

## Photochemical preparation of aluminium oxide layers via vacuum ultraviolet irradiation of a polymeric hexanoato aluminium complex

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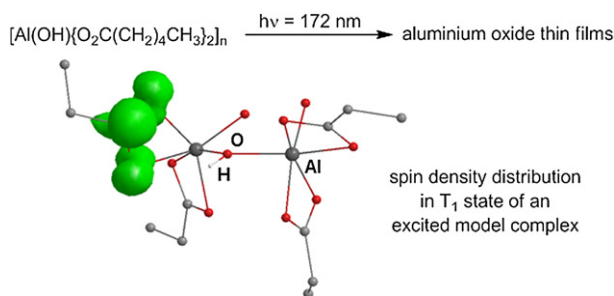
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### HIGHLIGHTS

- ▶ A polymeric aluminium complex was synthesized and characterized by NMR, FTIR, XPS and ICP.
- ▶ Thin layers of the compound were irradiated using vacuum-UV radiation and converted to AlO<sub>x</sub>.
- ▶ Quantum-chemical calculations explain the conversion mechanism.

### GRAPHICAL ABSTRACT



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### ABSTRACT

By means of photochemical conversion of thin layers of a polymeric hexanoato aluminium complex as the precursor, thin aluminium oxide layers were prepared onto silicon wafers. The precursor compound was synthesized and characterized by several analytical techniques like NMR, FTIR, XPS, ICP, and found to be a polymeric aluminium-containing coordination compound which has been proposed to be a hydroxo-bridged aluminium chain with pendant hexanoyl side-chains ascertained as catena-poly  $[\{\text{di}(\kappa\text{-}O,O\text{-hexanoato})\text{aluminium}\}(\mu\text{-hydroxo})]$  (PHAH). Thin layers deposited from a solution of PHAH in toluene onto silicon wafers were irradiated using VUV radiation from a xenon excimer lamp. The layers were characterized by XPS, XRD, XRR, and spectroscopic ellipsometry. VUV radiation with a radiant exposure of  $E = 36 \text{ J cm}^{-2}$  led to almost carbon-free amorphous layers with a composition close to that of alumina having a density of about  $2.1 \text{ g cm}^{-3}$ . Thus, using the example of a polymeric aluminium complex, the potential of the photochemical conversion of metal complexes into oxides could be shown as an alternative method, in addition to sol-gel techniques, for the generation of thin plane metal-oxide layers at normal temperature and pressure.

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## 1. Introduction

Flexible and transparent barrier coatings are essential for the protection of sensitive electronic devices, as, e.g., inorganic and

organic thin-film photovoltaic cells and organic light-emitting diodes (OLEDs), against oxygen and water vapour.

A popular approach is to deposit thin inorganic films onto polymer foils by different methods such as chemical or physical vapour deposition techniques (CVD, PVD) [1,2] or modifications of sol-gel procedures [3,4]. Inorganic layers with a thickness between 50 and 100 nm can achieve oxygen transmission rates (OTR) and water vapour transmission rates (WVTR) in the order of

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$10^{-1} \text{ cm}^3 (\text{m}^2 \text{ d bar})^{-1}$  and  $10^{-1} \text{ g} (\text{m}^2 \text{ d})^{-1}$ . The careful growth of nearly defect-free layers by means of atomic layer deposition (ALD) [5,6] allows the production of 10–20 nm thick barrier layers exhibiting WVTR values as low as  $10^{-3} \text{ g} (\text{m}^2 \text{ d})^{-1}$ . Typical materials used as inorganic gas barriers are binary metal oxides such as  $\text{SiO}_x$  or  $\text{AlO}_x$  [6–8]. The former is already commercially available on PET (CERAMIS<sup>®</sup>, Amcor). More complex compounds like  $\text{Si}_x\text{O}_y\text{C}_z$  [1] or  $\text{Zn}_x\text{Sn}_y\text{O}_z$  [7] have also been investigated.

Photochemical approaches to the production of inorganic barrier layers offer an attractive alternative because neither temperatures above 100 °C, i.e. in sol–gel techniques, nor low pressures, i.e. in vapour deposition techniques, are required. Roll-to-roll coating processes become technically feasible. In recent years, the oxidative conversion of perhydropolysilazane (PHPS), initiated by ultraviolet (UV) and vacuum ultraviolet (VUV) irradiation, has been studied and developed [9–11]. 100 nm layers of PHPS can be converted into  $\text{SiO}_x$  with  $x \approx 1.8$  and a density of  $\rho \approx 2.1 \text{ g cm}^{-3}$  on polymer substrates. OTRs of  $2 \times 10^{-2} \text{ cm}^3 (\text{m}^2 \text{ d bar})^{-1}$  and WVTRs of  $5 \times 10^{-1} \text{ g} (\text{m}^2 \text{ d})^{-1}$  were obtained. Apart from inducing the photochemical conversion, VUV light enabled the densification of the films. VUV annealing had already been observed in combined sol–gel/(V)UV processes [12–14].

Efforts to further improve the water vapour barrier of the photochemically produced  $\text{SiO}_x$  layers using PHPS as the precursor only showed a limited success. A probable reason is the inherent high concentration of silanol functionalities within the produced silica layer, which promotes diffusion of water molecules. To overcome these limitations, some further investigations of the photochemical path to alternative metal oxides seem to be a promising field of material research [15] and could help to make more complex oxides accessible.

Moreover, it has been well known for several years that inorganic coordination polymers can be used as precursors for the production of oxide and non-oxide ceramics via pyrolysis [16]. Kimura et al. described the fabrication of alumina fibres using poly [(acyloxy)aloxane]s as precursors [17,18]. In this process, a solution of the precursor in an organic solvent is spun and pyrolysed at  $T > 1000 \text{ °C}$ . This class of compounds thus seemed promising for our experiments to enlarge the range of inorganic thin films producible by our pure photochemical process to aluminium oxide. In order to obtain films with a low content of residual carbon, the ligand of the precursor should contain as few carbon atoms as possible. On the contrary, the solubility of the precursors increases with the carbon chain length [19], thus hexanoyl ligands were chosen as a compromise for the subsequent investigations.

The following described investigations focus on our first attempts to produce a polymeric aluminium-containing coordination compound, soluble in an organic solvent, its characterization by several spectroscopic methods and its deposition as thin layers on silicon wafers by spin-coating. After the conversion of the resulting layer into an almost carbon free oxide by means of VUV irradiation, the characterization of these photochemically modified layers in terms of chemical composition, structure, refraction index and density as a function of radiant exposure is intended.

## 2. Materials and methods

### 2.1. Synthesis of the polymeric hexanoato aluminium complex 1

A solution of 25 mmol tri-sec-butoxyaluminium (Alfa Aesar, Karlsruhe, Germany) in 20 ml of toluene was heated to 130 °C. 25 mmol distilled water were added in a drop-wise manner while stirring vigorously. Stirring at 130 °C was continued for 7.5 h to yield a white precipitate with very poor solubility. Then, 50 mmol

of hexanoic acid (Sigma Aldrich) were added and the reaction mixture was stirred for another 7.5 h. During this time the precipitate dissolved gradually forming a viscous solution. After cooling to room temperature an excess of dioxane was added whereupon the final product precipitated as a white powder. After filtration the powder was treated with dioxane in a soxhlet extractor, and then dried in vacuum. The product has been characterized by infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy:

IR  $\nu/\text{cm}^{-1}$ : 3690 (w), 2957 (w), 2924 (w), 2858 (w), 1586 (s), 1463 (s, sh), 1321 (w), 1113 (w), 980 (m), 725 (w), 650 (m, br).

<sup>1</sup>H NMR  $\delta(\text{C}_6\text{D}_6, \text{TMS})$ : 0.92 (3H, br,  $\text{CH}_3$ ); 1.33 (4H, br,  $\text{CH}_2$ ), 1.71 (2H, br,  $\text{CH}_2$ ), 2.31 (2H, br,  $\text{CH}_2$ ).

<sup>13</sup>C NMR  $\delta(\text{C}_6\text{D}_6, \text{TMS})$ : 14.7 ( $\text{CH}_3$ ), 23.2 ( $\text{CH}_2$ ), 25.8 ( $\text{CH}_2$ ), 32.1 ( $\text{CH}_2$ ), 38.1 ( $\text{CH}_2$ , br), 181.2 ( $\text{COO}$ , br).

As a result of the presented investigations, the aluminium complex **1** has been ascertained as (catena-poly[di( $\kappa$ -O,O-hexanoato)aluminium]( $\mu$ -hydroxo)] – PHAH) with the elemental formula  $[\text{Al}(\text{OH})\{\text{O}_2\text{C}(\text{CH}_2)_4\text{CH}_3\}_2]_n$ .

### 2.2. Characterization of 1

<sup>1</sup>H NMR (at 600.13 MHz) and <sup>13</sup>C NMR (at 150.9 MHz) measurements were carried out using an Avance II+ 600 spectrometer (Bruker Biospin, Karlsruhe, Germany).

The element concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), using Cirus Vision from SPECTRO, Kleve, Germany. For this purpose, 15 mg of the powder were dissolved in 4 ml  $\text{HNO}_3$  (65%, Suprapur, Merck KGaA, Darmstadt, Germany) as well as in 4 ml  $\text{HCl}$  (37%, ARISTAR for trace analysis, VWR) for comparison, and diluted with de-ionized water to a volume of 500 ml.

Attenuated total reflectance (ATR) FTIR spectra on powder were recorded using an IFS55 instrument (Bruker GmbH, Karlsruhe, Germany) and a Golden Gate diamond ATR accessory (Specac, UK).

### 2.3. Preparation, UV irradiation and characterization of thin layers of 1

A 1 wt.-% solution in toluene was spin-coated onto Si wafers (speed 3000 rpm, acceleration 300 rpm, duration 30 s) and dried for 5 min at 50 °C. White light interferometry (device F20 from Filmetrics, San Diego, USA) was used to determine thicknesses of the resulting layers. Those were found to be in the range of 50 nm. With the aim to improve signal-to-noise ratio in X-ray diffraction (XRD) and X-ray reflectivity (XRR) measurements, thicker layers up to 200 nm were prepared by repeating both the spin-coating and the subsequent irradiation procedure several times (2–4).

UV irradiation was carried out using a  $\text{Xe}_2^*$  excimer lamp XER-ADEX (Radium Lampenwerk Wipperfurth, Germany). It has a continuous emission in the vacuum ultraviolet (VUV) range at  $150 \text{ nm} < \lambda < 200 \text{ nm}$  with the emission maximum at  $\lambda_{\text{max}} = 172 \text{ nm}$ . In a distance of 2 cm from the lamp surface irradiance was  $25 \text{ mW cm}^{-2}$ . The irradiation chamber was flushed with nitrogen containing 0.25 vol.-% oxygen for minimizing VUV absorption by oxygen molecules and ozone formation [20] on the one hand and for maintenance of oxidative conditions on the other.

Fourier transform infrared (FTIR) spectra on pristine and irradiated layers were recorded using the spectrometer IFS55 (see above) in transmission mode.

Scanning electron microscopy (SEM) images were obtained with SEM system ULTRA 55 (Carl Zeiss SMT, Oberkochen, Germany).

X-ray photoelectron spectroscopy (XPS) was carried out with an Axis Ultra Probe (Kratos Analytical Ltd, Manchester, UK), equipped

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