

## Growth and stability of Ga<sub>2</sub>O<sub>3</sub> nanospheres

Simon Penner<sup>\*</sup>, Bernhard Klötzer, Bernd Jenewein, Frederik Klauser, Xianjie Liu, Erminald Bertel

*Institute of Physical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

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### Abstract

Gallium oxide thin films were prepared by thermal evaporation and deposition of Ga<sub>2</sub>O<sub>3</sub> on NaCl(001) cleavage planes at varying substrate temperatures, oxygen pressures and deposition rates. The structure of the so-prepared thin films was checked by Transmission Electron Microscopy and Selected Area Diffraction and also characterized by X-ray Photoelectron Spectroscopy and Atomic Force Microscopy, both in the as-deposited state and after different oxidative and reductive treatments. The substrate temperature proved to be most crucial for the structure of the gallium oxide films, ranging from low-contrast amorphous structures at low substrate temperatures (298 K) to nanosphere structures at higher temperatures (580 K). The stability of the films was found to be mainly determined by the interaction of substrate temperature and deposition rate. Crystalline β-Ga<sub>2</sub>O<sub>3</sub> structures were obtained after oxidative, reductive and annealing treatments at and beyond 773 K suggesting that the crystallization is mainly a thermal annealing effect.

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### 1. Introduction

Ga<sub>2</sub>O<sub>3</sub> has recently attracted increased interest due to its applications ranging from gas sensors [1,2] over optoelectronic devices [3] and nano-structured materials [4] to important materials in catalysis [5–8]. Concerning the latter, Ga<sub>2</sub>O<sub>3</sub>-based Pd catalysts have been shown to exhibit a high selectivity toward CO<sub>2</sub> in the methanol steam reforming process [6] and also a considerably increased turnover rate from H<sub>2</sub>/CO<sub>2</sub> to methanol compared e.g. to a Pd/SiO<sub>2</sub> reference catalyst [7]. It was even observed that pure gallia is able to dissociate hydrogen at temperatures above 500 K and to hydrogenate adsorbed CO<sub>2</sub> stepwise from formate to methoxy groups [9], important intermediate species in methanol synthesis. Hence, of particular catalytic interest are the oxidation state, location and type of the active Ga centers. Mobile Ga<sub>2</sub>O species [8], gallium hydrides [5] or Ga<sup>δ+</sup>–H species [10] have been discussed as active centers during catalytic reactions. Consequently, one of the most important issues concerns the preparation of the gallia

samples. Many different methods have been used, the most important ranging from thermal evaporation [11] over sputtering [12], sol–gel [13] and laser deposition [14] to chemical vapor techniques [15]. Oxidation of GaAs [16], CoGa [17] and GaN [18] surfaces has also been used.

In this contribution, we present our results on the preparation of gallium oxide films grown by thermal evaporation of Ga<sub>2</sub>O<sub>3</sub> on vacuum-cleaved NaCl(001) single crystal surfaces. We especially focused on the influence of deposition parameters (substrate temperature, film thickness, deposition rate) on the structure and morphology of the gallium oxide films and the stability of the so-prepared structures under oxidative and reductive conditions. These studies represent the first step to prepare self-supporting Pd/Ga<sub>2</sub>O<sub>3</sub> thin film model catalysts which will subsequently be used to prepare bimetallic Pd–Ga particles, closely connected to similar studies on Pd–ZnO [19].

### 2. Experimental details

A high-vacuum chamber (base pressure 10<sup>−4</sup> Pa) was used to prepare all gallium oxide films. The film thickness (usually 25 nm) was measured by a quartz crystal microbalance. Ga<sub>2</sub>O<sub>3</sub>

<sup>\*</sup> Corresponding author. Tel.: +43 512 507 5056; fax: +43 512 507 2925.

E-mail address: [simon.penner@uibk.ac.at](mailto:simon.penner@uibk.ac.at) (S. Penner).

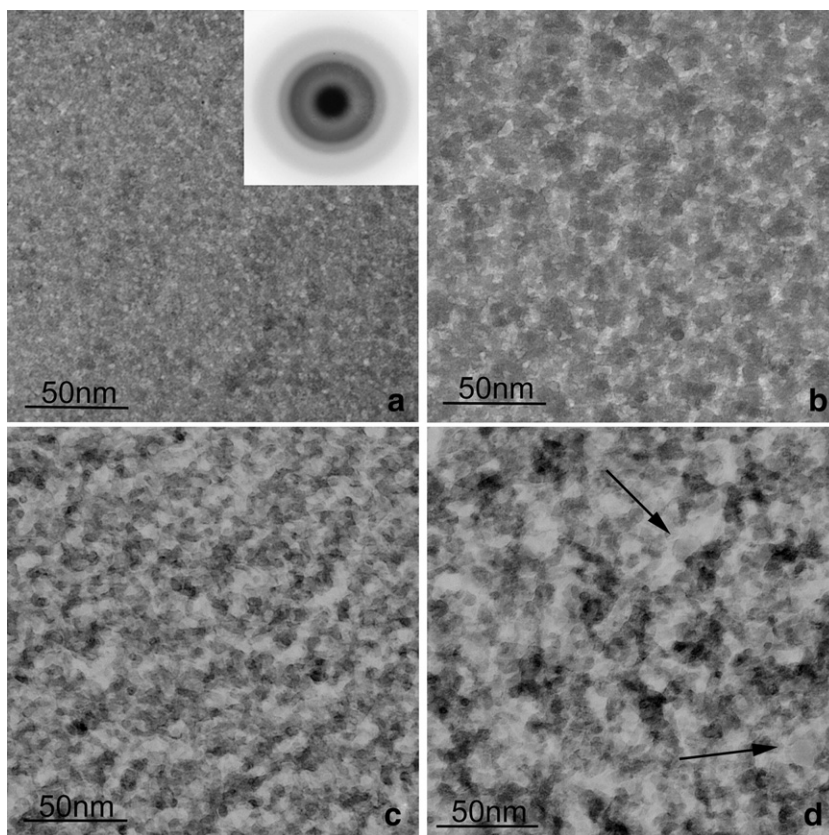


Fig. 1. TEM images of gallium oxide films prepared at 298 K (a), 430 K (b), 473 K (c) and 530 K (d) substrate temperature ( $10^{-2}$  Pa  $O_2$  pressure). A representative SAED pattern is shown as an inset in (a).

powder (Gallium (III) oxide, 99.99%, Alfa Aesar) was thermally evaporated from a tantalum crucible onto vacuum-cleaved NaCl (001) surfaces at varying substrate temperatures (298 K–580 K), deposition rates ( $\sim 0.3$ – $10 \text{ \AA s}^{-1}$ ) and  $O_2$  background pressures (up to  $10^{-2}$  Pa  $O_2$ ). The resulting films

were floated and rinsed with distilled water, dried and finally mounted on gold grids for electron microscopy. It should be noted that the prepared gallium oxide films are stable against hydrolysis, in contrast to their ZnO counterparts, which posed additional problems for preparing Pd/ZnO thin film catalysts.

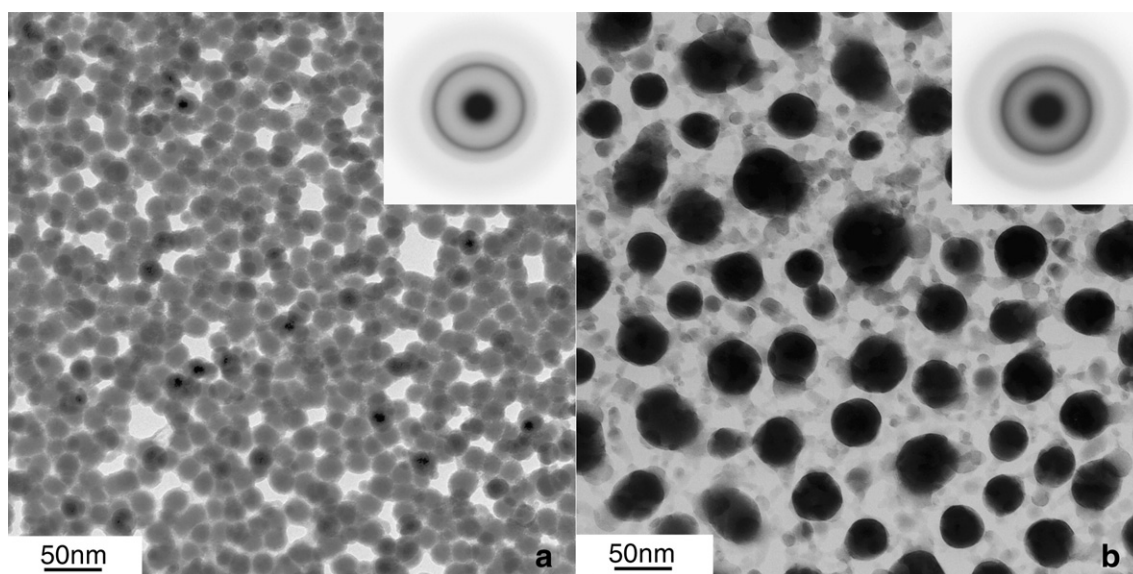


Fig. 2. TEM image of pure  $Ga_2O_3$  deposited at 580 K in  $10^{-2}$  Pa  $O_2$  (a) and in vacuum ( $10^{-4}$  Pa) without background oxygen (b). The corresponding SAED patterns are shown as insets.

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