FH – HES Fachhochschule – Hautes Ecoles Spécialisées

Chimia 58 (2004) 422–425

ISSN 0009–4293

NANO-Textured Functional Layers for Sustainable Products

Eva Maria Moser*, Jacques Painot, Anne Dimitrov and Edmond Goy

Abstract: The versatile role of nano-textured layers and their advanced performances have been elucidated in selected R&D projects. The aim was to overcome the limitation of conventional thin films due to micro defects like pinholes and scratches by nano-texturing the functional layers. Our concept allows the development of highly effective diffusion barrier layers for reactive gases in order to prevent their loss to the environment during storage. A second application describes the nanoactive corrosion protection for metallic products due to the combination of a passive physical barrier consisting of a highly cross-linked hydrocarbon layer and the adjustment of the electrochemical potential by incorporating metallic clusters. Tiny amounts of added metals like zinc substitute toxic metals used for conventional corrosion protection so far which enables a management of sustainable materials.

Keywords: Corrosion protection · Diffusion barrier layers · Hydrogen storage · Nanotechnology

1. Introduction

Thin films that provide the underlying material with specific mechanical, physical, and optical properties, such as wear-resistant coatings for tools and light-reflecting metallic surfaces can be used in a wide range of applications. In general, the properties of the thin films meet the product specifications and their inherent defects do not affect the performances in these protective or decorative application fields. However, tiny holes or scratches in the thin films can lead to a complete breakdown of the layer protection if a chemical reaction takes place at the interface. If the substrate needs to be entirely protected by a layer, the coverage of the thin films has to be provided under perfect conditions, such as avoiding the generation of dust in a 'clean room'. Another way is to inactivate the layer defects by a functional property of the layer itself.

In general, the aim of our research field is to combine the specific properties of a particular coating with the physical or chemical potential of a second material in order to enhance the properties and durability of the thin films. As a result, multifunctional coatings are obtained in which at least one function is adjusted to compensate the destructive impact of the micro defects in the coating. A positive side effect of the development of highly effective plasma-polymerized layers is the consequent development of sustainable products by the selection of an environmentally harmless basic material followed by surface treatment in well-defined closed systems. Several patent applications have been submitted to protect the production of the functional layer systems described in this article [1].

Hitherto, incorporated particles in conventional polymeric materials were, for example, widely used as scavengers for oxygen gas in packaging. On the other hand, plasma-polymerized thin films are of increasing importance in the field of transparent packaging. In particular, plasma-polymerized amorphous hydrocarbon coatings (a-C:H) proved to exhibit excellent diffusion barrier properties for gases and water vapor [2]. The incorporation of particles into hydrocarbon layers has been adapted for the high pressure CNG (compressed natural gas) vessel project [3] together with the concept of highly effective diffusion barrier systems which provide long-term storage for hydrogen gas. The non-linear relationship of a dense and elastic barrier layer forces the generation of multilayers containing varying amounts of metallic species to adsorb hydrogen gas at higher pressures. In that way, the functional layers 'blow up' and build up an intrinsic pressure that is able to withstand the high pressure inside the vessel to a certain extent. In particular, the creation of nano-textured functional layers enables their performance to be tailored to the desired product specification.

Another promising application is the development of active corrosion protective coatings based on metal-doped amorphous hydrocarbon thin films (Me-a-C:H). The basis for the nanoactive concept is provided

*Correspondence: Prof. Dr. E.M. Moser
University of Applied Sciences of Geneva
Ecole d'Ingénieurs de Genève (EIG)
Department of Chemical Process Engineering
4, rue de la Prairie
CH–1202 Genève
Tel.: +41 22 338 06 82
Fax: +41 22 338 06 11
E-Mail: moser@eig.unige.ch
www.eig.unige.ch

by two well-known corrosion protection methods: on one hand, passive corrosion protection by a dense barrier layer keeping away oxygen and water vapor, on the other hand cathodic or anodic protection like sacrificial zinc clusters or passivating metallic surfaces. By embedding metallic clusters into an amorphous hydrocarbon coating, it is possible to electrochemically protect the metallic surface if the added metal is in electric contact with the substrate to be protected. The amount of metal needed is usally very low and the formation of nano-clusters is suficient for most applications since the number of micro defects obtained during process procedures is small and correlates with the permeability of oxygen through the dense a-C:H matrix.

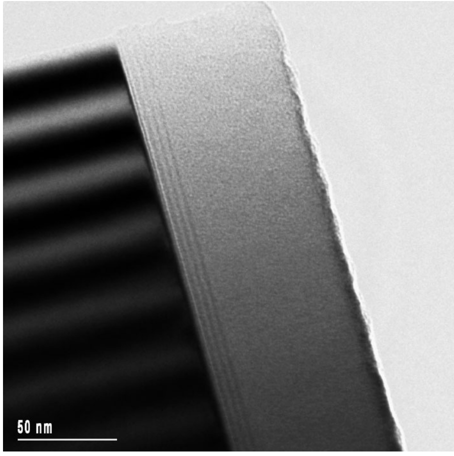
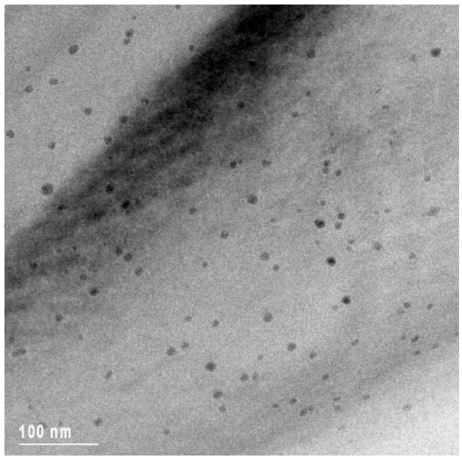


Fig. 2. a) TEM view picture of a nano-textured Zn-a-C:H thin film on a Si (100) wafer



b) TEM plane-view picture revealing the in-plane distribution of Zn-clusters in the a-C:H matrix

2. Experimental Details

The nano-textured thin films with a thickness in the range of 20 to 200 nm were deposited on various substrates in a high-vacuum deposition chamber, installed at the University of Applied Sciences of Geneva (EIG, Ecole d'Ingénieurs de Genève). In Fig. 1a, the magnetron sputtering discharge is ignited which allows the production of metal-doped hydrocarbon coatings by superimposing the magnetron sputtering method with plasma-stimulated gas-phase polymerization. The experimental procedure has been described in detail in previously published papers [2]. The barrier improvement factor (BIF) of the substrates is provided by the functional layer systems and is measured using the variable pressure permeability technique (VPP), as shown in Fig. 1b.

The structure of the thin films was analyzed using transmission electron microscopy (TEM) and ion beam analysis. TEM allowed the size and shape of the metallic dopants in the thin films to be determined as well as their distribution, whereas ion beam analysis using Rutherford backscattering (RBS) and electron recoil detection analysis (ERDA) revealed the molecular composition and stoichiometry of the thin films. TEM pictures were provided by the Centre Interdépartemental de Microscopie Electronique (CIME) at the Ecole Polytechnique Fédérale de Lausanne (EPFL), depth profiles were measured at the Centre d'Analyse par Faisceau Ionique (CAFI) at the Ecole d'Ingénieurs du Canton de Neuchâtel (EICN). Several functional tests regarding the corrosion protection were performed at the Eidgenössische Material- und Forschungsanstalt (EMPA), at the Eidgenössische Technische Hochschule Zürich (ETHZ), and at the Ecole d'Ingénieurs de Genève (EIG).

3. Results and Discussion

3.1. *Structural Aspects*

The TEM image depicted in Fig. 2a reveals the nano-textured sublayers of the amorphous thin film at the proximity of the silicon interface and a homogeneously structured pure hydrocarbon layer above. The darker textures are due to the zinc enrichment of about 1.5 at.% in the sublayers characterized by a thickness of 2–3 nm. The in-plane distribution of the metallic clusters and the distance of the clusters with a size of about 5–10 nm varying between 20 and 100 nm are exhibited in the TEM plane-view picture Fig. 2b.

The clusters can be distributed homogeneously in the thin films, enriched at the interface or vary along a gradient concentration, *i.e.* a decreasing metal content towards the outside of the coating can be obtained by choosing the appropriate process parameters. The enrichment of the metal at the interface is favorable for coatings with minimized overall metal content, whereas it is necessary to realize a homogeneous distribution of the metallic clusters at the thin film surface to obtain coatings with increased conductivity.

3.2. *Functional Aspects*

3.2.1. *Nano-Textured Diffusion Barrier Layers for the Storage of Reactive Gases*

In the current project financially supported by the Swiss Federal Office for Energy, the research and development of highly effective diffusion barrier coatings for the storage of hydrogen at extreme condi-

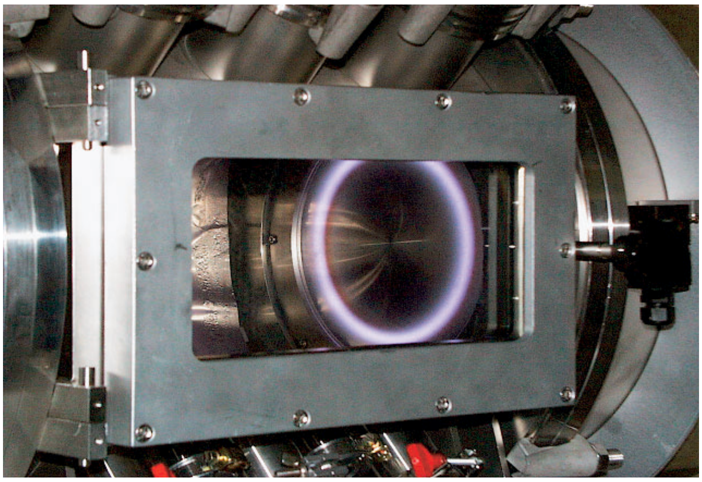
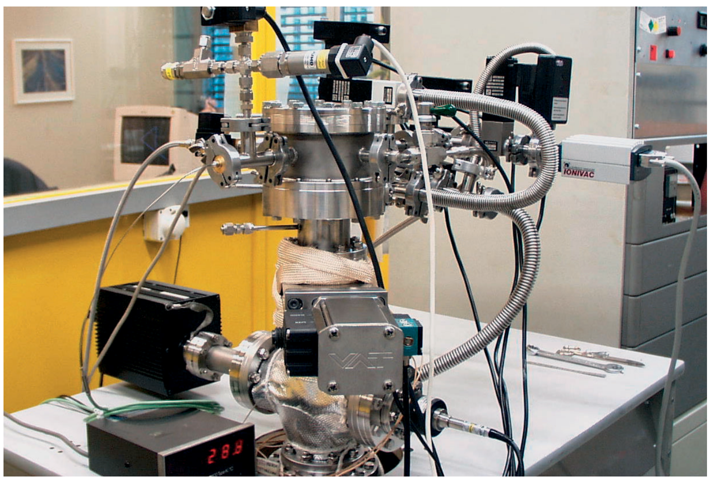


Fig. 1. a) Magnetron sputtering discharge in the plasma reactor at EIG



b) VPP-prototype realized and installed at EIG

CHIMIA 2004, 58, No. 6

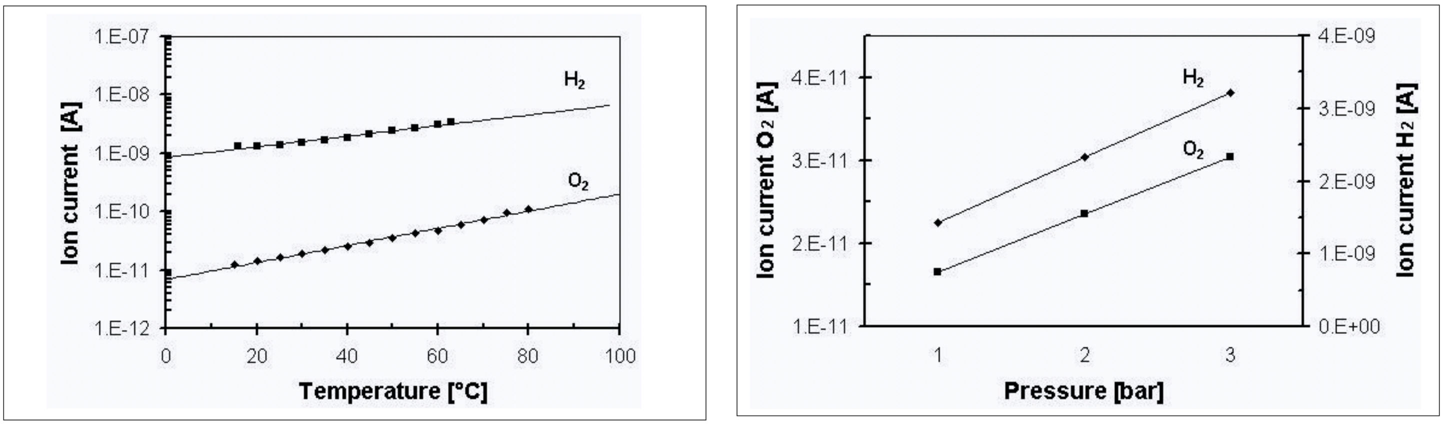


Fig. 3. a) Permeability of PET 12 μm at 1 bar in function of the temperature

b) Permeability of PET 12 μm at 23 °C in function of the pressure

tions is targeted. The physical data of hydrogen gas require a compression of up to 700 bar so as to provide economic energy storage. The French company Ullit S.A. produces high pressure CNG4-containers suitable for use in cars and buses. A modern car equipped with four of these containers of an empty weight of 4 × 50 kg and filled up with 8 kg of hydrogen gas at 700 bar would be able to cover a distance of 400 km. However, these fully polymeric containers reinforced with carbon fibers require a flexible diffusion barrier coating to withstand extreme storage conditions.

The hydrogen and oxygen permeability of PET (polyethylene terephthalate) increases linearly with increasing pressure up to 3 bar, whereas the permeability shows an exponential dependence if the temperature is increased up to 80 °C (Fig. 3).

The barrier improvement factor (BIF) defines the reduction of penetrating species through a coated sample with respect to the untreated sample. The measurements of the permeation behavior of the selected barrier layer systems shown in the Table demonstrate the importance of the material choice regarding the barrier effect for a particular gas. The impact of nano-texturing using metallic clusters in combination with multilayer systems provided a pronounced effect for the BIF on hydrogen gas while maintaining a remarkably high stretch failure of 15% before micro cracks could be detected in the multicoating system.

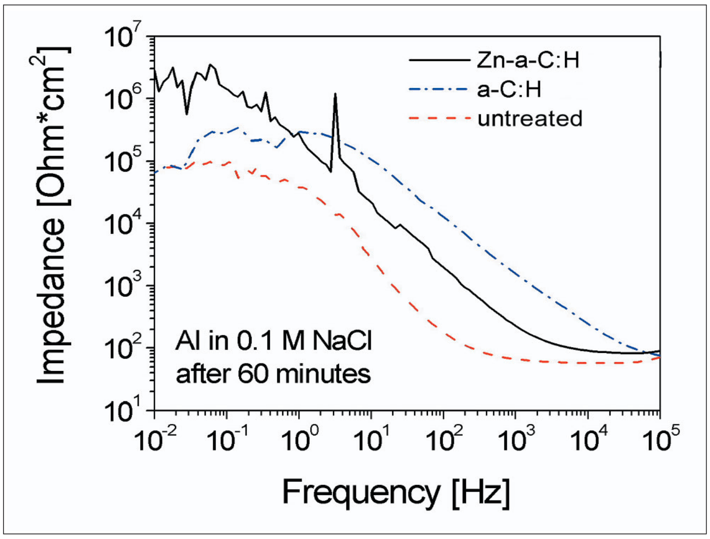


Fig. 4. Comparison of impedance spectra of a 50 nm thick Zn-a-C:H coated, a pure a-C:H coated, and an untreated Al-substrate

3.2.2. *Nano-Textured Active Corrosion Protection Layers for Metallic Components*

The influence of the protection layers on the corrosion behavior of aluminum substrates was investigated using impedance spectroscopy and optical microscopy. The graphic in Fig. 4 shows that a higher corrosion protection with an improvement factor of about 30, defined as the increase in impedance at low frequencies, is achieved for the zinc-doped a-C:H layer compared to the pure a-C:H layer. This effect is due to the metallic clusters since the barrier improvement factor is similar for both thin films.

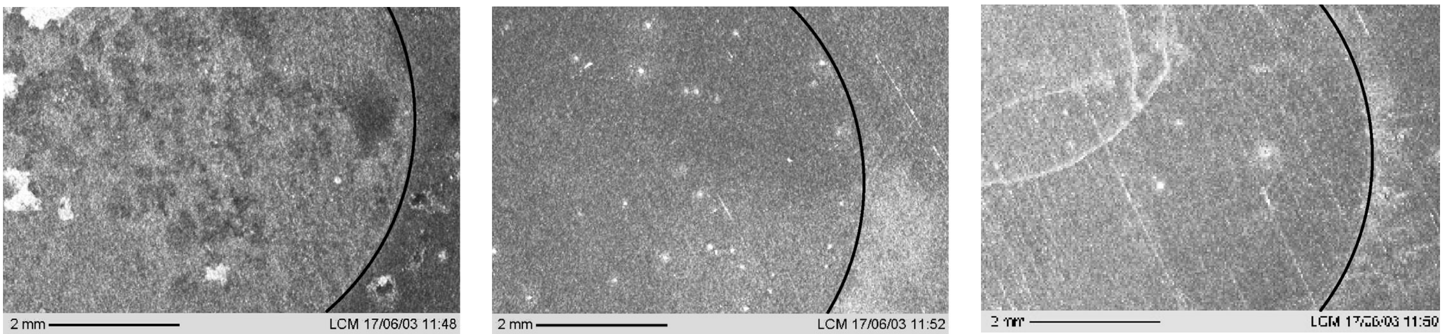
The optical comparison of the corroded areas on the aluminum substrates coated with 50 nm thick metal doped a-C:H coatings and a pure a-C:H coating demonstrates the differences between the various layers after exposure for 48 h in 0.1M NaCl solution (Fig. 5). Whereas the pure a-C:H thin film is completely undermined and delaminated, the substrates with the metal doped a-C:H layers exhibit a corrosion attack of less than 0.5% of the surface area. The coating does not lift off – even at pronounced defect sites in the substrate – if actively reacting metallic clusters are embedded at the interface. As a result, the protection performance of the metal-doped nanoactive layers is far higher than that of the passive pure a-C:H coating. The higher reflectivity of the coated substrates proves that the color and the reflection of the aluminum substrates remain unchanged. The spectroscopic data obtained of the very similar reflection spectra enabled to calculate the spectral reflectance of the coatings (Fig. 6).

Table. Gas-permeability of some selected plasma-coated PET-samples

Functional layer on PET 12 mm	Thickness [nm]	BIF[a] (H_2)	BIF[a] (He)	BIF[a] (O_2)	Stretch failure[b] [%]
Me	70	6	3	2	20
a-C:H	105	5	2	93	5
Me/Me-a-C:H	65	92	41	37	15

[a]Barrier improvement factor: Reduction of the permeability of the coated sample with respect to the untreated sample (PET 12 μm), measured at 23 °C and 1 bar.

[b]The interferometric detection method was used to determine the stretch failure leading to the formation of micro cracks in the coating of the sample.



a) pure a-C:H layer b) Zn-doped a-C:H layer c) Me-doped a-C:H layer

Fig. 5. Optical microscopy images of coated Al-substrates after 48 h in 0.1M NaCl solution. The curved line indicates the border of the exposed area.

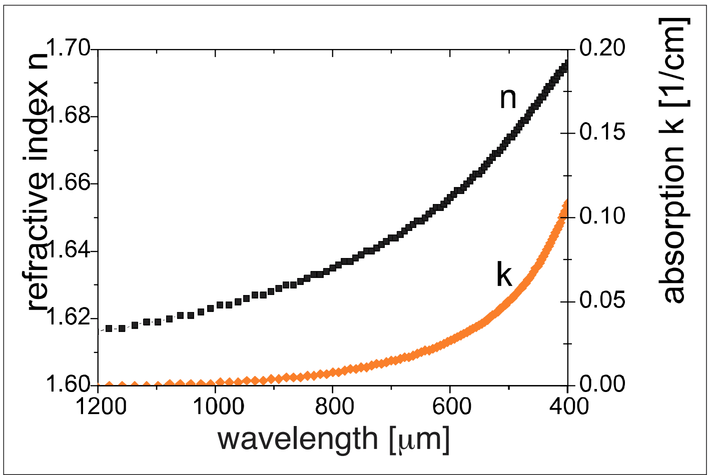
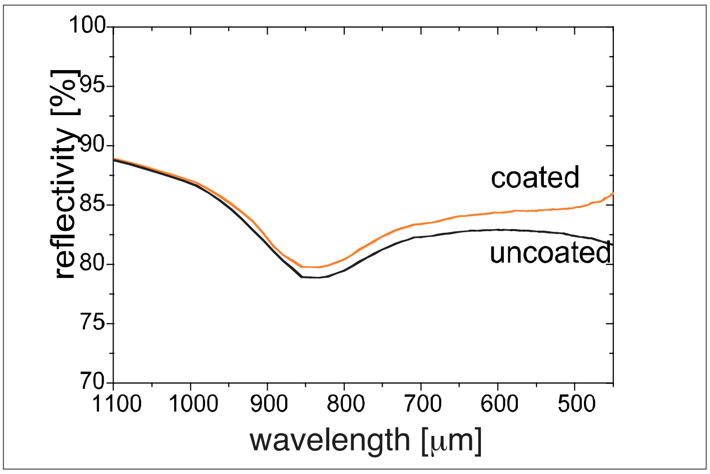


Fig. 6. Refractive index and absorption dispersion of a Zn-a-C:H layer (25 nm, 1 at%)



b) Reflection spectra of an uncoated and a Zn-a-C:H coated Al-substrate (25 nm, 1 at%)

Preliminary corrosion tests were also performed on silver and iron substrates. A significantly increased corrosion protection due to metallic doping of the hydrocarbon layers was also observed in these cases.

4. Conclusions

The improvement of functional properties is provided by nano-texturing conventional thin films. Multilayer diffusion barrier systems are suitable to overcome the extremely varying conditions in high-pressure vessels due to the adjustable stretch failure. The nano-texturing concept compensates the drawbacks of the physical barrier layers, namely coating defects like pinholes and scratches, which are compensated by the reaction of the embedded particles – such as adsorbing gas and oxidizing/reducing mechanisms.

The metal-doped a-C:H thin films exhibit an excellent corrosion protection compared to the non-active coatings. The nano-active corrosion protection concept is demonstrated for nano-textured amorphous hydrocarbon thin films deposited on aluminum substrates. The electrochemically active Zn-clusters provide an about 30-times higher corrosion resistance in the a-C:H layers for the aluminum surface and as a consequence prevent the delamination of the protection coating caused by undermining corrosion during the test conditions used so far. An amount of less than 10 mg of zinc per square meter is sufficient for a metallic surface to achieve an efficient corrosion protection and furthermore, to avoid the use of the toxic chromate or nickel containing layers.

In addition, the tests prove that the chemical and optical properties of the metal-doped thin films can be well adjusted so as to meet the product specific requirements. However, the selection of the most promising nano-texture to achieve the electrochemical activity and the chemical reactivity of the protecting coating for a specific product needs to be established taking into account the various correlations and mechanistic aspects.

Acknowledgements

The financial support by the Swiss Federal Office for Energy and the TOP NANO 21/CTI board is gratefully acknowledged. Special thanks are given to the specialists for corrosion protection and their contributions to the project: Dr. Markus Faller at EMPA, Prof. Dr. Sanna Virtanen, and Dr. Patrik Schmutz at ETHZ as well as to the experts in structure and composition analysis of the thin films: Prof. Dr. Patrick Buffat at EPFL, Prof. Dr. Armin Reller at the University of Augsburg, and Dr. Frans Munnik at CAFI/EICN. In addition, the authors wish to express their thanks to Dr. Martin Bösch, Adeline Hess, and Frédéric Jolliet at EIG, Hans-Peter Nau at Automotive Lighting Reutlingen, René Ziegenhagen at Les Manufactures Horlogères Cartier, and Claude Hembert at Ullit SA for their excellent and motivating collaboration.

Received: May 3, 2004

[1] PCT/CH01/00059 and PCT/CH02/00229.
[2] E.M. Moser, C. Faller, S. Pietrzko, F. Eggimann, *Thin Solid Films* **1999**, *355–356*, 49–54.
[3] E.M. Moser, Jahresbericht **2003**, BFE-Projekt Nr. 43648/83649.
[4] E.M. Moser, M. Faller, S. Mikhailov, S. Virtanen, Final Report, TOP NANO 21 Project No. 6325.1.