Temperature dependence of Hall mobility in indium–tin oxide thin films

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Carrier concentrations and mobilities of vacuum-prepared indium–tin oxide films have been measured to determine the effects of annealing. The apparent variation of electron mobility with temperature in these films is interpreted in terms of a grain-boundary barrier model. No grain growth was observed in the films studied; all changes in electron density and mobility may be explained by oxygen diffusion in the grain boundaries and, from them, into the grains themselves.

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Thin films of indium oxide doped with about 10% tin (ITO) are well known as transparent conducting coatings produced typically in a vacuum process by the radio-frequency sputtering of the compacted oxide onto heated substrates.[1–3]. Investigations of such films are often limited to their visible transmittance and electrical conductance. If such films are to be used as selective coatings allowing visible radiation to be transmitted but strongly reflecting that of the infrared, the parameters of the electrical conductance become important.

The optical properties used are those given by the free carriers in the material and are simply described by Drude free-electron theory applied to a thin film.[4] The density of free carriers determines the transition point through the plasma frequency and the sharpness of the transition is determined by the electrical mobility through the free-carrier relaxation time.

We have made films by reactive ion plating onto room-temperature substrates which have been established as transparent and highly conducting with microcrystallite sizes of the order of 10 nm.[5] The origin of reversible and irreversible changes in the conduction parameters with changes in temperature is important in determining the nature and stability of the optical properties and measurements to determine these are reported here. A model of intergrain boundaries being affected by the diffusion of an active gas has been used recently to explain the changes of conductance seen with polycrystalline silicon.[6] The model was of a boundary being a carrier-depleted region of the crystal with many interband states. This subject is reviewed in detail by Kazmerski.[7] Here the model is used for a degenerate semiconductor where the effects may be expected to be less profound, interface states will have little effect, and any large depletion layer barrier effect on conduction will be reduced by tunneling. Thermal emission over a small barrier is used to describe the intergrain conduction process and is illustrated in Fig. 1. This is adapted from the model of Anderson.[8] Carrier concentrations within the boundary between two microcrystallites, n_2, and that within the crystal n_1, are related by: $n_2 \simeq n_1 \exp[-(q\phi/kT)]$; ϕ is the potential boundary at the interface. When the mobility is limited by a mean free path constrained by the size of the grain, the conductance will be determined by the number of carriers able to cross the boundary. i.e., $\sigma = n_2 q\mu_B$; μ_0 is the intragrain mobility. Hall mobilities will give n_1 and μ_H. μ_H will show an apparent dependence on absolute temperature given by $\mu_H = \mu_B \exp[(-q\phi/kT)]$. μ_B will be expected to show some temperature dependence.

The experimental data to be discussed is summarized in Fig. 2 and Table I. They were obtained in a magnetic field of 0.6 T with a six-electrode configuration (current injection, voltage drop, Hall voltage V_H). Each run from 70 K to ambient includes a preliminary point at room temperature to check stability.

It was established by careful inspection of V_H as temperature changed that the variation of conductivity was entirely due to mobility changes to within the accuracy of the experiment. Carrier density N is, therefore, shown as constant for each experimental run. No significant thermal variation in N is expected for a degenerate semiconductor.

In most cases the films had a negative temperature coefficient of resistance (TCR) which was attributed to barrier effects. In no case was an "activation energy" greater than kT observed and in no case where a positive TCR was noted, was any simple relationship with T established to fit a scattering model for μ_B.

Film JR will be discussed first in terms of the grain-boundary model. When the temperature exceeds ambient in air, the film's grain boundaries absorb air and μ_H decreases (curve A) as ϕ is increased. This latter effect is shown when the process is repeated (curve B) which also clarifies the point that there appears to be some recovery of the mobility between two experiments. When room temperature is again

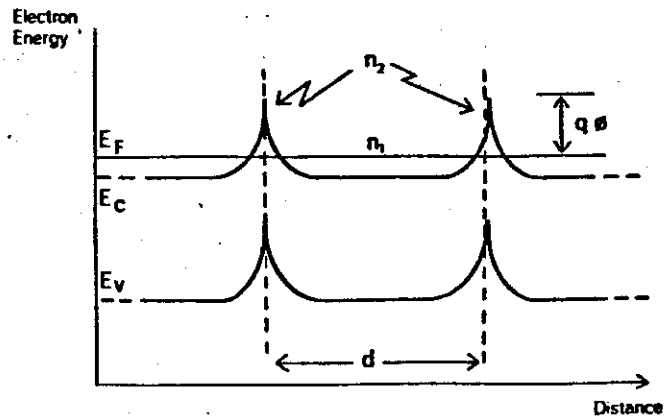

FIG. 1. Grain-boundary barrier model.

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TABLE I. Conductivity data for Fig. 2.

Film	Test	Electron density N ($\times 10^{26}$/m^3)	Mobility at 293 K μ_R ($\times 10^{-4}$ m^2/V s)	Conductivity at 293 K σ_R ($\times 10^4/\Omega$ m)
JR	A	2.72	11.8	5.1
	B	2.66	11.15	4.9
	C	2.55	11.3	4.6
	D	1.92	6.8	2.1
	E	10.00	12.9	20.6
KA/1	P	16.97	7.2	19.6
	Q	...	...	2–3
KJ	X	3.25	9.3	4.8
	Y.	18.20	9.8	28.4

exceeded, (curve B) mobility falls and then rises again during cooling to ambient. The first annealing reduced N (Table I), by oxygen compensation of donor centers, and this happened again throughout the second annealing. These results suggest that oxygen diffuses into the film along grain boundaries (increasing ϕ), and, from these, into the grains themselves (reducing N). As temperature falls after annealing (curve B), the barrier oxygen entering the grain is not replaced and ϕ partly recovers. Curve C shows the characteristics then obtained and curve D shows the results after heating in air at 403 K. The film was then warmed *in vacuo* for 18 h after which curve E was measured with a mixed positive/negative TCR. Here, it is suggested the oxygen has desorbed sufficiently from the film so that the barrier is only comparable with other scattering mechanisms at very low temperatures. The most significant result here, however, is that *both* absorption effects are reversible. At the relatively low temperatures employed, grain growth is not expected and it requires little imagination to visualize curves A–E having a common intercept μ_B.

It is widely known that very opaque brown ITO films may be made transparent by heating to 350–450 °C in air.[5] An experiment was performed to establish the mechanism for this change. We believe that the characteristic brown color of this type of film, which possesses a high carrier density, comes from optical scattering by excess metallic clusters. Either these occlusions or increased electron-electron interactions due to the high carrier density similarly limit the intragrain mobility. Two samples from the KA deposition were used, prepared by sputtering in an atmosphere with insufficient oxygen.

As the first sample (KA/1) was heated in air, it behaved similarly to film JR until 355 K (the minimum in curve P) when N began to fall and μ_H rose rapidly. At 355 K, $\mu = 6.9\times10^{-4}$ m^2/V s and $N = 17.0\times10^{26}$/m; at the next two points μ increased to 7.1×10^{-4} and 11.3×10^{-4} cm^2/V s as N fell to 14.4×10^{26} and then 8.2×10^{26}/m^3. As T was further increased to 835 K the resistance continued to rise. Only conductance could be measured later (curve Q relates to the right-hand scale) to show the form of mobility variations. Note that the absolute magnitude cannot be related to earlier measurements since the film partially broke up under thermal stress beyond 620 K.)

After the annealing, the film was transparent with a faint greenish tinge from interference effects. (At 650 nm it was much thicker than the 100-nm films described elsewhere here.) The results demonstrate that the oxidation of the metallic clusters which cause optical scattering also decreases N and increases μ. Again, grain growth is not expected to be significant at 355 K; certainly at these temperatures it is not likely to be as rapid as the change observed in μ. The alternative conclusion that μ_B was limited by scattering from the metallic content is preferred.

In a further experiment to establish these mechanisms, the second KA sample (KA/2) was annealed at around 650 K *in vacuo* with a second film (KJ) which began with very acceptable optical properties. KA/2 also broke up; once

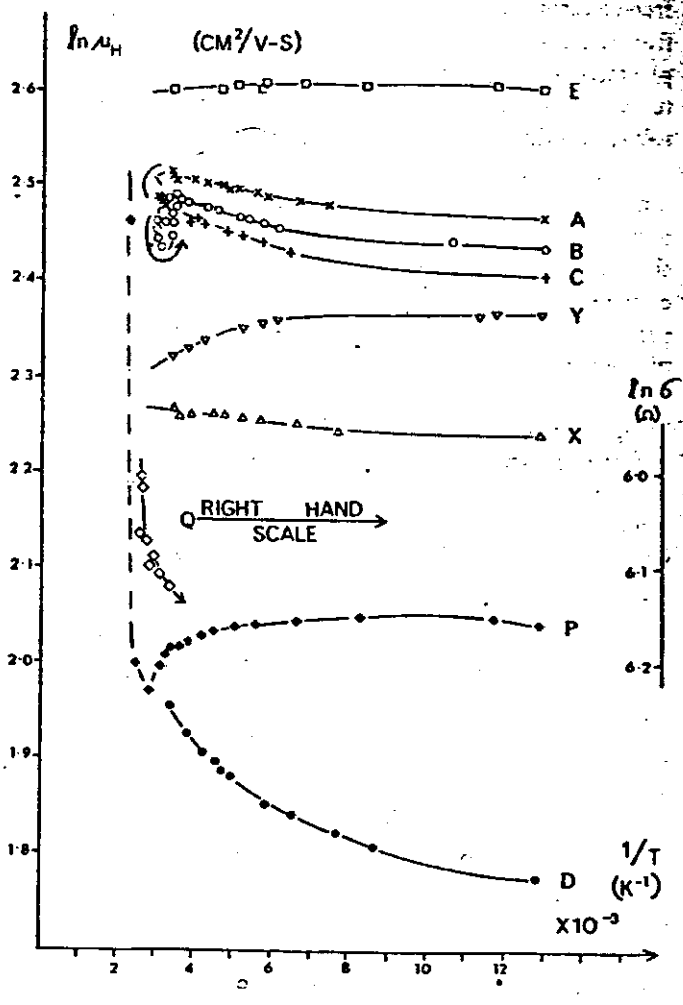

FIG. 2. Hall mobility (μ_H) and conductivity (σ) changes shown as a function of reciprocal temperature; the explanation of the legends is in the main text.

again both the resistivity and transparency increased. It would appear that there is sufficient free oxygen contained within the films to oxidize the surplus metal even *in vacuo*. While KJ changes appearance subtly from a slight yellowish tinge to a grey one, the cause is not obvious. The electron density increased significantly, but while mobility also arises due to oxygen desorption (curves X and Y) μ_B changes only slightly. There does not appear to have been any grain growth. The small reduction in μ_B may be caused by an increase in intragrain scattering by electron-electron interactions.

The results are important in that if mobility is limited by intragrain scattering, then the optical properties exhibited by the film will only deteriorate, due to surface roughness, if preparation methods are changed to give improved microcrystallite size. An estimate of the mean free path of these films suggest that this is of the same order as the grain size for these films measured here. Measurement of Hall mobility on films of indium oxide, which are twice those of indium tin oxide,[7] suggests that the mobilities are limited by bulk scattering rather than intergrain scattering. The influence of temperature on the properties of the films is well described by a view of reversible oxygen diffusion into and from the film through grain boundaries.

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