

Intrinsic performance limits in transparent conducting oxides

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Thin oxide films that are both transparent and electrically conducting have been studied extensively for over 20 years as a result of their wide range of technical applications. These include energy-efficient windows, burglar alarms and window heaters, as well as electrodes for solar cells and liquid-crystal displays. Efforts have concentrated on three systems: In_2O_3 , SnO_2 and ZnO . In each case there have been studies both of the pure oxides, where the conduction electrons result from oxygen vacancies acting as donors, and of mixed oxides, such as $\text{In}_2\text{O}_3:\text{Sn}$ or $\text{ZnO}:\text{Al}$, where the metal atom of higher valency is believed to form a donor state by substituting for an atom of the host metal. The aim of the present work was to examine the fundamental physical limits on the properties of these films, emphasizing the similarity between different oxides and showing that for all three systems mentioned here, the performance limits are now regularly being approached.

The basic physics of these transparent conducting films is now fairly clear, as was discussed by Hamberg and Granqvist [1]. The transparency results from a large bandgap (> 3 eV) which separates a full valence band from a conduction band partially filled by a degenerate electron gas with density 10^{25} – 10^{27} m^{-3} . The resistivity, ρ , of the films therefore depends on the scattering of the electrons in the degenerate gas according to

$$\rho = m^*/ne^2\tau$$

where m^* is the electron effective mass, n is the electron number density, e is the electronic charge and τ is the electron scattering time for Fermi surface electrons. The lowest attainable resistivity will be that resulting from those scattering mechanisms whose presence is essential to the combination of transparency and conductivity in the films. The most obvious such mechanism, ionized impurity scattering, will now be discussed, first to show that it must be present and secondly to estimate consequent limits on the resistivity.

In order to preserve charge neutrality in the films, there must be a number of positive charges sufficient to balance out the negatively charged free electrons. There are, of course, the ionized donor impurities from which the free electrons were originally produced. The Coulomb interaction between these impurities and the free electrons provides a source of scattering that is intrinsic to the doped material, and

which therefore sets a lower limit to the resistivity that can be achieved, regardless of scattering mechanisms such as neutral impurities, grain boundaries or other forms of structural disorder, the presence or absence of which depends on the precise details of the preparation procedure. A calculation of resistivity due to ionized impurity scattering will therefore give a lower limit to the attainable resistivity. In this letter we are concerned to illustrate the basic physics with the simplest and most transparent model, and consequently we use the calculation of Brooks [2] and Dingle [3], who used the Born approximation and Thomas–Fermi screening. The simplicity of the model also means that estimates of whether films will be able to meet a particular set of performance requirements can be made rapidly, without the need for complex calculation. Uncertainties (discussed below) in the values of material parameters and in our knowledge of the band structures also mean that the use of modern sophisticated free-electron theory is unjustified in this case.

Using the Coulomb interaction between the electrons and the impurities, Brooks and Dingle calculated independently in 1955 the resistivity for an electron gas of density n as

$$\rho = \frac{N_i Z^2 e^2 m^{*2}}{24\pi^3 (\epsilon_0 \epsilon_r)^2 \hbar^3 n^2} f(k_F)$$

where N_i is the number density of impurity centres with charge Ze , ϵ_r is the low-frequency relative permittivity and m^* is the conduction band effective electron mass. The function $f(k_F)$ is given by

$$f(k_F) = [\ln(1 + \beta^2) - \beta^2/(1 + \beta^2)]$$

and $\beta = 2k_F/\kappa_{\text{TF}}$, where κ_{TF} is the Thomas–Fermi screening wave vector.

To apply this to transparent conductors it is necessary to make certain assumptions about the doping. Most work has concentrated on doping by metallic substitution, as mentioned in the first paragraph. To calculate the resistivity in this case we put $Z = 1$ and $N_i = n$. This produces a lower resistivity than oxygen vacancy doping ($Z = 2N_i = n/2$) and is therefore appropriate for a calculation of lower limits as, in general, it is not clear to what extent the two possible doping mechanisms operate. The final parameters to be chosen are the effective mass and the low-frequency relative permittivity. For all systems, values of the effective mass lie in the range $0.25m_e$ to $0.4m_e$, with most around $0.3m_e$. Given the wide scatter, it is reasonable to take $0.3m_e$ for all of the substances. For the low-frequency relative permittivity there are much fewer literature

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data. However, a value of 8.14 for ZnO was given by Collins and Kleinman [4], 9 was given for In₂O₃ by Hamberg and Granqvist [1], and van Daal [5] gave 9 for SnO₂ along the *c*-axis, with a higher value of 14 along the *a*- and *b*-directions. To illustrate the resistivity limits, 9 will be taken for all of the systems. For a more complete discussion of the application of this calculation to transparent conductors, see Bellingham *et al.* [6].

The results of the calculation are shown as a function of carrier concentration in Fig. 1. Moore [7] calculated corrections to the original work of Dingle, based on second-order terms in the Born approximation; these have been included in the calculation for the plot in Fig. 1. The points are experimental data taken from the literature on all three substances; these have been chosen as showing low resistivity at any particular carrier concentration. The first point to make is that all three oxides show similar behaviour, strongly supporting the idea of a common scattering mechanism limiting the resistivity in all three cases. The second point is that, given the

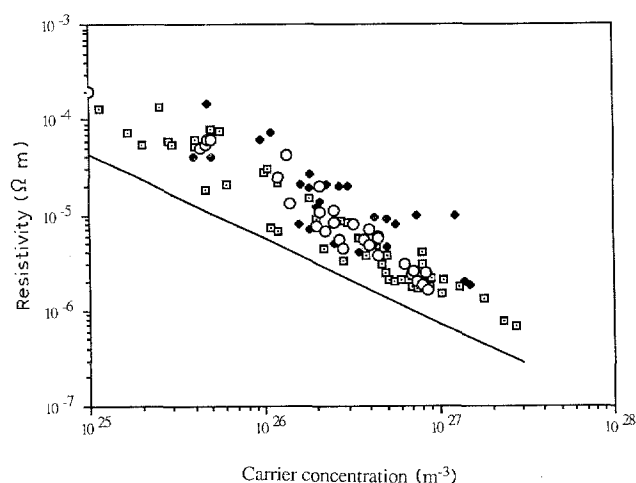


Figure 1 Literature data for the three oxide systems ((□) indium oxide, (◆) zinc oxide and (○) tin oxide) chosen as displaying low resistivity at any particular carrier concentration. The theory plot (—) is of the results of the calculation described in the text. The data for indium oxide were taken from [1, 6, 8–23]. The data for tin oxide were taken from [24–32] and the data for zinc oxide were taken from [33–41].

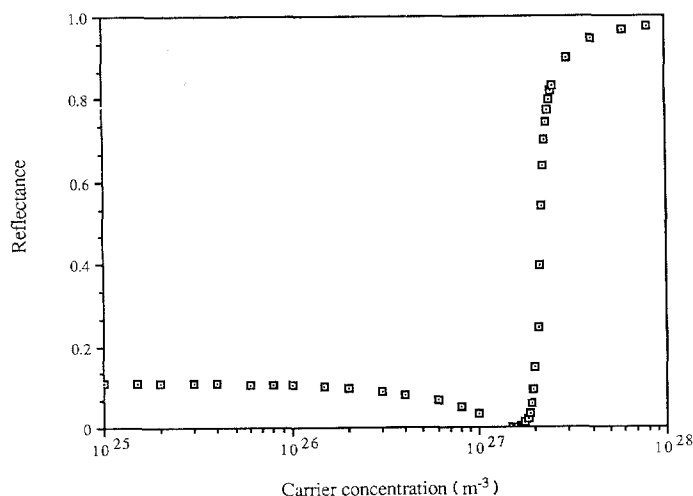


Figure 2 Reflectance at 800 nm for conducting oxides as a function of carrier concentration. The resistivity of the films was assumed to be given by the theory plot in Fig. 1.

uncertainties in the calculation, the data are totally consistent with the idea that this mechanism is ionized impurity scattering. It is therefore clear that, regardless of the oxide used, the details of the preparation process or the method of doping, the basic physics of these films sets a limit to the resistivity that can be achieved at any particular carrier concentration. As this limit is approximately inversely proportional to the carrier concentration, it can be seen as a limit on the electron mobility of about $9 \times 10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$.

From the argument presented above, it follows that lower-resistivity films can be produced by increasing the electron density, as the mobility stays roughly constant with the ionized impurity scattering. The problem, however, is that increases in carrier concentration lead to degradation of the optical properties. This occurs because any electron gas becomes reflective to radiation below the plasma frequency. This frequency is an increasing function of *n* and, consequently, as the electron concentration is increased, the films begin to reflect in the visible region as well as in the infrared. As an illustration of this, Fig. 2 shows calculations from the Drude theory of how the reflectivity at 800 nm (approximately the lowest-frequency visible radiation) varies as the carrier concentration of the films is changed. It is clear that values of *n* significantly above those presently achieved will result in reflective films that are useless for applications. The combination of a highest possible mobility (from the ionized impurity scattering alone) and a highest possible carrier density (from the requirement of transparency) results in there being an absolute lower limit on the resistivity. From the figures we see that this is about $4 \times 10^{-7} \text{ Ω m}$.

In conclusion, we have shown that a simple model illustrates the basic physics of the performance limits in transparent conducting oxide films. In particular, there is a well-defined limit to the achievable mobility resulting from the electron scattering, regardless of the system or the preparation method used. Experimental data show that this limit is now regularly approached. The requirement of transparency gives a further absolute limit to the conductivity of $2.5 \times 10^6 \text{ Ω}^{-1} \text{ m}^{-1}$. The simplicity of the

model also allows very rapid calculation of whether these oxides can meet any particular combination of required electrical or optical properties, since the performance limits are defined solely by the electron density in the films.

Acknowledgement

We thank Pilkington plc for financial support for this work.

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Received 24 April
and accepted 3 June 1991