Journal of the European Ceramic Society **11** (1993) 551–557

Application of Methods of Fuzzy Mathematics to the Determination of the Micromorphology of TiO_2 CVD Thin Films

P. Vaija,[a,b] J. Lahouidak,[b] J. Durand[b] & L. Cot[b]

[a] Helsinki University of Technology, Laboratory of Chemical Engineering, 02150 Espoo, Finland
[b] Ecole Nationale Supérieure de Chimie de Montpellier, Laboratoire de Physicochimie des Matériaux (CNRS-URA 1312), 8 rüe de l'Ecole Normale, 34053 Montpellier, France

(Received 3 March 1992; revised version received 7 September 1992; accepted 10 September 1992)

Abstract

The influence of the process parameters (temperature, total pressure, partial pressure of the TiO_2 precursor) has been studied. A columnar morphology is obtained above 500°C at low pressure, while equiaxial crystals are observed at high total pressure. The experimental morphology diagram derived from the experimental observations was completed applying a simple fuzzy expert system and a fuzzy extrapolation method.

Es wurde der Einfluß der Prozeßparameter (Temperatur, Gesamtdruck und Partialdruck des TiO_2—Prekursors) untersucht. Oberhalb 500°C ergibt sich bei geringen Drucken eine kolumnare Morphologie, bei hohen Gesamtdrucken werden dagegen equiaxiale Kristalle beobachtet. Das experimentell ermittelte Morphologie—Diagramm, das von den experimentellen Beobachtungen abgeleitet wurde, konnte mittels eines einfachen 'fuzzy'-Systems und einer 'fuzzy'-Extrapolationsmethode vervollständigt werden.

L'influence des paramètres de depôt (température, pression totale, pression partielle de précurseur de TiO_2) a été étudiée. Une structure de type colonnaire est obtenue au dessus de 500°C à basse pression, tandis qu'une structure de type granulaire est observée pour de fortes valeurs de la pression totale. Le diagramme de structure experimental est complété à l'aide d'un système expert flou et de la méthode d'extrapolation flou.

1 Introduction

In this study, layers of thin titanium oxide films were made by a thermal chemical vapor deposition (CVD) process starting from the titanium alkoxide $Ti(OPr^i)_4$, in the presence of nitrogen, which acts as a carrier gas as well as a diluant.

When studying the parameters of the layer deposition the following are taken into account:

—The temperature of the substrate, T_s;
—the nature of the substrate;
—the pressure under which the process is run, P_{trv};
—the relation between the partial pressure of the precursor and the pressure in the process, $\pi = P_{(Ti(OPr^i)_4)}/P_{trv}$;
—the time of the process.

The morphology model determination (thickness, columnar or equiaxial structural type) is based on the results of experiments on monocrystalline silicon used as substrate. The idea of this model is to extrapolate, starting from other models, morphologies determined by physical techniques.[1–3]

To predict the points which were not realized experimentally, the methods based on fuzzy mathematics were applied. Using the information obtained by these methods, the morphology diagram, consisting of experimental points, was completed.

2 Basic Principles of the Chemical Vapor Deposition Process

In the CVD process, the substrate to be coated is put into contact with a vapor phase containing one or several chemical species to perform a chemical reaction giving at least one solid product.

To produce chemical layers in a vapor phase the following are needed:

—The environment where the reaction is carried out (the reactor) and the heating system for the substrate (internal or external);

Journal of the European Ceramic Society 0955-2219/93/$6.00

—the feeding systems for the vapors;
—the pumping system to maintain the desired pressure in the reactor (in the low pressure CVD process, LPCVD).

The desired compound is deposited on the surface which is to be coated (the substrate) according to:

$$A_{(vapor)} + B_{(vapor)} \rightarrow C_{(solid)} \quad \text{reaction}$$

or:

$$AB_{(vapor)} \rightarrow A_{(solid)} + B_{(vapor)} \quad \text{decomposition}$$

The thermal CVD process has advantages which concern the properties of the coatings. Especially the homogeneity in the composition and thickness of the films is excellent, due to the low pressure. Furthermore, the chemical reaction takes place *in situ*, textural differences depend on the parameters of the deposition and processing costs are cheaper.

3 Morphology of the Layers Obtained by the Vacuum Techniques

The layer morphologies, obtained by physical techniques such as vacuum evaporation,[1] magnetron pulverization,[2] ionic layering,[3] can be described by models which define different zones in which the layer morphology is homogeneous.

In the first model, introduced by Movchan & Demchishin,[1] there are three essential zones depending on the temperature of the substrate. At low temperature the morphology is columnar and the columns are spaced. At high temperature an equiaxial morphology is prevalent.

Taking into account the pressure of argon, used when metallic layer films are produced by a magnetron pulverization process,[2] one transition area, between the areas 1 and 2, can be identified. It is called the T area and is shown in Fig. 1.

By using ionic layering,[3] a fourth area, called the vitreous area, can be obtained, which lies near the highest temperatures.

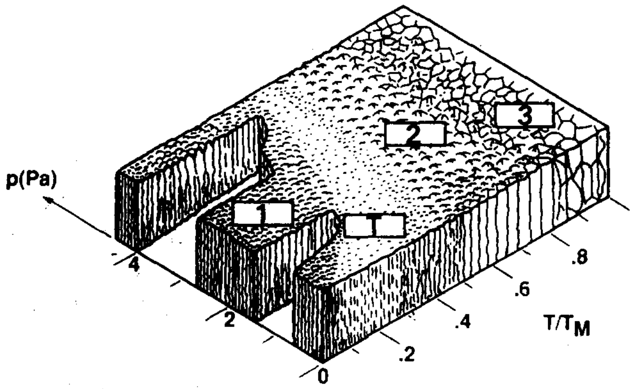


Fig. 1. Morphology diagram presenting different areas of metallic layers deposited by magnetron pulverization[2] as a function of normalized substrate temperature (T/T_m) and argon pressure.

4 Titanium Oxide Layers Produced by the Thermal CVD Process

The equipment required to produce titanium oxide layers consists of three parts:

(1) Vapor injection system: the precursor is heated by an oil bath. When the saturated vapor pressure is reached the alkoxide vapor is introduced by nitrogen gas.
(2) Reactor: a quartz tube in a horizontal furnace.
(3) Pumping system: the vapors are evacuated with the aid of an Alcatel vacuum pump ($12\,m^3/h$). The ultimate pressure is 1 Pa. The pumps are protected by a liquid nitrogen trap which allows the elimination of the reaction by-products.

5 Morphology Models of the TiO_2 Layers Deposited by the Thermal CVD Process

Titanium oxide layers were produced by the thermal CVD process on the silicon at three different temperatures: 400°C, 500°C and 600°C. The process pressure was varied between 25 and 2×10^3 Pa at each temperature. Each experiment was completed in 1 h. The partial pressure of the nitrogen was set at 20 Pa. Examination of the results revealed that the parameters of the CVD process influence several parameters of the resulting layers, such as:

—The morphology of the titanium oxide layers;
—the volume of the units which form columnar morphology;
—kinetics of the layer formation.

Figures 2 and 3 show the influence of the temperature, pressure and precursor partial pressure on the layer morphology obtained on silicon.

When both the total pressure (10^2 Pa) and the temperature (400°C) are low, the TiO_2 layer has the anatase morphology and is very compact. When the temperature rises the layer becomes columnar and the crystallite volume increases. Above 500°C, a rutile morphology is present, as shown by X-ray diffraction. The anatase–rutile transformation occurs near 500°C.

In contrast, at high temperatures, increasing pressure decreases the grain size (Fig. 2). At an intermediate temperature (500°C) an increase of the total pressure brings about firstly a columnar and then an equiaxial morphology.

Finally, Fig. 3 shows the influence of a decrease of the precursor partial pressure. At $T = 500$°C and total pressure $P = 10^2$ Pa a double effect can be observed: the dimensions of the units as well as the thickness of the layer decrease.

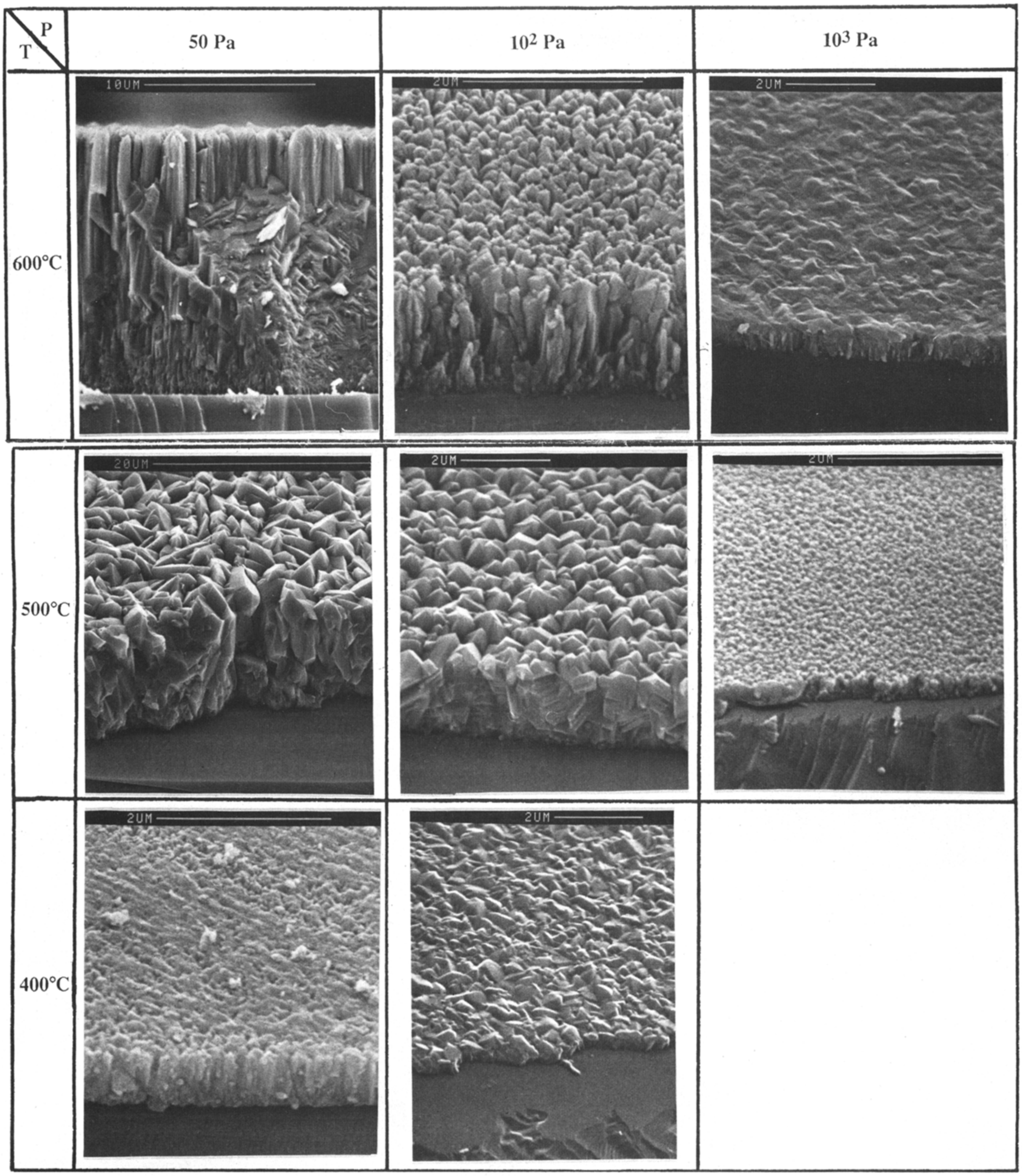
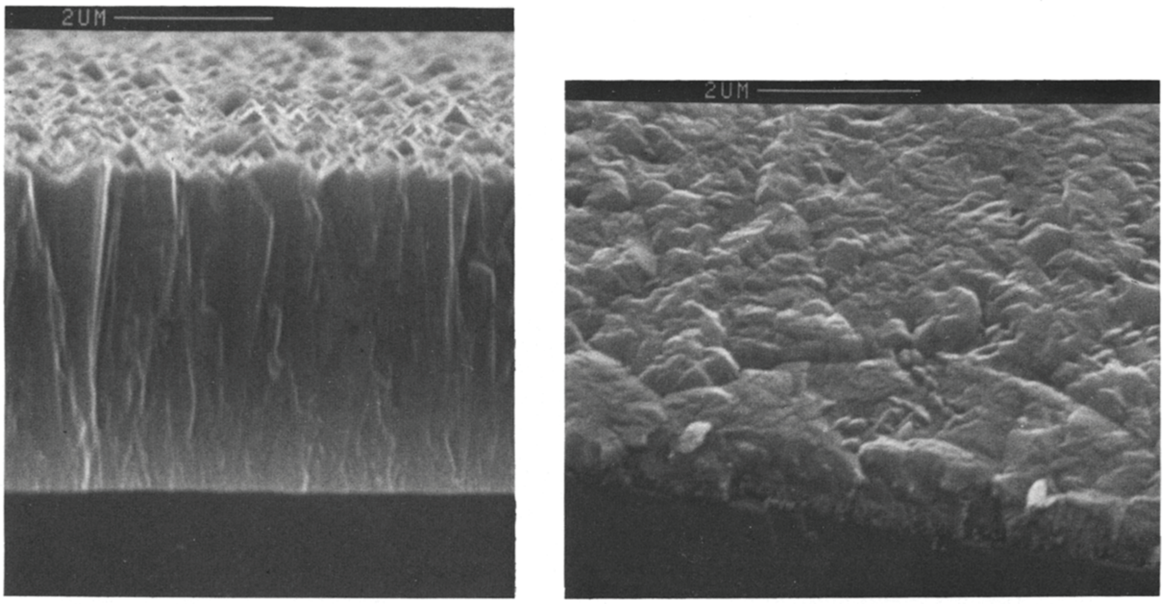


Fig. 2. Effect of the temperature and total pressure on the morphology of the TiO_2 layers deposited on monocrystalline silicon (partial pressure of precursor/total pressure = 0·1, $t = 1$ h).

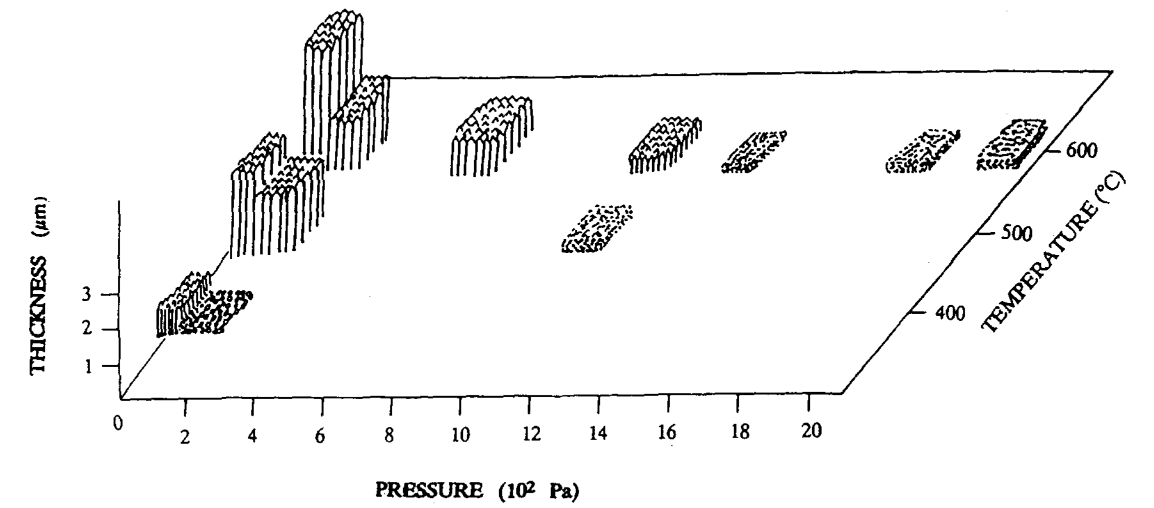
Figure 4(a) and (b) shows the combined effect of the temperature, the precursor partial pressure and the total pressure on the above parameters (morphology, volume of the units, thickness). The precursor partial pressure is indicated by the height of the boxes in Fig. 4(b). As can be seen in Fig. 4(a), the thickness of the layer decreases when the total pressure increases for a certain temperature (for example $T_s = 600°C$). The columnar morphology is dominant at low total pressure. At high total pressure equiaxial crystals are obtained.

The diagrams shown in Fig. 4 contain experimental results presented by discrete points. To complete the areas in this diagram where experimental results were not available, a simple fuzzy expert system was used which allows the prediction of the results in empty areas on the basis of the experimental data.

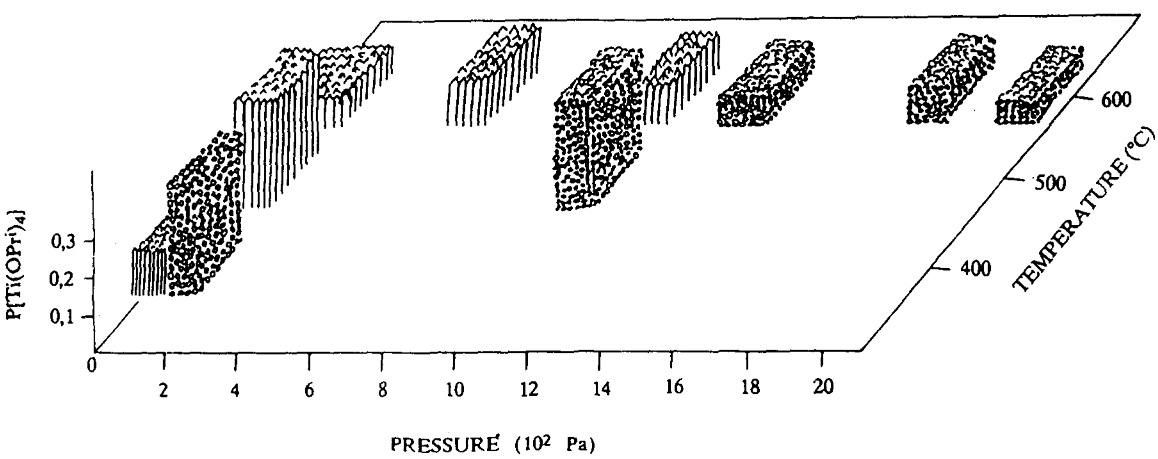


(a) (b)

Fig. 3. Influence of the precursor partial pressure at constant substrate temperature and total pressure $T_s = 500°C$, $P = 10^2$ Pa; (a) $\pi = 0{\cdot}2$, (b) $\pi = 0{\cdot}05$.



(a)



(b)

Fig. 4. Morphology diagram: (a) The thickness and the morphology of the TiO_2 layers as a function of total pressure and temperature; (b) the morphology of the TiO_2 layers as a function of total pressure, temperature and partial pressure of the precursor; columnar; faceted crystal; equiaxial texture.

6 Fuzzy Methodology Applied

The fuzzy methodology is developed for dealing with sources of uncertainty or imprecision that are non-statistical in nature. The application of fuzzy methods[4,5] allows heterogeneous data to be processed with a variable exactitude and reproducibility and to find the relations between the parameters faster and easier than by using other mathematical methods, e.g. by statistical theories. These methods are not created to deal with such uncertain data nor with subjective, expert knowledge and their application presupposes an extensive data set.

7 Application of Fuzzy Methods to the CVD Process

In order to develop an expert base to predict the thickness and another to predict the morphology of the layers produced by a thermal CVD process, the data from the previous experiments were transformed into sets of conditional statements.

if T_s and P_{trv} and π then THICKNESS
if T_s and P_{trv} and π then MORPHOLOGY (1)

Hence, the results of every experiment were described by one conditional statement in each expert base. The statements were weighted according to their reproducibility so that the weight was the highest for those experiments having the best reproducibility.

All values of independent variables and layer thicknesses were defined by triangular fuzzy numbers (TFN). The point a_2 of a triangular fuzzy number was determined by the measured values of that variable. Incertitude values, defined according to experience, are given in Table 1.

Table 1. Incertitude values, i.e. intervals a_1a_2 and a_2a_3 of the triangular fuzzy numbers (TFN)

Variable	*Incertitude*
T_s	20°C
P_{trv}	10%
π	10%
Thickness	5%

The layer morphologies were defined by discrete numbers, so that

0 = layer with an unspecified morphology
1 = compact columnar morphology
2 = non-compact columnar morphology
3 = equiaxial microcrystalline morphology
4 = large, faceted crystalline morphology

The morphology of a layer having a mixed morphology was specified by the prevalent morphology.

During the experimental study it was noticed that the layer morphology and thickness were very sensitive to variations of the temperature (T_s) and the pressure (P_{trv}) and less sensitive to that of the ratio (π). Hence, the independent variables in the expert bases were weighted. The weights of T_s and of P_{trv} were set to the maximum, i.e. to 1·00, and that of π to 0·60.

In all, there were 25 conditional statements describing the properties of TiO_2 thin films in both expert bases.

To complete the diagram, firstly the importance of the ratio π to the layer thickness and morphology in temperature intervals ($400°C \leq T_s \leq 500°C$ and $500°C \leq T_s \leq 600°C$) and at a constant temperature ($T_s = 600°C$) was studied. If answers were not found, the questions were fuzzified, widening the fuzzy intervals of the fuzzy numbers of the variables according to the definitions of Table 1.

It was noticed that at a constant pressure the morphology is dependent on the ratio π: it is columnar between $\pi = 0·01$ and $\pi = 0·02$, equiaxial at 0·035 and faceted crystalline at 0·04. At high total pressure the equiaxial morphology is prevalent.

Figure 5 presents the combined effect of the total pressure P_{trv} and the ratio π to the thickness and the morphology at a constant temperature ($T_s = 600°C$).

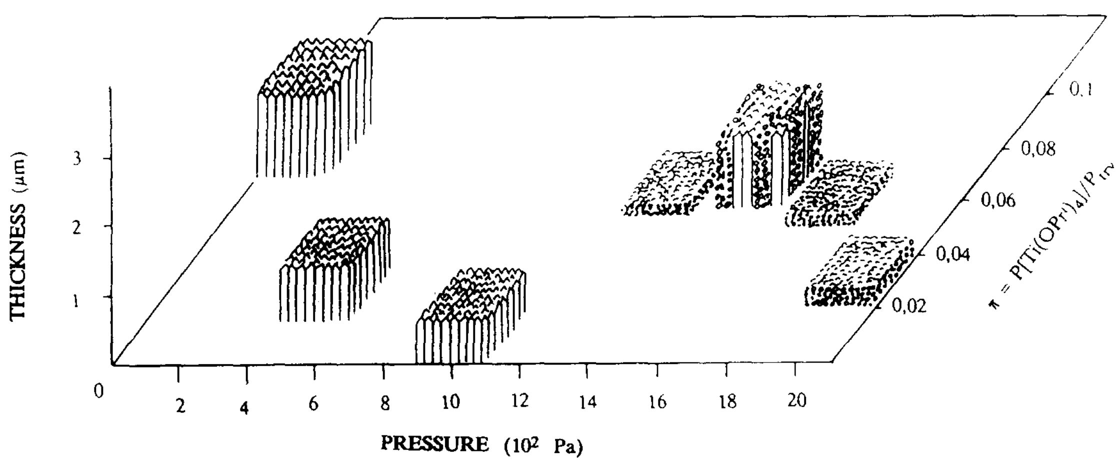


Fig. 5. Thickness and morphology of the TiO_2 layers as a function of the total pressure (P_{trv}) and of the ratio π.

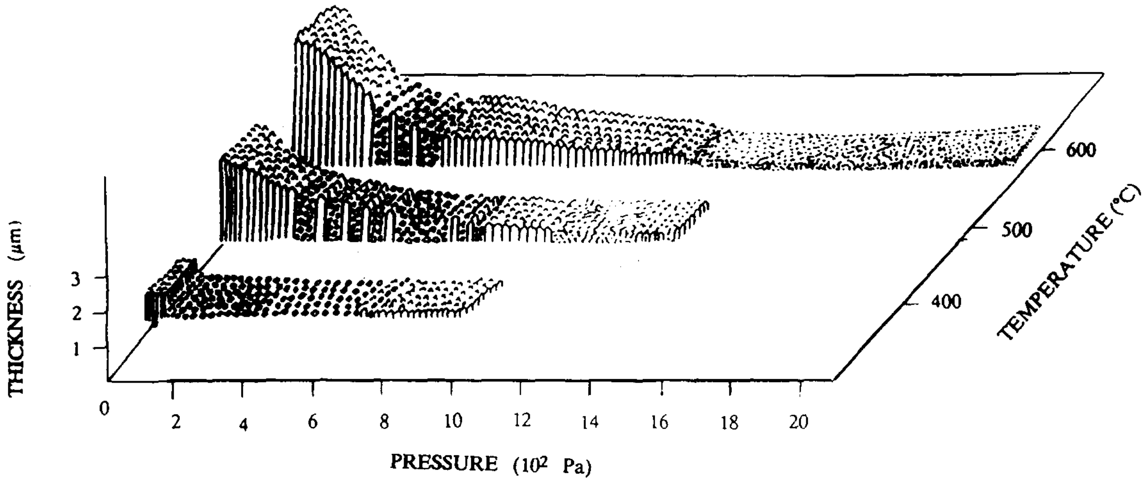


Fig. 6. The completed morphology diagram.

At low pressure values ($P_{trv} < 10^3$ Pa) the columnar morphology is dominant independently of the ratio π. At high pressure values ($P_{trv} > 10^3$ Pa) an equiaxial morphology was found. When the pressure is 15×10^3 Pa the thickness of the layer, obtained by this method, is approximately 1 μm. At this pressure, the fuzzy expert system predicted a mixed morphology, columnar and equiaxial. All these first estimations were included in the expert bases.

To find thicknesses and morphologies for the layer at low pressure and high temperature values, the clustering method was applied.[5] The answers of this method were included to the expert bases.

Finally, all values of the thickness and morphology were reviewed by the completed expert bases. The original diagram, presented in Fig. 4(a), completed by these values is shown in Fig. 6.

The completed diagram seems to be very logical, especially at the constant temperature ($T_s = 600°$C). At this temperature, it can be seen that the change in the morphology is progressive: at 9×10^2 Pa it is purely columnar, at $1{\cdot}2 \times 10^3$ Pa it is purely equiaxial, between $0{\cdot}9 \times 10^3$ and $1{\cdot}2 \times 10^3$ Pa a mixture of these morphologies is obtained.

The unexpected mixture of a columnar and faceted crystalline morphology, predicted by the fuzzy method between 2×10^2 and 4×10^2 Pa and at 600°C has been confirmed experimentally (Fig. 7). In these conditions, the morphology is globally columnar but the columns are disordered. The column shape is pyramidal.

It can be concluded that the thickness of the titanium oxide layers, deposited on the silicon, decreases when the pressure is increased, while the morphology modified is also changed. Analogous results were obtained for titanium oxide layers which had been deposited on carbon, only the thickness of the layer was found to be larger than that of the layer deposited on silicon.

The obtained results are in good agreement with the observed morphology shown schematically in Fig. 1. The double morphology expected in Fig. 7 corresponds to the transition zone T.

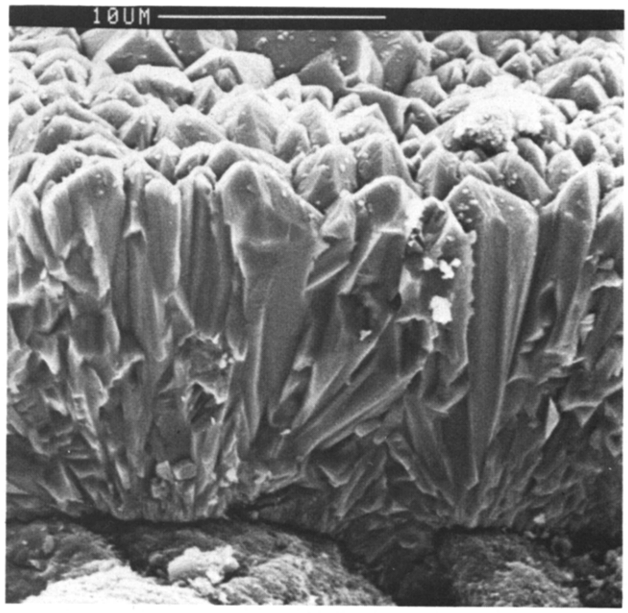


Fig. 7. Double morphology (columnar–faceted crystalline) obtained at $T_s = 600°$C, $P = 3 \times 10^2$ Pa, $\pi = 0{\cdot}1$ confirms the result of the fuzzy simulation.

The crystal shape is a function of the growth rate of the different crystalline faces. These growth rates depend on the temperature, the concentration of the gas phase and the total pressure.

8 Conclusion

The experimental morphology diagram completed by the results of a simple fuzzy expert system gives a global view of the importance of the parameters which are to be manipulated to obtain a precise morphology of a given thickness under operational conditions. It is shown that the temperature of the substrate, the ratio between the partial pressure of the precursor and the total pressure are particularly important.

References

1. Movchan, B. A. & Demchishin, A. V., Study of the structure and properties of thick vacuum condensates of nickel, tungsten, aluminum oxide, and zirconium dioxide. *Phys. Met. Metallorg.*, **28** (1969) 83.
2. Guentrher, H. K., Loo, B., Bruns, D., Edgell, J., Windham, D. & Muller, K. H., Microstructure analysis of thin films deposited by reactive evaporation and by reactive ion plating. In *SPIE* Vol. 1019, *Thin Film Technologies III*, 1988, pp. 73.
3. Harris, M., Macleod, H. A. & Ogura, S., The relationship between optical inhomogeneity and film structure. *Thin Solid Films*, **57** (1979) 173–8.
4. Vaija, P. & Dohnal, M., Fuzzy methods to compensate missing data and to evaluate the relative importance of different contributors in accident analysis. In *Acta Polytechnica Scandinavica, Chemical Technology and Metallurgy Series*, Helsinki, 1987, No. 179.
5. Vaija, P., Järveläinen, M. & Dohnal, M., Expert system and clustering of accident data. In *Proc. 5th Int. Symp. Loss Prevention and Safety Promotion in the Process Industries*, Paris, 1986, Vol. 3, pp. 228–42.