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Oriented aluminum nanocrystals in a one-step process ☆

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ABSTRACT

Aluminum coatings were deposited on glass substrates by chemical vapor deposition using N-methylpiperidine (nmp) stabilized dichloroalane [$Cl_2AlH \cdot 2nmp$] as aluminum precursor. With regard to temperature, the experimental conditions were varied between 75 °C and 125 °C for the precursor and between 250 °C and 450 °C for the substrate. Depending on these parameters, highly textured layers could be deposited. The substrates have been consistently covered by a layer of idiomorphic, mostly distorted octahedra of aluminum single crystals. The morphologies of the structures and the degree of orientation of the crystals were investigated by a scanning electron microscopy and X-ray diffraction measurements. The high order of [111] orientation was found to decrease with increasing precursor and substrate temperature. We propose a mechanism for the generation of the octahedral structures based on the formation of mesocrystals. On heating, the dichloroalane (stabilized with nmp) loses the nmp ligands together with hydrogen and chlorine. The amine (nmp) seems to trigger the formation of aluminum crystals depending on the temperature and thus influences the texture of the Al-layer and the formation of well-formed octahedron-like structures.

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1. Introduction

To generate aluminum films in a chemical vapor deposition (CVD) process, a variety of precursors have been developed over the last decades. However, the thermal decomposition of often used metalorganic precursors containing an Al–C bond like trimethylaluminum, triethylaluminum, triisobutylaluminum [1], diethylaluminum chloride or dimethylaluminum hydride [2] goes along with a carbon contamination of the produced layer. It is important to note that, if the Al–C bonding is being replaced by an Al–H bond, the carbon contamination caused by the precursor can be avoided [3]. Furthermore, the coordination of a Lewis-base to the Lewis-acidic alane gives a relatively stable donor–acceptor complex [4]. Popular donors are amines like Me_3N, Me_2EtN or Et_3N that lead to trimethylamine alane, triethylamine alane or dimethylethylamine alane [4–11]. In CVD, the listed types of adducts are believed to generate alane, AlH_3, and related compounds in situ, either in the gas phase or on the surface of a substrate by means of the dissociation of the amine ligand. The absence of a direct Al–C bond in the molecules as well as the relatively weak bond between Al and N allows the deposition of high purity Al layer after elimination of hydrogen [12].

It has generally been observed that when the abovementioned alane derivatives are decomposed by thermal CVD, a statistical orientation of the crystallites in the Al layer is obtained. To generate a layer with oriented Al crystals, so far, either epitaxial growth on Si [2,4], or Al [10], or TiN [6] has to be induced, or an interface layer of a growth enhancement material like Ti [13], TiN [5], or $TiCl_4$ [11,14] has to be used.

Here, we report on a generation of high purity octahedral aluminum crystals with a dominant [111] orientation on almost any surface. The textured Al coatings could be realized on different materials like glass, metals, or graphite without any restrictions for the substrate material or without any need for a pretreatment of the substrate. Depending on the experimental parameters, also other shapes could be observed. In the present paper, we focus on the formation of nanoscaled octahedra of aluminum on a glass substrate.

2. Experimental details

2.1. Chemical synthesis of the precursor

Alane derivates of the formula H_xAlX_{3-x} (x = 0,1,2,3; X = Cl, Br, I) and the mixed halogen species [HAlClBr] stabilized as N-methylpiperidine (nmp) adducts [$H_xAlX_{3-x} \cdot z$nmp] (z = 1,2) and [HAlClBr·2nmp] have been recently described [15,16]. Among them, the nmp adducts of $HAlCl_2$ and H_2AlCl were used as precursors for aluminum formation by CVD.

The decomposition of both molecules leads under almost the same experimental conditions to similar forms of aluminum films. In the following, we concentrate on dichloroalane [$HAlCl_2 \cdot 2nmp$] (see also Section 3).

☆ Dedicated to Prof. Werner Uhl on the occasion of his 60th birthday.
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2.2. Sample preparation

Using a thermal CVD process, the decomposition of [$HAlCl_2 \cdot 2nmp$] was carried out in a low pressure "cold wall" reactor [17]. In a preliminary test series, the inductively heated substrate holder (graphite) was adjusted to temperatures between 250 °C and 300 °C. The substrates used were small laboratory glass plates (from the company Menzel) with a typical size of 10 × 10 mm. Prior to each deposition, they were first washed in an acetone bath, then cleaned in a supersonic bath with ethanol, and finally dried on air. They were heated indirectly through the contact with the substrate holder.

The precursor flask was heated in three steps (each step equal to a difference of 25 °C) between temperatures of 75 °C and 125 °C. To avoid any condensation of the precursor on the glass wall, the temperature of the reaction chamber was adapted to the temperature of the precursor flask.

After evacuating the reaction tube down to a pressure of $3 \cdot 10^{-1}$ Pa, the substrate was heated to the desired temperature. When the substrate temperature became constant, the precursor valve was opened allowing a constant precursor flow regulated by the temperature of the flask.

At a substrate temperature between 250 °C and 300 °C, a precursor temperature of 75 °C or 100 °C, respectively, and a deposition time between 20 and 30 min, a metallic film of well-shaped aluminum octahedra could be generated. To evaluate the influence of the nmp on the formation of Al octahedra, an additional experiment with an excess of nmp was performed [18].

2.3. Sample characterization

During the CVD process, mass spectroscopic measurements were performed on a Vacom GAPAS spectrometer which was connected to the reaction tube. After the determination of the background, two separate measurements have been performed. In the first place, the precursor alone was heated to a temperature of 100 °C, followed by a second measurement in which in addition to the heating of the precursor, the substrate was brought to a temperature of 300 °C.

The morphology of the Al films was evaluated by field emission scanning electron microscopy (SEM) using a JEOL JSM 7500F instrument. The SEM micrographs were taken at an accelerating voltage of 4 kV.

The diffraction intensity data in Bragg–Brentano measurement geometry, as starting point for the phase, structure and texture analysis of the films under study, were collected on a Bruker AXS D8 powder diffractometer equipped with a silicon strip detector (LynxEye). The structural and micro-structural parameters were extracted by a profile analysis of related diffraction patterns without application of a standard using the program TOPAS (Bruker Analytical X-ray Systems GmbH, Karlsruhe, Germany). The scale factor, the background coefficients, the sample displacement and the unit cell parameters were simultaneously refined. The intermediate crystallite size broadening of the line profile shapes for the volume-weighted column heights calculation of the crystallite sizes was modeled by a Voigt function using the Scherrer equation [19].

The texture measurements were undertaken on an X-ray Philips (by now PANalytical GmbH) X'Pert MRD diffractometer, equipped with a sample cradle, on a 5° × 5° grid with the polar angle ψ ranging from 0° to 85°, the azimuthal angle φ ranging from 0° to 360° and a counting time of 200 s per point. The measurements were conducted in the parallel beam geometry with a set-up using an X-ray lens as incident beam module combined with a diffracted beam collimator in combination with a point focus. The calculation of pole figures, inverse pole figures and orientation distribution functions were performed by means of the commercially available software package X'Pert Texture from PANalytical (Analytical module for texture analysis by means of X-ray diffraction, PANalytical GmbH, Nürnberger Strasse 113, 34123 Kassel, Germany).

The pole figure measurements were corrected for background and defocusing. Measured defocusing correction data were collected with Si powder having the mass absorption coefficient of 62.07 cm^2/g, slightly higher than Al with an absorption coefficient of 48.67 cm^2/g. The utilized diffractometers were operated at 40 kV and 40 mA, using Cu Kα radiation ($\lambda = 0.154$ nm).

3. Results

3.1. Chemistry

The two compounds $H_2AlCl \cdot 2nmp$ and $HAlCl_2 \cdot 2nmp$ are representatives of base stabilized chloroalanes. Both compounds have a trigonal bipyramidally coordinated Al atom in the center with the hydrogen and chlorine atoms occupying the equatorial plane and nitrogen atoms of

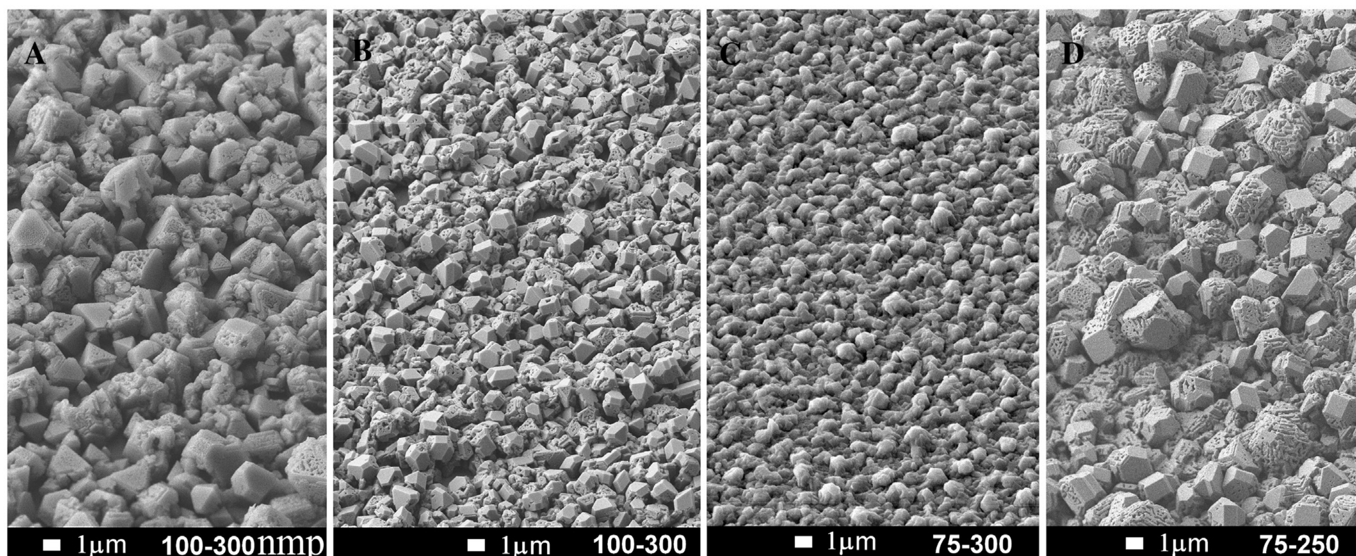

Fig. 1. Representative SEM images of the coatings. The samples pictured in images A, B and C were deposited at a substrate temperature of 300 °C and a precursor temperature of 100 °C (A, B) and 75 °C, respectively. The substrate temperature of the sample displayed in micrograph D was reduced to 250 °C. The applied precursor temperature was 75 °C. For sample 100–300 nmp (image A) additional supply of nmp in the CVD process was used.

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