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SEM EBIC INVESTIGATIONS OF ZnO VARISTOR CERAMICS

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Résumé - Le courant induit (EBIC) obtenu sur des varistances à base d'oxyde de zinc est étudié au microscope électronique à balayage (SEM). On trouve que seuls des joints de grains particuliers produisent un signal EBIC et que l'intensité du signal enregistré sur une ligne, présente une forte variation avec la polarisation appliquée. Les résultats des expériences sont discutés en termes d'émission Schottky des porteurs majoritaires sur la barrière de potentiel des joints de grains.

Abstract - The electron beam induced conductivity (EBIC) of zinc oxide varistor ceramics is studied in the scanning electron microscope (SEM). It is found that only particular grain boundaries give rise to an EBIC signal and that the signal strength and its linescan profile show strong variation with bias voltage. The experimental results are discussed in terms of Schottky emission of majority carriers across the grain boundary potential barrier.

Introduction

ZnO varistor ceramics exhibit strongly non-linear electrical characteristics /1,2/. Responsible for the non-linear behaviour are the grain boundaries (GB's) in the ceramics, where double Schottky barriers are formed due to charged GB interface states /3/. Basic methods for the investigation of the space charge structures associated with these barriers are measurements of the current-voltage, current-temperature and capacitance-voltage characteristics, which have rendered most of the existing knowledge about the electrical properties of the GB's /4,5/. The main disadvantage of these methods results from the fact that local variations in the GB properties are not detected and even have to be excluded in the interpretation of the data. Therefore an improved understanding of the GB's requires spatially resolving methods to enable a local evaluation of their electrical properties. A most promising method for this purpose is offered by EBIC measurements in the SEM as will be reported on in this paper.

Experimental

The investigated sample is a commercial ZnO varistor (SIOV-S05K11), which has been cut perpendicular to the two contacted surfaces. The cross sectional area obtained in this way was carefully polished for the investigation in the SEM but due to the material structure a large number of pores proved unavoidable. The experimental arrangement is schematically depicted in fig. 1. The sample is connected in series with a constant voltage source and a current preamplifier. The EBIC signal is separated from the dc bias current by chopping the electron beam and using a lock-in-amplifier. The measurements were performed at 30keV primary electron energy, 50nA beam current and 100kHz chopping frequency.

Results

Figs. 2a,b show micrographs of the same sample area at a bias voltage of 0V and 10V respectively. While at 0V the complete grain structure is imaged with the pores appearing as bright dots the micrograph at 10V reveals only particular GB's or sec-
Fig. 1 - Schematic representation of the experimental arrangement for the measurement of the electron beam induced conductivity.

Fig. 2 - Micrographs of the same sample area at a bias voltage of a) 0V and b) 10V.

rected for the absorbed current. But in view of curve (a) and many similar ones the signal increase is better classified in a general way as superlinear. The maximum occurs at different bias voltages for different GB’s and it may be pronounced as in curve (b) or flat and resembling a saturation behaviour as in curve (a). The decreasing branch of the curves terminates at that value of the bias voltage, where the current amplifier is driven into saturation due to the large dc bias current (1mA). Due to aging effects this value decreases gradually during hours of applied bias, and for this reason curve (a) and (b) terminate at different voltages.

Fig. 4 shows two linescans across an individual GB running parallel to the contacts at a bias voltage of 8.5 and 12V respectively. The voltages correspond to similar signal levels at the increasing and decreasing branch of the curves in fig. 3 with the maximum for this particular GB being at 10V. The linescan profiles are symmetrical here but in most cases asymmetrical profiles have been observed due to the fact that the GB’s are in general not exactly normal to the irradiated surface. As can be seen from fig. 4 the shape of the linescan changes slightly with increasing voltage and the peak width is becoming smaller.

Discussion

At 0V bias voltage the signal is constituted of that part of the absorbed primary electrons which flows to ground via the current amplifier (see fig. 1). The other part of the absorbed electrons flows to ground via the voltage source and is not detected. The magnitude of these two components is given by the ratio of the resistance values for the current path from the e-beam position to the right and left con-
tact respectively. This ratio changes only when the e-beam moves across a GB, since the resistance is exclusively controlled by the GB's. Thus the signal is different from grain to grain and for suited interconnections from the left to the right contact drops stepwise at each GB.

At non-zero bias the excess charge carriers generated by the pulsed e-beam lead to a periodical increase of the dc bias current which is detected as the EBIC-signal. Inside the grains the effect of carrier generation is negligible since there is a large concentration of free electrons (~10^{17} cm^{-3}) even before. At the GB's, however, there is a depletion of free carriers due to the acceptor-like, negatively charged interface states \(/3,5/\). The holes generated by the e-beam can be captured there into these states resulting in a reduction of the interface charge density \(Q\) and the associated electrical barrier \(V_B\) (see fig.5), which in a simplified approach can be written \(/5,6/\):

\[
V_B = V_{B_0} \left( \frac{Q}{Q_0} - \frac{1}{4} \frac{Q}{Q} \frac{V}{V_{B_0}} \right)^2
\]

\(V\) is the voltage drop across the GB which is a certain fraction of the voltage applied to the ceramics. \(Q\) is expected to increase with \(V\) or to remain constant \(/3,6/\) and \(Q_0\) and \(V_{B_0}\) are the values of \(Q\) and \(V_B\) at \(V=0\). The EBIC signal resulting from a reduction of \(Q\) or \(V_B\) by an amount \(\Delta Q\) or \(\Delta V_B\) respectively depends on the current-voltage relationship, which in terms of Schottky emission \(/6/\) and for \(V \gg kT/q\) is given by

\[
J = A^* T^2 \exp \left[ - \frac{(E_C - E_F) + qV_B}{kT} \right]
\]

\(A^*\) is the effective Richardson constant, \(T\) the absolute temperature and \(E_F\) the Fermi level in the bulk of the grains. With eq.(2) the EBIC signal becomes

\[
\Delta J = J \left[ \exp \left( \frac{q \Delta V_B}{kT} \right) - 1 \right]
\]

Since the varistor ceramics constitutes a complicated resistor network only those GB's which decisively control the current transport \((J \neq 0)\) will give an EBIC signal. This implies that the voltage drop is different from GB to GB. Along the same GB no difference in the voltage drop should exist, however, due to the high conductivity of the grains. Therefore the variation of the EBIC signal between adjacent sections of the same GB must be related to local changes in the electrical properties i.e. in \(Q\) and \(V_B\).
According to eq. (1) - (3) the EBIC signal $\Delta J$ depends on $V$ both via $J$ and via $AVB$. To enable a calculation of $\Delta J$ we have introduced the assumptions that $Q$ remains approximately constant or increases only slightly with $V$ and that the $\Delta Q$ induced by the e-beam is independent of $V$, which seems very reasonable for constant $Q$. The resulting $\Delta J(V)$-dependence (fig. 6) first increases superlinearly and for $V \rightarrow 4VB_0$ ($V_B \rightarrow 0$) gradually turns into a saturation value, which is qualitatively in good accordance with the experimental result up to the maximum of the curves. A quantitative comparison between the theoretical and the experimental result in this voltage range is prevented by the fact, that in the experiment the actual voltage drop across the GB is not known and additionally not even needs to vary proportional to the total voltage applied to the ceramics. Probably this is also the reason for the different curves of EBIC signal vs. bias voltage. For a clarification of this problem further investigations are necessary where the uncertainty in the voltage drop across the investigated GB is eliminated. This can be realized experimentally by contacting adjacent grains such that the applied voltage drops entirely across the appropriate GB. As mentioned above the calculated $\Delta J(V)$-dependence tends toward a saturation value but does not decrease again as is observed in the experimental curves. A possible cause for the latter effect might be that in the corresponding bias voltage range the potential drop at the reverse biased side of the particular GB reaches the threshold for impact ionization by the electrons emitted across the barrier. The minority holes generated thereby would compete with those generated by the e-beam and tend to diminish their modulation effect on the barrier $V_B$, which finally might result in the observed decrease of the EBIC signal. This proposal is further supported by the result of fig.4 where the narrowing of the linescan profile at the higher voltage indicates a shrinkage of the space charge layer as is expected when $Q$ is diminished by the capture of holes.

Conclusion

EBIC measurements at ZnO varistor ceramics enable the localization of those grain boundaries which control the transport of the electrical current. Inhomogeneities of their electrical properties are revealed on a micron scale.

References

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