Neural Network Modeling of Plasma Processes

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Plasma polymerized thin films are of increasing importance in the field of transparent packaging. In particular, hydrocarbon coatings prepared by the reactive magnetron sputtering method combined with plasma-stimulated gas-phase polymerization have proved to have excellent diffusion barrier properties for gases and water vapor.

However, the non-linear relationship between stretch failure and permeation properties poses a challenge when it comes to modeling the functional coatings to meet the required product specifications. An improvement in the functionality of these films has been achieved using the general regression neural network GRNN. The method employs the input parameters of the coating such as gas flow, pressure and process time. To improve the prediction performance the training input and output vectors were linearily transformed into the space defined by the principal components of the given training data.

In conclusion, it can be stated that modeling of plasma processes according to the film characteristics makes possible a more controlled and systematic production of thin films. The neural network being used as a tool to determine the process parameters is able to enlighten the understanding of their influence on the film properties which is of particular importance for optimization and scaling up of a defined functional thin film in a web coater.

Introduction

Amorphous hydrogenated carbon thin films generated by plasma-enhanced chemical vapor deposition have attracted a large amount of interest due to their desirable mechanical, physical and chemical characteristics and properties. The attributes of hydrogenated carbon films (a-C:H) vary from the extremes of hard diamondlike films (often called DLC) to soft polymerlike films. A number of groups have extensively characterized the chemical structure and investigated the macroscopic properties of hydrogenated carbon films using a wide variety of analytical methods. However, the detailed structure of the bonding network is still under study. A random covalent network model and a two phase model consisting of threefold coordinated sp^2 hybridized carbon clusters embedded in a randomly oriented tetrahedrally sp^3 bonding matrix, with the sp1 amount small enough to be ignored have been suggested. The matrix largely controls the mechanical properties governed by the hydrogen and sp^3 content while the planar rings control the band gap. Many of the properties of these films, such as hardness, density, high degree of transparency to infrared radiation, and high electrical resistivity have been correlated with the hydrogen content and the sp^2 to sp^3 ratio.

In previous work we have shown that dense hydrocarbon coatings can act as excellent diffusion barriers for oxygen and water vapor permeation [1-3]. Due to the diverse nature of these thin films their intrinsic flexibility can be tailored to meet the product specifications. This barrier type is, therefore, a potential candidate for extending the existing application fields for transparent packaging.

The non-linear relationship between input parameters of the coating process and properties of the resulting coating prevent an exact mathematical description and optimization. However, artificial neural networks mimic the behavior of biological neural nets, and have successfully solved problems through generalization of a limited quantity of training data, overall trends in functional relationships. In semiconductor manufacture, a multilayer perceptron trained by backpropagation is by far the most popular network architecture [4-6]. Based on a general regression neural network (GRNN) it is equally well to model a real deposition process and to calculate the effect of the parameters according to their specific probabilities based on a reasonably small data set [7, 8]. This mathematical model was also used to generate process parameters for thin films with the desired functional performance.

The aim of this work was to the properties of the coatings using a model based on a neural network and to obtain a deeper insight into their func-

tionality when acting as a diffusion barrier. However, the project was started without knowing that neural networks were suitable for modeling our process. After having evaluated the usability of neural networks and more specifically GRNN the general potential of their application in plasma processes was investigated *(Figure 1)*.

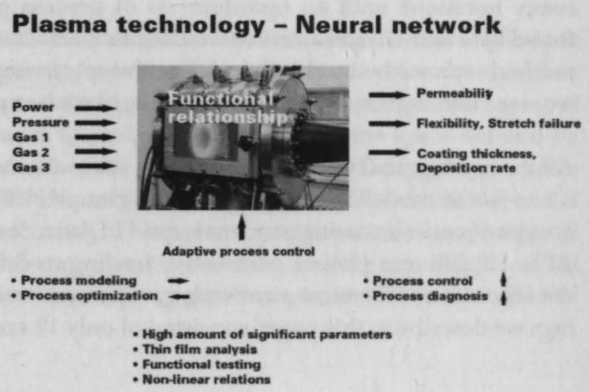

Figure 1: Schematic drawing of possible applications for neural network in plasma technology.

Experimental Procedure

All samples were prepared in a low temperature, plasma-enhanced chemical vapor deposition (PE-CVD) reactor and are described in detail in previous papers [1–3]. The starting pressure in the reactor was about 3×10^{-6} mbar. The discharge power density was maintained between 0.3 and 0.6 W/cm^2, and a pulse frequency of 2.5 kHz; a reverse voltage of 15 % of operating dc input voltage, and a reverse recovery time of 2 µs were chosen. The samples were either grounded (samples A1, B1) or were biased using a capacitively coupled radio frequency (rf = 13.56 MHz, Vb = –90 V). The target consisted of a circular hot pressed carbon disc (purity of 99.999). The total flow rate of gas mixtures (acetylene, helium, argon) was not higher than 72 sccm. The working pressure in the range from 1 to 15 µbar was regulated by a butterfly valve controlled by a baratron gauge. Polyethylene terephthalate (PET) film, DuPont-MYLAR® type A, with a thickness of 12 µm, aluminum foil, and a piece of silicon wafer [100] were used as substrates. The film thickness varied from 20 nm up to 3 µm to allow analyses by the various techniques. Oxygen permeability was measured using a Mocon OX-TRAN 2/20 instrument at 0 % and 85 % rel. humidity, respectively. Water vapor transmission measurements were conducted with a Lyssy Vapor Permeation Tester L 80–4000 at 90 % rel. humidity.

Neural Network Modeling of the Plasma Processes

The process of making coatings and analyzing their properties is expensive and time consuming. The average time from making the coatings until measurements of their properties were available was about two weeks. The high degree of complexity of the PE-CVD process would require many iterations until an optimum set of process parameters could be found by a human operator and would thus lead to very high costs. Linear methods cannot be used for modeling the sputtering process. Therefore, we were looking for a suitable non-linear, black box modeling approach.

All the coatings that were available at the time when we started looking for a non-linear modeling method could be grouped into about half a dozen groups of various coating processes, each of them described by a group of 10 to 30 different plasma parameters leading to different coatings. The data for some of the most promising groups were rare. The group of coatings we describe in this paper consisted of only 12 samples.

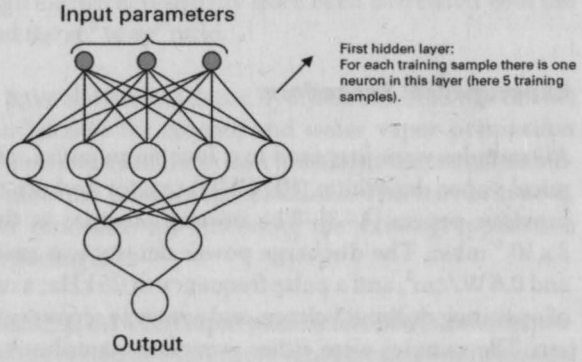

Figure 2: The General Regression Neural Network for a scalar output.

The General Regression Neural Network (GRNN, *Figure 2)* was found to be the most suitable for modeling our coating processes for the following reasons:

- We could use our rare data for training and verification at the same time, without the problem of overfitting (cross validation error measure).
- The same programs could be used without modification to model various groups of coatings, since the structure was only dependent on the training data.
- The clear analytical-statistical theory underlying the GRNN approach.

The training set consisted of 12 different plasma processes which were prepared by reactive dc magnetron sputtering processes combined with plasma stimulated gas-phase polymerization. The input parameters were (gas flow 1, gas flow 2, gas flow 3, pressure, process time) and the output (i.e. the desired properties) consisted of (permeation, stretch failure, coating thickness).

The training input vectors (process parameters) and the training output vectors (resulting coating properties) were first centered and normed to unit variance. To improve the prediction performance, the training input and output vectors were linearily transformed into the space defined by the principal components of the given training data. During the gradient-based training the GRNN predicted the properties of each coating as if it were a new unknown coating. This gave us a measure indicating how well the GRNN could predict new coatings before creating new samples. This was possible by minimizing a cross validation error measure during training *(Figure 3)*.

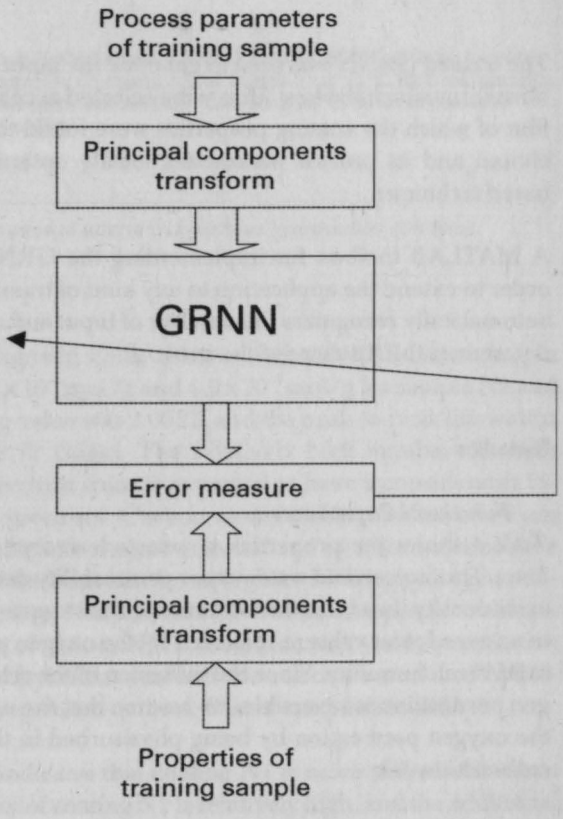

Figure 3: The training process.

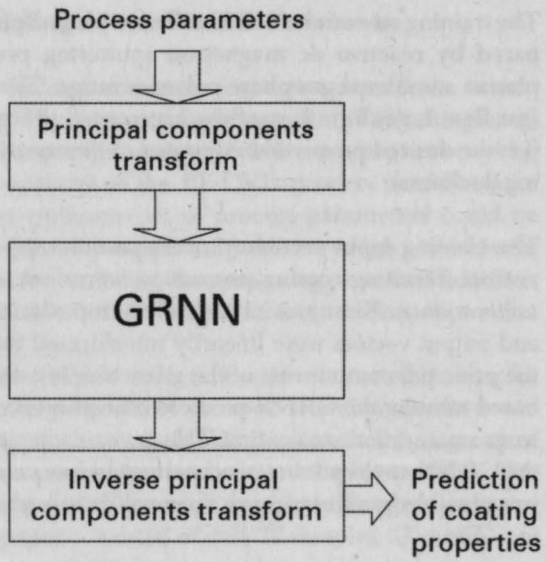

Figure 4: The trained GRNN used to predict process parameters.

The trained GRNN was used to generate the input parameters for a set of films from which the best films were selected according to *(Figure 4)*. The film of which the coating properties were found to be most suitable was chosen and its process parameters locally optimized using a gradient-based technique.

A MATLAB toolbox for implementing the GRNNs was developed in order to extend the application to any kind of training data. The program automatically recognizes the number of input and output parameters and determines the structure of the network.

Results

Functional Performance

Table 1 shows the properties of selected amorphous hydrocarbon thin films. The oxygen and water vapor permeability decreases with increasing mass density. In a humid environment, the oxygen permeation is reduced to an even lower value as indicated by the oxygen permeability measured at 85 % rel. humidity. Since the influence of the rel. humidity on the oxygen permeation is reversible, we assume that the water molecules reduce the oxygen permeation by being physisorbed in the voids of the hydrocarbon network.

The stretch failure factor of the coatings – defined as the % elongation permissible before permeation failure – decreases with increasing mass density and increases with the hydrogen content. Sample N1 exhibits an optimal functional performance that would be of interest for various applications and is characterized by a relatively high mass density and hydrogen content, as well as a lower nanohardness compared to the other coatings.

Sample	Thickness[a]	OXTR[b]	OXTR[c]	WVTR[d]	Stretch[e]	Density[f]	Hardness[g]
A1	20 ± 3	< 2.2 ± .2	< 1.7 ± .2	< .6 ± .2	> 2.5 ± .2	1.58	13.3
B1	35 ± 3	< 39.3 ± .2	< 18.7 ± .2	< 12.1 ± .3	> 8.8 ± .2	1.03	–
B2	58 ± 3	< 1.8 ± .2	< 1.6 ± .2	< .3 ± .2	> 2.8 ± .2	1.21	–
C2	76 ± 3	< 1.1 ± .2	< .7 ± .2	< .4 ± .2	> 2.8 ± .2	1.46	8.1
N1*	78 ± 3	< 1.2 ± .2	< .8 ± .2	< .6 ± .2	> 3.7 ± .2	1.48	7.5
N2*	89 ± 3	< 1.8 ± .2	< .9 ± .2	< .7 ± .2	> 3.0 ± .2	1.34	8.1
N3*	90 ± 3	< 2.4 ± .2	< 1.5 ± .2	< .7 ± .2	> 3.4 ± .2	1.18	8.8
PET-film	12 µm	< 123.9 ±.3	< 93.0 ± .3	< 20.4 ± .3	–	1.36	

*Samples prepared according to parameters suggested by GRNN

Legend:

a Thickness [nm]
b Oxygen permeability [ccm/(m^2 x d x bar)]: ASTM D 3985-81 @ 23 °C, 0 % rel. humidity
c Oxygen permeability [ccm/(m^2 x d x bar)]: ASTM D 3985-81 @ 23 °C, 85 % rel. humidity
d Water vapor permeability [g/m^2 x d]: ASTM F 1249-90 @ 23 °C, 90 % rel. humidity
e Stretch failure, Elongation [%]
f Mass density [g/cm^3]
g Nanohardness [GPa]

Table 1: Functional performance of selected amorphous hydrocarbon thin films.

Characterization

The density of paramagnetic spins, as measured with ESR (electron spin spectroscopy), was 7.2×10^{-5} mol/g and 4.9×10^{-5} mol/g for sample N1 and C2, respectively. The g-value was 2.0023, and the peak-to-peak linewidths were measured to be 11 Gauss. The relatively high number of about 1020/cm^3 unpaired electron spins is expected to have a considerable influence on the NMR spectrum. Carbon atoms inside a radius of ~1 nm around an unpaired electron are not detected and as a consequence the fraction of undetected carbons can be as high as 50 % in hydrogen deficient structures. Therefore, NMR results have to be interpreted with caution. The combination of various NMR measurements yields quantitative information about the hybridization and the relative amount of hydrogenated and non-hydrogenated carbon. This is compiled in *Table 2.*

The NMR spectrum indicates that coating N1 is more polymerlike than coating C2. The density of coating N1 is relatively high, and the additional

hydrogen is bonded to carbon atoms and not incorporated into the network interstitially as molecular hydrogen. In contrast, sample A1 contains more tetrahedrally bonded sites coordinated in a diamondlike carbon network according to Raman data. The effect of hydrogen incorporation into hydrocarbon films can be interpreted using a structural model, in which hydrogen appears to increase the number of network terminating bonds. An increase in hydrogen content leads to a higher polymeric content of the film and as a result to a flexible barrier, as long as the mass density is not reduced below a certain level.

Sample	$sp^2:sp^3$	sp^2 (C-graphite)	sp^2 (CH-polymer)	sp^3 (C-diamond/ CH_3)	sp^3 (CH-/CH_2-polymer)
C2	47:53	40	7	19	34
N1	45:55	34	11	13.5	41.5

Table 2: Hybridization and hydrogenation of carbon atoms in plasma polymerized hydrocarbon coatings as determined by NMR measurements in [at %].

Discussion

When we started using the GRNN approach some of the coatings exhibited a good performance as diffusion barriers (*Table 1:* coatings B2, C2). However, the stretch failure of these coatings was less than the 3% minimum value required by the packaging industry. The non-linear relationship between excellent diffusion barrier and elongation behavior prevents a straightforward optimization for the process engineer.

As shown in *Table 1*, excellent barrier coatings combined with a high stretch failure have been produced on the basis of the process parameter adjustments predicted by the GRNN (coatings N1, N2, and N3). In addition, the GRNN model as developed enabled us to study the correlation between the coating properties and the process parameters.

Outlook

Our aim was to establish a set of process parameters that optimizes barrier and stretch performance for an individual application. The GRNN was able to predict the process parameters for an excellent diffusion barrier suitable for flexible packaging. Further work will show to what degree GRNN is able to optimize process parameters for data sets concerning

functional thin films with different properties. Moreover, we intend to enhance the current GRNN structure so as to regulate the deposition processes in the web coater BABE 1 in an time-adaptive way *(Figure 5)*. The stabilization of the reactive magnetron sputtering method combined with plasma-stimulated gas-phase polymerization is a challenge we are going to elaborate a suitable model for in the near future *(Figure 6)*.

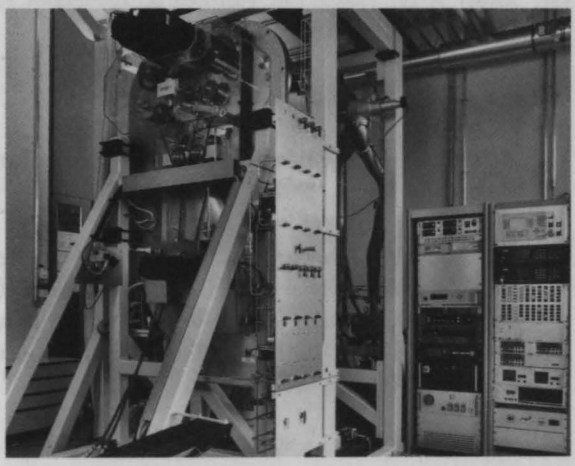

Figure 5: High vacuum web coater BABE 1.

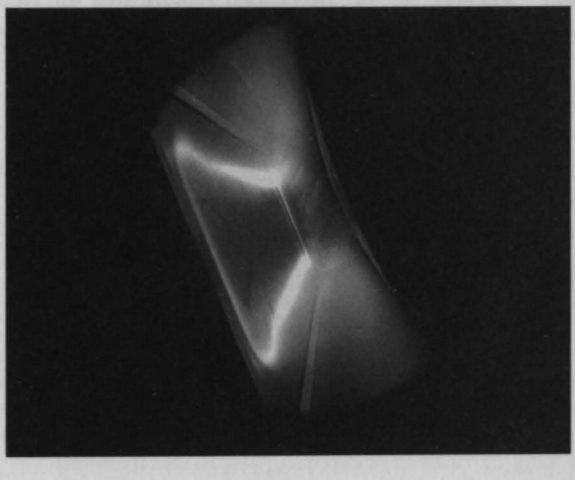

Figure 6: Pulsed dc-magnetron sputtering discharge in web coater BABE 1.

Literature

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