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THE ANOMALOUS BEHAVIOUR OF Ag-Al_2O_3 CERMET ELECTROFORMED DEVICES

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Abstract

Cermet coating consisting of silver particles in an aluminium oxide matrix were prepared on glass substrates by vacuum deposition. Variation of the circulating current with potential difference was obtained in evaporated Al/Ag-Al_2O_3/Cu sandwich structures, 100 to 200 nm thick containing 10 wt % Ag. It was observed that the investigated sandwich structures exhibit anomalous behaviour such as electroforming with Voltage-Controlled-Negative Resistance (VCNR) in vacuo of $\sim 4 \times 10^{-6}$ torr. The formed characteristics were explained on the basis of filamentary model.

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1 Introduction

It is well known that a metal-insulator-metal (MIM) sandwich structure can undergo a forming process under certain conditions, during which the electrical conductivity of the sample increases by several orders of magnitude [1]. This process is known as electroforming (or simply 'forming'). Forming is possible normally under an ambient pressure of less than 10^{-3}torr, although certain fluorides [2] and oxides [3] have been reported to be electroformed at atmospheric pressure. The forming process depends on ambient pressure, temperature, electric field, cermet thickness and on electrode materials used in the MIM and MCM structures. After forming,the conduction process in the MCM structure exhibits anomalous behavior. These devices are known as electroformed devices. The present investigation is concerned with metal-cermet-metal (MCM) sandwich structures, in particular, the Al/Ag-Al_2O_3/Cu combination. Electroforming with Voltage-Controlled-Negative Resistance (VCNR), switching and memory have been studied in detail in thin insulating films-MIM structures $\sim$ 20 to 300nm thick [4, 5, 6, 7] but less completely in metal-doped insulating films [8].

Models, which attempt to explain the origin of the electronic properties of electroformed insulating films can be divided into two groups. In the first group, Hickmott [9], Simmons and Verderber [10] and Barriac et al. [11] postulated that conduction is associated with the formation of an impurity or a defect band in the forbidden gap of the insulator. In the second group, Dearnaley et al. [4], Ralph et al. [12] and Rakhshani et al. [13] required the presence of conducting filaments and postulated that conduction is based upon the growth and thermal rupture of many filaments penetrating the insulator. Ray and Hoggarth [5] suggested that filaments are formed when metal particles from the anode of the MIM structure diffuse into a porous insulator. It is the filamentary model which has proved most suitable for describing the experimental observations, excluding electron emission in the present report.

Ray and Hoggarth [5] developed a poly-filamentary model. In this model, the circulating current I_c through a formed sample is expressed as a polynomial in potential difference V by the following equation,

$$I_c(V) = \sum a_n V^n \tag{1}$$

where n is the zero or an integer and a_n are coefficients.

2 Experimental

Cermet sandwich structures containing a mixture of silver powder and aluminium powder were deposited by electron bombardment heating technique in vacuum coating unit at ambient pressure of 1-3x10^{-6}torr. The Ag-Al_2O_3 cermet films were deposited at about 0.4nm sec^{-1} to a thickness of 100 to 200nm containing 10 wt% Ag. The lower Al electrode and upper Cu electrode were evaporated during the same pump down cycle. In our present investigation,the procedure for forming the devices were placed in the vacuum chamber at a pressure of $4x10^{-6}$torr. The I-V characteristics of these films during electroforming were usually obtained by measuring the circulating current with manually increasing the sample Pd slowly, maintaining a regular time interval (one minute for each 0.5V steps) so that the increasing current reached its steady state value. This method was repeated until a sharp increase in the circulating current (I_c) at a particular voltage initiated the forming process. The procedure was adopted to further increase the bias Pd across the electroformed device until the peak current dropped suddenly to its minimum value.

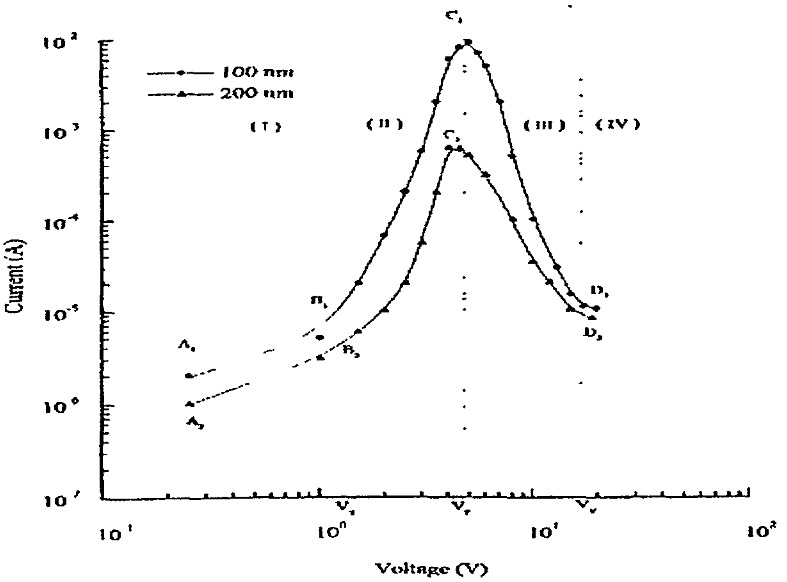

Figure 1: DC I-V curves for electroformed sandwich devices (5wt% Ag) of different thicknesses at ambient pressure $\sim$ 4 X 10^{-6} torr and at room temperature.

3 Results and discussion

The cermet thickness has a pronounced effect on electroforming under the ambient pressure $\sim$ $4x10^{-6}$torr as shown in Fig. 1. The forming voltage V_F was found to lie between 3.5 volt and 5 volt irrespective of the composition and cermet thickness. In the present case ,the forming voltage V_F is found to decrease with increase of cermet thickness but in MIM devices the reverse is usually the case. The decrease in V_F with increasing film thickness may arise from the formation of large metallic islands and the decrease in the inter-island separation. Both of which assist in the process of filament formation. Temperature also affects electroforming. In our investigated temperature range (298 to 338K), the peak circulating current (I_p) of the formed sample was found to increase during the voltage cycling and the forming voltage (V_F) was lower ($\langle$ 5V) beyond the room temperature 298 K, i.e. V_F was shifted to the lower voltage

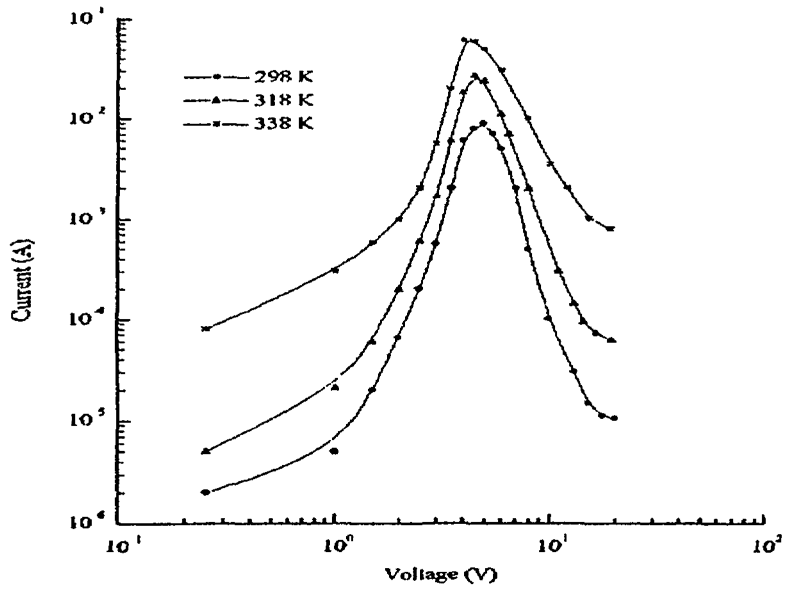

Figure 2: DC I-V curves for electroformed sandwich devices 5wt % Ag $\sim$ 100nm of different temperature at ambient pressure $\sim$ 4 X 10^{-6} torr showing VCNR regions.

with increasing temperature [Fig.2]. At temperature 318K and 338K, the initial impedances were slightly lower than the room temperature (298K) values. As a result the forming voltage (V_F) was found to be lower, especially in lower Ag content samples and the peak current (I_p) also increased the room temperature values.

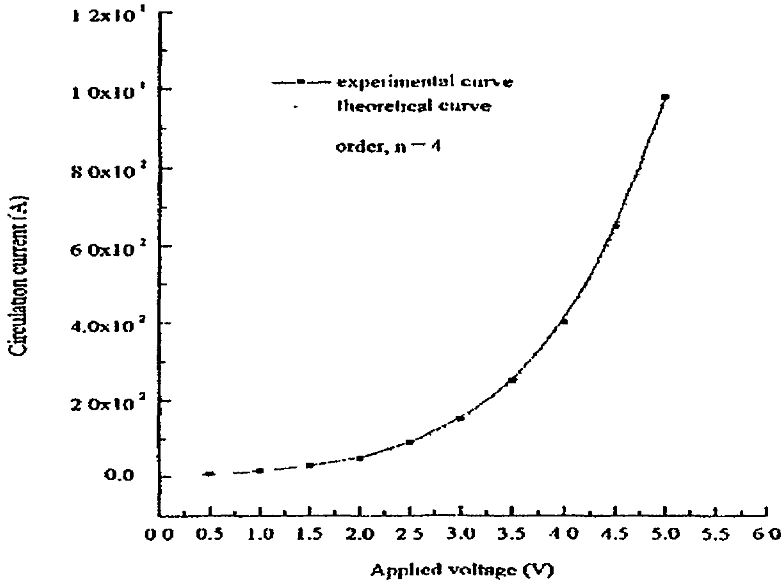

Figure 3: Fitting of filamentary model for a 10 wt %Ag formed device of cermet thickness $\sim$ 100nm at room temperature.

The I-V characteristics developing a VCNR region [Figs. 1 and 2] can be conveniently divided into four voltage regions, such as (I) pre-threshold voltage V_T; (II) forming voltage V_F at the peak circulating current I_p; (III) the valley voltage V_v i.e. VCNR region and (IV)

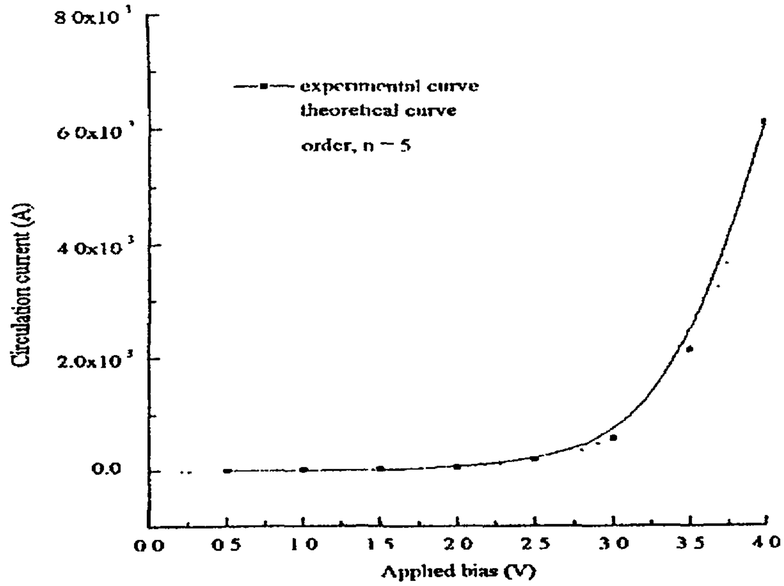

Figure 4: Fitting of filamentary model for a 10 wt %Ag formed device of cermet thickness ~ 200nm at room temperature.

the maximum applied voltage V_{max}. This anomalous behavior in the I-V graph was discussed by many authors [14], [15], [16]. The experimental results on formed devices are found to be consistent with the poly-filamentary model by Ray and Hoggarth [5]. The results of fitting this model to formed cermet devices are shown in Fig. 3 and Fig. 4. The best fit was obtained for n=4 and 5 in equation (1). The corresponding values of the coefficients a_n of V^n are presented in Table 1.

Thickness (nm)	order n	Values of the coefficient a_n						Error
		a_0	a_1	a_2	a_3	a_4	a_5	
100	4	2.14 $\times 10^{-4}$	1.99 $\times 10^{-4}$	1.72 $\times 10^{-3}$	7.77 $\times 10^{-4}$	2.42 $\times 10^{-4}$	- -	4.77 $\times 10^{-4}$
200	5	-7.23 $\times 10^{-5}$	4.68 $\times 10^{-4}$	-1.01 $\times 10^{-3}$	9.21 $\times 10^{-4}$	-3.65 $\times 10^{-4}$	5.37 $\times 10^{-5}$	1.78 $\times 10^{-5}$

Table 1: Values of coefficients a_n in expression of $\sum a_n V^n$ for (10 wt % Ag). The first row is calculated using Fig. 3 and second row using Fig. 4.

Therefore, the best agreement was obtained with n equal to 4 to 5 and the corresponding values of the coefficient a_n of V^n are displayed in Table 1.

4 Conclusion

In our study the presence of a peak current and a VCNR region indicates that the sample is being electroformed. It is believed that electroforming is a consequence of structural changes occurring in the present films. In the present work it was observed that only the Al/Ag-Al_2O_3/Cu sandwich structure held under vacuum of $4x10^{-6}$torr had undergone electroforming. These features are properly explained by a poly-filamentary model of Ray and Hoggarth [5]. Electroforming was found to depend on electric field, ambient pressure, cermet thickness and electrode materials respectively.

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