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Introduction

Chemical changes due to plasma treatment were studied by several surface sensitive techniques like XPS, UPS and MIES. UPS and valence band XPS spectra of wood and its main components cellulose and lignin have not been considered so far in order to interpret chemical changes due to surface treatment on wood surfaces.

The interpretation of the valence band spectra of wood, cellulose and lignin was done by comparison of several so-called "fingerprint" spectra. They were obtained from less complex molecules with similar chemical structures and functional groups.

The functional groups of cellulose in the valence band were identified by fingerprints from glucose and cellobiose, the fingerprints for lignin were obtained by coniferyl alcohol, cinnamyl alcohol, phenol and benzene.

The plasma treatment in ambient air has different effects to the surface of cellulose and lignin. A plasma containing oxygen reduces the cellulose surface and causes loss of hydroxyl groups and formation of C=O double bonds.

Experimental Techniques

MIES: Metastable Impact Electron Spectroscopy

Principle:

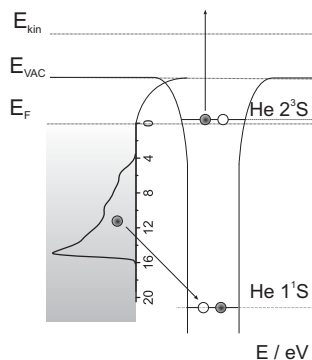
- ▶ Slow metastable atoms ($\text{He}^* 2^3\text{S}$) interact with surface
- ▶ electron transfer leads to emission of electrons [4]

Special features:

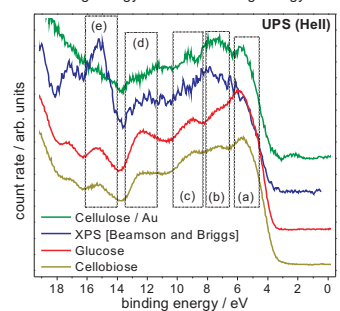
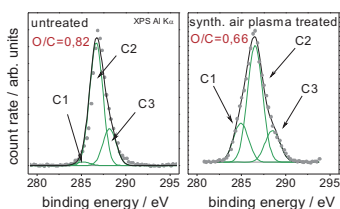
- ▶ Selective information about the electronic structure of surface species
- ▶ Non-destructive
- ▶ Rather low charge-up analyzing insulators
- ▶ Easy to combine with UPS (He I)

XPS: X-ray Photoelectron Spectroscopy

UPS: Ultraviolet Photoelectron Spectroscopy (He I, He II)



Cellulose and Cellobiose

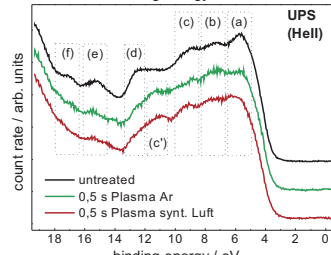
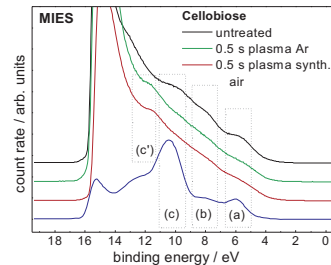


Untreated cellulose and cellobiose (XPS)

- ▶ Plasma in synth. air reduces cellulose
- ▶ Generation of C=O and C=C bonds

UPS / MIES

- ▶ Contributions between 5 and 12 eV are due to emissions from π MOs localized on the oxygen [1]
- ▶ Control: XPS from Beamson and Briggs

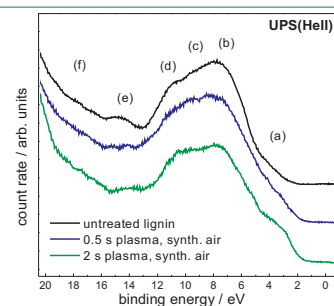
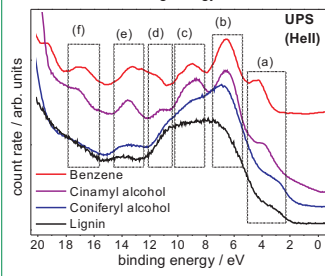
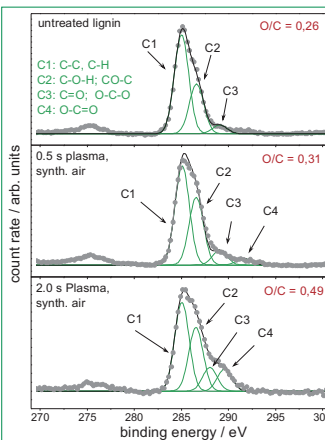


- ▶ Plasma treatment primarily causes changes in oxygen derived states of cellulose
- ▶ (a) based on ionization of hydroxyl groups
- ▶ (b) dominated by emissions from ether groups
- ▶ (c) and (d) ether and hydroxy
- ▶ Plasma treatment causes new peak (c') which is due to emissions from carbonyl groups
- ▶ Identification of hydroxyl groups is confirmed by MIES of Methanol

References

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- [3] Carlsson, C. M. Gilbert and Ström G., Langmuir 7 (1991) 2492-2497
- [4] Wolkenhauer, A., Avramidis, G., Cai, Y., Militz, H., Viöl, W., Polymer (2007) 470-474
- [5] Wolkenhauer, A., Avramidis, G., Hauswald, E., Militz, H., Viöl, W., in press Int. Journal of Adhesion and Adhesives (2008)

Lignin



Sample preparation

- ▶ Lignin was prepared by spin coating on Au using DMSO.
- ▶ Coniferyl alcohol and cinnamyl alcohol was prepared using a thermal evaporator (Kentax)

XPS treated and untreated lignin

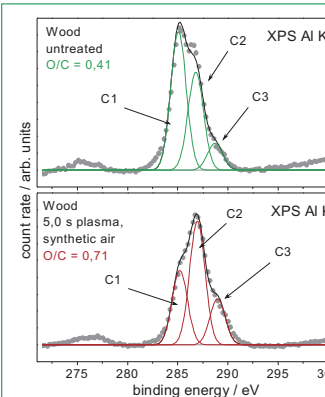
- ▶ Plasma treatment oxidizes the lignin surface.
- ▶ Formation of C-C and C=C bonds.
- ▶ Formation of carbonyl groups
- ▶ Formation of carboxyl groups

UPS (HeII) lignin, plasma treated in air

- ▶ Plasma treatment causes changes in oxygen derived states (4 - 13 eV) [5]
- ▶ Formation of carbonyl groups (d)
- ▶ Formation of C=C (a)

	(a)	(b)	(c)	(d)	(e) + (f)
Benzene	1e _{1g} (π)	3e _{2g} (σ CH) 1a _{2u} (π)	3e _{1u} (σ CH); 1b _{2u} (σ CC) 2b _{1u} (σ CH)	3a _{1g} (σ CH)	C2s
Phenol	4a ₁ (π) 3a ₁ (π)	2a ₁ (π) 21a ₁ 20a ₁	1a ₁ 17 a ₁ , 16a ₁ 15 a ₁	phenyl methoxy methoxy	C 2s C 2s
Cinnamyl benzene	phenyl	benzene hydroxy	benzene methoxy methoxy	phenyl methoxy methoxy	C 2s C 2s
Coniferyl phenyl	phenyl	hydroxy	hydroxy	phenyl methoxy methoxy	C 2s C 2s
Lignin	phenyl	hydroxy	hydroxy	phenyl methoxy methoxy	C 2s C 2s

Wood



- ### XPS - treated and untreated spruce
- ▶ Plasma treatment oxidizes the surface
 - ▶ Percentage of C1 in total C 1s decreases
 - ▶ Generation of hydroxyl or ether groups is indicated by growth of C2
 - ▶ Percentage of carbonyl groups increases
- ### Wetting behavior
- ▶ In general, oxyge-rich surfaces are hydrophilic
 - ▶ Increase of double bonds leads to polarizable surface.
 - ▶ Wettability increases

UPS - treated and untreated spruce

- ▶ UPS spectra of wood can be interpreted as the sum of lignin and cellulose

Untreated

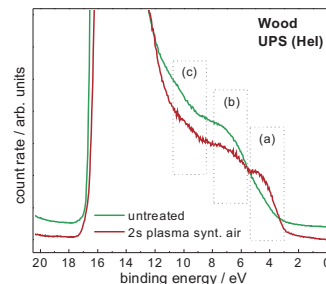
- ▶ Peak (a) not present
- ▶ Peak (b) hydroxyl groups

Air plasma treated

- ▶ Peak (a) is due to emissions from π MOs of carbon double bonds
- ▶ Peak (b) can be attributed to hydroxyl groups

Wetting behaviour

- ▶ Formation of polar bonds like carbonyl bonds and carbon double bonds was also shown by contact angle measurements [4, 5]



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