GENERATION RECOMBINATION NOISE IN REDUCED RUTILE (TiO_2)

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Generation recombination noise was observed in reduced rutile doped with aluminum in the frequency range of 25 Hz - 40 kHz and at temperatures ranging from 77°K up to 300°K.

Reduced rutile is a n-type semiconductor for which band-conduction has been amply demonstrated. There are authors, who interprete their experimental Hall coefficient, resistivity and thermoelectric power data in terms of single-band conduction [1], whereas Becker and Hosler assume multiple-band conduction [2]. As far as the type of donors centers is concerned there have been authors in favour of oxygen vacancies although recent publications all agree upon titanium interstitials [1,3]. It was felt worthwhile to study the noise behaviour of reduced rutile partly in view of the controversies quoted above.

Samples were obtained cut from crystals grown in the 001-direction. These crystals, with and without alumina added, were manufactured by the National Lead Company, South Amboy, N.J., USA. The samples were polished with carborundum and subsequently reduced at a temperature of 600 - 800°C in vacuum of 0.1 - 1 mm Hg pressure. In order to apply ohmic contacts we availed ourselves of a method due to Acket [1,4]. At first the samples were polished in molten KOH in order to eliminate high-resistance surface layers. Next indium contacts were soldered on the samples.

Noise measurements were performed using separate current and voltage probes in order to eliminate contributions due to contact resistance.

By passing a current through the samples, where the direction of the current was perpendicular the cristallographic c-axis, generation recombination noise could be observed [5].

This g-r noise gave rise to at most three relaxation times [5] in the frequency range of 25Hz-40kHz. Since samples were available with different aluminum dopes and since the reduction as well as the temperature could be varied the relaxation times could be studied in dependence of this dope, reduction and temperature. The results

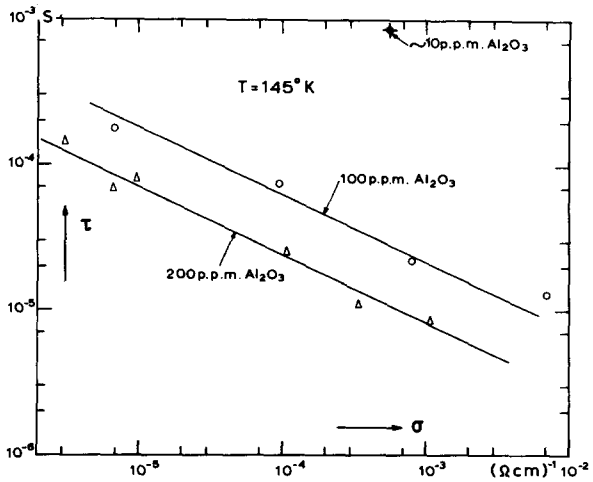

Fig. 1. The relaxation time τ_2 versus conductivity at a temperature of 145°K with the aluminum dope as parameter.

can be summed up as follows:

a) Samples with the lowest aluminum dope showed in general two relaxation times τ_1 and τ_2, where $\tau_1 < \tau_2$.

b) τ_1 was found to be independent of temperature in the whole temperature range considered.

c) τ_2 depends on the aluminum dope and on the conductivity of the material. Comparing results from different samples with different aluminum dopes but with the same conductivity at the same temperature ($T < 160$°K) it turned out that τ_2 is roughly proportional to the inverse aluminum concentration. Comparing results from one sample at the same temperature but with different conductivities obtained by varying the reduction, τ_2 decreased with increasing conductivity. Figs. 1 and 2 show this behaviour.

d) τ_2 increases with decreasing temperature starting from 300°K. At temperatures below 170°K τ_2 was independent of temperature.

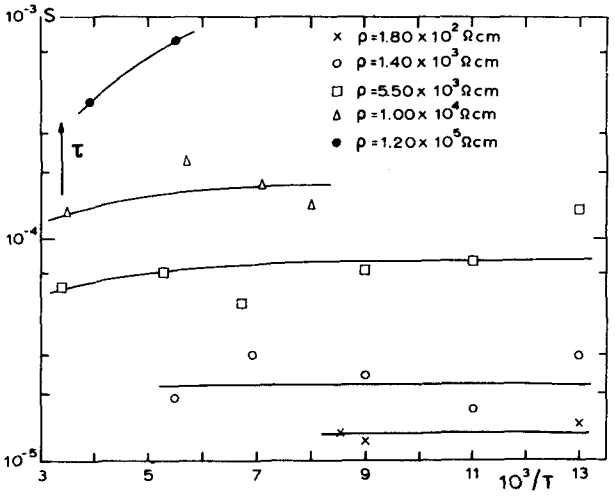

Fig. 2. The relaxation time τ_2 versus $10^3/T$ for a sample doped with 100 ppm Al_2O_3.

e) A third relaxation time was observed at a temperature of about 80°K in aluminum free material (about 10 ppm) with a room temperature resistivity of 2000 Ωcm.

The results quoted could be interpreted in terms of single band conduction and in general two "active" levels in the forbidden band. In a particular case (see under e) a third level apparently came into play. Also a double band conduction model as proposed by Becker and Hosler [2] would give rise to g-r noise caused by fluctuations in band to band transitions since the product between mobility and density of states in much larger for the upper band than for the lower band [2]. These fluctuations, however, should be very rapid and therefore indistinguishable in our frequency range. As a consequence our results are not understandable in terms of band to band fluctuations. As far as levels in the forbidden band are concerned several authors agree upon a donor level at 0.006 eV below the bottom of the conduction band which should be fully ionised in our case and should not contribute to the fluctuations. A second activation energy observed in Hall effect data is interpreted as the difference between the bottoms of their conduction bands by Becker and Hosler [2], whereas we follow Acket [1,4] in associating this energy with a 0.03 eV donor level. At 0.05 eV there is an acceptor level associated with aluminum centers. This fact is firmly established by Acket and Volger [1] and supported by Yahia [6] who makes plausible that aluminum centers should at least give rise to one additional acceptor level, besides a deep lying one. The latter is responsible for p-type conductivity at high temperatures (~ 1000°K) [6] and acts as a compensating level in our case. In order to explain our results we need an extra donor level. The possibility of such a level is indicated in the literature [1,2] although there is considerable uncertainty about the energy of the level. Our low temperature results can be explained only if we assume that the position of the Fermi level is in between this level and the 0.05 acceptor level. Since the position of the Fermi level was known in our experiments we estimate the energy at about 0.15 eV. On the basis of this analysis consistent with visualizing titanium interstitials as donor centers, the capture cross sections of the acceptor and donor centers with energies at 0.05 eV and 0.15 eV respectively, could be calculated. Room temperature values of about 10^{-22} cm^2 and 10^{-19} cm^2 were obtained, whereas at 100°K the respective values were 10^{-22} cm^2 and 10^{-15} cm^2. Apparently the cross section of the aluminum center, which should be repulsive [6], is almost independent of temperature, which indicates capture by tunneling. The donor, cross section, an attractive center [1] increases strongly with decreasing temperature, a behaviour predicted by Lax [7].

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