Nitrogen doping in biomaterials by extreme ultraviolet (EUV) surface modification for biocompatibility control

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INTRODUCTION:

Various studies show that employment of nitrogen coatings on certain biomaterials can noticeably increase the degree of biocompatibility (particularly for vascular repair) [1]. Chemical and laser ablation surface modification techniques are used for introduction or enrichment of nitrogen. However alteration of bulk material is reported which is undesirable for biomedical engineering applications. Extreme Ultraviolet (EUV) radiation with low penetration depth (less than 100 nm) can be successfully utilized to avoid bulk properties alteration. In this study Polyvinyl fluoride (PVF) and Polytetrafluoroethylene (PTFE) were treated by EUV radiation in the presence of ionized nitrogen. X-ray photoelectron spectroscopy (XPS) measurements demonstrate a notable amount of nitrogen on treated polymer surfaces.

METHODS:

In this study a 10-Hz laser-plasma EUV source is used. This source is based on a double-stream gas-puff target, irradiated with the 3 ns/0.8J Nd:YAG laser pulse. The source is equipped with an auxiliary gas-puff valve to inject nitrogen into EUV – sample interaction region. Using a gold-plated grazing incidence ellipsoidal collector, an effective radiation focus and spectral coherence centered at 10±1 nm acquired. More detailed source setup information can be found in another place [2]. PTFE and PVF samples were irradiated by 50, 200, and 300 EUV shots and 50 and 200 EUV shots respectively. Pristine and EUV irradiated samples were examined by x-ray photoelectron spectroscopy (XPS).

RESULTS & DISCUSSION:

Direct photoetching by EUV photons result in formation of micro and nanostructures onto the polymer sample surfaces. Moreover in the presence of reactive gas (such as nitrogen), chemical modification in surface layers observed. Table 1 summarized the XPS spectra results of pristine and EUV treated samples. Pristine samples of PTFE ad PVF do not contain nitrogen atoms. It can be observed that in case of PTFE samples, at 300 EUV shots N1s (0.67% atomic weight) along with O1s (0.57% atomic weight) incorporates on polymer surface. Whereas in case of PVF samples nitrogen atom incorporation is demonstrated at 200 EUV shots (N1s=3.36 % atomic weight) forming polar covalent bond with carbon.

Table 1. Summarized results from XPS spectra

Material	No. of shots	Element	Atomic Weight %
PTFE	Pristine sample	C1s	24
		F1s	74
	50	C1s	23.17
		F1s	76.83
	200	C1s	24.99
		F1s	75.01
	300	C1s	29.46
		F1s	70.54
		O1s	0.57
		N1s	0.67

PVF	Pristine sample	C1s	66.73
		F1s	31.43
		O1s	1.85
	50	C1s	64.59
		F1s	34.74
		O1s	0.67
	200	C1s	76.6
		F1s	13.3
		O1s	6.74
		N1s	3.36

CONCLUSIONS:

Nitrogen enrichment or doping in polymeric biomaterials is possible through EUV surface modification. EUV photons carry enough energy to simultaneously ionized and excite nitrogen gas molecules. This results in incorporation of nitrogen atoms in polymer chain as demonstrated by results therefore biocompatibility enhancement is foreseen.

REFERENCES:

[1] W.-H. Liao et al. (2012) *J. Biomed. Mater. Res., Part A* **100(11)**:3151–6 [2] A. Bartnik et al. (2011) *Nucl Instrum Meth A* **647**:125–131

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