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POLYCRYSTALLINE GAS SENSORS PROPERTIES BASED ON DC & AC ELECTRICAL MEASUREMENTS

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Abstract: Electrical properties of polycristalline gas sensors are analyzed by dc and ac measurements. DC electrical conductivity values compared with those obtained by admitance spectroscopy methods help to get a detailed analysis "*on line*" of conductivity modulated gas sensors. Electrical behaviour of grain boundaries are obtained and a new design of sensors can be achieved by enhancing the activity of surface states in the detecting operation.

A Schottky barrier model is used to explain the grain boundaries action under the presence of surrounding gases. The height of this barrier is a function of gas concentration due to trapping of excess charge generated by gas adsorption at the interface. A comparison between this dependence and a plot of the real and imaginary components of the admittance versus frequency, at different gas concentration, gives information of the different parameters that play a role in the conduction mechanisms, i.e. trapping centers, Schottky barriers, number of carriers, etc. The analysis of this plot for several gases, different concentrations and temperature, allows us to determine the nature of the detection mechanism and the behaviour of the barriers, energy activation and deep trapping centers, and finally compute their value.

These methods have been applied to the design of a CO sensor based on Tin oxide films for domestic purpose, the characteristics of which are presented.

Introduction

Transport mechanisms of majority carriers in polycrystalline semicoductor compounds constitute the basis for understanding the sensing function of semiconductor gas sensors.

Important progress has been made in the last few years on the characterization of grain boundaries in some devices such as ZnO varistors, capacitors and solar cells. Taking these studies into account, complex impedance measurements have allowed improvements to be made in the knowledge of the interface microstructure associated with Schottky barriers, and have produced information on the trapping centres deep in the bulk [1-4] and on the activation energy and capture cross section as a function of temperature.

In the present paper we apply the technique to SnO_2, where the electrical properties of grain boundaries modulate the conduction mechanisms.

We have measured the response of the sensors in different atmospheres and temperatures. The

spectra obtained give us information related to band bending in the grain boundaries.

Localization of adsorption sites could be followed by this technique, taking into account the modification of the real or imaginary part of the impedance as the material detects the presence of different gas concentrations. The influence of the various components can be deduced from their change in value. At intermediate frequencies the capacitance value is enhanced by the charge trapped at the interface. The charge in the intergrain zones causes further resonances (peaks in the impedance plot), the importance of which is a function of the nature of the adsorbed gases. The conductance of the samples is increased at low frequencies, where the conductivity relative to that of the bulk material governs all the conduction mechanisms.

Measuring Methods

An a.c. variable-frecuency low-voltage signal (10μHz up to 32 MHz) is applied to the samples to obtain the complex impedance or admittance spectrum. The analysis of the poles and zeros of the transfer function can be applied to identify the values of the components of the equivalent circuit. Plots are made of the imaginary component of Z versus $\log\omega$.

We have considered three types of samples:

1 Electron beam deposited films. Base material: SnO_2 powder (99.999% purity). Alumina substrate. Thermally anealed in synthetic air at 400 ° C.

2 Serigraphic thick films. Base material: SnO_2 + organic ligant paint. Alumina substrate.

3 Reactive sputtering thin films. Base material: Sn metallic. Reactive gas Oxigen (15%) + Argon. Alumina substrate. Thermally anealed in synthetic air at 400 ° C.

Samples were placed in a chamber with the temperature and the gas mixture computer monitorized.

Basic considerations on conduction mechanisms

Because of the abrupt discontinuity of the lattice structure at the surface, a large number of localized energy states or generation-recombination centers may be introduced at the surface region. These energy states may greatly enhance the recombination rate at the surface region [5]. An understanding of the surface recombination process is important because it has strong effect on the characteristics of gas sensors.

In gas sensors, the impurities that act as localized states in the generation recombination process are mainly those which act as catalysts for the specific gas. This means that the generation of carriers due to gas detection takes place when this interaction is produced. Impurities for gas sensors must, then, be selected among those materials which introduce a localized energy state in the band gap. The best choice is when this energy level lies near the center of the band gap. For gas sensors it is convenient to produce a material whose surface recombination velocity be high, so that a large number of free carriers may interact with surface states. The sensor has to be fabricated so that the detection mechanism would be enhanced. Any method for fabricating thin or thick films, pellets or sintered materials may be adapted to

produce such a rough surface [6].

However a more important influence of surface in conduction mechanisms may be found in polycrystalline materials. These materials may be considered as a set of different resistivity domains connected in such a way that the total resistivity will be the series resultant of grains, ρ_1, and their boundaries, ρ_2. The value of the resistivity should be computed by the composition of forward and reverse current through the potential barrier of the grain boundary. If d is the inter grain distance, it may be shown that

$$\sigma_1 = e \cdot n_1 \frac{e \cdot v \cdot d}{K_B \cdot T} \cdot \exp\left[-\frac{\phi_B}{K_B \cdot T}\right] = e \cdot n_1 \cdot \mu_0 \cdot \exp\left[-\frac{\phi_B}{K_B \cdot T}\right] \quad (1)$$

$$\sigma_2 = \frac{n_1 \cdot e^2 \cdot d}{\left(2 \cdot \pi \cdot m^* \cdot K_B \cdot T\right)^{1/2}} \cdot \exp\left[\frac{\phi_B}{K_B \cdot T}\right] \quad (2)$$

If we consider μ_0 as a mobility, expression (1) can be interpreted in two different ways:

1.- All carriers contribute to the current trough the barrier, and there is a thermally activated mobility, $\mu = \mu_0 \cdot \exp(-\Phi_B / K_B \cdot T)$. Or

2.- There is only a reduced number of carriers, $n = n_1 \cdot \exp(-\Phi / K_B \cdot T)$, with a mobility μ_0.

It may be shown that for case 1, if $\sigma_1 \ll \sigma_2$, the number of carriers of the grain governs the conduction in the material. In the other case n will be thermally activated.

In quite a similar way we may consider as carriers thermally activated or mobility thermally activated the case of surface states acting as trapping centers. In fact the surface states N create a potential barrier, the energy bands bend in the vicinity of surface. If l is the size of grain and N the superficial density of states, it may be shown that

if $n_1 \cdot l \ll N_t$ Surface states capture a big amount of charge, and this leads to carrier density thermally activated.

if $n_1 \cdot l \gg N_t$ Carrier density inside the grain does not vary too much, this leads to mobility thermally activated.

For gas sensors it is convenient to achieve the case of carriers thermally activated. In this case the surface states will govern the conduction process enhancing the gas sensing mechanism [7].

Model proposed

The frequency response of different samples are resumed in Figures 2 to 7. Linear system analysis leads to the equivalent circuit of figure 1.

R_1 and C_1 constitute a cell that assumes the grains action on the conduction mechanism; R_3 and C_3 performs the bulk behaviour cell, and C_2 takes into account the barrier activity due to grain boundaries (grain

to grain, and grain to bulk) [8].

The impedance function of such a circuit is:

$$Z(s) = R_3 \cdot \frac{1 + A \cdot s}{1 + b \cdot s + a \cdot s^2} \qquad (3)$$

$$A = R_1 \cdot (C_1 + C_2)$$

$$a = R_1 \cdot R_3 \cdot (C_1 \cdot C_3 + C_2 \cdot C_3 + C_1 \cdot C_3)$$

$$b = R_1 \cdot (C_1 + C_2) + R_3 \cdot (C_2 + C_3)$$

It is necessary that $a \leq (b/2)^2$, in order to assure real solutions.

If $a \ll (b/2)^2$ there is only a pole in the measurable spectrum, that means that in a plot of the imaginary part of the impedance vs $\log\omega$ will lead to a single peak.

If $a \approx (b/2)^2$ there two poles which center the frequency value of $(b/2)^{-1}$.

If $A \approx (b/2)$ there is a zero between two poles.

For $\omega = 0$ $R(0) = R_3$ and $C(0) = (C_2 + C_3)$

All these characteristics related to the different response of our films allow an interpretation of their surface structure and their behaviour on a gas stimulus.

Discussion

The first samples in which there is a chrystallite structure over an amorphous bulk material (Fig 2 & Fig.3) exhibits only one peak at high frequencies, which means that $a \ll b^2$, that is the grain action is more important than that of the bulk, because A has to be of the same order than b, the interaction of grain boundaries to the bulk becomes very important (C_1 & $C_2 \gg C_3$).

The second kind of samples have a grain structure and a rough and porous surface (Fig. 4 & Fig. 5), the frequency response presents only one peak that in some cases can split in two very close, and the frequency is lower than the former. a is of the same order than $(b/2)^2$. The bulk participates slightly in the conduction mechanisms. C_3 is smaller than C_1 or C_2, but not negligeable, this contributes to increase the value of b and then to reduce the frequency value of peak.

Finally in the case of microchrystalline structures (Fig. 6 & Fig. 7), there are two peaks in the frequency response, that is the values of all components of the equivalent circuit are comparable in magnitude. The activity of grains and bulk is indistinguisable (there is no bulk structure detected by electron microscopy), and the sensibility less important.

Conclusions

The best structure for a gas sensor is that of material with a chrystallite structure, made either by electron beam or sputtering in which the grain activity dominates the conduction mechanisms.

Acknowledgements

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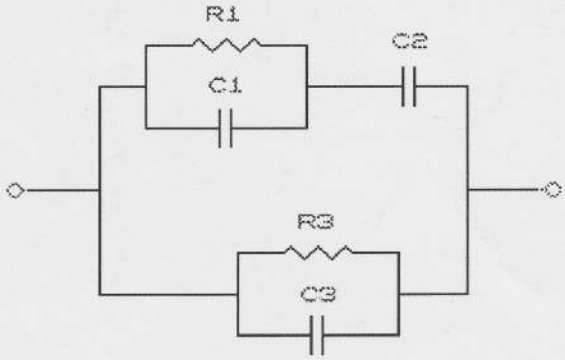

Fig.1 Equivalent circuit

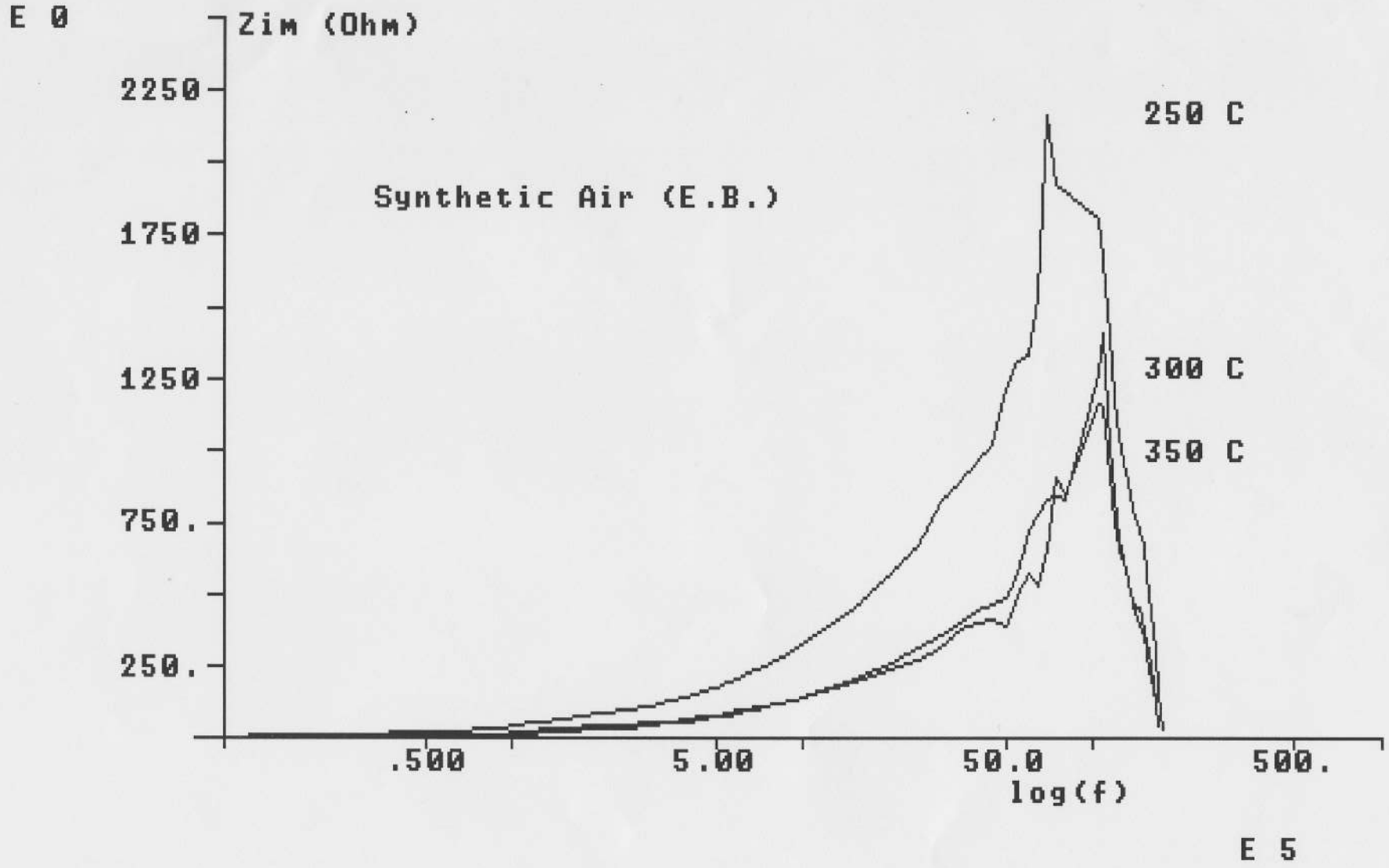
E 0
Zim (Ohm)
2250
1750
1250
750.
250.
Synthetic Air (E.B.)
250 C
300 C
350 C
.500
5.00
50.0
500.
log(f)
E 5

Fig.2

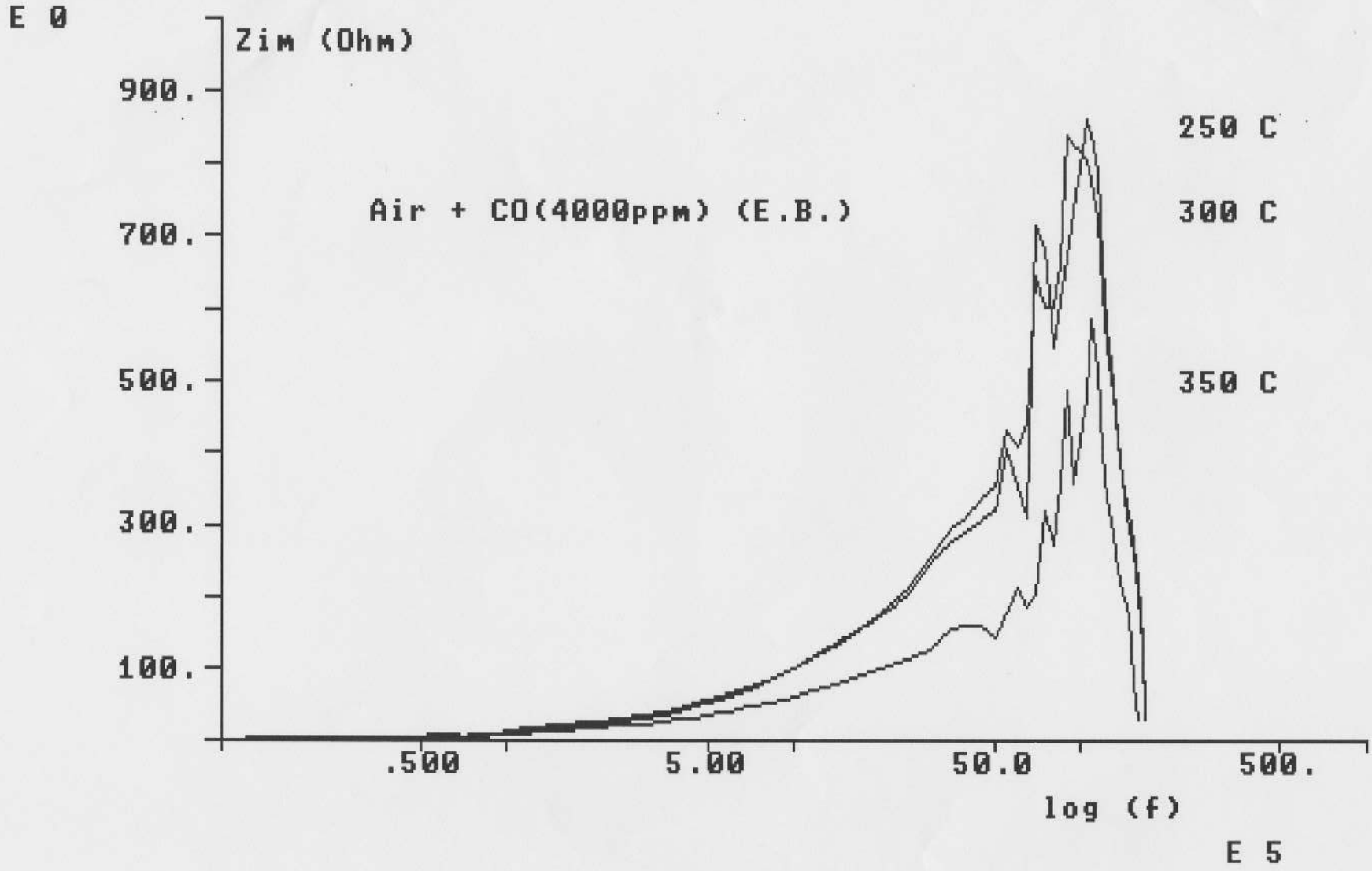
E 0
Zim (Ohm)
900.
700.
500.
300.
100.
Air + CO(4000ppm) (E.B.)
250 C
300 C
350 C
.500
5.00
50.0
500.
log (f)
E 5

Fig.3

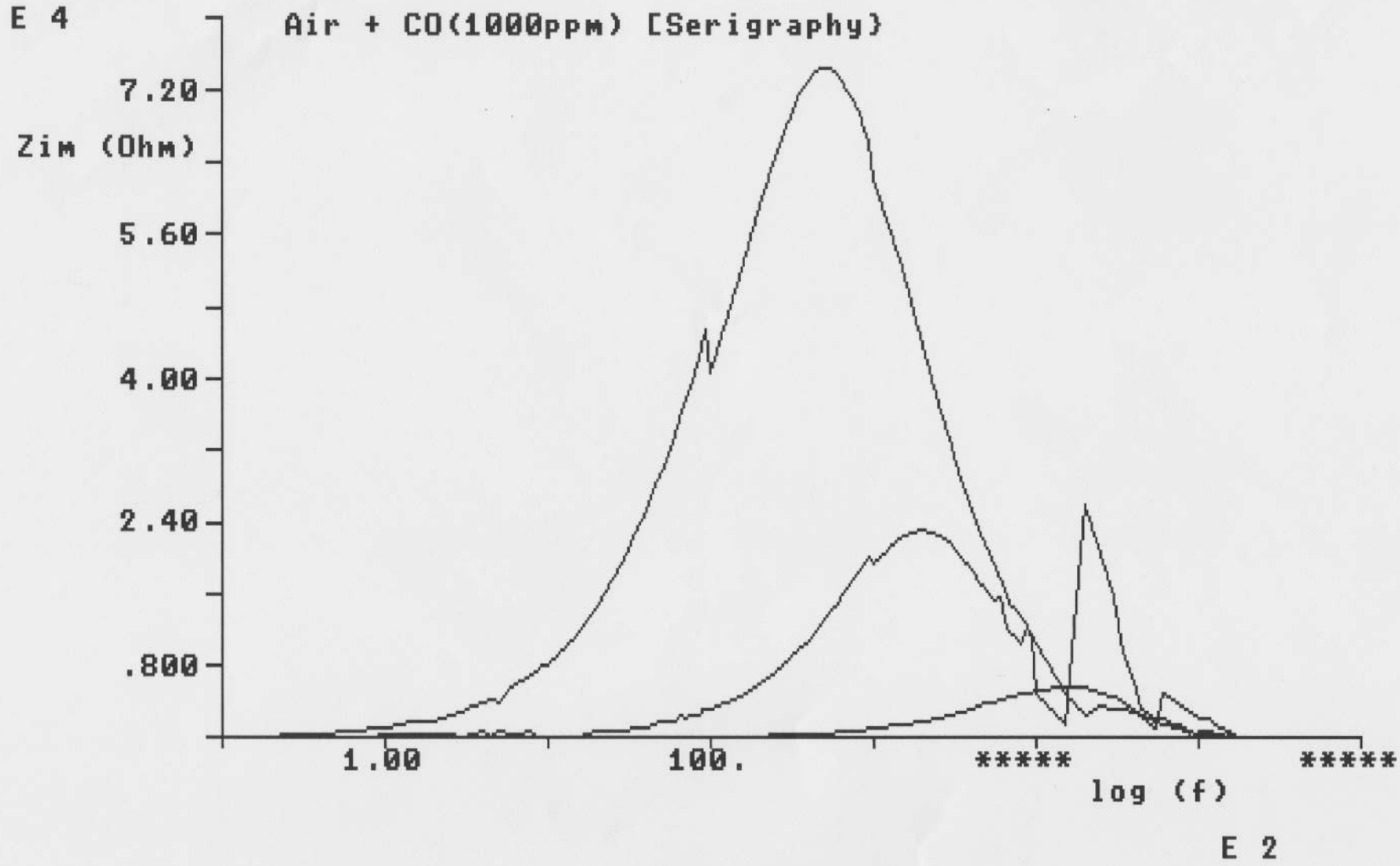
E 4
Air + CO(1000ppm) [Serigraphy)
7.20
Zim (Ohm)
5.60
4.00
2.40
.800
1.00
100.
*****
*****
log (f)
E 2

Fig.4

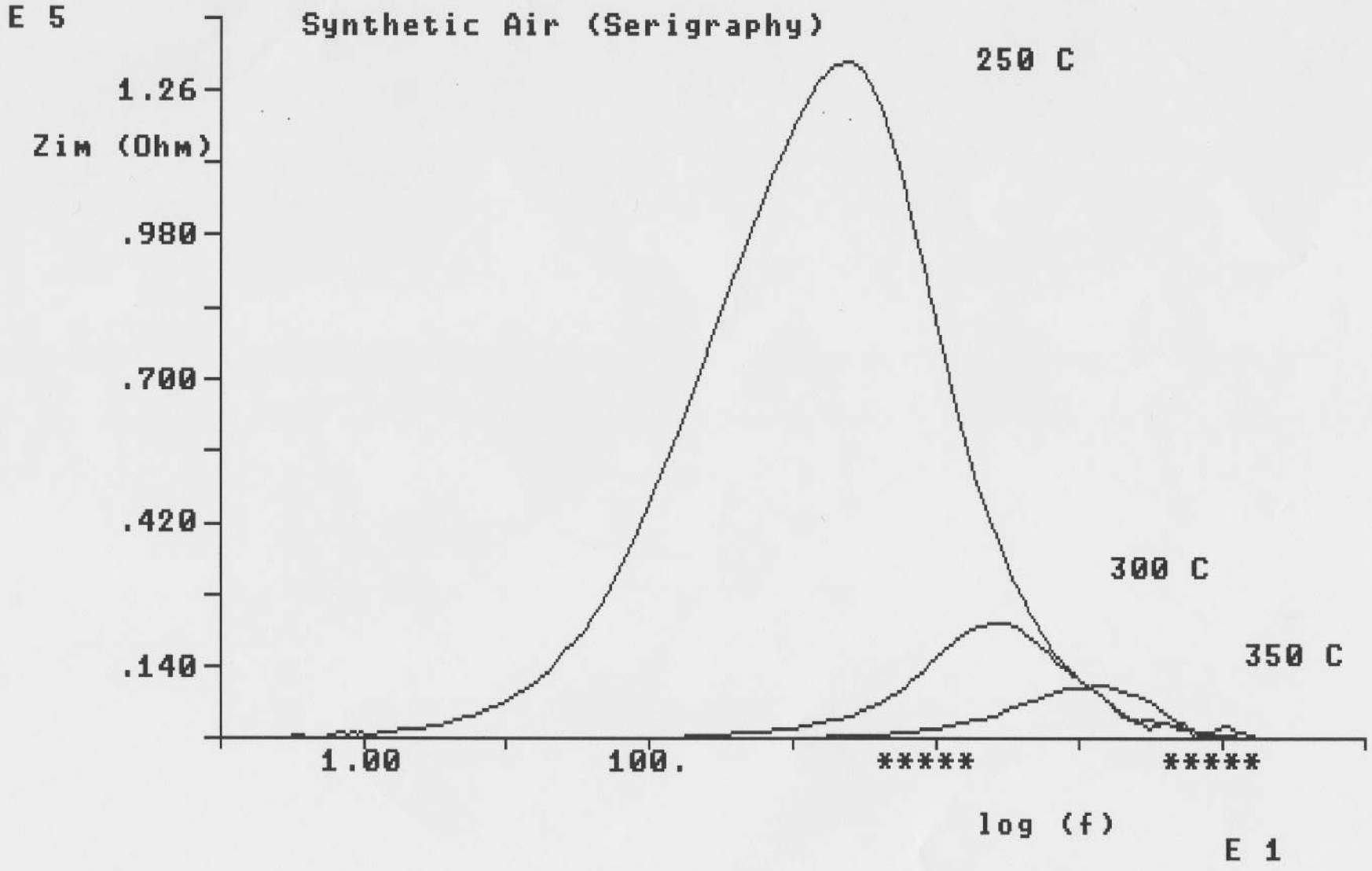
E 5
Synthetic Air (Serigraphy)
250 C
1.26
Zim (Ohm)
.980
.700
.420
300 C
350 C
.140
1.00
100.
*****
*****
log (f)
E 1

Fig.5