INVESTIGATION ON DIELECTRIC BARRIER DISCHARGE SURFACE FUNCTIONALIZATION BY XPS-ANALYSIS

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Abstract: *The plasma aided flame retardation of wood, wooden products and cellulosic fibrous materials has been conceived and developed as a result of a plasma aided process of capillary impregnation. The dielectric barrier discharge surface pre-treatment modifies the chemical and capillary activity and improves such characteristics of the impregnation process as the penetration depth, speed of solution spreading and adsorption, and capacity of adsorbed solution. The effect of plasma pre-treatment onto the wood surface activation (or functionalization) was investigated on Tzalam wood (Lysiloma bahamensis). The alteration of the wood surface chemical composition or the surface functionalization as a result of the cold plasma pre-treatment at atmospheric pressure and room temperature was monitored by X-ray photoelectron spectroscopy (XPS -analysis, ESCA).*

Keywords: DIELECTRIC BARRIER DISCHARGE SURFACE TREATMENT, PLASMA AIDED CAPILLARY IMPREGNATION, FLAME RETARDATION OF CELLULOSIC FIBROUS MATERIALS, X-RAY PHOTOELECTRON SPECTROSCOPY

1. Introduction

The plasma aided flame retardation of wood, wooden products and cellulosic fibrous materials has been developed as a result of a new plasma aided process of *capillary impregnation*, [1, 2].

The plasma-chemical surface pre-treatment modifies the chemical activity of wood surface as well as its electrical (ionic) and capillary activities, and in general improves the technological characteristics of the capillary impregnation process. A system of plasma device and applicators has been created to produce cold technological plasma through dielectric barrier discharge (*DBD*) at atmospheric pressure and room temperature [1, 2].

The cold plasma pre-treatment by non-equilibrium *DBD* of such soft wood, like *White pine* (Bulgaria) and *Douglas fir*, (Canada) improves technological characteristics such as a solution spreading and adsorption speed, as well as a specific amount of the adsorbed flame retardant. In this way, the plasma pre-treatment of wood and wooden materials improves its flame retardation [1, 4].

Tzalam wood is largely used in non-structural constructions, flooring and panelling. *Tzalam* is harder than softwoods. This wood is highly durable (service life of more than 25 years) and easy to work with, finishes smoothly and takes a fairly high natural polish. Hardwoods have a more complex structure than softwoods. The vessels may show considerable variation in size, shape of perforation plates, and structure of cell wall. But due to its relatively high density, fine-texture and surface inactivation it is difficult to apply flame retardants through capillary impregnation. The plasma-chemical surface pre-treatment by dielectric barrier air discharge at atmospheric pressure (*DBAD*) was specify as new good way to *Tzalam* wood surface functionalization and activation [5].

The objective of this paper was to study the effect of plasma *DBAD* pre-treatment by *X-ray photoelectron spectroscopy* (*XPS*) or *electron spectroscopy for chemical analysis* (*ESCA*) on the wood surface functionalization. *X-ray photoelectron spectroscopy* is a very powerful non-destructive surface analytical technique which provides valuable data on chemical surface composition and surface reorganization after plasma-chemical pre-treatment.

X-ray photoelectron spectroscopy is a surface chemical analysis technique that can be used successfully to analyze the surface chemistry of a material in its "as received" state, or after some treatment such as cold plasma pre-treatment. *The binding energy* is a characteristic of the atoms, which can be used for elemental identification on the plasma chemically modifying wood surface.

The interpretation of the curve fit of the carbon C_{1s} peak after *Kazayawoko* (1998) was used to interpret the changes of wood surface chemistry after plasma *DBAD* pre-treatment. This study was developed as part of a large investigation on plasma-chemically activated and flame retarded wood surface [1, 2, 3, and 5].

2. Experimental Investigation

Subject of research was an oxidative cold plasma treatment accompanied with an accumulation of oxygen containing groups on the surface an effect depending on the operation conditions, Fig. 1.

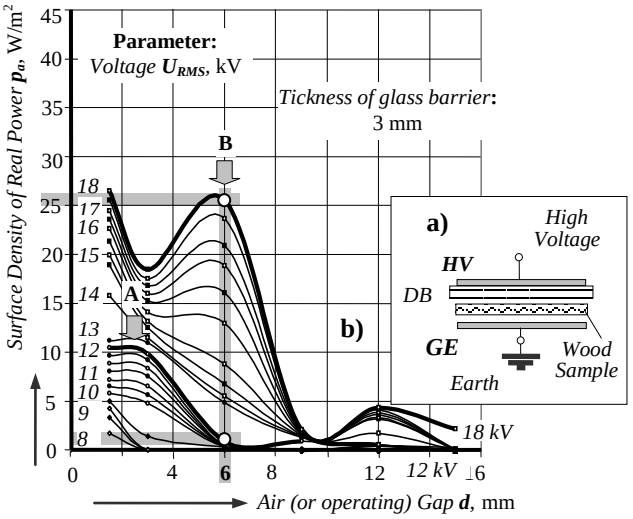

Fig. 1. *Plasma-chemical surface modification of wood sample by non-equilibrium dielectric barrier air discharge at atmospheric pressure in asymmetric coplanar system with one glass barrier (**a**), technological discharge characteristic "p_a - U_{RMS}", and regime of plasma pre-treatment at industrial frequency (**b**): **A** - transitional regimes (stage, area) from electron avalanche to cathode directed streamers; **B** - regime (stage, area) of cathode directed streamers.*

Similar changes ware the basis of the expecting *DBAD*-surface functionalization effect on the *Tzalam* wood surface. Cold plasma pre-treatment in two types of dielectric barrier discharge in air at atmospheric pressure was performed: *i*) *DBAD* at industrial frequency (50 Hz) and relatively low voltage (12 kV *RMS*; 17 kV *Peak Value*) - *the discharge regime* is transitional from electron avalanche stage to cathode directed streamers stage; *ii*) *DBAD* at relatively high voltage (15 kV *RMS*; 21 kV *PV*) characterizing the regime (stage) of cathode directed streamers, Fig. 1.

For this investigation *XPS*-analysis was carried out using a photoelectron spectrometer *VGS ESCALAB Mk II* with monochromatic *AlKα* radiation source (*FWHM* = 0.5 eV). The angle between the directions of the incident *X-ray* and that of the observations (fixed by analyzer entrance slit) was 50. *XPS-spectra* ware obtained by irradiating a wood sample with a beam of *X-rays*

Table 1: *Elemental composition of* ***Tzalam*** *(hard wood),* ***Pine*** *and* ***Douglas fir*** *(soft wood) heart wood surfaces before (K) and after plasma pre-treatment (SO, SN, SHF) determined from wide XPS-spectra.*

Kind of Wood: Density, kg/m³	*Samples*		*Chemical Surface Composition*, at. %						
			Peaks	***C***	***O***	***N***	*Si*	***nO/nC***	***nN/nC***
Heart **Tzalam** wood (*Lysiloma bahamensis*, Yucatan, Mexico): 780 *kg/m³*	*K-Tzalam* (Bare or Non-Treated)			**83.71**	**14.49**	**1.530**	**0.274**	**0.17**	**0.0183**
	DBD-pre-treated	*SO1*	12 kV (50 Hz)	66.55	32.43	1.027	0.000	0.49	0.0154
		SN1	18 kV(50 Hz)	61.38	37.63	0.990	0.000	0.61	0.0161
Heart **Pine** wood (*Pinus Sylvestris*, Bulgaria): 371 *kg/m³*	*K-Pine* (Non-Treated)			**74.80**	**24.40**	**0.700**	**0.000**	**0.33**	**0.0094**
	DBD-pre-treated	*SO*	10 kV (50 Hz)	70.10	28.50	0.600	0.000	0.41	0.0086
		SN	15 kV(50 Hz)	70.40	29.00	0.600	0.000	0.41	0.0058
		SHF	10 kV (10 kHz)	73.50	26.10	0.400	0.000	0.36	0.0049
Heart **Douglas Fir** wood (*Pseudotsuga menziesii*, Canada): 678 *kg/m³*	*K-Douglas fir* (Non-Treated)			**77.69**	**21.79**	**0.520**	**0.000**	**0.28**	**0.0067**
	DBD-pre-treated	*SO*	10 kV (50 Hz)	68.30	31.70	0.000	0.000	0.46	0.0000
		SN	15 kV(50 Hz)	69.10	29.90	1.000	0.000	0.43	0.0145
		SHF	10 kV (10 kHz)	74.00	25.50	0.500	0.000	0.34	0.0068

while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the sample being analyzed [1].

3. Results and Discussion

The surface chemical composition changing after such plasma pre-treatment was monitored by comparative *XPS*-analysis on two kind of soft wood - *white pine* (*Pinus sylvestris*) and *Douglas fir* (*Pseudotzuga*), and one hard wood - *Tzalam* (*Lysiloma bahamensis*) wood samples and some results are presented in Table 1 and 2.

The *XPS-wide spectra* of pre-treated and untreated wood samples show three characteristic peaks at 285.0, 533.2, and 400.4 *eV* attributed respectively to C_{1s}, O_{1s} and N_{1s}. The elements carbon (*C*), oxygen (*O*) and nitrogen (*N*) were detected on the investigated *Tzalam* wood surfaces. The nitrogen detected on the non plasma treated - control sample is most probably adsorbed on the surface from the ambient air.

The atomic percents of the carbon components (i.e., *C1*, *C2*, *C3*, and *C4*) were determined from the high-resolution *XPS*-spectra of C_{1S} peak - Fig. 2.

The presented in Table 1 and 2 data confirms the expected functionalization-oxidation of the *Tzalam* surface:

i) the surface oxygen content of *Tzalam* and all other woods plasma treated samples was higher (*Tzalam*: 32.43; 37.63; *Pine*, *Douglas fir*: from 25.5 to 31.7 at. %) as compared to that of the non-treated sample (*Tzalam*: 14.49; *Pine*: 24.4; *Douglas fir* 21.79 at. %);

ii) the total percentage of the surface carbon bonded to oxygen (the last column, Table 2) was also higher (42.4; 40.1 at. %) for *Tzalam* plasma treated samples compared to that (36.2 %) of the non-treated one;

iii) the *nO/nC* ratio (Table 1) of *Tzalam* plasma treated samples was higher (0.49; 0.61) compared to that (0.17) of the non-treated one. The plasma pre-treatment provoked oxidation of the *Tzalam* wood surface is similar but in different degree to the plasma enhanced oxidation of the *White pine* and *Douglas fir* wood surface, Table 1 and 2.

The high-resolution spectrum of the carbon peak C_{1s} showing the presence of different chemical states, or classes, of carbon (*C*) on the bare wood surface (*K*). According to *Kazayawoko* et al., the C_{1s} peak was observed to consist of four main components, which were ascribed to four classes of carbon atoms present on wood surface: *C1* (285.0±0.4 eV) – carbon atoms are those bonded to *carbon* (*C*) or *hydrogen* (*H*) atom; *C2* (286.0±0.4 eV) - carbon atoms are bonded to a single non-carbonyl oxygen atom; *C3* (288.7±0.4 eV) - carbon atoms are bonded to *two non-carbonyl* or to a *single carbonyl oxygen atom*, and *C4* (289.5±0.4 eV) – carbon atoms are ascribed to the *carboxyl oxygen group*. *C1*, *C2* and *C3* states of carbon are the main components of the C_{1s} peak whereas the *C4* component detects in some cases, Table 2.

XPS-measurement results, Table 1, and carbon (C_{s1}) and oxygen (O_{s1}) peaks analysis, Table 2 and 3, lead to the conclusion that the surface air plasma-chemical modification of wood at atmospheric pressure by *DBAD* is a useful and effective method for surface chemical activation of inactivated wood (*Tzalam*, *Douglas fir*, *White pine*) by oxidation of lignin, resin and extractive materials.

XPS-analysis of the bare wood surface reveals by the *nO/nC* and *C1/C2* ratios the existence of cellulose (*nO/nC* = 0.83; *nC1/nC2* = 0), lignin (*nO/nC* = 0.10; *nC1/nC2* = 1), and resin and extractive materials (*nO/nC* = 0.33; 1 < *nC1/nC2* < 10) on the wood surface. For *Tzalam* wood *nO/nC* was closed to 0.1 than to 0.33 - 0.17; while for *White pine* and *Douglas fir* this ratio was the opposite - 0.28 and 0.33. But for all three kinds of wood the ratio *nC1/nC2* was greater than one - *nC1/nC2* >1.0: *Tzalam* - 1.439; *White pine* - 1.554; and *Douglas fir* - 2.068. These results demonstrate conclusively the importance of resin and extractive materials for the plasma-chemical wood surface modification. It could be argued that an additional role in element alternation of *Tzalam* wood surface plays the lignin - the ratio *nO/nC* was closed to 0.1 but greater than 0.1 and the ratio *nC1/nC2* was greater than 1.0 but closed to 1.0, Table 2.

It is evident from the data in Table 3, different type of *oxygen to carbon bonding* (C-O; C=O; O-C-O; or O-C=O) is observed for the plasma pre-treated under different operation conditions *Tzalam* wood samples, indicating the impact of the discharge operation conditions on the wood surface oxidation.

The C_{1s} peak was observed to consist a maximum increased *C2* state of carbon (C-O) and increased *C3* state (C=0, O-C-O) on the plasma functionalized surface of *Tzalam* wood samples (*SO1*) under the *A* operating condition of *DBAD* (12 kV *RMS*). The second operating condition of *DBAD* (15 kV *RMS*) increased in maximum degree the *C3* (C=0, O-C-O) and *C4* state of carbon (O-C=O), but decreased the C2 state. The third operating condition of *DBAD* (10 kHz, 10 kV) increased the third C2, C3 and C4 together Table 2.

The *Sum (C2;C3)* covers quantitatively all different type of oxygen to carbon bonding - C-O; C=O; and O-C-O, Table 2. The alternative *Sum (O1;O3)* covers quantitatively this oxygen to carbon bonding plus H-O-H (water), Table 3. The difference between *Sum (O1;O3)* and *Sum (C2;C3)* gives the amount of chemically bound water on the wood surface and the changing after plasma-chemical pre-treatment. The surface plasma modification by *DBAD* at atmospheric pressure decreases the amount of water on the wood surface, Table 3.

Table 2. *Carbon peak C_{s1} components or proportions of oxygen (O) and carbon (C) functional groups of Tzalam, Pine and Douglas fir heart wood surfaces before (K) and after plasma pre-treatment (SO, SN, SHF) determined from high-resolution XPS-spectra.*

Kind of Wood: Density, kg/m³	*Carbon peak C_{s1} components area, %*										
	Peak position, eV (±0.4)		**C1** (C-C or C-H): **285.0**	**C2** (C-O, C-OH): **286.0**	**C2-3** (ND): **287.2**	**C3** (C=O, O-C-O): **288.7**	**C4** (O-C=O): **289.5**	**C4-5** (ND): **293.5**	**nC2/ nC1**	**nC3/ nC1**	**Sum (C2;C3)**
Heart **Tzalam** wood (*Lysiloma bahamensis*, Mexico): 780 *kg/m³*	*K* (Non-Treated)		**50.2**	**34.9**	**13.6**	**1.3**	**0.0**	**0.0**	**0.6900**	**0.0258**	**36.2**
	DBD-pre-treated	SO1	**35.0**	**27.1**	**22.0**	**15.3**	**0.0**	**0,6**	**0.7740**	**0.4386**	**42.4**
		SN1	**42.3**	**30.9**	**15.3**	**9.2**	**0.0**	**2.2**	**0.7304**	**0.2175**	**40.1**
Heart **Pine** Wood (*Pinus Sylvestris*, Bulgaria: 371 *kg/m³*	*K* (Non-Treated)		**54.1**	**34.8**	**0.0**	**8.8**	**2.3**	**0.0**	**0.6435**	**0.1626**	**43.6**
	DBD-pre-treated	SO	**50.9**	**37.2**	**0.0**	**9.8**	**2.1**	**0.0**	**0.7310**	**0.1925**	**47.0**
		SN	**45.2**	**40.4**	**0.0**	**11.9**	**2.6**	**0.0**	**0.8936**	**0.2633**	**52.4**
		SHF	**45.4**	**40.1**	**0.0**	**12.0**	**2.5**	**0.0**	**0.8834**	**0.2643**	**52.1**
Heart **Douglas fir** wood (*Pseudotsuga menziesii*, Canada): 678 *kg/m³*	*K* (Non-Treated)		**64.1**	**31.0**	**0.0**	**4.9**	**0.0**	**0.0**	**0.4836**	**0.0764**	**35.9**
	DBD-pre-treated	SO	**55.4**	**38.9**	**0.0**	**5.7**	**0.0**	**0.0**	**0.7022**	**0.1029**	**44.6**
		SN	**58.1**	**23.5**	**0.0**	**12.8**	**5.6**	**0.0**	**0.4045**	**0.2203**	**36.3**
		SHF	**57.5**	**35.0**	**0.0**	**6.2**	**1.3**	**0.0**	**0.6086**	**0.1078**	**41.2**

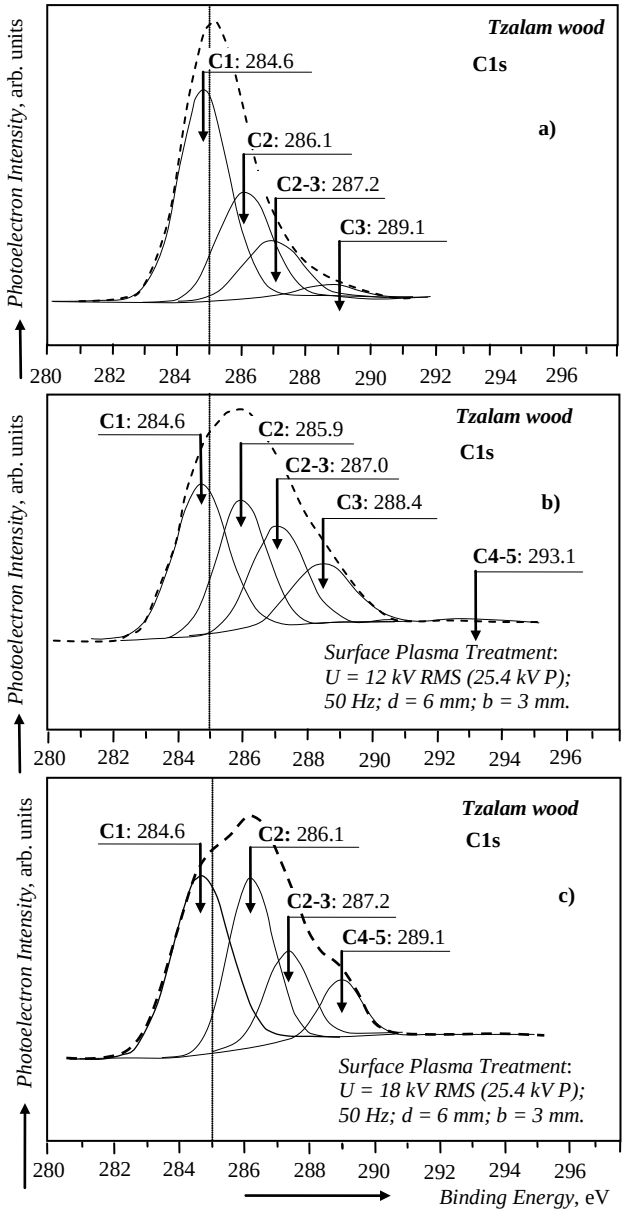

Fig. 2. *XPS/ESCA* high-resolution spectra of carbon (*C1s*) peak: **a** - bare sample of *Tzalam* heart wood; b - *DBAD* pre-treated sample at 12 kV *RMS*; c - *DBAD* pre-treated sample at 18 kV *RMS*.

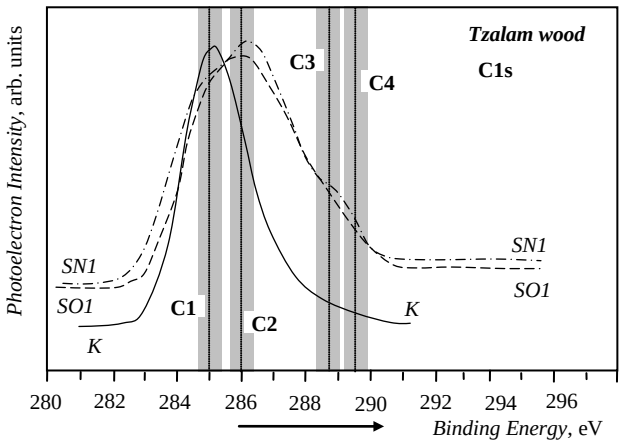

Fig. 3. *Carbon C1s peak in photoelectron XPS/ESCA spectra:* ***a*** *- bare sample of Tzalam heart wood;* ***b*** *- DBAD pre-treated Tzalam sample at 12 kV RMS; c - DBAD pre-treated Tzalam sample at 18 kV RMS.*

The air plasma-chemical functionalization of Douglas fir wood surface examined in the daylight of the alteration of carbon to oxygen bonding holds out opportunities for its controlling by the operating condition of *DBD* pre-treatment.

Conclusion

Plasma-chemical treatment of the surface of *Tzalam wood* with *DBAD* at atmospheric pressure is connected to: *i* - the characteristic oxidation of the surface of the wood, as the ratio *nO/nC* varies mostly on ***B***- regime (stage) of processing; *ii* – the growth of the degree of oxidation after plasma-chemical treatment at the expense of changes determined by carbon peak *C2* (C-O, C-OH) and *C3* (C=O; O-C-O); *iii* - the most oxidation is in *Tzalam wood*, although *bare Tzalam wood* is characterized by the lowest degree of oxidation from the three kinds of tested woods; *iv* - characteristic reducing of the amount of chemically bound water (H-O-H) to the surface of the wood, as the reduction is in the greatest degree in ***B***- regime (stage) of processing; *v* - with significant changes on the surface that the *XPS*-analysis covers and exhibits.

Table 3. *Oxygen peak O_{s1} components or proportions of oxygen (O), carbon (C) and hydrogen (H) functional groups of Tzalam and Douglas fir heart soft wood surfaces before (K) and after plasma pre-treatment (SO, SN, SHF) determined from high-resolution XPS-spectra.*

Kind of Wood: Density, kg/m³	*Oxygen peak O_{s1} components area, %*								
	Peak position, eV (±0.4)		**O1** (O=C): **531.5**	**O2** (O-H): **532.5**	**O3** (O-C; H-O-H): **533.0**	**O4** (ND): **534.5**	**Sum (O1;O3)**	**Sum (C2;C3)**	**Sum (O1;O3) - Sum (C2;C3): (H-O-H)**
Heart **Tzalam** wood (*Lysiloma bahamensis*, Mexico): 780 *kg/m³*	*K* (Non-Treated)		**0.0**	**58.5**	**41.5**	**0.0**	**41.5**	**36.2**	**5.3**
	DBD-pre-treated	SO1	**0.0**	**56.2**	**43.8**	**0.0**	**43.8**	**42.4**	**1.4**
		SN1	**0.0**	**58.7**	**41.2**	**0.0**	**41.2**	**40.1**	**1.1**
Heart **Douglas fir** wood (*Pseudotsuga menziesii*, Canada): 678 *kg/m³*	*K* (Non-Treated)		**0.0**	**0.0**	**100**	**0.0**	**100.0**	**35.9**	**64.1**
	DBD-pre-treated	SO	**3.2**	**0.0**	**91.8**	**5.0**	**95.0**	**44.6**	**50.4**
		SN	**5.5**	**59.9**	**34.6**	**0.0**	**40.1**	**36.3**	**3.8**
		SHF	**12.2**	**51.2**	**36.6**	**0.0**	**48.8**	**41.2**	**7.6**

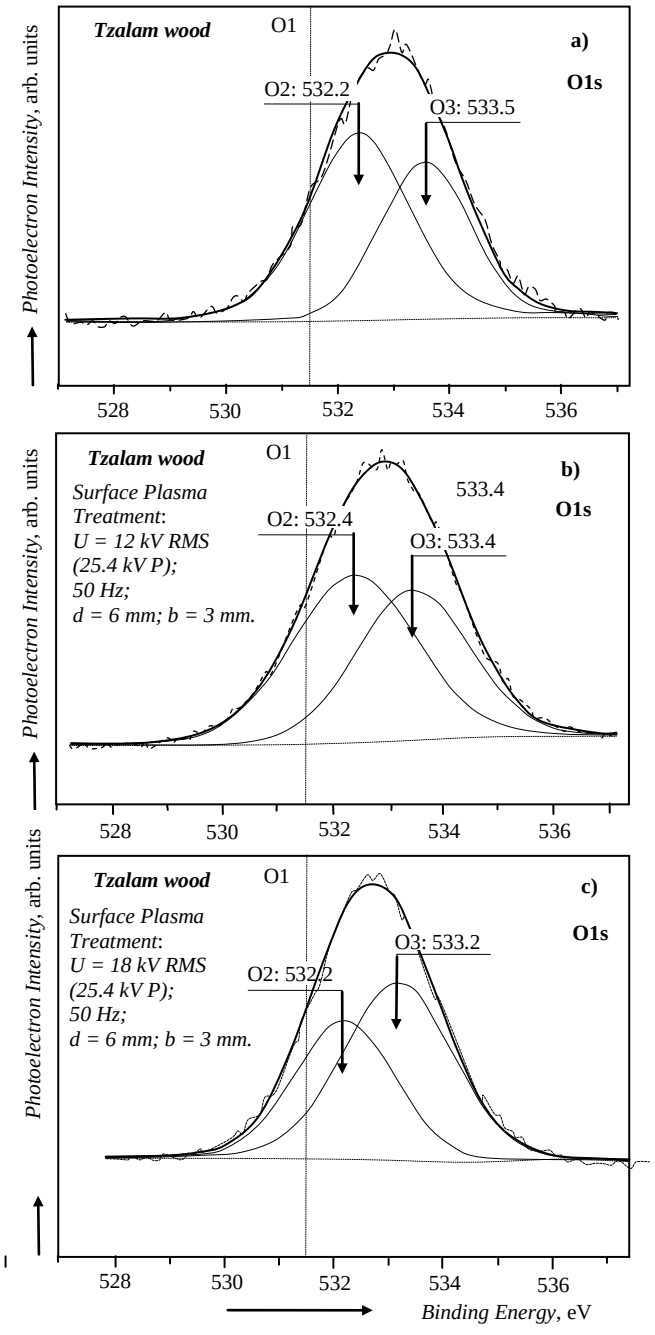

Fig. 4. *XPS/ESCA high-resolution spectra of oxygen (O1s) peak:* ***a*** *- bare sample of Tzalam heart wood;* ***b*** *- DBAD pre-treated sample at 12 kV RMS;* ***c*** *- DBAD pre-treated sample at 18 kV RMS.*

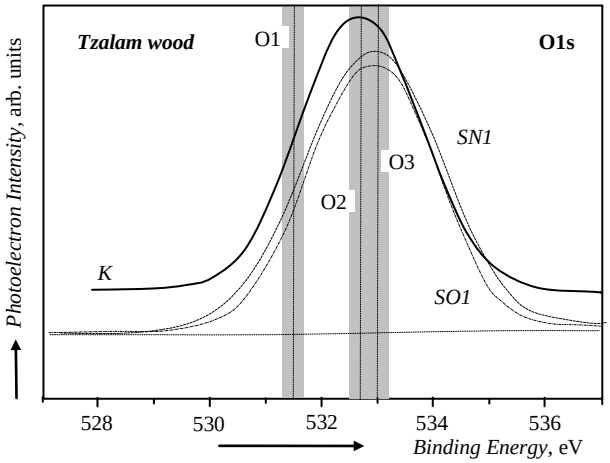

Fig. 5. *Oxygen O1s peak in photoelectron XPS/ESCA spectra: K - bare sample of Tzalam heart wood; SO1 - DBAD pre-treated Tzalam sample at 12 kV RMS; SN1 - DBAD pre-treated Tzalam sample at 18 kV RMS.*

Acknowledgments

The authors gratefully acknowledge the financial support of Technical University - Sofia, for the Research Project 132ПД0051-01.

References

[1] Dineff, P., D. Gospodinova, L. Kostova, T. Vladkova, and E. Chen., *Plasma aided surface technology for modification of materials referred to fire protection*, Problems of Atomic Science and Technology, Series Plasma Physics (14), 2008, 6, pp. 198÷200.

[2] P. Dineff, L. Kostova. *Method for Plasma Chemical Surface Modification*. H05H 1/24, Bulgarian Patent Publication No.: BG 66022 B1; International Patent Publication No.: WO Patent 2006/133524 A2; Priority Date: 14.06.2005 (BG No. 109189).

[3] Dineff, P., D. Gospodinova, I. Avramova. *Energy Characteristics and Parameters of Non-Uniform (Pin-to-Plate) Dielectric Barrier Discharge*. XVI-th International Symposium on Electrical Apparatus and Technologies "SIELA'09", June 04÷06, 2009, Bourgas, Bulgaria. Proceedings of Papers, 2009, Vol.: 2, pp. 30÷39.

[4] Динев, П., Д. Господинова, И. Аврамова. *Електродни конфигурации на бариерен разряд и ефект на повърхностно химично активиране*. XIX. Международна конференция по авангардни материали и обработки „АМО'09", 25÷27 юни, 2009, Кранево, България. Сборник с доклади, ДМТ-Продукт, 2009, стр. 191÷196.

[5] Господинова, Д., И. Иванов, П. Динев, Л. Велева, А. Гутиерес, *Плазмено подпомогната огнезащита на дървесина от ТЦАЛАМ (Lysiloma Bahamensis) - I и II.* Годишник на Техническия университет - София, София, България, Том: 62, Кн.: 4, 2012, стр. 103÷122.