Rapid Note

Electron scattering mechanisms in ITGO (Sn+Ge doped In₂O₃) thin films for low emittance window coatings

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Abstract. Electronic properties of ITGO (Sn+Ge doped In_2O_3) thin films have been investigated for various compositions with decreasing doping levels (molar ratios $[Sn]/[In] \leq 0.05$ with $[Ge] = 0.2\,[Sn]$). Conductivity and Hall measurements *versus* temperatures ranging from 77 to 500 K have shown that two electron scattering mechanisms are to be considered. Even though ionised impurities dominate the electron scattering in the whole temperature range, the influence of optical phonons cannot be neglected. It appears gradually from 200 to 250 K and involves a marked decrease of the electron mobility with temperature. The influence of the doping level on the electron mobility has also been studied. It can be correlated with the effective mass variations deduced from the evolution of the thermoelectric power *versus* temperature [1,2] and with the observation by optical absorption of localised states for the lowest doping levels [1,8].

PACS. 73.50.-h Electronic transport phenomena in thin films – 73.50.-Jt Galvanomagnetic and other magnetotransport effects – 63.20.Kr Phonon-electron and phonon-phonon interactions

Introduction

When preparing low emittance window coatings based on Sn doped In_2O_3 (ITO) thin films, the main problem concerns the drop of their electronic properties when decreasing the doping levels. It is well-known that the performances of such coatings are improved when the electron relaxation time τ is as large as possible. This concerns IR reflectivity (the Hagen-Rubens rule states $R \approx 1 - 2\sqrt{\dfrac{2\omega}{\varepsilon_\infty \omega_p^2 \tau}}$) as well as visible and near IR absorption ($\alpha \approx \dfrac{\varepsilon_\infty \omega_p^2}{2c\omega^2 n\tau}$ when $\omega^2 \gg \omega_p^2$) or the absorption peak near $\omega = \omega_p$ (with its maximum $\alpha_M \approx \dfrac{1}{c}\sqrt{\dfrac{\varepsilon_\infty \omega_p}{2\tau}}$). In every case, once ω_p fixed, increasing τ is the only way to improve the performances.

A lot of papers have been published on ITO thin films [3,4] which generally admit that electron scattering by ionised impurities is the only mechanism to take into account in order to justify the τ values observed. Consequently, decreasing the doping level to shift the plasma frequency towards lower IR values should decrease the concentration of the scattering centers and increase τ. This, however, is not observed and ITO performances drop when using low doping levels.

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Previous works have shown that Ge doping of either ITO, giving a material we have called ITGO [5,6], or of In_2O_3 [7], allows the electron mobility $\mu = \dfrac{q\tau}{m^*}$ to be improved. The present paper is devoted to the study of the electron mobility in ITGO thin films and its variation with temperature for various compositions using lower doping levels than in usual ITO (molar ratios $[Sn]/[In] \leq 0.05$ and $[Ge] = 0.2\,[Sn]$).
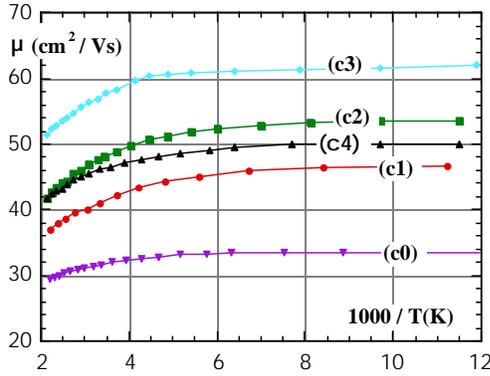
Experiments

A series of ITGO thin films with thicknesses from 340 nm to 1340 nm was deposited using constant experimental conditions: starting from a classical vacuum (limit $\approx 5 \times 10^{-7}$ mbar) with a 5 cm diameter target, deposition by RF magnetron sputtering ($P_{RF} = 20\,\text{W}$) in argon plasma (1 Pa) on glass substrates heated to $T = 320\,°\text{C}$. Five compositions were studied with the molar ratios $[Sn]/[In] = 0.05$ (composition $c1$), 0.025 ($c2$), 0.01 ($c3$), 0.005 ($c4$) et 0 ($c0 = $ pure In_2O_3), with $[Ge] = 0.2\,[Sn]$ in every case. The electron mobility and concentration were determined *versus* temperature from 77 to 500 K by conductivity and Hall measurements [1]. The results for $T = 300\,\text{K}$ are given in Table 1.

It is worth noting that the mobilities are higher than that usually obtained for sputtered ITO (about $\mu \approx 20\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ with $n \approx 1.5 \times 10^{21}\,\text{cm}^{-3}$) and that

Table 1. Conductivity and Hall results at 300 K.

Composition	thickness d (nm)	resistivity ρ ($10^{-4}\,\Omega$ cm)	electron concentration n (10^{20} cm^{-3})	electron mobility μ (cm^2 V^{-1} s^{-1})
$c1$	1340	1.49	10.5	40
$c2$	463	2.40	5.13	51
$c3$	583	4.23	2.62	56
$c4$	506	8.44	1.59	47
$c0$	340	17.23	1.15	32

Fig. 1. Electron mobility *versus* temperature for various ITGO film compositions.

Fig. 2. Verifying the relation $\mu_L(T) = \mu_L^O[\exp(h\nu_o/kT) - 1]$ for every ITGO composition.

the resistivity of composition $c1$ is quite low. The mobility reaches a maximum for composition $c3$ and then decreases with the doping level.

The electron concentration is higher than expected in films with $c0$ composition supposed to be "pure" In$_2$O$_3$ films. It points out the role played by oxygen vacancies giving this high doping level. This role is confirmed by the variation of the electronic properties obtained when slightly changing the initial pressure before to introduce argon: this initial pressure which mainly corresponds to water vapour, is one of the main parameters defining the rate of oxygen vacancies formation during sputtering. Optimizing the sputtering conditions (initial pressure, argon flow rate...) it has been possible to obtain as high mobility value as $\mu = 69\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ for composition $c3$ at 300 K.

Electron mobility dependence on temperature

The dependence of the electron mobility on temperature is plotted in Figure 1. The electron concentration is constant for every sample. In every case the mobility, constant at low temperatures, decreases for increasing temperatures. Electron scattering by ionized impurities alone would give a constant mobility with the value of the low temperature limit. It is thus easy to subtract this constant contribution μ_I from the total mobility $\mu(T)$ so as to obtain the contribution $\mu_L(T)$ of the other mechanism(s): $\mu_L(T)^{-1} = \mu(T)^{-1} - \mu_I^{-1}$. To check

if $\mu_L(T)$ has the temperature dependence involved by optical phonons scattering ($\mu_L(T) = \mu_L^O[\exp(h\nu_o/kT) - 1]$ with $\mu_L^O = Km^{*-3/2}$ [9]) we have plotted (Fig. 2) the variation of $\ln[1 + \mu_L(T)/\mu_L^O]$ *versus* $1000/T$. The constant μ_L^O had to be determined for every composition so as to obtain in every case a straight line crossing the origin. The whole set of points gives then a unique straight line whose slope ($h\nu_o/k$) allows the limiting frequency ν_o of longitudinal optical vibrations to be calculated. We obtain $\nu_o = 1.2 \times 10^{13}$ Hz to be compared to previously published values [3].

Electron mobility dependence on doping level

The electron mobility dependence on doping level is interesting to examine. The study of the thermoelectric power variations *versus* temperature [1,2] has shown that the electron effective mass m^* depends on the doping level. In the case of scattering by optical phonons, the μ_L^O term of the electron mobility depends on m^*: $\mu_L^O = Km^{*-3/2}$. Assuming $K \approx$ constant, its value has been determined by using $m^* = 0.52\,m_0$ obtained from thermoelectric power measurements [1,2] for composition $c1$. As shown in Table 2, the variation with composition of μ_L^O is well correlated with the m^* variation already observed [1,2].

Concerning ionized impurities scattering if the impurity concentration is supposed to be equal to the carrier one, neither the Conwell-Weisskopf [10] nor the Brooks-Herring [11] models can explain the mobility variation

Table 2. Effective mass dependence on ITGO composition.

Composition	$c1$	$c2$	$c3$	$c4$	$c0$
$\mu_L^O (\text{cm}^2/\text{V}^{-1}\text{s}^{-1})$	65.1	80.4	130.0	98.8	86.8
m^*/m_0 (from μ_L^O)	0.52	0.45	0.33	0.39	0.43
m^*/m_0 (thermoelectricpower [1])	0.52	0.42	0.31	0.36	0.45

obtained with its maximum at intermediate composition and its decrease for decreasing doping levels.

Another approach is suggested by the optical absorption results [1,8]. Absorption by localized states has been observed for compositions $c3$, $c4$ and $c0$. It can be explained as resulting of neutral defects corresponding to electronically occupied states due to oxygen vacancies. It means that, due to a relatively large ionisation energy, these oxygen vacancy states are not ionised. Electron scattering by these neutral defects then decreases the mobility. Their influence diminishes when increasing the doping concentration, the vanishing of this additive scattering mechanism for high doping levels being due to two main reasons: first doping by SnO_2 (and GeO_2) supplies oxygen excess (1 excess O for 2 Sn or Ge) causing the oxygen vacancy concentration to decrease and second, increasing the screening effect due to high carriers concentrations involves a broadening of the conduction band [1,8] and tends to delocalise the electrons on the oxygen vacancy states. These states are then probably merged into the conduction band and thus included into the carrier concentration N.

Conclusion

Studying the dependence of the electron mobility on temperature and composition in ITGO films, we have shown that optical phonons scattering has to be considered together with ionized impurities to explain the transport properties. The variation of the mobility with composition is well correlated with the effective mass variation already observed [1,2]. The mobility decrease observed for low doping concentrations can be understood by considering the neutral defects corresponding to occupied localized states due to oxygen vacancies. The oxygen vacancy concentration in the sputtered films is a fundamental parameter to be controlled in order to improve the properties for low doping levels.

References

1. C. Marcel, Ph.D. thesis, University of Bordeaux I, 1998.
2. C. Marcel, J. Salardenne (to be published).
3. I. Hamberg, C.G. Grandqvist, J. Appl. Phys. R **123**, 60 (1986).
4. H.L. Hartnagel, A.L. Dawar, A.K. Jain, C. Jagadish, in *Semiconducting transparent thin films*, Institute of Physics, (Publishing, Bristol and Philadelphia, 1995).
5. Y. Xu, Ph.D. thesis, University of Bordeaux I, 1994.
6. Y. Xu, J. Salardenne, S.J. Wen, G. Campet, T. Buffeteau, B. Desbat, S.S.I. Lett. (1992).
7. T. Maruyama, T. Tago, Appl. Phys. Lett. **64**, 11 (1994).
8. C. Marcel, J. Salardenne, P. Boy, E. Monterrat (to be published).
9. V.I. Fistul, in *Heavily doped semiconductors* (Plenum Press, New York, 1969).
10. E.M. Conwell, V.F. Weiskopf, Phys. Rev. **77**, 388 (1950).
11. H. Brooks, Phys. Rev. **83**, 879 (1951).