

ELECTRONIC PROPERTIES OF Sn- OR Ge-DOPED In₂O₃ SEMICONDUCTORS

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The thermoelectric power and Hall effect of In₂O₃ single crystals, either undoped or Sn doped, and of In₂O₃ ceramics, either undoped or Sn or Ge doped, are investigated. All doped samples have negative thermoelectric power values. The metal-type conductivity occurs when the carrier concentration exceeds 10¹⁹ cm⁻³. The correspondence between the values of the thermoelectric power and those of the carrier mobility and carrier concentration is given. Most interestingly this study puts into light the enhanced carrier mobility occurring for Ge-doped In₂O₃ samples compared with ITO samples (Sn-doped In₂O₃) widely used in optoelectronic devices.

I. INTRODUCTION

Over the past 30 years, a great interest has focused on the development of transparent electrode materials such as Sn-doped In₂O₃ commonly labeled ITO, and their optical and electrical properties have been investigated in detail [1–4]. Indeed, the optical and electrical properties of transparent conductive electrodes are very important for optoelectronic-related applications such as electrochromic applications, and could limit the performances for large surface devices such as smart windows. One indeed needs to obtain the lowest possible resistance associated with the highest possible optical transmission in the visible spectrum. Closely related to that, one has to emphasize that the influence of the nature of the doping element on the electronic properties of In₂O₃ based semiconductors is not yet clearly established. Therefore, an important question still arises: can the electrical and optical properties of well-known ITO be improved by using dopants other than Sn (partially or totally substituted to Sn)? With the aim in mind to answer this question, we investigate here the thermoelectric power and Hall effect on a series of In₂O₃ based samples either undoped or doped with Sn or Ge. For sake of clarity, this preliminary investigation will be carried out here on single crystals and ceramics only.

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II. PRELIMINARY CONSIDERATIONS RELATED TO THE THERMOELECTRIC POWER

The thermoelectric power α is proportional to the thermo-emf, $\Delta E_E - \Delta E_T$, divided by the temperature drop ΔT across the sample:

$$\alpha = (\Delta E_E - \Delta E_T)/\Delta T \quad (1)$$

One considers here that electron-carriers predominantly influence the evolution, with temperature, of the thermo-emf (as it occurs for Sn-doped In_2O_3). The terms on the right-hand side refer to potential (ΔE_E) and kinetic energy (ΔE_T) respectively; they are both measured relative to the energy at the edge of the band (namely the conduction band for the In_2O_3 -based semiconductors investigated here [1–4]).

In the case of a non-degenerate semiconductor, to a first approximation one can write:

$$\alpha_1 = -k(2 - \mu^*)/q \quad (2)$$

$$\alpha_i = -k(4 - \mu^*)/q \quad (3)$$

where α_1 and α_i symbolize the thermoelectric power for the case of carrier scattering mainly limited by phonons and by ions respectively, k is the Boltzmann constant, and q the electronic charge. μ^* is dimensionless and is known as the reduced electrochemical potential. Under such a circumstance, the dependence of α as a function of the conduction-band electron density n can be evaluated. Indeed, n can be expressed as:

$$n = (\pi N_c e \mu^*)/2 \quad (4)$$

where N_c represents the effective density of states in the conduction band. Therefore, expressions (2) and (3) become, respectively:

$$\alpha_1 = k/q\{2 - \ln(2n/\Pi^{1/2}N_c)\} \quad (5)$$

$$\alpha_i = k/q\{4 - \ln(2n/\Pi^{1/2}N_c)\} \quad (6)$$

In the degenerate-semiconductor case ($\mu^* > 0$), we have:

$$\alpha_1 = -k\pi^2/(q3\mu^*) \quad (7)$$

$$\alpha_i = -k\pi^2/(q(\pi^2 + \mu^{*2})) \quad (8)$$

Equations (7) and (8) are rather similar to those generally used for metals [5].

III. EXPERIMENTAL PROCEDURE

(i) Single crystal manufacturing

Either undoped or Sn-doped In_2O_3 (IO) single crystals have been manufactured. The undoped IO single crystals were grown by two methods: (i) the flux method

as described by J.P. Remeika [6], (ii) the vapor phase technique as described by R.L. Weiher [7]. These two methods generally yield high- and low-carrier concentration, respectively [2]. In order to get appropriate high conductivity, the flux method, uniquely, was used to grow the Sn-doped IO single crystals.

(ii) *Ceramics manufacturing*

Either undoped In_2O_3 (IO) ceramics or IO ceramics doped with Sn or Ge have been manufactured. The undoped ceramics were prepared by sintering pellets (10 mm diameter, 1 mm thick) in air at various temperatures (1100 °C, 1200 °C, 1300 °C and 1350 °C) during 24 h with a heating and cooling rate of 100 °C/h. The doped In_2O_3 ceramics were prepared by intimately mixing the starting material oxides (i.e., $\text{In}_2\text{O}_3 + \text{SnO}_2$ or GeO_2). The mixed powders were cold-pressed in a steel die and then submitted to an isostatic pressure of 5 bars. The obtained pellets were sintered in air at 1350 °C for 24 h after heating to temperature at 100 °C/h; they were subsequently cooled at 100 °C/h.

All electrical measurements were performed using equipment described elsewhere [2, 8].

IV. RESULTS AND DISCUSSION

(i) *Single crystals*

Values of the room temperature conductivity σ , carrier concentration n , and carrier mobility μ of undoped In_2O_3 single crystals and of Sn-doped In_2O_3 single crystals are given in table I. The reported values were deduced from Hall effect measurements [2].

The thermoelectric power of all samples has similarly been investigated at room temperature. Fig. 1 illustrates the dependence of the thermoelectric power α on the electron density n . For $n \leq 10^{19} \text{ cm}^{-3}$, α varies proportionally as $\log(n)$ (straight line on fig. 1). Such an evolution is predictable, as it obeys relation (5) and/or (6). On the other hand, for higher carrier concentration the proportionality is not observed because equations (2)–(6) are no longer valid; in fact α varies as $n^{2/3}$, as it often occurs for strong degeneracy ($n \geq 10^{20} \text{ cm}^{-3}$, [9]).

These experimental results enable us to find the degree of degeneracy of the electron gas depicted by μ^* . Using the values of μ^* , deduced from equation (3) for instance, and the dependence of μ^* on the carrier density (equation (4)), we can evaluate, for the non-degenerate situation, the evolution of the carrier effective mass m_N as a function of the density of the conduction-band energy-states N_c . As an illustrative example, one would get for (totally) non-degenerated n-type In_2O_3 : $m_N/m_0 = 0.42$ ($m_0 =$ free-electron mass). This ratio is indeed calculated from the values $\mu^* = -1.3$ and $n = 10^{18} \text{ cm}^{-3}$, obtained by extrapolating the dotted line (non-degenerated case) of Fig. 1. All these values of m_N/m_0 , μ^* , and n are in good agreement with the literature report for slightly n-type doped In_2O_3 thin films [1].

TABLE I
 Values of the room temperature conductivity, carrier concentration and carrier mobility for the undoped (1 to 5) and Sn doped In_2O_3 (A to D) single crystals [2].* The ratio $\text{Sn}/(\text{In} + \text{Sn})$ corresponds to 10^{-2} in $\text{In}_{2-2x}\text{Sn}_{2x}\text{O}_3$ [2].

Sn/(In + Sn) ratio* (% values)	Sample symbol.	μ ($\text{cm}^2\text{v}^{-1}\text{s}^{-1}$)	n (cm^{-3})	σ ($\text{cm}^{-1}\Omega^{-1}$)
Sn/(In + Sn) = 0	1	85	2.5×10^{18}	3.4×10^1
Sn/(In + Sn) = 0	2	70	3.98×10^{18}	4.5×10^1
Sn/(In + Sn) = 0	3	65	1.0×10^{19}	1.04×10^2
Sn/(In + Sn) = 0	4	58	1.4×10^{19}	1.3×10^2
Sn/(In + Sn) = 0	5	45	1.8×10^{19}	1.3×10^2
Sn (In + Sn) = 0.25	A	48	3.8×10^{19}	2.92×10^2
Sn (In + Sn) = 0.5	B	62	7.8×10^{19}	7.74×10^2
Sn (In + Sn) = 0.8	C	100	1.6×10^{20}	2.56×10^3
Sn (In + Sn) = 0.9	D	81	2.8×10^{20}	3.63×10^3

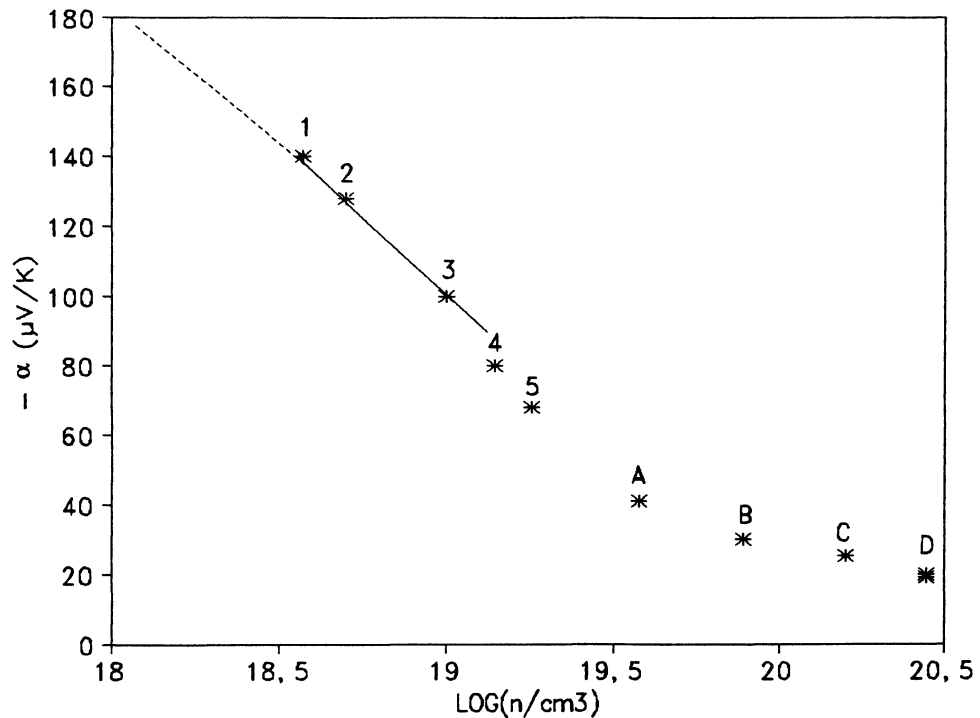


FIGURE 1 Dependence of the thermoelectric power on the electron density in undoped and Sn doped In_2O_3 single crystals at 300K. The sample symbolization is similar to that depicted in table I.

(ii) *Polycrystalline ceramics*

Values of the room temperature conductivity, carrier concentration, and carrier mobility, measured by Hall effect [3] for undoped and for Sn- or Ge-doped In_2O_3 are shown in Table II. Fig. 2 illustrates, for samples a to n (Table II), the dependence of the thermoelectric power on the electron density.

The thermoelectric power, like the mobility, is governed by the scattering mechanism of carriers; therefore, we could expect different values of α for In_2O_3 doped with different impurities. That is illustrated hereafter for heavily doped samples. It is indeed evident from Fig. 2 that α values, referring to samples k–n and symbolizing In_2O_3 doped with Ge for which $n = 10^{20} \text{ cm}^{-3}$, are somewhat higher than those referring to samples f–i, which represent In_2O_3 doped with Sn and for which $n = 10^{20} \text{ cm}^{-3}$. This can be understood using, for the sake of simplicity, equation (7), which is valid in the strongly degenerate case ($n = 10^{20} \text{ cm}^{-3}$). Using equation (7), the basic nature of the effect can indeed be foreseen. One can write:

$$\alpha_{\text{Ge}}/\alpha_{\text{Sn}} = \mu_{\text{Sn}}^*/\mu_{\text{Ge}}^* \quad (9)$$

On the other hand, μ^* depends upon the carrier mobility, the carrier effective mass, and the scattering cross section Q according to:

$$\mu^* = e^2/(2m_N n^2 \mu Q^2) \quad (10)$$

TABLE II
Room temperature resistivities, carrier concentrations and carrier mobilities for undoped and Sn or Ge doped In_2O_3 ceramics [3]. The ratio $M/(\text{In} + \text{Sn})$ has same meaning as in table I.

$M/(\text{In} + M)$ ratio ($M = \text{Sn}$ or Ge)	Sample symbol.	μ ($\text{cm}^2\text{v}^{-1}\text{s}^{-1}$)	n (cm^{-3})	σ ($\text{cm}^{-1}\Omega^{-1}$)
Sn/(In + Sn) = 0 sintered at 1100 °C	a	40	1.3×10^{17}	8.32×10^{-1}
Sn/(In + Sn) = 0 sintered at 1200 °C	b	45	1.5×10^{17}	1.08
Sn/(In + Sn) = 0 sintered at 1300 °C	c	28	2.5×10^{18}	1.12×10^1
Sn/(In + Sn) = 0 sintered at 1350 °C	d	25	4.0×10^{17}	1.6
Sn/(In + Sn) = 0.125	e	35.1	4.5×10^{19}	2.53×10^2
Sn (In + Sn) = 0.25	f	30.9	1×10^{20}	4.94×10^2
Sn (In + Sn) = 0.5	g	29	1.86×10^{20}	8.63×10^2
Sn (In + Sn) = 1	h	28	1.9×10^{20}	8.51×10^2
Sn (In + Sn) = 2.5	i	25	1.91×10^{20}	7.64×10^2
Ge/(In + Ge) = 0.125	j	45	3.2×10^{19}	2.3×10^2
Ge/(In + Ge) = 0.25	k	50	8.0×10^{19}	6.4×10^2
Ge/(In + Ge) = 0.5	l	55	1.8×10^{20}	1.58×10^3
Ge/(In + Ge) = 1	m	52	1.88×10^{20}	1.56×10^3
Ge/(In + Ge) = 2.5	n	50	1.9×10^{20}	1.52×10^3

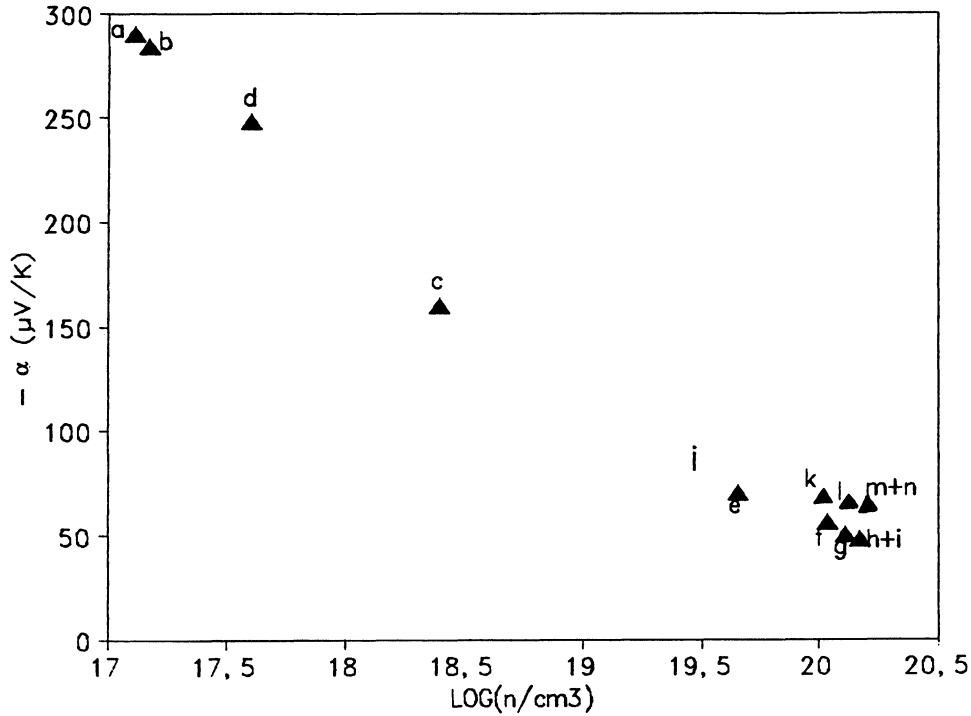


FIGURE 2 Dependence of the thermoelectric power on the electron density in undoped and Sn or Ge doped In_2O_3 ceramics at 300K. The sample symbolization is similar to that depicted in table II.

Consequently, we can obtain the following expression after certain transformations:

$$\alpha_{\text{Ge}}/\alpha_{\text{Sn}} = (\mu_{\text{Ge}}/\mu_{\text{Sn}})^2(Q_{\text{Ge}}/Q_{\text{Sn}})^2 \quad (11)$$

The ratio of the scattering cross sections is not known exactly, but we can reasonably assume that it is less than unity; thereby the ratio between the thermoelectric power of germanium-doped and tin-doped samples will be lower than the square of the mobility-ratio.

V. CONCLUSIONS

We must now emphasize again that, most interestingly, the α values observed for In_2O_3 heavily doped with Ge are higher than those observed for In_2O_3 heavily doped with Sn: this result gives another strong evidence, as the Hall effect measurements (table II), of the enhanced carrier mobility in Ge-doped In_2O_3 (according to (11)). It clearly means that the optoelectronic properties of the widely used "conventional" ITO (ITO symbolizing, as pointed above, Sn doped In_2O_3) films should be improved if Sn is partially, or totally, substituted by Ge.

Finally let us note that, for similar carrier concentrations, the values of the thermoelectric power of polycrystalline ceramic samples are higher than those of the related single crystals. This difference would be depicted by equation (10) and, thereby, would arise from the lower effective mass and scattering cross section occurring for single crystals.

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