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Interaction of electrochemically deposited aluminium nanoparticles with reactive gases

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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 $AlCl_3$ 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.

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 O_2 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*(trifluoromethylsolfonly) imide ([BMP]Tf_2N), 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]Tf_2N 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 $AlCl_3$ (Fluka, 99%) was used as a source of aluminium. A concentration of 1.6 Mol per litre $AlCl_3$ was used in this study. The electrochemical cell with a geometric surface area of 0.79 cm^2 was made of polytetraflouroethylene and clamped over a teflon covered viton *o*-ring onto the hydrogen terminated Si(1 0 0) substrate. The hydrogen termination was achieved by immersion in HF and NH_4F 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. $Al/AlCl_3$ 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 OriginPro7 (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(1 0 0) 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

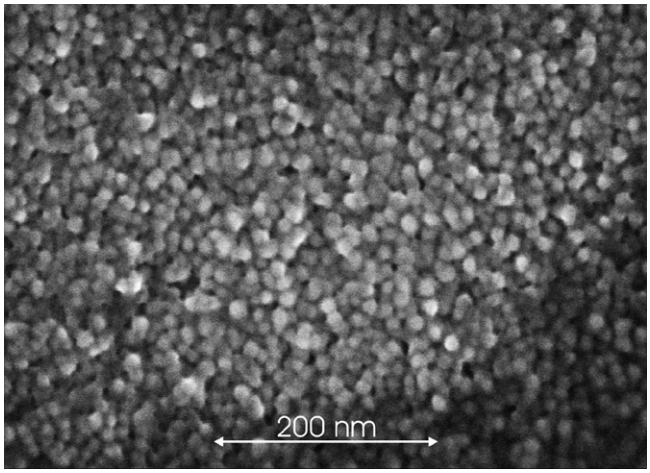

Fig. 1. HRSEM micrograph of a nanocrystalline aluminium film.