

Fundamental study of the interaction of Ti atoms with spruce surfaces

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Abstract

Metastable induced electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were applied to study the interaction of Ti metal atoms with spruce surfaces. Spruce surfaces were produced by planing splints from a spruce bar. Ti atoms were adsorbed from a metal evaporator under ultra-high vacuum conditions. The amount adsorbed corresponds to 10 monolayer equivalents. Strong interactions between the spruce surface and metals atoms occurred. Impinging Ti atoms were oxidized by the spruce surface. No Ti agglomeration or particle formation was observed. The surface was smoothed by the Ti applied and was completely covered by a titanium oxide film.

Keywords: adsorption; metastable induced electron spectroscopy (MIES); photoelectron spectroscopy (UPS, XPS); spruce surfaces; titanium.

Introduction

The classical tools of wood preservation against aging (weathering) and attack by microorganisms are lacquering and impregnation. Alternative methods in terms of higher ecoefficiency and less environmental damage are permanently under investigation.

It is known that metal oxide particles such as TiO₂, SiO₂ and ZnO are very useful in protection against UV-B radiation and bacterial and fungal hazards (Miyafuji et al. 2004; Jaroenworalluck et al. 2006; Popov et al. 2005). Furthermore, such particles can decompose volatile organic compounds via photocatalytic processes (Zhang et al. 2005). Up to now, these particles have been applied to wood surfaces as additives in lacquers.

The surface properties of wood can be changed by applying a dielectric barrier discharge at atmospheric

pressure (Klarhöfer et al. 2005). Depending on the gas utilized, surface tension, and chemical activity, the surface can be changed drastically (Bente et al. 2004). In such a discharge, metal atoms can also be applied to wood surfaces.

The goal of the present study was to contribute to the development of lacquer-free surfaces covered directly with metals via a dielectric barrier discharge. Before such processes can be applied, basic knowledge of the adsorption and stability of metals and metal oxides on wood surfaces is required.

This study investigates the fundamental interactions between Ti atoms and spruce surfaces. Surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) are well known in the context of surface analysis (Dorris and Gray 1978; Johansson et al. 2004; Fardim et al. 2006). We also used metastable induced electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS), which offer detailed insight into the interaction processes between wood and metals (Klarhöfer et al. 2005).

Experimental

The apparatus for spectroscopy was described in detail previously (Friedrichs et al. 2006). Briefly, the system is equipped with a hemispherical analyzer (VSW HA 100) in combination with He^{*}/HeI and an X-ray source. The base pressure of the apparatus is 2×10^{-11} mbar.

MIES and UPS are performed by applying a cold-cathode discharge adapted to the ultra-high vacuum chamber via a two-stage pumping system. A time-of-flight technique is integrated to separate electrons emitted by He^{*} (MIES) and HeI (UPS) upon interaction with the surface. MIES and UPS spectra are recorded with a resolution of 220 meV under normal emission within 280 s. The angle of incidence for the mixed He^{*}/HeI beam is 45°. All MIES and UPS spectra are displayed as a function of the electron binding energy (E_b) with respect to the Fermi level, which is determined by the high-energy cutoff obtained for metallic samples in UPS. The surface work function can be determined from the low-energy onset of the MIES or UPS spectra with an accuracy of ± 0.1 eV.

Metastable He^{*} atoms may interact via different mechanisms, depending on the surface electronic structure and work function. For the clean and Ti-covered wood surfaces studied in this paper, only Auger de-excitation (AD) occurs. During AD an electron from the sample surface fills the 1s orbital of the impinging He^{*}. Simultaneously a He^{*} 2s electron carrying the excess energy is emitted. Detailed descriptions of the He^{*}-surface interaction processes may be found in literature reviews (Harada 1997; Morgner 2000).

XPS was performed using a commercial X-ray source (Specs RQ20/38C). The photons hit the surface at an angle of 80° and emitted electrons are analyzed at 10° to the surface normal. Spectra are recorded with a resolution of 1.1 eV for detail spectra and 2.2 eV for survey spectra.

All AFM pictures were taken using an Omicron UHV AFM-STM system in contact mode and a base pressure of 4×10^{-10} mbar.

The samples were prepared in the spectroscopy apparatus. After spectroscopic measurements, they were transferred to the microscope.

Spruce specimens were cut using a planer. Typically, splints had a thickness of between 0.1 and 0.2 mm. To avoid charging of the sample during MIES and UPS measurements, splints were slightly heated at approximately 120°C. This temperature is sufficient for charge compensation and does not alter either the chemical composition of the wood or the spectra.

Ti films were produced by evaporating 99.99% pure Ti (Chempur GmbH) from a commercial metal evaporator (Omicron EFM3) at a flux of approximately 2.5 monolayer equivalents (MLE) per minute *in situ*; 1 MLE corresponds to one complete surface Ti layer. These layers were produced on freshly prepared spruce splints at room temperature. All measurements shown here were obtained with 10 MLE Ti.

Results

Figure 1a shows an overview XPS spectrum of the Ti-covered spruce surface. The main features identified cor-

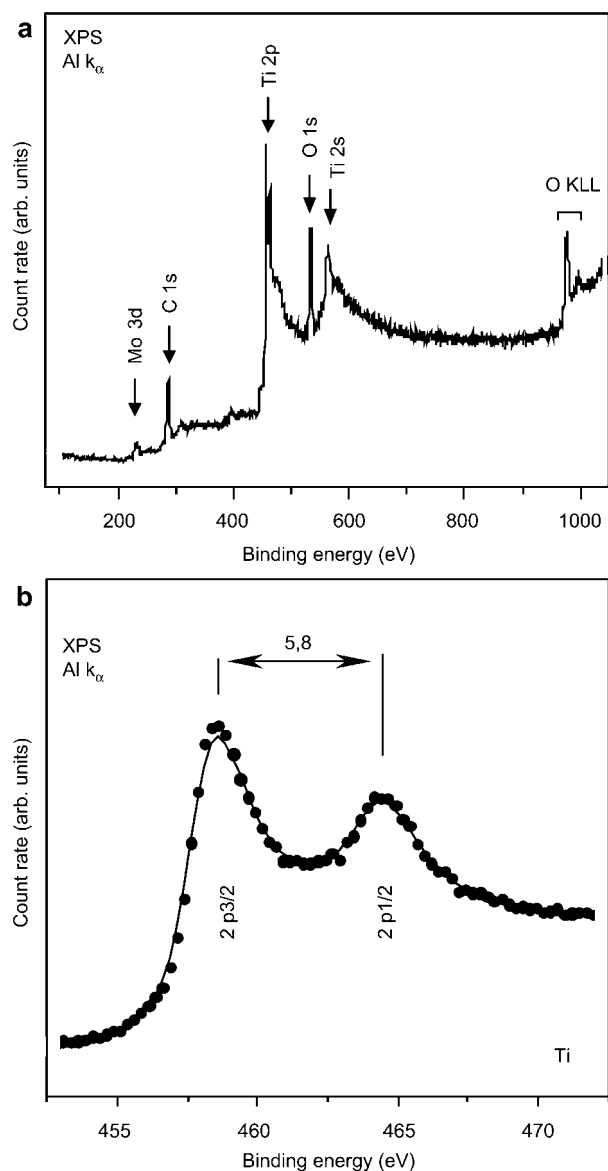


Figure 1 XPS spectra of a Ti-covered spruce surface: (a) overview (0–1100 eV) and (b) Ti 2p (450–470 eV).

respond to carbon (C 1s at $E_B=287.3$ eV), titanium (Ti 2p_{3/2} at $E_B=456.4$ eV, Ti 2p_{1/2} at $E_B=462.0$ eV, Ti 2s at $E_B=563.7$ eV), and oxygen (O 1s at $E_B=532.7$ eV). Furthermore, some contributions from the molybdenum sample holder at $E_B=231$ eV are visible, which are not of importance for the further discussion. Figure 1b shows a detail spectrum of the Ti 2p_{3/2} and 2p_{1/2} peaks. The distance between these peaks amounts to 5.8 eV.

MIES spectra of pure and Ti-covered surfaces are illustrated in Figure 2a. Besides secondary electrons, the clean spruce surface shows peaks at $E_B=10.5$ and 6.1 eV. Its work function amounts to 4.5 eV. Such spectra are typical for surfaces terminated by alkanes or hydroxyl groups. The emissions between 5 and 11 eV are attributed to C 2p-derived molecular orbitals (MOs). Part of the emission beyond 11 eV is attributed to C 2s-derived MOs (Harada 1997; Günster et al. 1999). After Ti deposition, two main peaks are visible at $E_B=8.1$ and ~2.8 eV. The surface work function decreases to 3.7 eV on Ti deposition. The peak at 8.1 eV is similar to that observed for rutile TiO₂(110) single crystals and is attrib-

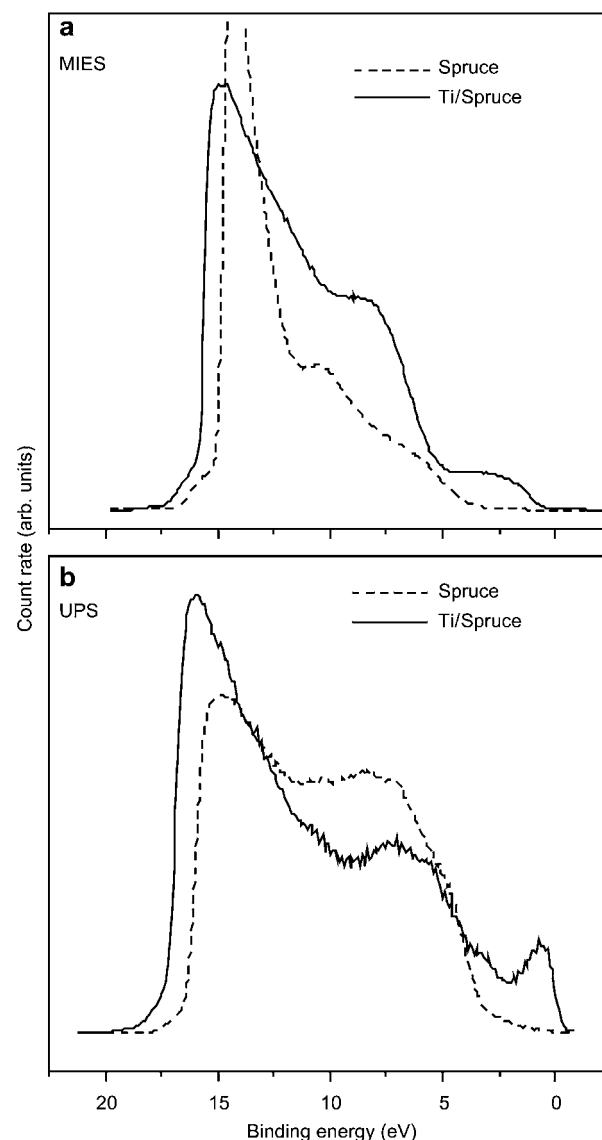


Figure 2 MIES (a) and UPS (b) spectrum of pure and Ti-covered spruce surfaces.

uted to O 2p MOs. In contrast to TiO_2 , the peak at ~ 2.8 eV must be attributed to occupied Ti 3d orbitals (Suzuki et al. 2000). This means that the oxide formation is not complete and stoichiometric.

UPS spectra of pure and Ti-covered spruce surfaces corresponding to the MIES spectra in Figure 2b reveal the following. Besides secondary electrons, the clean spruce surface shows peaks at $E_B = 10.5$, 8.4, and 7.0 eV. As for the MIES results, the features between 5 and 11 eV are attributed to C 2p-derived MOs and the peaks beyond 11 eV to C 2s-derived MOs (Harada 1997; Günster et al. 1999). After Ti deposition, four main peaks are visible at $E_B = 7.1$, 5.5, 3.1, and 0.6 eV. O 2p-derived MOs are responsible for the peaks between 5 and 10 eV (Suzuki et al. 2000). The structures between 5 eV and the Fermi level are attributed to occupied Ti 3d orbitals.

The AFM image ($200 \times 200 \text{ nm}^2$) of a clean spruce surface in Figure 3a is typical of complex surfaces.

Wood is composed of cellulose, hemicelluloses, and lignins. The microfibrils on the surface are oriented more or less in the same direction, as visible in the image. The maximum height difference between the lowest areas (dark) and highest areas (light) amounts to 40 nm. Figure 3b shows a typical AFM image of the Ti-covered surface. Again, the microfibrils are clearly visible. Here, however, the maximum height difference amounts to 20 nm. The surface appears to be smoother than the uncovered one. We estimated the mean surface roughness r_{msr} for both surfaces by applying SPIP 3.2.11.0 software, which yielded results of 3.7 nm for clean spruce 2.2 nm for Ti-covered spruce.

Discussion

The quality of wood surfaces is usually assessed in terms of the C 1s/O 1s peak ratio. The value found in this paper

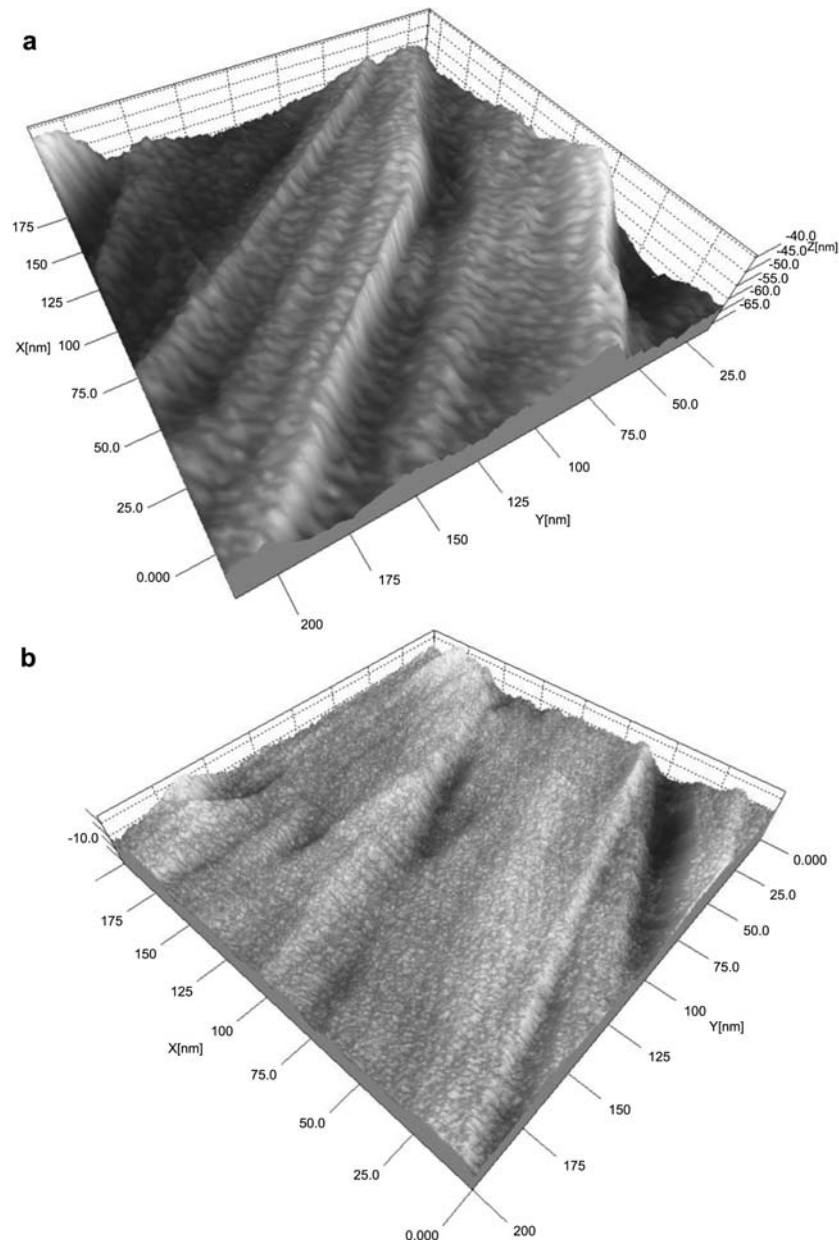


Figure 3 AFM images of uncovered (a) spruce surface ($200 \times 200 \text{ nm}^2$) and Ti-covered (b) spruce surfaces ($200 \times 200 \text{ nm}^2$).

(0.35) corresponds very well to data in the literature (Johansson 2002).

MIES and UPS spectra of the Ti-covered spruce surface appear to be similar to MIES and UPS results for TiO₂ surfaces beyond $E_b = 5$ eV. This indicates that treatment with metallic Ti leads to the formation of a layer of titanium oxide (TiO_x) on top of the surface.

The emission near 6 eV in the UPS spectrum in Figure 2b is due to the emission from oxygen-induced states (Shirotori et al. 2004), indicating that there is no bonding to carbon atoms of the wood substrate to form TiC. Detailed XPS C 1s spectra were recorded before and after metal evaporation; however, no changes were observed in the C 1s region, so these spectra are not presented.

Evaporation of the complete Ti layer takes place within 240 s. MIES and UPS measurements were performed immediately after Ti evaporation. Residual gas was analyzed in parallel during sample preparation. From this it can be estimated that the amount of oxygen containing residual gas components (H₂O, CO, O₂, CO₂) being offered to the surface during preparation is 0.8 L (1L = 10⁻⁶ torr/s = 1.3 mbar/s). This implies that the TiO_x observed on the surface is not induced by oxygen uptake by the residual gas. Therefore, we conclude that the Ti atoms deoxidize the underlying spruce, thus forming TiO_x.

AFM images demonstrate that the surface is smoother after Ti evaporation. We were not able to find any particles on the entire surface. This means that no Ti agglomeration occurs during evaporation, but that the spruce surface is immediately reduced by approaching Ti atoms. The surface undergoes significant smoothing upon Ti evaporation and the surface roughness is decreased by 40%.

UPS reveals a contribution from TiO_x and, most likely, small contributions from the underlying spruce substrate. MIES does not show any substrate contributions. MIES is extremely surface-sensitive and only shows results from the interaction of He* atoms with the very outermost surface wave function. From the MIES results it can be safely concluded that the spruce surface is completely covered with a TiO_x film, a finding that is also supported by the AFM images. Nevertheless, substrate contributions in UPS cannot be explained by a homogeneously distributed Ti film, because the information depth of UPS does not exceed approximately 4 MLE. It is likely that the surface smoothing observed by AFM is induced by preferred Ti adsorption in surface pores and cavities.

UPS and MIES indicate high electron densities just below the Fermi level. In contrast, TiO₂ would show a bandgap of 3.1 eV. The XPS measurements in Figure 1b reveal a peak distance between Ti 2p_{3/2} and 2p_{1/2} of 5.8 eV. Metallic Ti has a distance of 6.17 eV and TiO₂ 5.54 eV (Moulder et al. 1992). We interpret the results as indicating that oxide formation is not complete and that metallic-like Ti states remain on the surface.

Summary and outlook

Spruce surfaces were covered with 10 monolayer equivalents of Ti under clean ultra-high vacuum conditions. A titanium oxide film was formed by the immediate oxida-

tion of impinging Ti at the spruce surface. No Ti agglomeration or particle formation was observed. From the MIES and AFM results it can be concluded that the surface was completely covered by the titanium oxide. Future investigations should show the practical relevance of our promising basic research. Although Ti may perfectly protect wood surfaces, the well-known formation of micro-cracks in wood remains a potential route for attack by microorganisms.

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References

- Bente, M., Avramidis, G., Förster, S., Rohwer, E.G., Viöl, W. (2004) Wood surface modification in dielectric barrier discharges at atmospheric pressure for creating water repellent characteristics. *Holz Roh- Werkst.* 62:157–163.
- Dorris, G.A., Gray, D.G. (1978) The surface analysis of paper and wood fibres by ESCA. II. Application to cellulose and lignin. *Cellul. Chem. Technol.* 12:721–734.
- Fardim, P., Heijnesson Hulté, A., Boisvert, J.-P., Johansson, L.-S., Ernstsson, M., Campbell, J.M., Lejeune, A., Holmbom, B., Laine, J., Gray, D. (2006) Critical comparison of methods for surface coverage by extractives and lignin in pulps by X-ray photoelectron spectroscopy (XPS). *Holzforschung* 60:149–155.
- Frerichs, M., Voigts, F., Maus-Friedrichs, W. (2006) Fundamental processes of aluminium corrosion studied under ultra high vacuum conditions. *Appl. Surf. Sci.* 253:950–958.
- Günster, J., Liu, G., Stultz, J., Goodman, D.W. (1999) Interaction of methanol and water on MgO(100) studied by ultraviolet photoelectron and metastable impact electron spectroscopies. *J. Chem. Phys.* 110:2558–2565.
- Harada, Y., Masuda, S., Ozaki, H. (1997) Electron spectroscopy using metastable atoms as probes for solid surfaces. *Chem. Rev* 97:1857–1952.
- Jaroenworarluck, A., Sunsaneeyametha, W., Kosachan, N., Stevens, R. (2006) Characteristics of silica-coated TiO₂ and its UV absorption for sunscreen cosmetic applications. *Surf. Int. Anal.* 38:473–477.
- Johansson, L.-S. (2002) Monitoring fibre surfaces with XPS in papermaking processes. *Microchim. Acta* 138:217–223.
- Johansson, L.-S., Campbell, J., Koljonen, K., Kleen, M., Buchert, J. (2004) On surface distributions in natural cellulosic fibres. *Cellul. Chem. Technol.* 36:706–710.
- Klarhöfer, L., Frerichs, M., Maus-Friedrichs, W., Kempter, V., Viöl, W. (2005) Investigation of pure and plasma treated spruce with surface analytical techniques. In: *Proceedings of the European Conference on Wood Modification*, Vol. 2. pp. 339–345 (ISBN 3-00-017207-69).
- Miyafuji, H., Kokaji, H., Saka, S.J. (2004) Photostable wood-inorganic composites prepared by the sol-gel process with UV absorbent. *J. Wood Sci.* 50:130–135.
- Morgner, H. (2000) The characterization of liquid and solid surfaces with metastable helium atoms. *Adv. At. Mol. Opt. Phys.* 42:387–488.
- Moulder, J.F., Stickle, W.F., Sobol, P.E., Bomben, K.D. *Handbook of X-Ray Photoelectron Spectroscopy*. Perkin-Elmer Corporation, Eden Prairie, MN, 1992.
- Popov, A.P., Priezzhev, A.V., Lademann, J., Myllylä, R. (2005) TiO₂ nanoparticles as an effective UV-B radiation skin-protective compound in sunscreens. *J. Phys. D Appl. Phys.* 38:2564–2570.

Shirotori, Y., Sawada, K., Ozawa, K., Edamoto, K. (2004) Electronic structure and reactivity of the TiO thin film formed on a TiC(100) surface. *Thin Solid Films* 464–465:76–79.

Suzuki, T., Souda, R., Maus-Friedrichs, W., Kempter, V. (2000) TiO(001) single-crystal film formation by the incorporation of oxygen from MgO into the deposited Ti film. *Phys. Rev. B* 62:8306–8312.

Zhang, C., He, H., Tanaka, K. (2005) Perfect catalytic oxidation of formaldehyde over a Pt/TiO₂ catalyst at room temperature. *Catal. Commun.* 6:211–214.

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