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# CONTENTS

ADVANCED DESIGN AND TECHNOLOGY FOR PRODUCTION OF SENSOR ELEMENTS IN DEVICES BASED ON SURFACE PLASMON RESONANCE Maslov V.P., G.V. Dorozinsky
PLASMA SURFACE TECHNOLOGY PROMOTING CAPILLARY IMPREGNATION OF WOOD: XPS ANALYSIS OF DIFFERENT PLASMA PRE-TREATED WOOD SURFACES
Ivanov I., D. Gospodinova, P. Dineff, L. Veleva
INFLUENCE OF THE POSITION OF THE SWASH PLATE ROTATION AXIS ON THE VOLUMETRIC EFFICIENCY OF THE AXIAL PISTONS PUMPS Zaluski P
MODELING AND OPTIMIZATION OF THE PROPERTIES AND COMPOSITION OF TITANIUM-BASED ALLOYS
Tontchev N., Y. Kalev, R. Lazarova
INTELLIGENT DECISION-MAKING FOR ENERGY AND ECONOMIC EFFICIENCY OF INNOVATIVE MANUFACTURING PROCESSES BASED ON MULTI-ATTRIBUTE KEY PERFORMANCE INDICATORS Grzelak D., R.Freund, H. Wiemer, K. Großmann
INVESTIGATION OF MECHANICAL PROPERTIES OF TITANIUM ALLOYS BASED ON GENETIC OPTIMIZATION AND PARETO FRONT Ivanov M., N. Tontchev
SOFWARE MODEL FOR SELECTION OF THE APPROPRIATE CHEMICAL COMPOSITION OF TITANIUM ALLOYS UNDER DEFINES REQUIREMENTS FOR MECHANICAL CHARACTERISTICS Ivanov M., N. Tontchev
THERMAL STRESSES IN THE BLADES WITH AND WITHOUT TBC BASED ON THE TEMPERATURE DISTRIBUTIONS MEASURED USING THERMAL IMAGING CAMERA Maś K., M. Woźny, S. Dudek, M. Marchewka, D. Płoch, W. Bochnowski, E. M. Sheregii
APPLICATION OF EA SIGNAL TO EVALUATE THE DEGRADATION OF X6CrNiTi18-10 STEEL DURING TENSILE TEST Pachnowski W A Driedric S Adomick E Szerzeji
PVD DEPOSITION OF HAFNIUM IN ALUMINIDE COATINGS Romanowska J
CVD AND EB-PVD AS A METHODS OF THE ZIRCONIUM INTRODUCING TO THE ALUMINIDE COATINGS Zagula-Yavorska M., J. Sieniawski
THE TERMOGRAPHIC ANALYSIS OF THE WELDING BY TIG Maś K., M. Woźny, M. Marchewka, D. Płoch, E. MSheregii
THE SCANING NOZZLE HOT AIR SYSTEM FOR THERMOGRAPHIC DETECTION OF THE SURFACE INCORPORATED HIDDEN DEFECTS Prokhorenko S., K. Maś, M. Woźny, E. M. Sheregii
BELT CONVEYOR DESIGN AND ANALYSIS Gerdemeli İ., S. Kurt, E. T. Dayan
LATTICE (CAGE) BEAM DESIGN AND FINITE ELEMENT ANALYSIS OF GANTRY CRANE Gerdemeli İ., S. Kurt, B. Bige

# PLASMA SURFACE TECHNOLOGY PROMOTING CAPILLARY IMPREGNATION OF WOOD: XPS ANALYSIS OF DIFFERENT PLASMA PRE-TREATED WOOD SURFACES

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**Abstract:** X-ray Photoelectron Spectroscopy (XPS) also referred to as Electron Spectroscopy for chemical analysis (ESCA) was used to characterize the surfaces of plasma-chemical treated wood in air by dielectric barrier discharge (DBD). The plasma-surface pre-treatment of wood, wooden products and cellulosic fibrous materials has been developed for promoting capillary impregnation and plasma-aided flame retardency. In this study, XPS has been used since it has proved to be suitable investigation method to characterize the composition of a plasma pre-treated material surface. This method is a powerful analytical and non-destructive technique which has already been used for the analysis of plasma modified wood surfaces and in the characterization of wood's reactions. Changes due to the plasma-chemical process were identified from the survey large spectra as well as from the detailed  $C_{1s}$  and  $O_{1s}$  spectra. The oxidative changes were quantified with the atomic ratio of oxygen to carbon and with a detailed analysis of the contributions to the  $C_{1s}$  and  $O_{1s}$  peaks.

**Keywords**: ATMOSPHERIC DIELECTRIC BARRIER DISCHARGE (*DBD*), FLAME RETARDANT, CAPILLARY IMPREGNATION, TROPICAL (RAIN-FOREST) WOOD, X-RAY PHOTOELECTRON SPECTROSCOPY (*XPS*).

#### 1. Introduction

The plasma aided flame retardation of wood and wood products has been developed as a result of a new plasma-aided process of *capillary impregnation* that comprises a surface plasma pre-treatment for alteration of the chemical, electrical (ionic), and capillary activities of wood surface, in general for improvement the technological characteristics of the capillary impregnation process. This study has been developed as part of a large research on plasma-chemically activated wood surface and flame retardant treated rain-forest wood.

A technological system of air plasma device and applicators has been created to produce cold technological plasma through dielectric barrier discharge (*DBD*) at atmospheric pressure and room temperature. The cold plasma pre-treatment by nonequilibrium *DBD* of wood, like rain-forest woods - *Tzalam*, *Caoba Mahogany*, and *Mexican White Cedar* (Mexico, Yucatán), improves technological characteristics such as solution spreading and wicking speed, as well as specific amount of the sorbed flame retardant. Due to its fine-texture and surface inactivation it is difficult to apply flame retardants directly through capillary impregnation. In this way, the plasma pre-treatment of wood and wooden products improves its flame retardation. The plasmachemical surface pre-treatment by dielectric barrier air discharge at atmospheric pressure (*DBD*) was specified as a new good way for wood surface functionalization and activation [1, 2, 3, and 4].

Wood is a complex material constituted mainly of three biopolymers: lignin, cellulose and hemicelluloses. In addition to these polymeric components, wood may contain extractives in more or less large quantities including several classes of organic compounds like sugars, flavonoids, tannins, terpenes, fats or waxes. Well-suited for the study of surface chemistry of complex organic materials, *X-ray photoelectron spectroscopy (XPS)* also referred to as *Electron Spectroscopy for chemical analysis* (*ESCA*) has been widely used in order to investigate the surface chemical composition of numerous lignocellulosic materials especially in the field of pulp and paper, where the surface chemistry is of considerable importance for the properties of the final products. Similarly, some reported studies investigate the changes of surface chemistry after different wood transformation processes and processing [4 and 5].

*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 plasma-chemical surface pre-treatment.

The binding energy is a characteristic of the atoms, which can be used for elemental identification on the plasma chemically modified 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 *DBD* pre-treatment. To obtain a deeper insight into the various functional groups, the C 1s signal is usually deconvoluted into four components according to the number of oxygen atoms bonded to *C*, [5]:

 $\Box$  The C<sub>1</sub> class corresponds to carbon atoms bonded only with carbon or hydrogen atoms (C-C or C-H), and it is usually pointed out at a *binding energy (BE)* of 284.6 eV (some also use 285.0 eV as the nominal value for the binding energy of carbon);

□ The C<sub>2</sub> class reveals the carbon atoms bonded with one oxygen atom (C-O or C-OH), and it appears at a higher binding energy compared to  $C_I (\Delta_{BE} = +1.5 \pm 0.2 \text{ eV}) - 286.1 \pm 0.2;$ 

□ The C<sub>3</sub> class corresponds to carbon atoms bonded to a carbonyl (C=O) or two non-carbonyl oxygen atoms (O-C-O), and it appears at a higher binding energy compared to  $C_{I}$  ( $\Delta_{BE}$  = + 2.8 ± 0.2 eV) - 287.4 ± 0.2.

□ And finally, the C4 class is associated with carbon atoms bonded to a carbonyl and a non-carbonyl oxygen atom (O-C=O) - it appears at a higher binding energy compared to  $C_I (\Delta_{BE} = + 3.75 \pm 0.2 \text{ eV}) - 288.35 \pm 0.2$ .



**Fig. 1.** Plasma-chemical surface pre-treatment of wood sample by non-equilibrium dielectric barrier air discharge at atmospheric pressure in asymmetric coplanar system with one glass barrier (**a**), technological regimes (A and B) of cathode directed streamers (**b**).

 Table 1: Elemental surface composition of three heartwood species before (K) and 2 hours after plasma pre-treatment (DBD: 12/18 kV)

 determined from wide XPS-spectra.

Wood	Samples	Peaks on the Wide XPS-spectra - Chemical Surface Composition, at. %								
1100u	Sumpres	Peaks	С	0	Ν	Р	Si	nO/nC		
Tzalam Heartwood	K (Non-Treated)		83.71	14.49	1.53	-	0.27	0.17		
	DBD Pre- treated	12 kV (50 Hz)	66.55	32.43	1.03	-	-	0.49		
		18 kV (50 Hz)	61.38	37.63	0.99	-	-	0.61		
Caoba Mahogany	K (Non-Treated)		81.12	18.39	0.49	-	-	0.23		
	DBD Pre-	12 kV (50 Hz)	78.25	20.17	1.58	-	-	0.26		
Heartwood	treated	18 kV (50 Hz)	71.06	28.21	0.73	-	-	0.40		
	K (Non-Treated)		79.86	17.75	1.41	-	0.98	0.22		
Heartwood	DBD Pre-	12 kV (50 Hz)	61.34	35.17	1.44	2.05	-	0.57		
Treatwood	treated	18 kV (50 Hz)	66.83	29.92	2.24	1.01	-	0.45		

This is a necessary condition to get better knowledge of the chemical transformations occurring during plasma-chemical surface pre-treatment and to propose an interpretation in terms of existing and known mechanisms.

*The objective* of this paper was to study the effect of plasma chemical surface pre-treatment of DBD in air (oxidative atmosphere) at atmospheric pressure and room temperature at industrial frequency (50 Hz) and two voltages - 12 and 18 kV (RMS), on the wood surface functionalization monitored by surface chemical composition change. Therefore, we focused mainly on the O/C ratio evolution and on the changes in the various components of the C (1s) and O (1s) lines.

#### 2. Experimental Investigation

On basis of prior art, as well as on our own experience in plasma-aided impregnation of wood and wooden materials, [1, 2], an oxidative surface plasma pre-treatment has been applied on the test samples for 60 sec in a non-equilibrium cold plasma of *DBD* at atmospheric pressure. Similar changes are the basis of the expected *DBD*-surface functionalization effect on the three species of rain-forest wood samples, plasma pre-treatment in two types of *DBD* in air was performed: *i*) A - DBD at industrial frequency (50 Hz) and relatively low voltage (12 kV RMS; 16.9 kV PV) at which the discharge regime is transitionally from electron avalanche to cathode directed streamers; *ii*) B - DBD at industrial frequency and relatively high voltage (18 kV RMS; 25.4 kV *PV*) characterizing the regime of cathode directed streamers, Fig. 1.

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

Studies of *cold plasma functionalization phenomena on wood*, i.e. interactions of oxidative cold plasma with wood surface, may add valuable information about the capillary impregnation, gluing and coating properties of wood. Such information is essential in the development of efficient processing methods, and for the prediction of the functionality and durability of wood products.

Three species of Mexican rain-forest heartwood were investigated: *i* - *Tzalam* (*Lysiloma bahamensis*); *ii* - *Caoba Mahogany* (*Swietenia macrophylla*); and *White Cedar* (*Cupressus Lusitanica*).

#### 3. Results and Discussion

The results from the wide *XPS* survey spectra of investigated wood samples before (*DBD* non-treated) and two hours after plasma chemical treatment (*DBD* pre-treated) are presented in Table 1. Analysis of the survey spectra indicates the presence of carbon (*C*), oxygen (*O*) and small amounts of nitrogen (*N*), phosphor (*P*) and silicon (*Si*) which represent the expected elements in wood.

High-resolution scans of the *XPS* spectra of C (1s) and O (1s) levels are also presented with their decomposition into components, respectively Fig. 2 and 3.

Using the total areas of these peaks and the respective photoemission cross-sections, a quantitative determination of the O/C ratio can be calculated. By knowing the chemical composition of each of these components, it is possible to calculate *a priori* the theoretical O/C ratio characteristic of non-treated wood samples [5].

 Table 2. Carbon peak C (1s) components or proportions of oxygen (O) and carbon (C) functional groups of heartwood surfaces before (K) and 2 hours after plasma surface pre-treatment (DBD: 12/18 kV) determined from high-resolution XPS-spectra.

			Carbon peak $C_{sl}$ components, area %								
Woods Samples		ples	C1 (C-C or C-H)	C2 (C-O or C-OH)	C2-3 (ND)	C3 (C=O or O-C-O)	C4 (O-C=O)	C4- (ND)	nC1/ nC2	<b>Sum</b> (nC2+ nC3	nC2/ (nC2+nC3)
			( <b>285.0</b> ±0.4 eV)	( <b>286.0</b> ±0.4 eV)	(287.0 ±0.4 eV)	(288.7 ±0.4 eV)	( <b>289.5</b> ±0.4 eV)	(292.8 ±0.4 eV	-	-	-
	K (Untreated)		56.79	15.20	0.00	4.14	0.00	0.00	5.31	19.34	0.79
Tzalam Heartwood	DBD	12 kV	35.04	27.12	22.01	15.27	0.00	0.56	1.29	42.39	0.64
	treated	18 kV	42.33	30.92	15.35	9.23	0.00	2.17	1.40	40.15	0.77
Caoba Mahogany Heartwood	K (Untreated)		57.22	12.67	0.00	6.23	0.00	0.00	6.40	18.90	0.67
	DBD Bro	12 kV	49.65	26.14	0.00	14.71	9.50	0.00	1.90	40.85	0.64
	treated	18 kV	51.69	22.92	0.00	12.29	13.10	0.00	2.26	35.12	0.65
Maxican	K (Untreated)		54.22	17.40	0.00	4.60	0.00	0.00	4.48	22.00	0.79
White Cedar Heartwood	DBD Bro	12 kV	45.94	27.96	15.05	5.98	0.00	5.07	1.64	33.94	0.82
	treated	18 kV	50.23	20.74	15.22	13.10	0.00	0,71	2.42	33.84	0.61



Fig. 2. Carbon C (1s) peak in photoelectron XPS/ESCA spectra of bare samples of heartwood and 2 hours after plasma surface pre-treatment in atmospheric dielectric barrier discharge in air at industrial frequency (50 Hz) and 12 and 18 kV (RMS) voltage.

*Cellulose* comprises five carbon atoms of C<sub>2</sub> and one of C<sub>3</sub> with an O/C of **0.83**. *Hemicelluloses*, which are mainly represented by glucuronoxylans, are constituted of fewer than five carbon atoms of C<sub>2</sub>, less than one carbon atom of C<sub>4</sub> for the acetyl and carboxylic groups and one atom of C<sub>3</sub> with an O/C of approximately **0.80**. The contribution of *lignin* is more complex and therefore more difficult to quantify. Four types of carbons are present in its structure with a greater contribution from the C<sub>1</sub> and C<sub>2</sub> classes and an O/C ratio of roughly **0.33**. *Extractives* are also present in very small quantities in wood and their contribution to the overall *XPS* spectrum is relatively low - for example carbon atoms of C<sub>4</sub> class are present in *linolic* and *abietic* acid with an O/C of 0.11/0.10, respectively [**5**].

From the data of untreated wood samples, it appears that carbon atoms bonded with one oxygen atom (C2 class) are the

most abundant. Carbon atoms bonded with other carbon or hydrogen (C<sub>1</sub> class) or bonded with two oxygen atoms (C<sub>3</sub> class) are present in smaller proportions, while those bonded with three oxygen atoms are less abundant Table 2.

The O/C ratio may be estimated from the individual ratio and abundance of each component, or from the elemental composition determined experimentally in the case of untreated wood samples. According to these methods, the O/C ratios are found to be of and 0.17, 0.22 and 0.23, respectively, Table 1.

The O/C ratio and distribution of carbon atoms of plasma treated samples differ considerably from those obtained for untreated wood: 0.49, 0.26 and 0.57 (*DBD*:12 kV); 0.61, 0.40 and 0.45 (*DBD*: 18 kV). The increased O/C ratio is attributed to the important oxidation occurring during cold plasma-treatment: the C<sub>1</sub> (C-C; C-H) contribution decreased considerably while

**Table 3.** Oxygen peak O (1s) components or proportions of oxygen (O), carbon (C) and hydrogen (H) functional groups of heartwood surfaces before (Tzalam-K) and after plasma surface pre-treatment (DBD: 12/18 kV) determined from high-resolution XPS-spectra.

Woods		01 02 03		(			<b>O</b> 3 <sup>1</sup>	
	Samples	(O=C)	(O-H)	(O-C; H-O-H)	Sum1 O1;O3	Sum2 C2;C3	Sum1 01;03) Sum2 C2;C3 H-O-F	( <b>0-</b> C)
	Binding energy, eV	<b>531.5</b> ±0,4	<b>532.5</b> ±0,4	<b>533.0</b> ±0,4	)	)	9 90	(0 0)
Tzalam (Lysiloma bahamensis)	K: untreated	0.00	58.48	41.51	41.51	19.34	22.17	19.34
	DBD: 12 kV (50 Hz)	0.00	56.21	43.79	43.79	42.39	1.40	42.39
	<i>DBD</i> : 18 kV (50 Hz)	0.00	58.74	41.26	41.26	40.15	Line (Control (Contro) (Contro) (Contro) (Contro) (Contro) (Contro) (Contro) (Contro	40.15
Caoba Mahogany (Swietenia	K: untreated	0.00	58.00	42.00	42.00	18.90	23.10	18.90
	DBD: 12 kV (50 Hz)	0.00	58.62	41.38	41.38	40.85	0.53	40.85
macrophylla)	DBD: 18 kV (50 Hz)	0.00	56.72	43.28	43.28 35.12 8.16	35.12		
Mexican White Cedar (Cupressus Lusitanica)	K: untreated	0.00	53.22	46.78	46.78	22.00	24.78	22.00
	DBD: 12 kV (50 Hz)	0.00	61.43	38.57	38.57	33.94	4.63	33.94
	DBD: 18 kV (50 Hz)	0.00	56.70	43.30	43.30	33.84	9.46	33.84

the C<sub>2</sub> (C-O; C-OH), C<sub>3</sub> (C=O; O-C-O) contribution increased, and C<sub>4</sub> (O=C-O) appears in *Caoba Mahogany*, indicating that the content of C-O, C-OH, C=O, O-C-O and O=C-O groups becomes more important. This plasma modification can not be attributed to an increase of the lignin content due to preferential degradation of hemicellulose.

Figures 2 and 3 show typical *XPS* survey spectra and high resolution C (1s) and O 1s spectra of plasma-treated Tzalam, Caoba mahogany and White cedar wood. When comparing C 1s spectra presented in Fig. 2, it is clear that the contribution of the different types of carbons differs strongly between untreated and plasma-treated wood samples. C<sub>3</sub> and C<sub>2</sub> contributions increased highly, while the C<sub>1</sub> contribution (attributed to lignin) decreased seriously after plasma-treatment.

The contribution of the different types of oxygen atoms is much more difficult to analyze, Fig. 3. O<sub>1</sub> and O<sub>3</sub> classes report the contribution of two types of carbon atoms - O=C and O-C while C<sub>2</sub> and C<sub>3</sub> classes report the contribution similarly of different types of oxygen atoms - C-O, C-OH, C=O and O-C-O. The difference between *Sum1* (O<sub>1</sub> + O<sub>3</sub>) and *Sum2* (C<sub>2</sub> + C<sub>3</sub>) can be attributed to the amount of water on the wood surface (H-O-H), Table 3.

The plasma chemical surface modification removes successfully the water (H-O-H) from the wood surfaces. The difference (*Sum1-Sum2*) was decreased highly two hours after plasma pre-treatment: *Tzalam* - form 22.17 to 1.40/1.11; *Caoba Mahogany* - from 23.10 to 0.53/8.16; and *Mexican white cedar* - from 24.78 to 4.63/9.46, respectively, Table 3.

The O<sub>3</sub> class reveals the oxygen atoms bonded with one carbon atom and two hydrogen atoms (O-C and H-O-H). A new difference between O<sub>3</sub> class and the difference (*Sum1-Sum2*) reveals the abundance of oxygen atoms bonded with other carbon atom (O-C). From the data of untreated and plasma treated wood samples, it appears that carbon atoms bonded with one oxygen atom (C<sub>2</sub> or O<sub>3</sub><sup>+</sup> class) increase essentially its quantity after plasma treatment: *Tzalam* - form 19.34 to 42.39/40.15; *Caoba Mahogany* - from 18.90 to 40.85/35.12; and *Mexican white cedar* - from 22.00 to 33.94/33.84, respectively, Table 3.

When using high energy resolution experiment settings on *XPS* equipped with a monochromatic Al K-alpha X-ray source, the *Full Width at Half Maximum (FWHM)* of the main investigated *XPS*-peaks range from:

 $\Box$  The C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>, or C (1s) component, peaks of untreated (bare) woods have *FWHMs* that, in general, range from 1.3 eV to 2.0 eV: *Tzalam* - from 1.6 to 2.0; *Caoba Mahogany* - from 1.3 to 2.0; and *Mexican white cedar* - from 1.8 to 2.0;

 $\Box$  The C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> peaks of plasma treated (*DBD*: 12 kV) woods have *FWHM*s that, in general, range from 1.4 eV to 2.34 eV: *Tzalam* - from 1.8 to 2.2; *Caoba Mahogany* - from 1.98 to 2.16; and *Mexican white cedar* - from 1.4 to 2.34.

 $\Box$  The C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> peaks of plasma treated (*DBD*: 18 kV) woods have *FWHM*s that, in general, range from 1.4 eV to 2.34 eV: *Tzalam* - from 1.42 to 2.1; *Caoba Mahogany* - from 1.75 to 2.38; and *Mexican white cedar* - from 1.0 to 1.91.

 $\Box$  The O<sub>1</sub>, O<sub>2</sub>, and O<sub>3</sub>, or O (1s) component, peaks of untreated woods have *FWHMs* that, in general, range from 1.8 eV to 2.44 eV: *Tzalam* - 2.38; *Caoba Mahogany* - from 1.97 to 2.44; and *Mexican white cedar* - from 1.8 to 2.0;

 $\Box$  The O<sub>1</sub>, O<sub>2</sub>, and O<sub>3</sub>, or O (1s) component, peaks of plasma treated (*DBD*: 12 kV) woods have *FWHMs* that, in general, range from 2.24 eV to 2.67 eV: *Tzalam* - from 2.45 to 2.67; *Caoba Mahogany* - from 2.40 to 2.63; and *Mexican white cedar* - from 2.24 to 2.25;

 $\Box$  The O<sub>1</sub>, O<sub>2</sub>, and O<sub>3</sub>, or O (1s) component, peaks of plasma treated (*DBD*: 18 kV) woods have *FWHMs* that, in general, range from 1.3 eV to 2.0 eV: *Tzalam* - from 2.17 to 2.37; *Caoba Mahogany* - from 2.53 to 2.57; and *Mexican white cedar* - from 2.3 to 2.58;

#### Conclusion

Processes of woods preservation and bonding are usually achieved through the application of impregnation solution or adhesive on wood surface. Among the different mechanisms involved in the impregnation and bonding of woods, two synergistic effects seem essential in order to achieve good results:

□ The penetration and anchoring of the impregnation solution or adhesive in the void spaces of the wood surface;

□ The occurrence of a strong interaction or chemical reaction between the impregnate or adhesive and the major constituents of wood.

These conditions are governed by the surface properties that depend not only on the bulk composition, but also on the surface building and modification process.

X-ray photoelectron spectroscopy is a suitable investigation method to characterize the composition of wood surface. *XPS* is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation. It was used successively to investigate the interaction of three rain-forest wood surfaces with cold non-equilibrium plasma of *DBD* in air at atmospheric pressure and room temperature.

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Fig. 3. Oxygen O1s peak in photoelectron XPS/ESCA spectra of bare sample of heartwood and 2 hours after plasma surface pre-treatment in atmospheric dielectric barrier air discharge at industrial frequency (50 Hz) and 12 and 18 kV (RMS) voltage.

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