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Ceramic Titanate Rectifying Barriers

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A new method of fabricating silver-ceramic barium titanate rectifying junctions is described. Measurements of current voltage characteristics, barrier capacitance and distribution of donor density within the barrier are presented. The results indicate the possibility of a thin insulating layer within the barrier. The effect of trapping levels in the space charge region is also considered.

REPORTS on titanium dioxide rectifying barriers have been made by a number of investigators[1-5]. These reports indicate a diode type behaviour in metal-titanium dioxide junctions with considerable departures from an ideal diode theory. The standard methods to ascertain the nature of rectifying junctions have been by study of the volt-ampere characteristics and by differential capacitance measurements. These methods are based on a number of assumptions which are almost always violated in practice. To obviate this difficulty, the nature of the rectification process has been studied by observing the deviations of the diode behaviour from that predicted for an ideal diode and the results are reported in the present paper.

Fabrication of Diodes

The diodes studied were prepared from high dielectric constant ceramic barium titanate with traces of strontium and zirconium titanate as impurities. The word ceramic has been used to imply a polycrystalline substance with impurities and defects. These materials are being used widely in the industry for the manufacture of ceramic capacitors. The samples, usually of circular cross-section, 0·25 in. in diameter and 20 mils thick, were first reduced[6] in dry forming gas (75 per cent nitrogen plus 25 per cent hydrogen) at a temperature of about 1300°C. The temperature and duration of reduction, in general, depend upon the size of the chip. After the reduction process the resulting samples are called, for lack of a better name, reduced samples. During reduction, the colour of the chip changes from grey to dark blue indicating a loss of oxygen in the reduction process. After reduction, a marked increase in the conductivity of the sample is observed[7]; the greater the degree of reduction, the larger is the conductivity. For example, samples which were originally insulators exhibited a conductivity of 350 ohms per square after reduction. Even though the amphoteric nature of these titanate semiconductors is well known, the *n*-type conductivity of the samples under study has been established beyond doubt. On one side of these reduced semiconducting ceramic chips, a conducting silver paint was silk screened to cover an area of about 0·028 sq. in. The samples were dried in air and fired in a box furnace for a period ranging from 30 to 60 min. at 700° to 800°C. A blocking contact was observed at the silver-ceramic junction. A second electrode was added to the other side of the chip by painting with a conducting 'air-dry' silver paste. In selecting this silver paint care was taken to assure an ohmic contact. These diodes were then tested for their electrical characteristics.

Electrical Characteristics

Some typical, rather than favourable, volt-ampere characteristics have been chosen and plotted. Fig. 1 shows one such graph. If the junction were to be a *p-n* type junction, the forward current would depend on the voltage in an exponential manner according to the relation

$$I_f = I_0[\exp(qv/BkT)-1]$$

where B is a dimensionless coefficient which is determined from the slope of the ln I_f versus V graph. The classical value of B is unity. Allowing generation and recombination at traps in the space charge region, Sah *et al.*[8] predicted a value

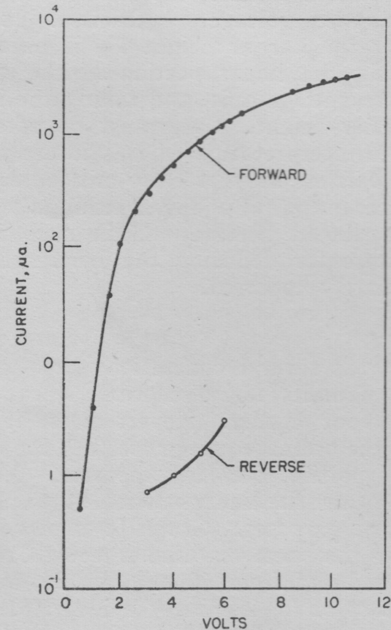

Fig. 1 — Semilog plot of d.c. current versus terminal voltage measured at room temperature [The area of the metallized portion is 0·028 sq. in. in all cases and the samples were fired at 800°C. for 60 min.]

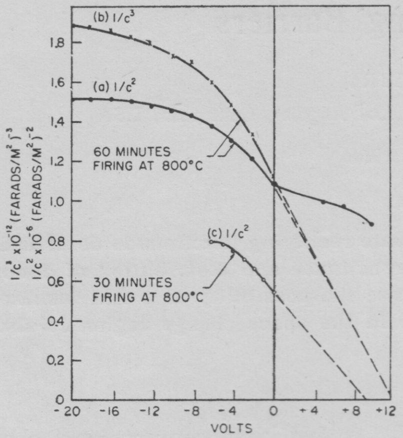

Fig. 2 — Variation of the voltage applied across the barrier with the reciprocal of the square and cube of capacitance (C)

of 2, but not more. From Fig. 1, the measured value of B is about 2·4 for low voltages and changes continuously with voltage for high voltages. This is a marked deviation from all known classical models and an attempt is made in the next section to obtain a description of the nature of the junction by studying this and other such effects.

The differential capacitance measurements were taken on a General Radio impedance bridge, model 1650 A. The values of capacitance and dissipation factors were measured at 1 kc/s. for various voltages across the junction. The independence of the series resistance of the diode with applied voltage causes very little change in the slope of $1/C^2$ versus V when compared with the $(1/C')^2$ versus V graph where C' and C are respectively the measured and actual capacitances of the reverse biased junction. Fig. 2 shows a plot of the square of the reciprocal of the barrier capacitance as ordinate and the applied voltage as abscissa. It is well known that the barrier height V_B is obtained by extrapolating the linear portion of the graph to intersect the voltage axis, and taking the intercept as the barrier height. Care must be taken, however, in the interpretation of this intercept value; composite barriers may produce misleading results. For instance, graph (a) of Fig. 2 exhibits very little perceptible linear portion and in such instances the procedure for deducing the barrier height is not immediately apparent.

Discussion

From Fig. 2 several conclusions can be drawn. Graph (a) exhibits no perceptible linear portion as pointed out earlier. Nevertheless, if $1/C^3$ is plotted as the ordinate [see graph (b)], the existence of a linear portion becomes apparent. Now it is more easy to see the linear portion of graph (a) for extrapolation purposes. Graph (c) shows the same relation for the same material but with the firing time now reduced from 60 min. to 30 min. The linear portion of (c) is clearly evident. It is well known that the capacitance of a linear graded junction varies as $V^{-1/3}$ whereas the capacitance of an abrupt junction varies as $V^{-1/2}$. Thus, it appears that samples fired for shorter durations behave like abrupt junctions [see graph (c)], and those fired for longer durations behave like diffused junctions [see graph (b)]. This gives reason to doubt the occurrence of some kind of ‘diffusion-like’ process of reoxidation of the reduced substrate during the silver firing stage.

Extrapolating the linear parts of graphs (b) and (c) of Fig. 2 one can see that the apparent barrier heights are respectively 9·5 and 12·5 V. These values are unusually high and casts some doubt about the validity of a model with a plain diffusion type junction.

A knowledge of the density of the uncompensated ionized donors is helpful at this stage. The density of uncompensated ionized donors at a depth x from the silver contact is given by the Schottky relation

$$N(x) = \frac{2}{\epsilon q}\,\frac{dv}{dC^{-2}}$$

where $x = \epsilon/C$; ϵ_t is the dielectric constant; q, the electronic charge; and C, the capacitance measured across the junction when the applied voltage is V. The doping profile (Fig. 3) can be obtained by plotting x as abscissa and $N(x)$ as ordinate. This graph indicates that the junction conforms more with the Bethe[2] model than the Shockley model. A Bethe model of a potential barrier is same as the Schottky model, except that a uniform insulating layer, with thickness t, separates the metal contact from the semiconductor. In the Bethe model, the potential varies linearly with distance throughout the insulating layer and quadratically with distance in the adjacent semiconducting region in which there is a space charge.

In the light of this result it is easier to interpret the results obtained from Fig. 2. Because the original ceramic was an insulator and the reduced ceramic a semiconductor, it is possible to expect

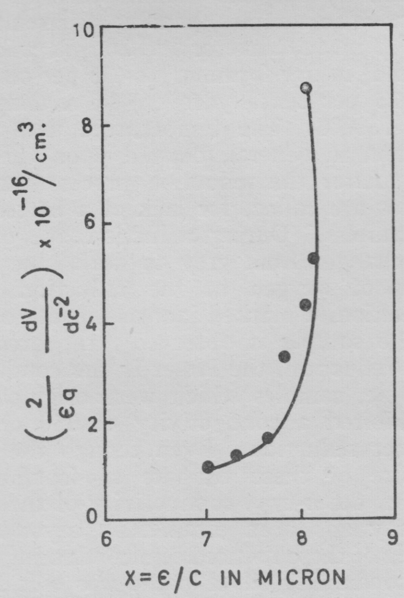

Fig. 3 — Variation of donor concentration $N(x)$ with barrier width x [The slope dV/dC^{-2} was approximately obtained from the slope between adjacent points in Fig. 2]

the reoxidized ceramic to behave once again like an insulator. This means that any model for a diode should include the presence of an insulating layer sandwiched between the metallic silver and the semiconducting titanate.

For the case of an insulating layer adjacent to a space charge region, it can be shown[9,10] that the intercept value[3] is

$$X = V_B + \left(\frac{Nq\epsilon_t^2}{2\epsilon_t^2}\right) + (2q\epsilon NX)^2 \frac{t}{\epsilon_t}$$

where X is the intercept of the linear portion of the graph (see Fig. 2) on the voltage axis; t, the thickness of the insulating layer; ϵ_t, the dielectric constant of the insulating layer (assumed to be the same, i.e. 1250, as that of the original unreduced titanate, which is designated by ϵ); N, the carrier concentration; and q, the electronic charge. Ref. 9 gives a slightly different formula than the one in ref. 10. Both formulae, however, give approximately the same result. The value of N is obtained from the inverse slope of $1/C^2$ versus V graph. Assuming the unknown value of V_B as approximately 1 V., which is a reasonable guess, and substituting 12·5 for X, a value of 2-3 μ is obtained for the thickness of the insulating layer. From graph (c) of Fig. 2, the intercept value is about 9·5 and the corresponding thickness of the insulating layer, as calculated from the above formula, is about 1 μ. This indicates that the thickness of the insulating layer at the interface increases with longer durations of firing. This result gives support to the assertion that some kind of diffusion like reoxidation takes place during the silver firing stage. It has been established that the values of the thicknesses obtained above were correct within an order of magnitude. Once the value of t is established, its contribution to the reverse biased junction can be calculated. The total capacitance of the junction, then, is the series combination of this capacitance and that due to the space charge region. The extremely thin insulating layer with a large dielectric constant, therefore, contributes substantially to the overall capacitance of the junction.

While discussing the volt-ampere characteristics it has been pointed out that the variation of B from the classical value is probably due to trapping effects. If it is assumed that a large deep trap density exists adjacent to the blocking contact, then the space charge region will be quite narrow, resulting both in a fairly high reverse bias capacitance and relatively large reverse bias leakage current. This is precisely what was observed by the author. Fig. 4 shows plots of leakage current and capacitance as a function of voltage.

It is not surprising, therefore, that extremely large values of capacitance were observed. Indeed, it was reported some time ago[11] that reduced barium titanate exhibits extremely large dielectric constants. In the light of the present investigation it appears that this ' increase ' in dielectric constant is perhaps not due to hydrogen reduction as asserted in the said reference but due to the thin insulating layer at the interface and the narrow space charge region. Measurements indicated that the absolute value of this capacitance at a given d.c. voltage is exactly twice the capacitance obtained by having blocking contacts on both sides of the chip. The capacitance measured with two blocking contacts was found to be almost the same as the value that would be obtained by assuming a hypothetical ' increase ' in the dielectric constant of the reduced ceramic.

A study of the reverse characteristics also revealed some interesting points. All the reverse characteristics, without exception, exhibited a pronounced hysteresis which increases with increasing temperature or increasing voltage. The ' hysteresis loop ' as observed on the oscilloscope was extremely unstable and was found to oscillate vigorously and never at equilibrium. The forward current, however, was found to be substantially uneffected with changes in temperature. No satisfactory reason was found to explain this phenomena. This may perhaps be due to an excessive density of states with small activation energies. If, however, the reverse bias were maintained for a long time, the transient subsided, resulting in a slightly lower capacitance and lower reverse current than at the instant immediately following the application of voltage. It is tempting to ascribe this behaviour to some kind of space charge limited electron flow with trap filling and emptying phenomena where the trap density varies nonlinearly with energy, or else to space charge limited double injection of mobile carriers into the insulating layer. This suspicion is supported by the near-cube law (strictly speaking, greater than square law) variation[12] of current with applied voltage (see Fig. 5).

Two-carrier space charge limited currents require a cathode and an anode which are capable of injecting electrons and holes. If holes were injected from the rectifying barrier into the semiconducting ceramic substrate, the hole storage effect could be expected to make the capacitance under forward bias increase very sharply. As this is not the case, it appears that conduction is dominated by electrons. It seems that injection occurs only at one contact, viz. at the fired on silver contact, and the injected carriers are electrons. Under these conditions the problem can be considered as one of the determination of the volt-ampere characteristics for space charge limited currents through an

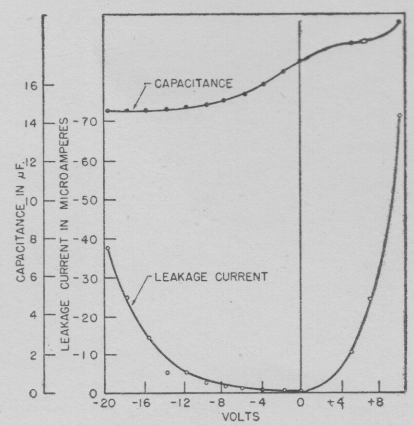

Fig. 4 — Plot of capacitance (C) and leakage current versus applied voltage

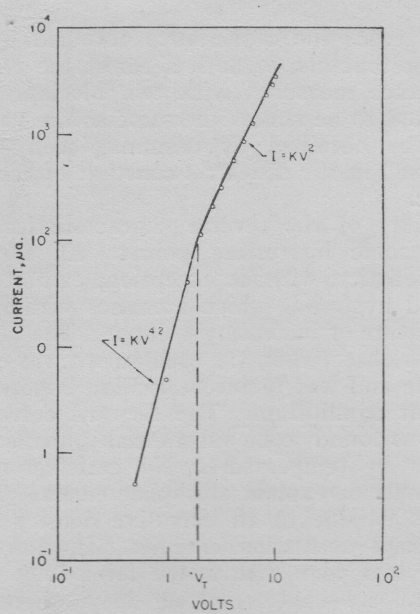

Fig. 5 — Log-log plot of d.c. current versus terminal voltage [The failure of the square law behaviour below a threshold voltage V_T is evident]

insulating layer. The problem greatly simplifies if one considers anode charge as a function of voltage rather than current as a function of voltage. If traps are assumed to exist at a discrete level, a square law relation can be established[13] between current density J and applied voltage V.

$$J = (\text{constant}).V^2$$

If traps are, more or less, distributed in energy, a power law behaviour that is greater than a square law should appear[14]. Fig. 5 indicates a square law behaviour above a threshold voltage V_T. This threshold voltage may be interpreted as the voltage at which all the traps get completely filled and the volt-ampere characteristics approach the square law region in an asymptotic manner.

Conclusion

It seems reasonable to conclude, in the light of the present evidence, that an insulating layer indeed exists adjacent to the blocking contact. In ceramic materials trapping effects are likely to play a prominent role in the determination of the nature of the junction. There is scope for further study. For example, the feasibility to transmit currents of useful magnitudes through the insulating layer by Schottky emission should be investigated. This may be a step towards the development of a ceramic triode. An attractive feature of the method of fabrication presented here is in the simplicity of the technology involved and a feasibility for batch processing.

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