

## Investigation of pure and plasma treated spruce with surface analytical techniques

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### ABSTRACT

Surface properties of wood can be changed using a dielectric barrier discharge at atmospheric pressure. Depending on the utilised gas the surface tension and chemical activity can be increased or hydrophobic surfaces can be obtained by plasma-polymerisation. For characterising the altered wood surfaces different electron spectroscopic methods are used. XPS or ESCA is a well known technique for analysing the chemical composition of wood surfaces. UPS and MIES are largely unknown methods on cellulosic materials. As UPS reflects the Density Of States (DOS), MIES the Surface Density of States (SDOS) respectively, these methods are useful to characterise changes of wood surfaces based on plasma treatment. It is shown that these techniques yield indeed reproducible results and, in particular, possess the potential to give information on the interaction of molecules with wood surfaces.

### INTRODUCTION

During recent years plasma technology has become more and more important and has expanded into various technical fields. For generating light, cleaning, surface coating, creation of special functional groups or where fundamental adhesion problems occur, plasma technology is an all-rounder. Yet up until now its full potential has not been fully tapped. By use of plasma-treatment, surfaces are cleaned, heated and activated. Thereby, the surface is influenced by electrons, ions, molecules and radicals, which by direct pulse transmission remove impurities. Chemical reactions also reduce impurities and generate special functional groups. As a result of these systematically generated groups or the destruction of chemical bonds, the surface tension and chemical activities increase. In this way surface properties can be modified without influencing the volume characteristics (Hippler *et al.* 2001). A new innovative application of plasma technology is the treatment of sensitive, organic materials such as timber.

As a result of temperature sensitivity, large dimensions and vacuum unsuitability, the renewable resource wood caused problems in the technical realisation and was not satisfactorily treatable. The treatment has now be facilitated by a dielectric barrier discharge (DBD) and a particular, customised setup. By plasma-treatment prior to any coating, process wood and derived timber products can be conditioned in such a way that coatings (paints, lacquers, glues) will be absorbed quicker and the levels of adhesion will increase. Thus, the fracture strength of laminated wood can be increased significantly and a reduction of the amount of required glue is feasible. Even with only a slight percentage reduction a substantial cost saving can be achieved, in addition to a decrease in the environmental pollution levels. Another conceivable application could be the partial abandonment of frequently used primers. Furthermore, the utilisation of new materials and material combinations will be possible. Newly-made materials are the wood-plastic-compounds. Investigations have proven that plasma-treatment can completely solve many problems of varnishing. Due to the fact that no visual alteration on the surface occurs by plasma-treatment, this technology is applicable on surfaces where the aesthetic character needs to be preserved. Because gas temperatures are less than 100°C a thermal influence through pyrolysis is excluded; rather a slight heating can improve the quality of adhesion additionally (Rehn *et al.* 2003, Rehn and Viöl 2003, Rehn *et al.* 2004).

Hydrophobic surfaces are obtained by plasma-polymerisation under atmospheric pressure utilising gases such as methane, ethane and silane-mixtures. These water repellent layers can substitute the conventional, protective coatings (Bente *et al.* 2004).

In order to optimise the plasma-treatment and used coatings, glues etc. basic investigations need to be carried out. If the fundamental effectiveness and modification of wood surfaces are understood, the parameters of treatment and coatings can be altered for achieving optimal results. To investigate surface properties and modifications X-Ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS) and Metastable Impact Electron Spectroscopy (MIES) have been applied to clean, untreated and plasma-treated spruce surfaces.

The traditional preservation by means of coating and impregnation, as well as the adhesion, can be optimised in durability and in function by the plasma-treatment. With the plasma-treatment the quality of wood and derived timber products is improved, thereby heightening competitiveness relative to other materials.

## EXPERIMENTAL

The ultrahigh vacuum (UHV) apparatus is evacuated by a combination of a turbo molecular and a ion getter pump. The base pressure is better than  $5 \cdot 10^{-11}$  mbar which is achieved after bake-out to 150°C for at least 24h. It is equipped with a commercial Low Energy Electron Diffraction (LEED) system (LEED Electronics PHI Model 11-020), a commercial X-ray source (Specs RQ-20/38C) for X-Ray Photoelectron Spectroscopy (XPS), providing Mg  $K_{\alpha}$  or Al  $K_{\alpha}$  with photon energies of 1253,6eV and 1486,6eV, respectively. These photons hit the sample surface under 80° to its normal. Metastable Impact Electron Spectroscopy (MIES) and Ultraviolet Photoelectron Spectroscopy (UPS) are performed applying a combined source which provides He\*  $2^3S$  atoms (excitation energy 19.8eV) and HeI photons (excitation energy 21.2eV). The source is schematically shown in Figure 1. Besides ground state He the cold cathode discharge produces He\*  $2^1S$ , He\*  $2^3S$ , HeI and He<sup>+</sup> in the source chamber. The He beam is formed by a skimmer between source and buffer chamber. He<sup>+</sup> are removed from the beam by a condenser inside the buffer chamber. Within the source a He par-

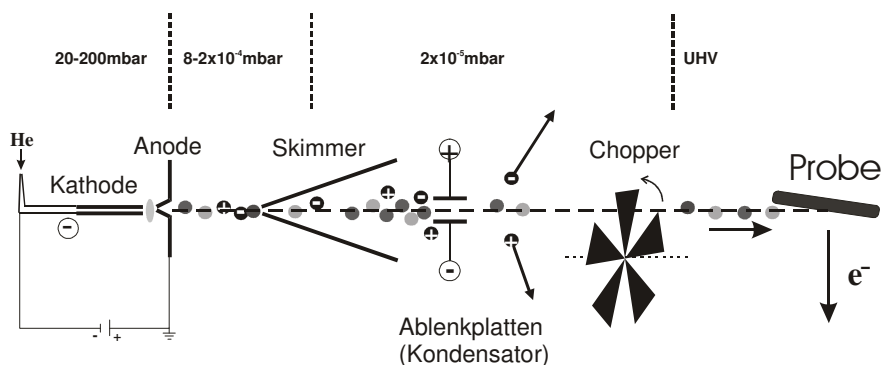


Figure 1: Schematic representation of the combined  $\text{He}^*/\text{HeI}$  source

tial pressure of about 10-20 mbar is necessary. The source chamber provides a He pressure of about  $1.5 \cdot 10^{-3}$  mbar, the buffer chamber  $1 \cdot 10^{-5}$  mbar. Inside the UHV chamber the He partial pressure rises to about  $3 \cdot 10^{-9}$  mbar. This does not affect any measurement because He is unreactive.

$\text{He}^*$  and HeI are separated from each other by a time-of-flight chopper system. Applying a separation electronics and a two-channel counter system MIES and UPS are measured simultaneously.  $\text{He}^*$  atoms and HeI photons hit the sample under  $45^\circ$  to surface normal.

Electrons emitted under  $90^\circ$  by photons or metastable atoms impact on the sample are analyzed by a hemispherical analyzer (VSW HA 100). The acquisitions of all spectra are performed computer controlled. MIES and UPS spectra are measured under normal emission within 100s. XPS spectra are measured under  $10^\circ$  with respect to the surface normal within 2-3h, typically, depending on resolution requirements. The sample position within the UHV chamber is adjusted by a commercial system (Aerotech UNIDEX 11) under computer control. This guarantees a high reproducibility.

The principles of photo electron spectroscopy (UPS and XPS) are well known. Briefly, photon impact on the surfaces results in the emission of electrons with characteristic energies (Ertl and Küppers 1985). XPS provides information on the chemical composition while UPS in principle shows the Density of States (DOS) averaged over about  $15 \text{ \AA}$  depth, in the energy range between the Fermi level and less than 20 eV which is corresponding to the valence band.

In MIES,  $\text{He}^*$  atoms, most of them in  $\text{He}^* 2^3\text{S}$  states, approach the surface with thermal velocity. Interaction takes place in distances between  $3 \text{ \AA}$  and  $10 \text{ \AA}$  from the surface on the impinging trajectory with the very outermost surface wave functions (Harada *et al.* 1987, Morgner 2000). Therefore, MIES is extremely sensitive for surface states. This is important for the study of the interaction of water molecules with the surfaces presented here. In principle three different processes occur during the interaction of  $\text{He}^*$  with surfaces depending on the surface work function, its conductivity and its possible coverage with molecules. Because of the insulating nature of the surface under study, only Auger de-excitation (AD) is observed in the investigations presented in this contribution. Therefore we restrict our description of the interaction on this process. Figure 2 shows the interaction process schematically. The  $\text{He}^*$  atom approaches the surfaces. As soon as the overlap between surface wave functions and the He 1s orbital becomes significant, a surface electron fills the He 1s vacancy, thus emitting the electron in the He 2s state. This electron carries the excess kinetic energy  $E_{\text{kin}}$ . The energy balance is similar to the one for UPS with a different excitation energy  $E^*$  (19.8 eV instead of 21.2 eV):

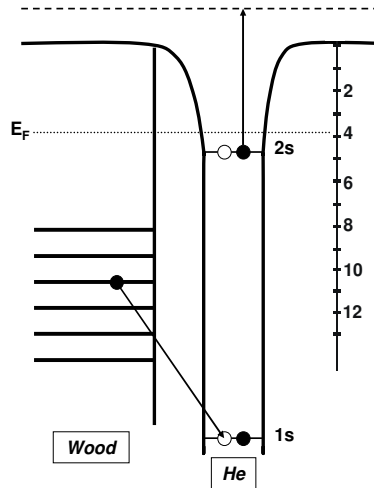


Figure 2: Schematic representation of the Auger de-excitation process in front of an insulating

$$E_{\text{kin}} = E^* - E_B - \phi \quad (1)$$

Hereby  $\phi$  denotes the surface work function and  $E_B$  the electron binding energy with respect to the Fermi level. The spectral distribution  $N(E)$  reflects the Surface Density of States (SDOS) which is responsible for the surface interaction with impinging atoms or molecules from the ambience.

For the plasma treatment of the wood surfaces, a prototype of a plasma reactor was developed in order to meet several industrial applications. Figure 3 shows the set-up for an industrial application (Viöl 1999, 2002, 2004). The speed of the wood motion is can be varied between 3 m/min and 18 m/min. Timber materials up to a thickness of 30 mm and a broadness of 150 mm can be treated and are guided through two vertical movable pairs of electrodes. As a result, the wood can be treated from both sides simultaneously. In order to get a homogeneous discharge the gas gap has to be held constantly at 2 mm. This is realised by rollers running over the wood surface. In order to chill the electrodes, to collect and destroy generated ozone and to homogenise the discharge, air is drawn centrally through the two pairs of electrodes. A high voltage generator, with a 30kHz, 20kV AC output, is connected to each pair of electrodes, which are placed under and over the wood. Whilst the wood is grounded, a phase shift of  $180^\circ$  among the two pairs of electrodes implicates a potential difference of 40kV. With this arrangement power densities over  $25\text{W}/\text{cm}^3$  are realised. With a discharge width of  $2 \times 30\text{mm}$ , the treatment times vary between 0.2s and 1s.

The oval form of the electrodes, the consistent air flow and the exact alignment of the wood between the upper and the lower electrodes lead to a nearly homogeneous discharge without hot filaments. In order to treat single, small, specimens for XPS, UPS and MIES, it was required that a cavity was milled into a large plank where this small specimens were deposited. The wood specimens were prepared of 0.1mm thick splinters, which can be produced by a planer. Out of these splinters the specimens for the measurements were cut.

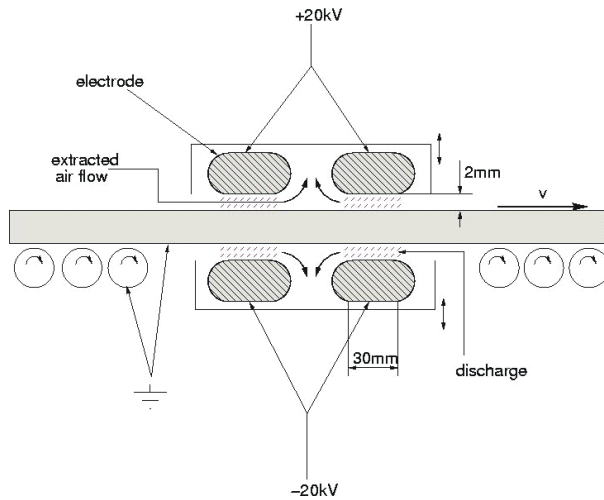


Figure 3: Schematic sketch of the plasma discharge set-up

## RESULTS AND DISCUSSION

Figure 4 shows XPS survey spectra of spruce surfaces which are untreated, treated in silane ( $\text{SiH}_4$ ) plasma and treated in synthetic air plasma from the top to the bottom, respectively. The experimental details of the plasma treatments are described in the experimental section. The spectra are shown as a function of the binding energy. The untreated spruce surface mainly shows C(1s) and O(1s) peaks at binding energies

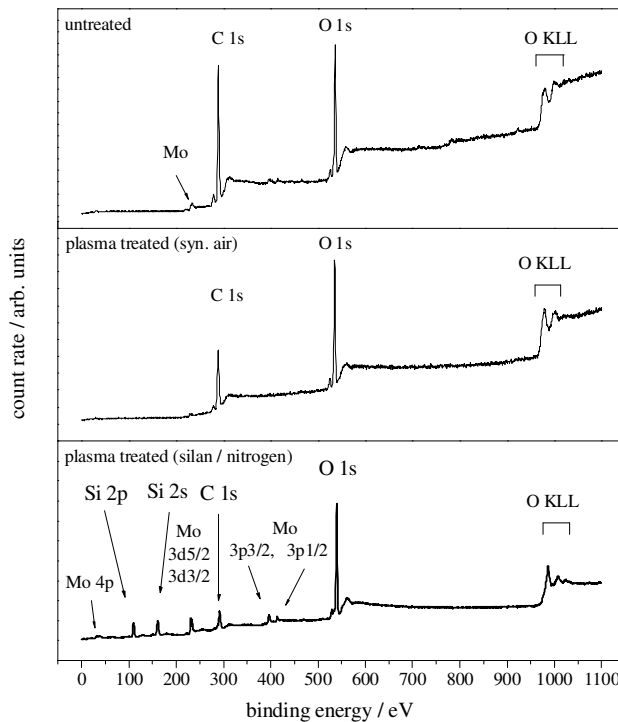


Figure 4: XPS spectra of spruce surfaces which are treated in silane ( $\text{SiH}_4$ ) plasma, untreated and treated in synthetic air plasma, respectively

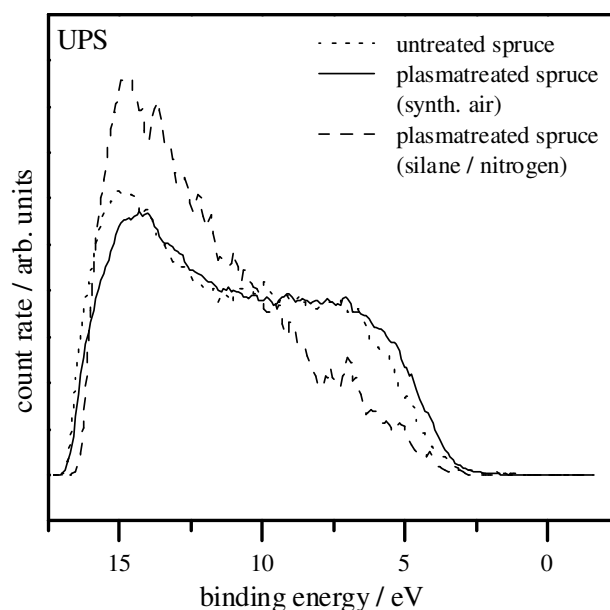
$E_B$  of  $(288.6 \pm 0.3)$  eV and  $(536.1 \pm 0.3)$  eV, respectively. The peak ratio  $O(1s)/C(1s)$  amounts to 0.32. A decomposition of the  $C(1s)$  peak into its 3 components  $C_1(C-C)$ ,  $C_2(C-O)$  and  $C_3(C=O)$  will be made in forthcoming publication. Additional structures around  $E_B \approx 233$  eV, 397 eV and 416 eV are due to emission from the sample holder made of molybdenum. These structures do not affect the following discussions.

The surface treated in synthetic air plasma also shows two main structures:  $C(1s)$  at  $E_B = (288.6 \pm 0.3)$  eV and  $O(1s)$  at  $E_B = (535.2 \pm 0.3)$  eV. The  $C(1s)$  peak position fits very well with the untreated surface while the  $O(1s)$  peaks position is shifted to lower binding energies by 0.9 eV. The peak ratios  $O(1s)/C(1s)$  amount to 0.57. This is significantly higher than for the untreated surface which means, that a significant amount of oxygen must be adsorbed on or incorporated into the spruce surface.

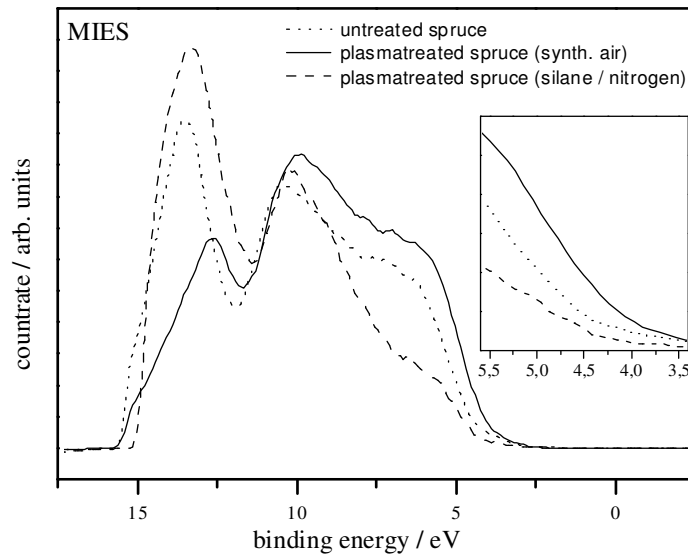
The surface treated in a plasma containing silane also shows more than two structures.  $C(1s)$  is found at  $E_B = (287.6 \pm 0.3)$  eV and  $O(1s)$  at  $E_B = (536.3 \pm 0.3)$  eV. The  $C(1s)$  peak position and the  $O(1s)$  peak position fits well to the ones for the air treated surface. The relative peak ratios  $O(1s)/C(1s)$  amount to 5.1. This is even significantly higher than for the air treated surface and is due to the partly  $SiO_2$  covered surface. Besides the small Mo contribution two additional peaks at  $E_B = (106.4 \pm 0.3)$  eV and  $E_B = (157.8 \pm 0.3)$  eV occur. These are due to emission from  $Si(2p)$  and  $Si(2s)$ , respectively. The further enhanced oxygen uptake compared with the other spruce surfaces, together with the incorporation of silicon, suggests, that during silane plasma treatment a Si-O complex is formed.

Figure 5 shows UPS spectra of spruce surfaces treated in the same manner as described with Figure 4. During UPS / MIES measurements the surface was kept at 130°C. Prior to the studies the surface was carefully dehydrated by heating at 100°C under UHV conditions until the QMS water signal has reduced to less than 5 percent of its original value. In auxiliary experiments to be described in our forthcoming publication, we have verified that we do indeed study the wood surface, not adsorbate water, segregating to the surface.

The surface work function (WF) can be estimated from the low-energy offset of the spectra (4.4 ( $\pm 0.1$ ) eV for untreated and air treated surfaces and 4.7 ( $\pm 0.1$ ) eV for the silane treated surface). All spectra show a gap of about 3.1 ( $\pm 0.1$ ) eV between valence



**Figure 5:** UPS spectra of spruce surfaces which are treated in silane ( $SiH_4$ ) plasma, untreated and treated in an synthetic air plasma, respectively



**Figure 6:** MIES spectra of spruce surfaces which are treated in silane ( $\text{SiH}_4$ ) plasma, untreated and treated in a synthetic air plasma, respectively

band maximum (VBM) and the Fermi level (corresponding to the binding energy  $E_B=0\text{eV}$ ). The band gap amounts to  $3.1\text{eV (VBM)}+4.4\text{eV(WF)}=7.5\text{eV}$  for the untreated and air treated surfaces and  $7.8\text{eV}$  for the silane treated surface. All UPS spectra are relatively unstructured. The spectrum of the silane-treated surface is quite different from the both others, which are very similar to each other. The XPS results suggest a Si-O-formation on the surface which is however not confirmed by the UPS results. The main change of the Bulk Density of States (BDOS), in the region accessible to UPS, for the silane treated surface is a strong reduction of the intensity up a binding energy of  $10\text{eV}$  and an increase of the band gap.

Figure 6 shows MIES spectra of the surface characterized in Figure 4 by XPS. The MIES spectra are induced by the Auger De-excitation process, because the MIES and UPS spectra show comparable band gap widths. The spectra are dominated by a strong emission between  $12\text{eV}$  and  $14\text{eV}$  and a broad structured emission between  $3\text{eV}$  and  $12\text{eV}$ . The MIES spectra directly reflects the SDOS of the surface which is responsible for any electronical interaction between surfaces and impinging molecules.

Inspection of Harada *et al.* 1997 and Günster *et al.* 1999 shows that the MIES spectra are typical for surfaces terminated by carbohydrates and/or hydroxyl groups whereby the emission between  $E_B=5$  to  $10\text{eV}$  can be attributed to C(2p) derived molecular orbitals (MOs), while that for  $E_B>11\text{eV}$  is due to C(2s) derived MOs. Emission in the region around  $E_B=6\text{eV}$  may also come from the ionization of O(2p) MOs.

Summarizing, we have shown that the combination of XPS, UPS and MIES can be applied to the study of the surface of untreated and plasma-treated spruce and yields reproducible results.

In future work we will study the interaction of water with well-characterised wood surfaces by applying the same combination of techniques.

## ACKNOWLEDGEMENTS

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