2/In_2O_3 = 1%	C_5	1.3×10^{20}	30
SnO_2/In_2O_3 = 2.5	C_6	1.3×10^{20}	26
SnO_2/In_2O_3 = 5	C_7	1.5×10^{20}	28

III.2. Ceramics

III.2.1. Undoped ceramics. Various undoped ceramics of In_2O_3 were sintered at different temperatures ranging between 1000 and 1350°C. The room temperature resistivity and the carrier concentration deduced from the Hall mobility measurements depend on the sintering temperature. The resistivity of C1 prepared at 1300°C reaches a minimum of about 10^{-1} Ω cm as the donor concentration exhibits a maximum of 2×10^{18} cm^{-3} for the same sample (Fig. 3). The Hall mobility is practically constant with a value corresponding to a 30–40 $cm^2\ V^{-1}\ s^{-1}$ range (Table II). As for single crystals we may assume that high temperature induces in In_2O_3 some oxygen vacancies and that their number increases with rising temperature. Figure 3 shows the variation of the resistivity with temperature for two samples (C1, C2) sintered at 1200 and 1300°C. Both samples behave in a degenerated manner. At low temperature (80 K $< T <$ 200 K) for Cl, ln σ is roughly proportional to $T^{-1/4}$, according to the prediction of a Davis–Mott model (*15*). This means that the Fermi level E_F lies below a mobility edge, E_C, and that, consequently, the conduction mechanism is variable-range hopping in the bottom of the conduction band. Electrons associated with oxygen vacancies are obviously responsible for the occupied states. At higher temperatures, ln σ has a linear $1/T$ dependence with an activation energy of $\simeq$ 9 meV. We have checked by Hall effect measurements that this activation energy corresponds to an increase of the carrier concentration, the mobility being constant. As a consequence $E_C - E_F \simeq 9$ meV.

Sample C2 sintered at 1300°C behaves slightly differently: the $T^{-1/4}$ law is no longer observed. However, ln σ still has a linear $1/T$ dependence at high temperature, but the activation energy is reduced and a value of about 2 meV may be deduced. For this sample the Fermi level is very close to the mobility edge.

Although the carrier concentration in ceramics ($\approx 2.5 \times 10^{18}$ cm^{-3}) is smaller than that in single crystals ($\approx 10^{19}$ cm^{-3}), the mobility is lower. We may point out that in ceramics, the mobility does not depend only on the carrier concentration measured by the Hall effect, which does not involve scattering by ionized impurities or acoustical phonons likely appearing in single crystals. In our ceramics, scanning electron microscopy reveals a large amount of voids between the grains and shows a grain size of about 100 nm. This value is only 10 times larger than the electron mean free path. We can deduce that scattering at the grain boundaries should also contribute to the mo-

bility and account for the lower value observed.

II.2.2. Pb-doped ceramics. We have found that undoped crystals contained some lead traces, as a result of the growth process. It has also been mentioned that a higher carrier concentration ($\approx 10^{19}$ cm^{-3}) was measured in such crystals. In order to determine the influence of lead on In_2O_3 single crystals, various lead-doped In_2O_3 ceramics were prepared by mixing PbO and In_2O_3 powders. The PbO/In_2O_3 molar ratio ranged between 0.1 and 5%. All ceramics were sintered at 1300°C. It was found that the carrier concentration measured by the Hall effect did not drastically change in presence of lead: it is about 2×10^{18} cm^{-3} for PbO/In_2O_3 = 0.012% and 1.55×10^{18} cm^{-3} for PbO/In_2O_3 = 2.3%. The mobility is for both samples about 30 cm^2 V^{-1} s^{-1}, a value only slightly lower than that measured for the "undoped" crystals (Table I). From those results we can conclude that the higher carrier density which is measured in the single crystals is not related to some lead traces but results more probably from the amount of oxygen vacancies.

II.2.3. Sn-doped ceramics. Five SnO_2/In_2O_3 molar fractions have been selected between 0.1 and 5% (Table II). The variation of the carrier concentration measured by the Hall effect vs the tin rate in the starting mixture is given in Fig. 4. The tin concentration was calculated assuming a density of 5. The determined carrier concentration is lower than the Sn concentration even at low dopant concentrations due to the presence of an excess of nonreacting SnO_2. The electron concentration is limited to about 1.3×10^{20} cm^{-3}, a value slightly smaller than that in the single crystals (2.8×10^{20} cm^{-3}) but in agreement with the order of magnitude of the solubility limit which was found to correspond to Sn/In $\approx$ 1%. As in single crystals, we have to assume here that all Sn atoms are not electrically active. This phenomenon seems even to be enhanced in ceramics. The mobility does not depend significantly on the Sn concentration; it is roughly the same as that in undoped ceramics, i.e., 30 cm^2 V^{-1} s^{-1}. This confirms that it is limited neither by ionized impurity scattering nor by neutral impurity scattering. It probably depends on the grain boundaries.

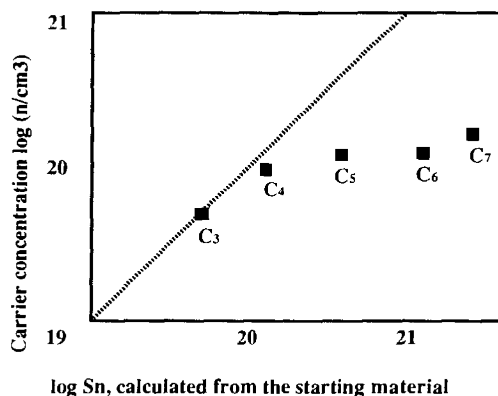

FIG. 4. Carrier concentration vs Sn concentration in the starting mixture for ceramics.

IV. Conclusion

Undoped and Sn-doped single crystals of In_2O_3 were grown by a flux method. Although the single crystals contain some traces of lead, the conductivity variation may be explained by oxygen vacancies in undoped crystals. Lead is apparently electrically inactive, this point having been clarified by studying lead-doped In_2O_3 ceramics.

The presence of small amounts of Sn in single crystals leads to an increase of the conductivity due to the higher number of electrons in the conduction band, but with a maximum of about 3.5×10^3 Ω^{-1} cm^{-1}. The mobility is enhanced as the carrier concentration increases, but it attains a maximum of about 100 cm^2 V^{-1} s^{-1} for an electron concentration of 1.6×10^{20} cm^{-3}. This phenomenon may be related to a change of the effective mass vs the dopant concentration. The solubility limit of SnO_2 in In_2O_3

was estimated to be 2%, but it seems that only a part of the Sn atoms present are electrically active for the highest Sn concentrations. At higher tin rates the mobility decreases, the presence of neutral $(SnO)_n$ clusters having been suggested to explain this behavior.

Finally, we have mentioned some results obtained with Sn-doped In_2O_3 ceramics. The electron concentration is of the same order of magnitude as that in single crystals. However, the mobility is lower, about 30 $cm^2\ V^{-1}\ s^{-1}$, and it does not depend on the dopant concentration. Grain boundaries are likely responsible for these low values. A careful X-ray diffraction study would probably show presence of SnO_2 (*16*).

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