# DLC Biocompatible thin Films for Cardiovascular Implants

S.T. SHISHIYANU<sup>1</sup>, T.S. SHISHIYANU<sup>1</sup>, P.S. STEFANOV<sup>2</sup>, V.K. GUEORGUIEV<sup>3</sup>

<sup>1</sup>Department of Microelectronics, Technical University of Moldova, 2004 Chisinau, Moldova <sup>2</sup>ISMA Ltd., 1138 Sofia, Bulgaria <sup>3</sup>Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria

sergeteo@mail.utm.md

Abstract – Diamond-like carbon films (DLC films) for cardiovascular implants have successfully been prepared by dual-target unbalanced magnetron sputtering and Rapid Photothermal Processing (RPP). It is found that the sputtering current of target plays an important role in the DLC film deposition. Deposition rate of 3.5  $\mu$ m/h is obtained by using the sputtering current of 30 A. Rapid Photothermal Processing at 400°C essentially reduced the carbon content and have improved the surface morphology structure of deposited coatings, which depend on the intensity of the ion impingement on the growing interface.

Index Terms - Diamond-like carbon, nanocomposite DLC, RPP.

## I. INTRODUCTION

Diamond-like carbon (DLC) films have found widespread application in biological coatings for implantable medical devices, as a result of their good chemical resistance, temperature stability and biocompatibility. The biological behavior of an implant can be tuned by modifying the element composition. DLC can be easily alloyed with other biocompatible materials such as titanium as well as toxic materials such as silver, copper and vanadium by normal codeposition methods [1]. Nanocrystalline diamond-coated medical steel has shown a high level resistance to blood platelet adhesion and thrombi formation [2]. Diamond and DLC coatings have successfully been proposed for applications as artificial heart valves, prosthetic devices, joint replacements, catheters and stents, orthopedic pins, roots of false teeth, surgical scalpels and dental instruments [3-6].

#### **II. EXPERIMENTAL**

Pulsed direct current (p-DC) magnetron sputtering in combination with an unbalanced magnetron configuration has become a major technique in the deposition of advanced coatings during the last decade. It has the significant advantage over DC magnetron sputtering in suppressing arcing at the targets during reactive sputtering and in sputtering non-conductive materials.

In this paper we present the results on the microstructural control of Ti/DLC nanocomposite coatings with pulsed direct current (DC) magnetron sputtering. The sputtering system was configured of Ti target (99.7%), and graphite target (99.99%). The diameter of all the targets was 3 inches. All the power supplies for sputtering were operated at current regulation mode via a computer-controlled system. The thin metal layers were deposited on nonannealel and annealed stainless steel. Annealing was performed according the technology sequence for stents-electropolishing and high temperature annealing for grain enlargement and improving of the stents elasticity. A number of analytic methods were applied SEM, AFM and EDX.

The Ti/DLC films were deposited onto pre-etched nonannealed and high temperature annealed stainless steel

type 316L. The morphological analyses demonstrated the essential grain enlargement. The high temperature annealing increase the grain size from 10 to 60  $\mu$ m, which is necessary for the required elasticity of the arterial stents. The grain structure can influence the structure of the deposited biocompatible nanolayers, which is demonstrated further for deposited at high temperatures layers on stainless steel substrates.

The images of the grain structure of the preetched 316L type stainless steel annealed at high temperatures and the initial non-annealed sample are shown in Fig. 1.

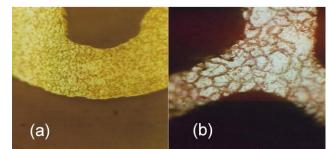


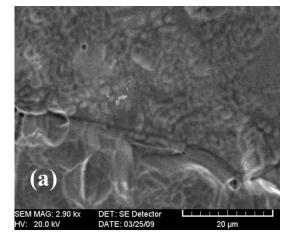
Fig. 1 (a,b). Grain structure of preetched high temperature annealed (a) and non-annealed (b) 316L type stainless steel.

The SEM images of the DLC layers deposited on stainless steel at temperatures higher than 230°C. T1<T2, the RPP was performed at 300°C in vacuum, are presented in Fig. 2.

The thermal annealing of the stainless steel substrate during deposition at high temperatures do not change essential the elemental content of the substrate. Only a small oxidation is observed. But the surface and the structure of the deposited carbon layers is not smooth, as it is for layers deposited on the glass and these temperatures are not applicable for the stents technology.

AFM study images of the DLC layers deposited on stainless steel at 250°C, RPP 400°C are presented in Fig. 3.

The AFM study of DLC layers deposited at high temperatures on nonannealed and annealed stainless steel have shown that the roughness of the layers is up to 300 nm on nonannealed substrates and up to 3500 nm on annealed substrates.



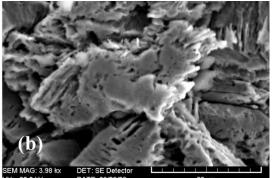
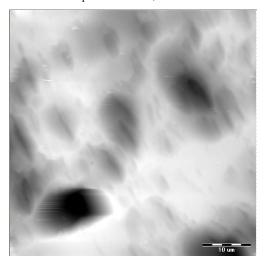


Fig. 2 (a,b). SEM of RPP DLC layers on stainless steel deposited at temperatures: a - T1, b - T2.



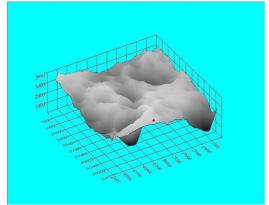


Fig. 3 (a,b). 2D and 3D AFM images of layer deposited at 250°C on nonannealed stainless steel.

The roughness on nonannealed samples is due to the nonpolished surface, wile on the annealed substrates-to the much larger grain size after annealing.

TABLE 1. INFLUENCE OF RAPID PHOTOTHERMALPROCESSING ON THE CARBON CONTENT IN DLC.

	Non annealed		Furnace 400°C 3 min		RTP 300°C 3 min		RTP 300°C 1 min + 400°C 1 min	
Ele me nt	W %	A %	W %	A%	W %	A%	W %	A%
С	27. 51	39. 46	28. 24	39. 64	30. 30	42. 99	16. 59	25. 45

The RPP at 300°C and the furnace annealing at 400°C up to 3 min do not change essentially the carbon content, but RPP at higher temperature even up to 1 min change/reduce the carbon content.

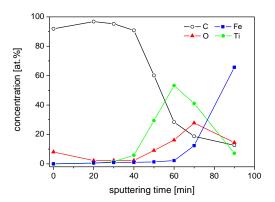


Fig. 4. Auger depth analysis for 65min deposition of DLC.

Auger depth analysis of DLC layers deposited on stainless steel for different deposition times at low plasma densities were also carried out, and the Auger spectra are presented in Fig. 4. The Auger analyses have shown existence of relative thick carbon layer, thin transition C/Ti layer and thin Ti layer.

#### **III. CONCLUSIONS**

The reliable technology for magnetron deposition of biocompatible Ti/DLC nanolayers for coating of implantable medical devices has been established. RPP at 300÷400°C improved the microstructure and properties of deposited coatings, which strongly depend on the intensity of the concurrent ion impingement on the growing interface.

#### **ACKNOWLEDGEMENTS**

Authors gratefully acknowledge ISMA Ltd. Sofia for providing the magnetron sputtering system and the cardiovascular STENTs produced by ISMA Ltd. Sofia, Bulgaria. Authors also gratefully acknowledge Dr. E.Monaico, Dr. M.Enachi and National Center for Materials Study and Testing for carefully provided SEM and AFM measurements.

### REFERENCES

- I.D. Scheerder, et al., "The Biocompatibility of Diamond-Like Carbon Nano Films," J. Invasive Cardiology, vol. 12, pp.389-394, 2000.
- [2] W. Okroj, M. Kamińska, L. Klimek, W. Szymański, B. Walkowiak, "Blood platelets in contact with nanocrystalline diamond surfaces," Diamond & Related Mater., vol. 15, Issue 10, pp.1535-1539, 2006.
- [3] A.Grill, "Diamond-like carbon coatings as biocompatible materials—an overview," Diamond & Related Mater., vol. 12, Issue 2, pp.166-170, 2003.
- [4] R. Hauert, "A review of modified DLC coatings for biological applications," Diamond & Related Mater. vol. 12, Issue 3-7, pp.583-589, 2003.
- [5] R.A. Freitas, Foresight Update, 39 Foresight Inst. Palo-Alto, CA, USA, 1999.
  P.A. Dearnley, "A review of metallic, ceramic and surface treated metals used for bearing surfaces in human joint replacements," Proc. of Institution of Mechanical Engineers. Part H, Engineering in Medicine, vol. 213, pp.107-135. 1999