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DIRECT OBSERVATION OF VOLTAGE BARRIERS IN ZnO VARISTORS

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Abstract

Voltage barriers in a ZnO varistor have been imaged by voltage contrast scanning electron microscopy. They are due to grain boundaries and are capable of supporting voltage differences of up to about 4 V.

Ever since the discovery by Matsuoka[1,2] of highly non-ohmic V-I behavior of polycrystalline ZnO sintered with various metal oxide additives, the so-called varistors have attracted attention as potential electronic circuit protectors against transient overvoltages.[3,4] The 10^6 to 10^8-fold increase in conductivity with a 50 per cent increase in applied voltage is normally explained by breakdown of voltage barriers at grain boundaries.[2,5,6]

Einzinger[7] has shown through direct contact measurements that the resistivity across a grain boundary is much higher than within a single grain. Wong[8] has compared the V-I behavior of several GE-MOV® varistors of different grain size and concluded that the maximum voltage drop per grain boundary is 2.3 V, and is largely independent of the exact grain size of the varistor. In this letter we report on a direct observation of the voltage barriers by voltage contrast scanning electron microscopy.

The voltage contrast technique[9,10] was originally developed for observing voltage distributions in semiconductor devices, but it can measure the voltage distribution on any surface. In its refined, quantitative forms the technique is capable of voltage resolution up to 50 mV[10] at spatial resolution better than 1 μm, but it is used much more often as a qualitative technique with voltage resolution of about 0.5 V. In either of the two forms the technique is well suited to studying the voltage distribution across an activated varistor.

Fig. 1 shows the experimental arrangement. The varistor surface was polished and lightly etched to reveal the grain boundaries, and gold electrodes 1 μm thick were vapor deposited onto it. The voltage observations were made on a 0.1 mm wide gap between the electrodes (produced by the shadow of a 0.1 mm wide wire). The resistor in series with the variable power supply served as a circuit protector against discharges, and for monitoring the current through the varistor.

The varistor used in this study contained 10 mol % CoO, 0.2 mol % Nd_2O_3 and 0.25 mol % Sm_2O_3. These compositions were verified by energy-dispersive X-ray (EDX) microanalysis in a scanning transmission electron microscope.[11] The additives were found mostly concentrated in second phase particles. The grain boundaries were free of intergranular phases wider than 10 Å (as determined by high resolution imaging[11]), and no grain boundary segregation of any of the additives above the sensitivity of the EDX technique (∿ .5 mol %) was found. Average ZnO grain size was about 20 μm.

Typical voltage contrast images are shown in Fig. 2. As usual in voltage contrast imaging, regions at negative potential appear brighter. Fig. 2(a) shows the gap between the two electrodes at no applied voltage. The gold electrodes are brighter than the ZnO grains because of their higher secondary electron emission coefficient. When 10V is applied across the gap (Fig. 2(b)), the grains in contact with the negative electrode become brighter, and the brightness is reduced in a series of steps at each grain boundary all the way to the grains in contact with the positive electrode. When the voltage is reversed (Fig. 2(c)), the direction of the brightness steps reverses also. The discrete nature of the steps proves that the voltage was discontinuous across the grain boundaries. To check that the voltage steps were not caused by the etching of the ZnO, we imaged the voltage distribution across an unetched sample. The results were the same as the ones shown here.

Precise measurements using the quantitative voltage contrast method are in progress. In the meantime, approximate quantitative results on the magnitude of the voltage drop at each grain boundary were obtained by separating the voltage contrast from the topographic contrast as follows. Microdensitometer traces were taken between the points A, A' shown in Fig. 2(a) for a range of applied voltages from -25V to +25V. The negative bias traces were then substracted from the positive bias ones. The resultant traces are shown in Fig. 3. They are due mainly to voltage differences, although the relationship between the trace height and the voltage is not necessarily linear.

It can be seen from Fig. 3 that at 10 V applied voltage, just one grain boundary barrier between A and A' is responsible for about half the voltage difference. At 20 V the voltage drop at this boundary is again about 3-5 V, while the remaining 15 V are distributed evenly across the ZnO grains. The total varistor current at 20 V indicated a resistivity of the ZnO grains of $\sim$ 100 Ω-cm, in good agreement with the high-current resistivities measured on bulk varistors of the present composition,[11,13] which were also rather higher than the 1 Ω-cm typical of pure ZnO.[12] The resistance of the gold electrodes was found by a simple calculation to be negligible, but it is possible that the resistance of the ZnO-Au contact was quite large.

A possible criticism of our work might be that the conduction between the two electrodes is three-dimensional, and that examining the voltage distribution on an open surface neglects possible conduction paths through interior grains. However, since a path between two neighboring surface grains through a third (volume) grain involves the crossing of at least one extra grain boundary, we believe that the barrier breakdown will occur first across the exposed grain boundary, and the conductive contribution of the volume boundaries will not be important.

In summary, our results demonstrate that in a 10 mol % CoO, 0.2 mol % Nd_2O_3, and 0.25 mol % Sm_2O_3, ZnO varistor, grain boundaries constitute voltage barriers capable of supporting voltage differences of up to ∿4 V. At higher applied voltage per grain boundary the barriers break down and the conduction is mainly limited by the resistance of the ZnO grains. Since no continuous intergranular films thicker than 10 Å were found in the varistor,[11] we conclude that the voltage barriers were formed by a depletion layer[6] rather than an insulating oxide film.[5]

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Figure Captions

Fig. 1. Voltage contrast imaging set-up.

Fig. 2. SEM images of the same area of a ZnO varistor. a) No applied voltage; b) +10 V; c) -10 V. The gold electrodes are at lower left and upper right.

Fig. 3. Voltage profiles along the line A-A' (see Fig. 2(a)).

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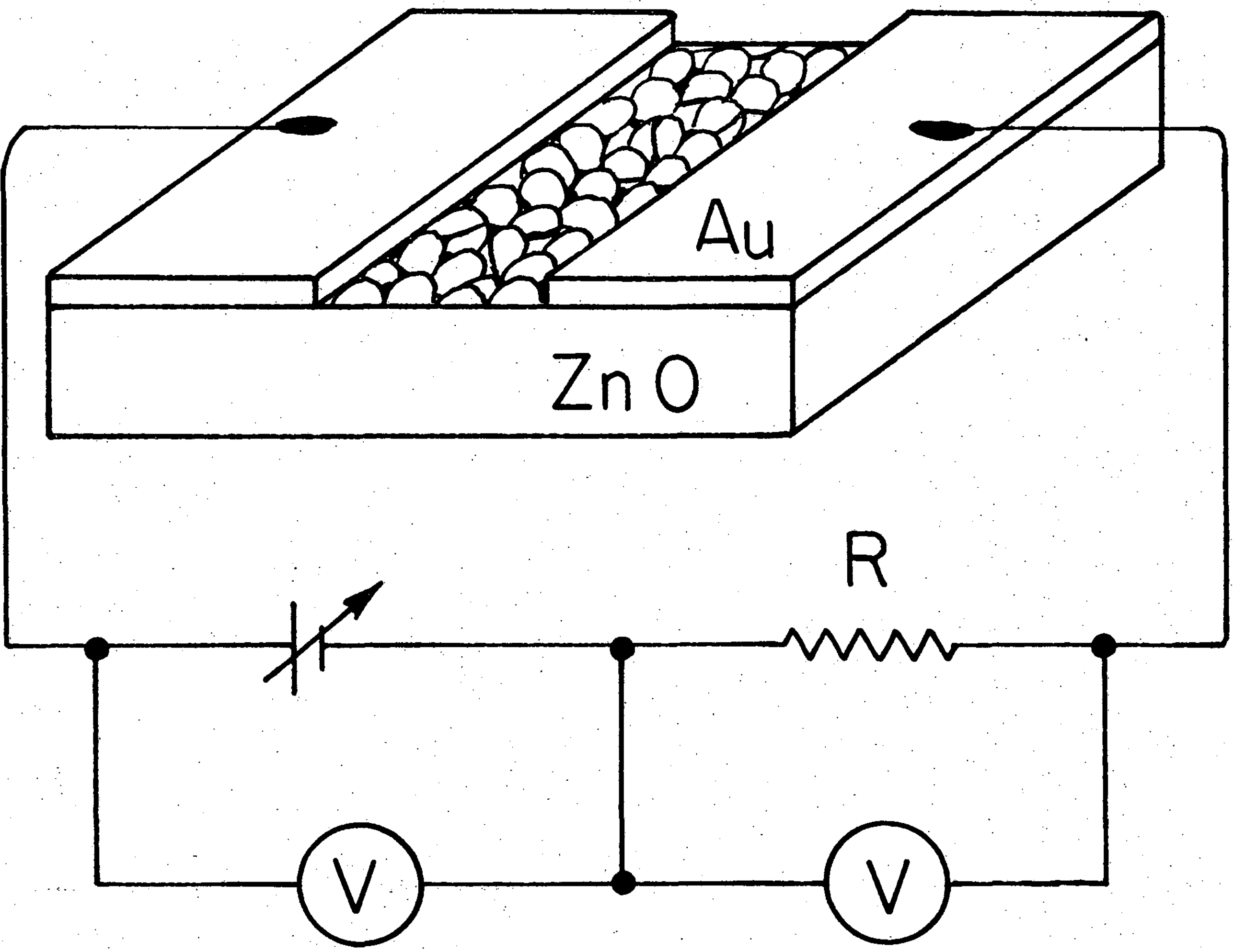

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Fig. 1

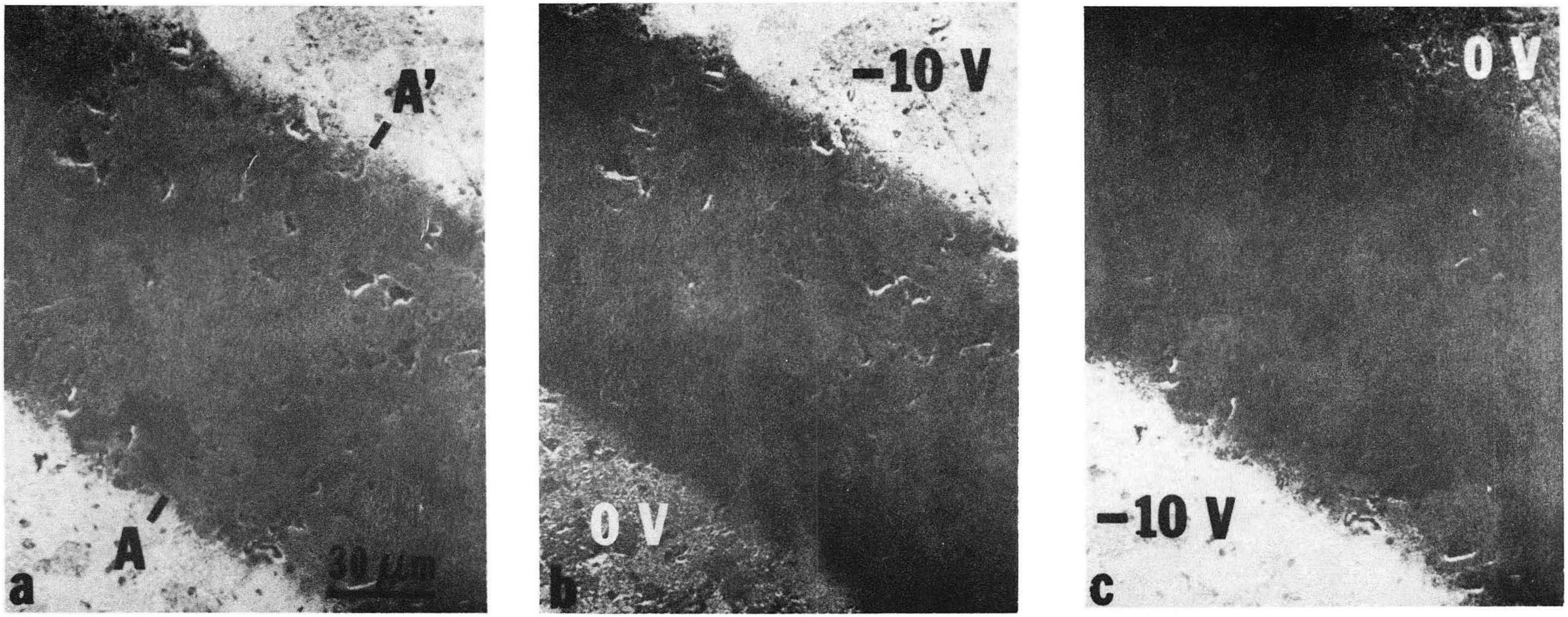

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Fig. 2

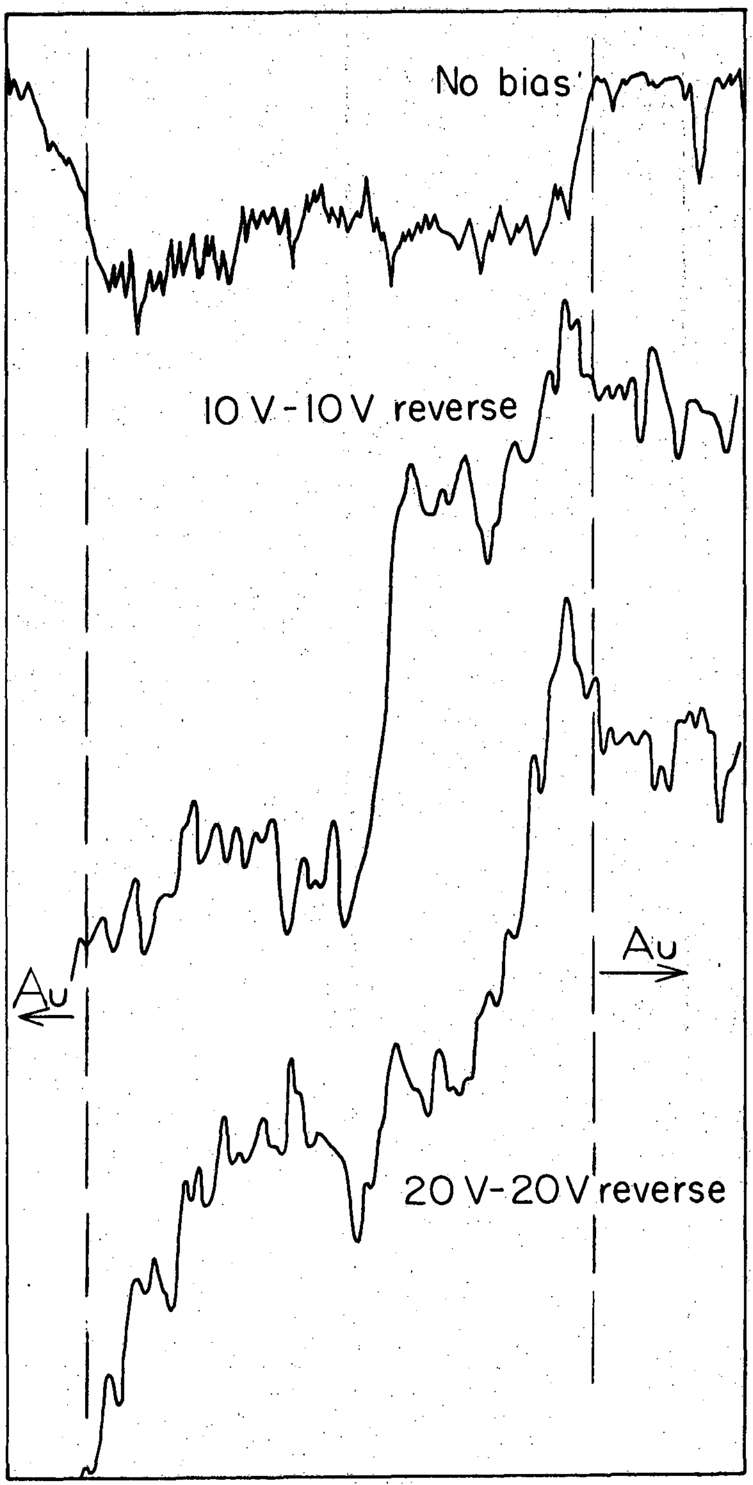

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Fig. 3

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