# „DEPOSITION OF CARBON NITRIDE LAYERS BY PLASMA METHODS AND SURFACE MODIFICATION OF POLYETHYLENE BY FAST ATOM BOMBARDMENT”

Summary of Ph.D. theses

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Budapest, 2004.

## Introduction

The surface engineering is the important interdisciplinary area of chemical and physical researches.

In this work we studied two topics of surface engineering, namely the deposition of carbon nitride coatings and the modification of polyethylene surface. These are related fields of studies, because both systems are carbon-based ones. The practical reasons of choice of subject are the potential microelectronic application of carbon nitride layers, and the fact that ultra-high molecular-weight polyethylene (UHMWPE) is a frequent component of orthopedic implants.

Predictions made by Liu and Cohen in 1989 of the extreme hardness and high elastic modulus of the $\beta$-$C_3N_4$ initiated a large number of studies in the field of carbon nitride research.

X-ray photoelectron spectroscopy is often used for both chemical analysis and chemical structural characterization of $CN_x$ layers. In spite of the large number of publications, there is no agreement on the assignment of the variety of N1s component peaks to well-defined structural units with $sp^3$- $sp^2$- and sp-type C-N bonds.

In this work $CN_x$ layers were prepared by using DC sputtering, reactive DC and RF magnetron sputtering, PECVD and ion beam assisted deposition methods at varying temperatures and plasma parameters. The $CN_x$ layers were studied by XPS and FTIR focused attention to the decomposition of the N1s peak.

The interaction of polymers with energetic ion or atom beams is of theoretical and practical interest. The related physical and chemical changes induced with high yields may lead to large modifications in the various characteristics of polymers. These include electrical and optical properties, surface wettability, adhesive bonding, biocompatibility, surface hardness and wear resistance, etc. In particular there are several studies on the various effect induced in polyethylene

by ion beams. No reports have been found, however, on the effects induced in PE by fast atom beams (FAB), during which some phenomena arising on ion beam treatment of PE –like surface charging of the target and coulombic repulsion of the projectiles- are greatly diminished or eliminated.

In this work we studied the interaction of PE with low-energy H, He, Ar and N atom beams. The aim was to reveal the surface chemical changes and the alterations in the surface nanomechanical properties of PE induced by low-energy FAB treatment.

## Theses

### *Results obtained in field of carbon nitride research*

1. Layers of $CN_x$ with a high nitrogen content reaching 47-50 atom% have been prepared by reactive DC sputtering of a graphite target. According to XPS and FT-IR measurements, these layers are polymeric-like containing a large amount of $sp^2$-type C=N bonds.
2. The local plasma parameters of DC magnetron source by a Langmuir probe have been determined. Dependence was found between the plasma parameters and the chemical bonding mode of N in the $CN_x$ layers. The total nitrogen concentration decreased with increasing plasma density, while the ratio of $sp^3$ type nitrogen (C-N) to $sp^2$ type one (C=N) increased.
3. The N1s XPS regions were very broad, manifesting several bonding states. After the decomposition of the N1s peak the component at 398.3 eV B.E. was assigned to $sp^2$ type N and that between 400,2-400,6 eV B.E. to $sp^3$ type one. The concentration ratio of the $sp^3/sp^2$ type N atoms correlates to the IR intensity ratio at 1300 $cm^{-1}$ / 1530 $cm^{-1}$ corroborating the XPS assignments.

4. In the $CN_x$ layers grown by RF-PECVD from C-H containing precursors, a high amount of nitril-type bonds is observed, while in the presence of benzene, additional C-H and N-H states formed.

5. For $CN_x$ layers prepared by using ion beam assisted deposition in combination with thermal activation, the increase in the deposition temperature from 200°C to 600°C resulted in a decrease in their N-content. Upon increasing the deposition temperature, the concentration of the $sp^2$-type N component decreased significantly, implying the preferential loss of C=N type bonds. Accordingly, the relative amount of $sp^3$-type bound increased.

***Results obtained in field of surface modification of polyethylene:***

6. Ultra-high molecular-weight polyethylene (UHMWPE) was treated by fast atom beams (FAB) obtained from He, Ar, H, N with about 1 kV accelerating voltage. Each applied FAB treatment results in the increase of the bulk plasmon loss energy of the C1s peak. This implies the formation of graphitic-type material and/or hydrogenated amorphous carbon, or carbon nitride in case of treatment by N atoms.

7. The incorporation of N is about three times higher upon 1 keV FAB treatment of UHMWPE than upon its nitrogen ion-beam treatment performed under similar conditions. The difference is probably due to the lack of the coulombic repulsion during FAB treatment.

8. Angle-dependent XPS studies of the nitrogen-FAB-treated UHMWPE reveal the presence of a N-rich subsurface layer with a topmost layer containing less N. This is in agreement with the depth distribution of N atoms calculated by the TRIM code, according to which the intensity maximum of the built-in N is in the subsurface region.

9. FAB treatment of UHMWPE results in a significant (from two to threefold) increase of its nanohardness, and a decrease of more than one order of magnitude in the volume loss during wear tests.

***Publications directly related to the PhD. thesis:***

I. I. Bertóti, A. Tóth, M. Mohai, **T. Ujvári**, Comparison of composition and bonding states of constituents in $CN_x$ layers prepared by d.c. plasma and magnetron sputtering, Surf. Interface Anal. 30 (2000) 538.

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VI. I. Bertóti, G. Radnóczi, M. Mohai, A. Tóth, **T. Ujvári**:
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VIII. I. Bertóti, A. Tóth, M. Mohai and **T. Ujvári**: Comparison of composition and bonding states of constituents in $CN_x$ layers prepared by d.c. plasma and magnetron sputtering, 8$^{th}$ European Conference on Applications of Surface and Interface Analysis 4-8 October 1999, Sevilla/Spain, Poster, Abstr. p. 227

IX. I. Bertóti, A. Tóth, M. Mohai, **T. Ujvári**: Composition and Chemical Structure Characteristics of $CN_x$ Layers Prepared by Different Plasma

Assisted Techniques, XIV$^{TH}$ International Symposium on the Reactivity of Solids, 27-31 August 2000 Budapest/Hungary; Oral presentation 12 (Abstr. p. 23)

X. A. Kolitsch, **T. Ujvári**, A Tóth, M. Mohai, I. Bertóti:
XPS characterization of the composition and bonding states of elements in $CN_x$ layers prepared by ion beam assisted deposition
12th European Conference on Diamond, Diamond-Like Materials, Carbon Nanotubes, Nitrides & Silicon Carbide; (2-7 september 2001; Budapest Marriott Hotel, Budapest, Hungary) Poster presentation 15.11.03

XI. **T. Ujvári**, B. Szikora, M. Mohai, Zs. Keresztes, A. Tóth, I. Bertóti;
Effect of plasma-parameters on the structure of $CN_x$ layers deposited by DC magnetron sputtering
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XV. Tóth András, Bertóti Imre, Mohai Miklós, **Ujvári Tamás**, Nagy Piroska Mária (ELTE), Szikora Béla (BME); Részecskesugárral aktivált felületi folyamatok: polietilén felület módosítása és $CN_x$ rétegek növesztése MTA KK AKKL Szeminárium, 2001. Nov.6.

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XXI. Bertóti Imre, Mohai Miklós, Tóth András, Ujvári Tamás: Új típusú felületkezelési módszer: a plazmaimmerziós ionimplantáció (PI3), MTA AKKL szeminárium, Budapest, 2002. nov. 21.

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XXV. Mohai, M.; Tóth, A.; Sajó, I.; Ujvári, T.; Bertóti, I., Plasma Surface Modification of Titanium and Ti-alloys, 10th European Conference on Applications of Surface and Interface Analysis (ECASIA), Berlin, Germany, October 5-10, 2003.