

Interaction of electrochemically deposited aluminium nanoparticles with reactive gases

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Available online 7 April 2007

Abstract

Metastable induced electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) were used to study the interaction of nanocrystalline aluminium with oxygen and carbon monoxide, respectively. High resolution scanning electron microscopy (HRSEM) was used to investigate the morphology of the nanocrystalline aluminium films. These films were prepared by electrodeposition from the ionic liquid 1-butyl-1-methylpyrrolidinium *bis*(trifluoromethylsulfonyl)imide containing 1.6 Mol per litre AlCl₃ in an argon filled glove box.

Only a slight oxidation under exposure to oxygen and carbon monoxide was observed. After carbon monoxide dosage, no significant amount of carbon contamination was detected on the sample. These results indicate that the nanocrystalline aluminium is rather inert. © 2007 Elsevier B.V. All rights reserved.

Keywords: MIES; UPS; XPS; SEM; Aluminium

1. Introduction

The unique properties (optical, electrical, magnetic, mechanical and chemical) of nanomaterials, which are mostly a function of the grain size, have attracted a lot of interest. The increasing number of atoms located at grain boundaries with decreasing grain size leads to dramatic effects e.g., in the mechanical properties of the material. The oxidation behaviour of various nanoscale metals has been found to be strongly dependent on the particle size [1] and according to Natter et al., the microhardness of nanocrystalline aluminium showed grain size dependent values between 1.44 GPa (100 nm average grain size) and 3.40 GPa (14 nm average grain size) [2]. This gives support to a potential use of nanocrystalline aluminium in corrosion resistance applications, which is interesting considering that aluminium is already widely used in technical

products. A good example for the use of aluminium is the remarkable increase in wear resistance of stainless steel after dip coating with sols prepared from dispersed boehmite nano-powders observed by Hubert and co-workers [3].

The corrosion behaviour of aluminium compounds with surface science methods (MIES, UPS, XPS) has been investigated by Frerichs et al. [4], the interaction of aluminium films prepared by physical vapour deposition with reactive gases under UHV conditions has been investigated intensively by Frerichs et al. [5]. In this paper, we present the first MIES/UPS-data on the interaction between nanocrystalline aluminium and O₂ and CO, respectively.

Nowadays, a considerable amount of procedures for the generation of nanoparticles of various kinds exist: thermal spraying, sputter deposition, laser ablation, electrodeposition from ionic liquids and many more. The advantages of electrodeposition from ionic liquids of the second generation, such as 1-butyl-1-methylpyrrolidinium *bis*(trifluoromethylsulfonyl) imide ([BMP][Tf₂N]), include the feasibility of deposition at room temperature and the possibility to influence the mean grain size by controllable parameters

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such as deposition temperature and choice of the specific ionic liquid. The electrodeposition of aluminium was the subject of detailed studies in the past [6–8]. The air–moisture stability of newly developed ionic liquids render this technique interesting even for industrial applications (coatings).

2. Experimental

The ionic liquid [BMP]Tf₂N of the highest available quality was purchased. It was subsequently dried at 100 °C under vacuum conditions to water-content below 3 ppm and stored in an argon filled glove box (water- and oxygen-content below 2 ppm). Anhydrous AlCl₃ (Fluka, 99%) was used as a source of aluminium. A concentration of 1.6 Mol per litre AlCl₃ was used in this study. The electrochemical cell with a geometric surface area of 0.79 cm² was made of polytetrafluoroethylene and clamped over a teflon covered viton *o*-ring onto the hydrogen terminated Si(100) substrate. The hydrogen termination was achieved by immersion in HF and NH₄F after extensive cleaning procedures. The deposition was carried out inside the glove box using a Parstat 2263 Potentiostat/Galvanostat (Princeton Applied Research) controlled by Power CV and PowerStep software at a voltage of –1.4 V (vs. Al/AlCl₃ quasi reference electrode) for a duration of 2 h. Upon deposition, the ionic liquid is removed by washing the sample with acetonitrile inside the glove box.

The surface morphology of the film was investigated with a high resolution scanning electron microscope (HRSEM) (Carl Zeiss DSM 982 Gemini). X-ray photoelectron spectroscopy (XPS), metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS) were performed at the “Institut für Physik und Physikalische Technologien”. For that purpose, the samples were transferred to a vacuum-tight transportation chamber inside the glove box. The transportation chamber could be docked to the load lock chamber of the spectroscopy apparatus, so that the samples were not exposed to the ambient atmosphere.

The spectroscopy apparatus with a base pressure of 2×10^{-11} mbar is equipped with a combined MIES-UPS(HeI)-source, X-ray source (combined Al and Mg cathode, Specs RQ-20/38C) and a hemispherical electron energy analyser (VSW HA100). Details on this apparatus can be found elsewhere [5].

A cold-cathode discharge adapted via two pumping stages to the chamber is utilized to perform MIES and UPS. An integrated time-of-flight technique is used to separate signals arising by electron emission from He* (MIES) and HeI (UPS) interaction with the surface. Both MIES and UPS spectra, are recorded under normal emission within 140 s with an energy resolution of 220 meV. The mixed H*–HeI beam exhibits an angle of incidence of 45°. All MIES and UPS spectra are displayed as a function of the electron binding energy with respect to the Fermi

level obtained from the high energy cutoff observed for metallic samples in UPS.

The fitting of XPS spectra was performed using Origin-Pro7 (OriginLab Corporation) including the PFM add-on. The full width at half maximum (FWHM) and the position for the metallic Al2p peak were obtained in previous measurements (not shown here) and used as fitting parameters in order to get more reliable results.

Several different mechanisms for the interaction of metastable He* atoms with surfaces are known. For the nanocrystalline aluminium samples studied here, only the Auger deexcitation (AD) occurs. During AD, an electron from the sample surface fills the 1s orbital of the impinging He*. Simultaneously, the He* 2s carrying the excess energy is emitted. Detailed descriptions of the different interaction processes between He* and surfaces may be found in recent reviews [9,10].

A commercial X-ray source is used for XPS. The photons hit the surface under an angle of 80° with respect to the surface normal. Electrons emitted from the surface are analyzed under 10° to the surface normal using a hemispherical analyzer. Survey spectra are recorded with an energy resolution of 2.2 eV, detail spectra with 1.1 eV, respectively.

3. Results

Fig. 1 shows an HRSEM micrograph of a nanocrystalline aluminium film deposited onto a Si(100) substrate in the manner described above. Manually size evaluation of about 100 particles gives a value of 16 ± 3 nm for the mean grain size. This size could also be corroborated with X-ray diffraction measurements (not shown here) giving a similar mean grain size. The particles constitute a film covering the substrate completely. In the micrograph, residues of neither the ionic liquid nor the solvent (acetonitrile) are visible.

Fig. 2 shows a XPS survey spectrum (0–1100 eV) of a nanocrystalline aluminium film after sputtering. All peaks are labelled with the corresponding element. Striking is

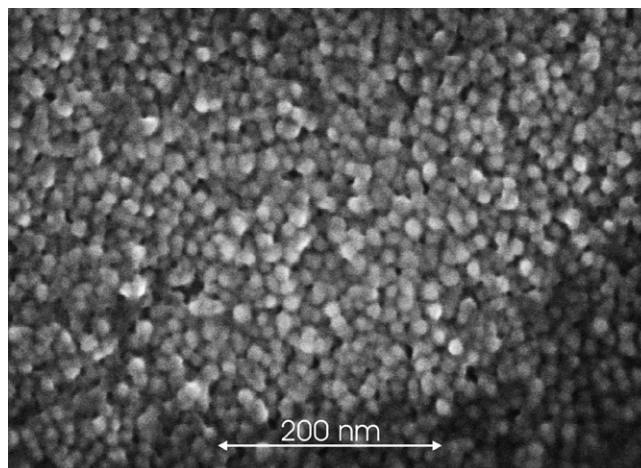


Fig. 1. HRSEM micrograph of a nanocrystalline aluminium film.

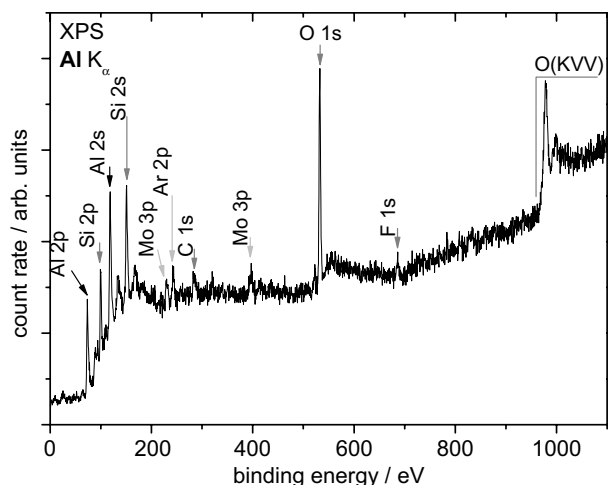


Fig. 2. XPS survey spectrum (0–1100 eV) of the nanocrystalline aluminium film.

the low contamination level – only small contributions from chlorine, carbon and fluorine are visible – indicating a clean aluminium film. The small molybdenum signal is caused by the sample holder and does not affect our further discussion.

Fig. 3 displays the MIES (a) and UPS (b) spectra recorded during oxygen exposure. The spectra are displayed in a waterfall manner, with the amount of oxygen indicated by the arrow on the right hand side. Two relevant features are visible in the MIES spectra: one clearly visible peak with a binding energy of 10.5 eV and a shoulder at a binding energy of 7.5 eV. In the UPS spectra, only the feature with a binding energy of 7.5 eV is visible. The only signifi-

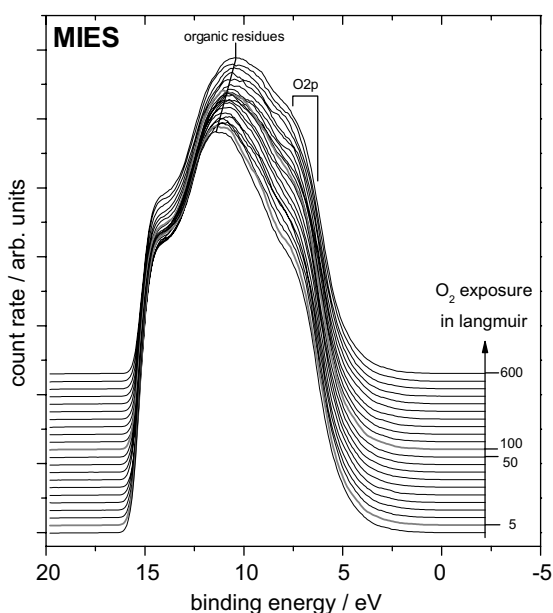


Fig. 3a. MIES spectra of the nanocrystalline aluminium film recorded during oxygen exposure.

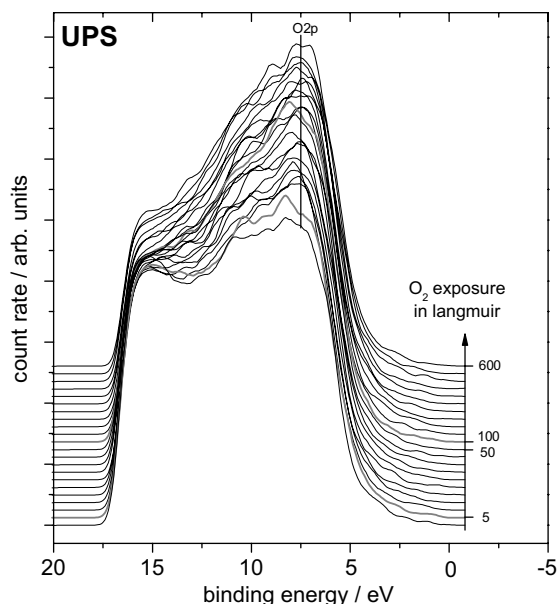


Fig. 3b. UPS spectra of the nanocrystalline aluminium film recorded during oxygen exposure.

cant change in the spectra with higher oxygen dosage is a rise in the feature at 7.5 eV binding energy, but only in the UPS spectra.

Fig. 4 shows detail XPS spectra of the Al2p peak before (a) and after (b) oxygen dosage. In both spectra, clear contributions arising from metallic (binding energy 74.4 eV) and oxidized (binding energy 77.0 eV) aluminium are visible. The relative areas and the individually fitted peaks change only slightly: the ratio of metallic to oxidized aluminium decreases from 0.30 to 0.28 after exposure to oxygen.

Fig. 5 displays the MIES (a) and UPS (b) spectra recorded during carbon monoxide exposure. Again, the arrow on the right-hand side indicates the amount of CO dosed. The MIES spectra display, similar to those shown in Fig. 4, two features: a peak at a binding energy of 11.5 eV and a shoulder at a binding energy of 7.5 eV. The UPS spectra display a single feature at a binding energy of 7.4 eV; again this feature is slightly increasing with dosage.

4. Discussion

The XPS survey spectrum depicted in Fig. 2 documents clearly that by the method described above, relatively clean, nanocrystalline aluminium films can be obtained. Only hints of contaminations from carbon, chlorine and fluorine are visible. Although the O1s peak appears to be rather large, the oxide layer thickness was estimated to be 2.1 nm from an XPS detail spectrum of the Al2p peak (not shown here).

The peak in the MIES spectra displayed in Fig. 3a are due to organic contaminations. The detection of this

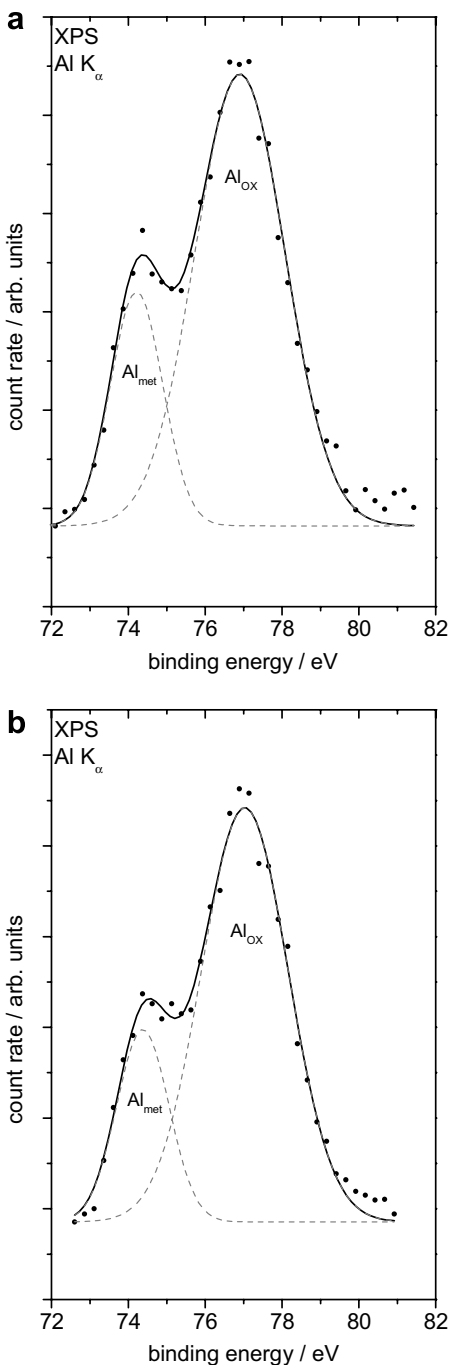


Fig. 4. XPS spectrum of the Al_{2p} peak of the nanocrystalline aluminium film: (a) before oxygen exposure and (b) after oxygen exposure.

contamination underlines the extremely high surface sensitivity of the MIES technique, because they are neither visible in the HRSEM micrograph (Fig. 1) nor in the XPS or UPS spectra. The second feature in the MIES spectra with a binding energy of 7.5 eV is attributed to electron emission from the O_{2p} orbital.

The UPS spectra in Fig. 3b only show one peak at a binding energy of 7.5 eV, which is also assigned to emission from the O_{2p} orbital. In contrast to the evolution of the MIES spectra, where basically no change is observable, this

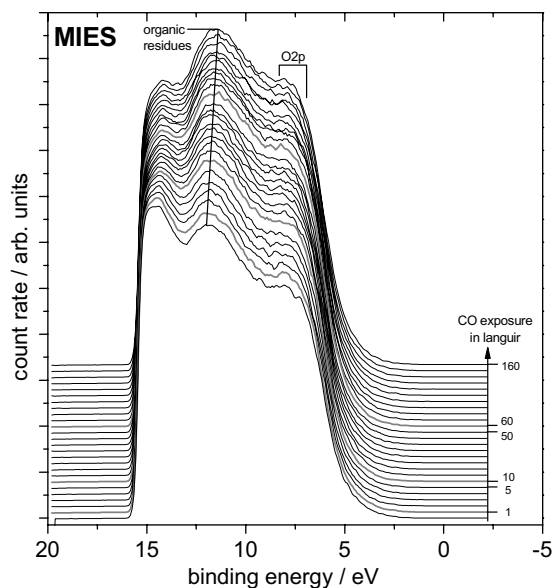


Fig. 5a. MIES spectra of the nanocrystalline aluminium film recorded during carbon monoxide exposure.

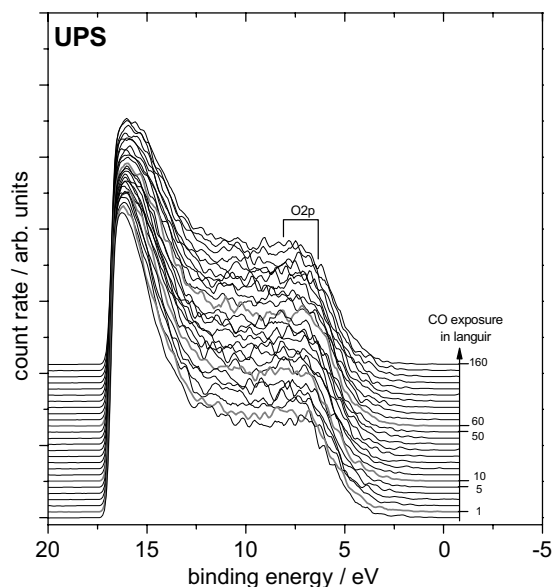


Fig. 5b. UPS spectra of the nanocrystalline aluminium film recorded during carbon monoxide exposure.

peak seems to enlarge with prolonged oxygen dosage. This suggests the sub-surface incorporation of oxygen.

The perception of a small amount of oxygen being incorporated into the bulk is corroborated by the XPS spectra in Fig. 4. The ratio of metallic to aluminium to oxidized aluminium is decreased slightly from 0.3 to 0.28.

The interpretation of the MIES and UPS spectra during CO exposure shown in Fig. 5 is similar: the peak with a binding energy of 11.5 eV is again attributed to organic contaminations. The feature at a binding energy of 7.5 eV attributed to the emission from the O_{2p} orbital is more

pronounced in this case. This is probably caused by a slightly higher degree of pre-oxidation in the glove box.

The UPS spectra, again show only the peak attributed to oxygen, which is slightly increasing with dosage of carbon monoxide. XPS spectra not shown here indicate a slight oxidation of the aluminium, while not a considerable amount of carbon accumulates on the surface.

5. Summary

Nanocrystalline aluminium films prepared by electrodeposition from the ionic liquid [BMP]Tf₂S have are exposed to oxygen and carbon monoxide under MIES and UPS monitoring. Additional XPS experiments are performed to determine the oxide layer thickness as well as possible contaminations. The experiments indicate a weak interaction of the nanocrystalline aluminium films with oxygen and carbon monoxide, respectively. In both cases, the oxidation level increases only slightly. After the exposure to carbon monoxide, not a significant amount of carbon was detected. The corrosion resistance of nanocrystalline aluminium films is thought to be good and a future application in corrosion protection seems possible, since the process could be easily adapted to existing routines.

Acknowledgements

The authors are thankful for the technical assistance of Mrs. Münster (HRSEM images) and D. Schwendt (spectroscopy lab). Furthermore, the authors thank Dr. S. Zein el Abedin for help with the ionic liquid.

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