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THE ANOMALOUS VARIATION OF THE RESISTIVITY OF THIN GOLD FILMS

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A B S T R A C T

Measurements of the variation of the resistance of thin discontinuous gold films, vacuum coated on amorphous organic substrates at ambient temperature, have been carried out in both vacuum and at atmospheric pressure up to several weeks after their initial deposition.

Evaporations made consecutively at 10 minute intervals, onto the surface of a given substrate in the region 10^{11}-10 ohms, demonstrated that the resistance varies spontaneously as a function of time with a critical region at about 10^5 ohms. Those films having a resistance at the end of an evaporation, higher or lower than 10^5, have their resistance values spontaneously increasing or decreasing with time,respectively. Examination of a particular area,immediately after the depositon by means of electron microscopy, revealed that the initial agglomeration changes quite sensitively as a function of time and according to the direction of the variation of the resistance.

R E S U M O

Foram feitas medidas da variação da resistência de filmes finos de ouro, descontínuos, obtidos por deposição em alto vácuo sobre subtrato orgânico amorfo e à temperatura ambiente. As medidas foram feitas à pressão atmosférica e em vacuo, durante várias semanas após a deposição inicial.

Evaporações feitas consecutivamente a intervalos de 10 minutos, sobre o substrato, na região de 10^{11}-10 ohms, mostraram que a resistência varia espontaneamente como uma função do

tempo, apresentando uma região crítica ao redor de 10^5 ohms. Filmes com resistências, ao final da evaporação, maior ou menor que que 10^5 ohms apresentam, respectivamente, aumento ou diminuição - dos valores de suas resistências, espontaneamente com o tempo. Exame ao miscroscópio eletrônico de uma particular área ,imediatamente após a deposição ,mostrou que os aglomerados iniciais variam sensivelmente em função do tempo e de maneira concorde com o sentido de variação da resistência.

Several papers on the electrical conductivity of discontinuous thin films evaporated on dielectric substrates have appeared in recent years (1) - (6). Recent reviews of the litterature have been published by Dittemer (2) and Morris (6). The anomalous variation as a function of time, of the electrical resistance of thin films has previously been mentioned by some authors. Neugebauer et al (1), working with thin films of the order of a few, to several tens of angstroms of different metals deposited on pyrex glass substrates, observed an increase of the resistance with time during the first few hours following the evaporation. Tosser et al (7) observed a spontaneous decrease of the resistance in zinc at a vacuum of 10^{-4} torr and Colas et al (8) have reported the slow evolution of the resistance during a 2 to 3 weeks period for a Au - Pd alloy film.

In the present communication, resistance measurements of thin gold films have been correlated with electron micrographs in an attempt to establish the relationship between the morphological behaviour and the anomalous variation of the resistance with time.

The preparation of the thin gold films was carried out by means of direct vapour deposition of gold metal onto dielectric substrates, i.e., a co-polymer of polyvinyl chloride and polyvinyl acetates (VYNS), having an estimated thickness of 10 $\mu g/cm^2$.

Substrates for the resistance measurements and specimens for the electron microscope were taken from the same VYNS film. The gold metal was evaporated from a tungstenhelix at a distance great enough (d=30cm) to prevent undue heating of the substrate. All of the evaporations were carried out in a vacuum better than 10^{-5} torr.

The resistance monitor shown in Fig. 1 consists of an aluminium ring covered with a VYNS substrate the central part of which is in contact with a gold disc. The ring and disc serve as the measuring electrodes and are taken out of the chamber to an electronic ohmmeter and strip chart recorder operating in the range $10^2\Omega$-$10^{14}\Omega$. Thickness determination of the gold films was realized using gravimetric mean values taken from 20 samples.

Consecutive evaporations were carried out at 10 minutes intervals and the results shown in Fig. 2. It is evident that we are dealing with three different kinds of behaviour of the spontaneous resistance variation which take place following the interruption of the evaporation and depends on the range of values in question, i.e., from values of $10^7\Omega$-$10^6\Omega$, it increases, while at $10^6\Omega$-$10^5\Omega$ it almost stabilizes and below this value, decreases. Therefore it would seem that these different phases are a function of the film thickness. Thus $e \simeq 70\text{Å}$ when $R \simeq 10^9\Omega$; $e \simeq 100\text{Å}$ when $R \simeq 10^6$ and $e \simeq 120\text{Å}$ when $R \simeq 10^4\Omega$. This same behaviour of spontaneous increasing and decreasing of the resistance as a function of time has been observed in many series of samples kept at atmospheric pressure over a period of several weeks.

In order to obtain evidence of a relationship between the film morphology and the spontaneous variation of the resistance, observations were made in the electron microscope immediately after the interruption of the evaporation for each of the three mentioned phases. Both the resistance measurements and the electron microscope observations were made under the same pressure conditions, taking into consideration the known influence of the particular parameter on thin film resistance values (9) - (11). All of the resistance values were recorded continuously while the electron micrographs were taken at time intervals of 15 to 90 mins.

In Fig. 3 can be seen the electron micrographs of the three observed phases. In order to determine the influence of the electron beam on the observed morphology, one of the micrographs was taken with an intense beam (I = 2 μA) during a 3 minutes period. No appreciable effect could be observed.

In the analysis of electron micrographs it is common practice to measure the size of the islands and the distance between them. In the present work, a method of measurement was developed whereby the micrograph in question is projected onto a sheet of millimeter paper and the area determined by the number of square millimeters counted within that particular area.

The ratio r between the total area and vacant area, was calculated for the same region of the film. The first three measurements given in Table 1 were made from selected micrographs recorded at t_i=45 min and t_f=135 min. assuming the interruption time for a given evaporation as 0, or the time of origin. The resistance values R_i and R_f were measured in relation to t_i and t_f and a variation factor, F, arrived at. The values for r and F, are listed in Table 1.

What can probably be considered remarkable in the present work is the order of magnitude of the resistance variation, i.e., + 36% and - 43%. It should be mentioned that in some prolonged experiments, of about three hours, variations of the order of 100% were observed, whereas the spontaneous decrease of resistance in the case of tin, as reported by Tosser et al., was only about 1% after several hours (7). In phases I and II of the above Table, it can be seen that the increase and decrease of the resistance corresponds to the variation in size of the vacant area. Kane et al (12), have stated that the resistance increase is caused by the process of agglomeration of the gold film and also by geome-

trical changes.

In the present case, the increase in resistance was more rapid than the decrease, consequently the variation factor at the time the micrographs were taken for analysis was only x 1.6. This time interval is indicated in Fig. 3. A close examination of the micrographs of phase II, shows a movement towards the shrinking of the vacant area and in some regions, a distincit tendency to grow. This is a phase of morphological instability.

Several experimental factors have contributed to the error of the resistance measurements, One of them is the dependence of the resistance on the pressure which is impossible to avoid where the experiments are not carried out on samples "in situ". Morris (10), has demonstrated the variation of resistance at the begining and end of the vacuum. This could well explain the small deviation in experiment II in which a discrepancy was observed between $\underline{r}$ and $\underline{F}$. The influence of the electron beam was found to be negligible and the ratio $\underline{r}$ is within the experimental error. Kehrer (11), confirmed the stability of the electron beam using tin films evaporated at 10^{-4} torr.

There can be no doubt that thin gold films undergo a spontaneous variation of their electrical conductivity as a function of thickness or initial resistance. Such a spontaneous variation is more pronounced immediately after the evaporation but can never the less be detected, at atmospheric pressure, up to several weeks after the deposition.

In the work presented here it is possible define three principal phases, namely,

1. $R > 10^6\Omega$ - spontaneous increase
2. $R \simeq 10^6\Omega$ - small and no regular variation
3. $R < 10^6\Omega$ - spontaneous decrease

The spontaneous variation of the resistance in the different phases is apparantly explained by changes in the film morphology.

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TABLE 1

Key: I - Spontaneous increase

II - Small and unstable variation

III - Spontaneous decrease

IV - Electron beam influence

PHASE	VACANT AREA VARIATION t = 90 min. (error 5%)	F
I	+ 36%	+ 1.6 x
II	- 8%	+ 1.2 x
III	- 43%	- 4.5 x
IV	Negligible	

FIGURE CAPTIONS:

Fig. 1 - Design of resistance monitor consisting of aluminium ring with VYNS substrate, electrodes and contact points.

Fig. 2 - Figure shows consecutive 10 min. interval evaporations and the spontaneous variation of the resistance after interruption of the gold deposition in vacuum.

Fig. 3 - The spontaneous variation of resistance of thin gold film following the interruption of the deposition at: a) $R \simeq 10^8\Omega$ (increase); b) $R \simeq 10^6\Omega$ (negligible variation) and c) $R \simeq 10^3\Omega$ (decrease)

Fig. 4 - The series of electron micrographs, I, II and III, in the figure should be correlated with fig. 3 a), 3 b) and 3 c). Thus:

Serie (I) a: 40; b: 70; c: 100; d: 130
(II) a: 50; b: 80; c: 190
(III) a: 35; b: 50; c: 120; d: 205

where the numbers represent the time in minutes since the termination of the deposition (mag: x 400.000).

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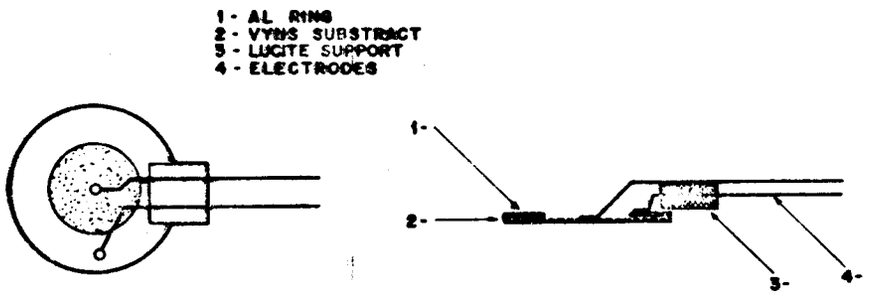
1 - AL RING
2 - VYNS SUBSTRACT
3 - LUCITE SUPPORT
4 - ELECTRODES
1-
2-
3-
4-

FIGURE 1

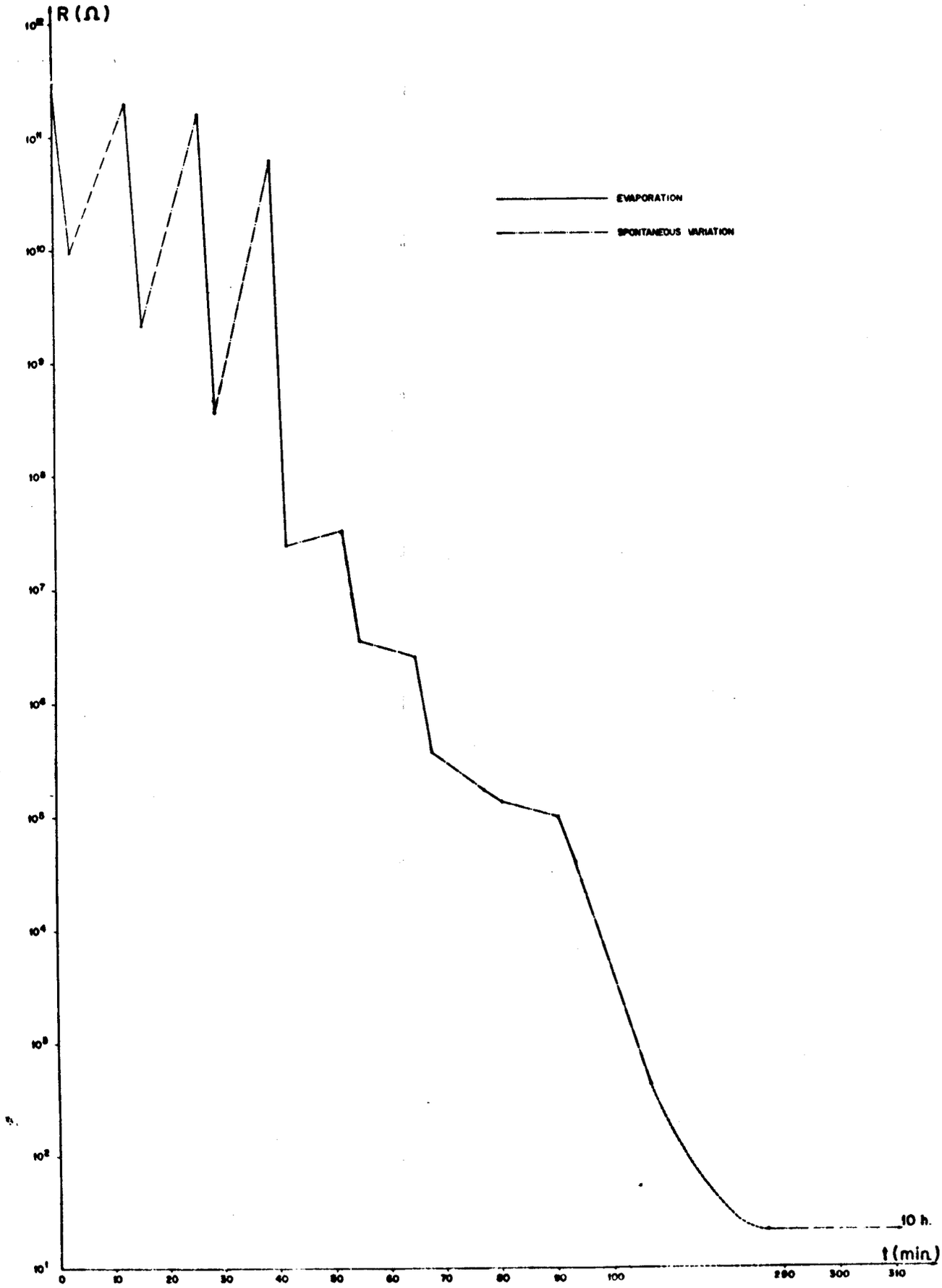
R (Ω)
EVAPORATION
SPONTANEOUS VARIATION
10 h.
t (min.)
0
10
20
30
40
50
60
70
80
90
100
290
300
310

FIGURE 2

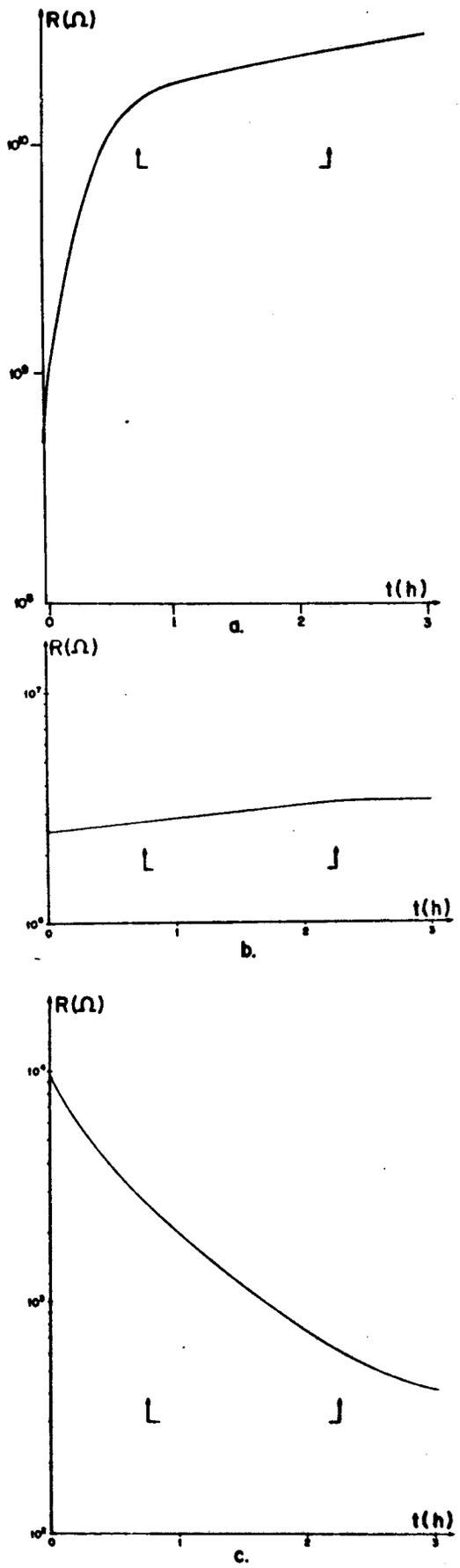

FIGURE 3

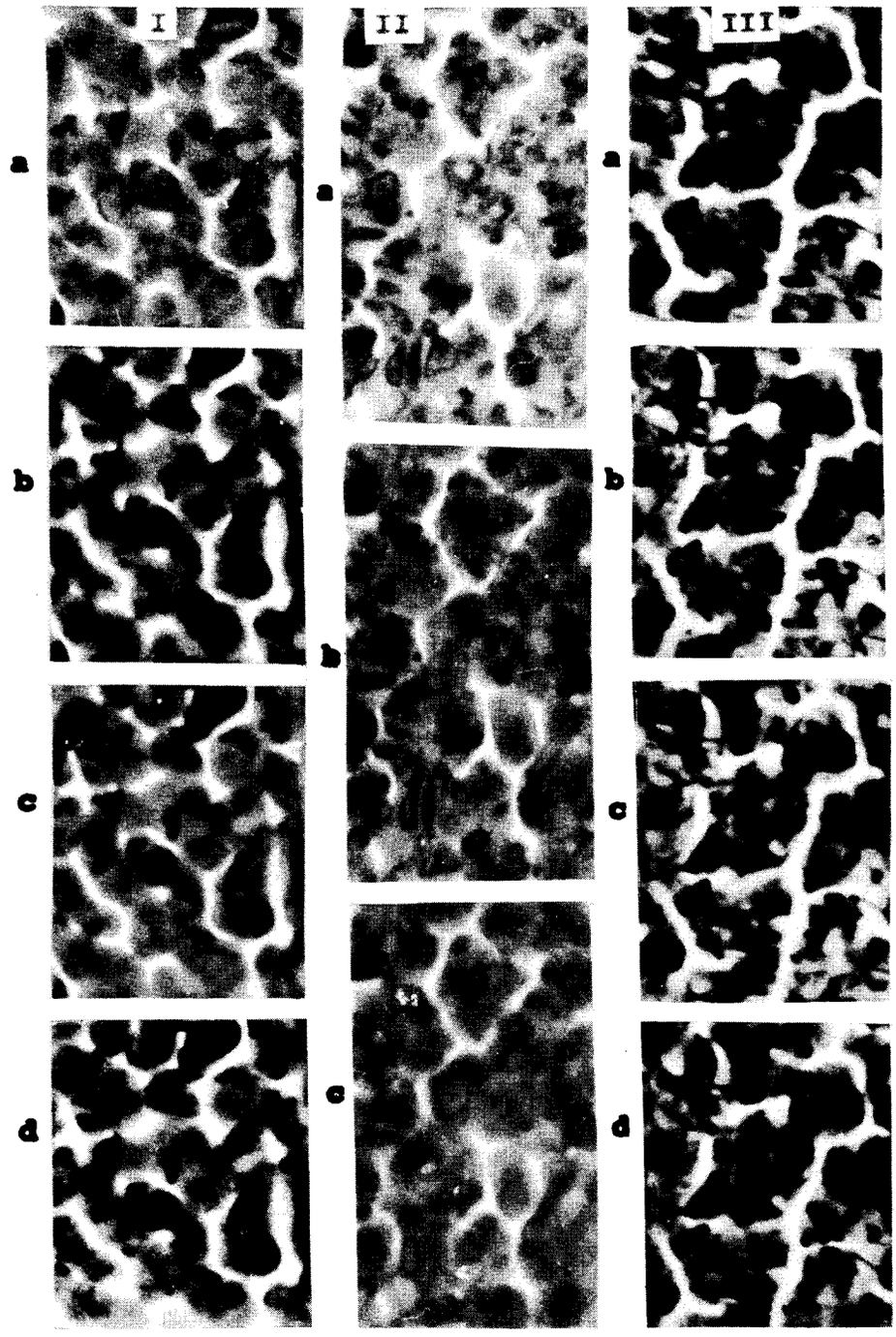

FIGURE 4