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Tungsten oxide nanoparticles synthesised by laser assisted homogeneous gas-phase nucleation

O. Alm [a,*], L. Landström [a], M. Boman [a], C.G. Granqvist [b], P. Heszler [b,1]

[a] Department of Materials Chemistry, The Ångström Laboratory, Uppsala University, P.O. Box 538, SE-75121 Uppsala, Sweden
[b] Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden

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Abstract

Tungsten oxide nanoparticles were generated by excimer (ArF) laser assisted chemical vapor deposition from $WF_6/H_2/O_2/Ar$ gas mixtures. The deposited particles were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy. The deposition rate as a function of the partial pressures of the reactants and of the laser fluence was measured by X-ray fluorescence spectroscopy. The mean diameter of the deposited tungsten oxide particles varied with the experimental parameters and was typically 23 nm. Particles with a higher degree of crystallinity were observed at a laser fluence exceeding 130 mJ/cm^2, and X-ray amorphous particles were obtained below 110 mJ/cm^2. The amorphous tungsten oxide had a stoichiometry ranging from $WO_{2.7}$ to WO_3. Deposits were formed only when hydrogen was present in the gas mixture.

Keywords: Tungsten oxide; Nanostructured materials; LCVD

1. Introduction

Nanosized particles have attracted much interest for several years. The physical properties of the particles—for example, magnetic, electronic, or optical characteristics—often differ when compared to the corresponding bulk material. The benefit arising from the size-dependent properties of these tiny particles has been one of the driving forces in nanotechnology. This technology gives the possibility to tailor the properties of a material consisting of nanoparticles/nanocrystals, often called nanostructured materials (NsM) [1]. Examples of applications of nanoparticles in nanostructured materials can be found, for example, in solar collectors [2], in photocatalytic films [3] and in high thermal flow stress materials used in engines [4].

It is also known that porous nanoparticle layers exhibit high surface area, and therefore, can be used as catalysts or for sensor applications. Semiconductor

* Corresponding author. Tel.: +46 18 4713737; fax: +46 18 513548.
E-mail address: oscar.alm@mkem.uu.se (O. Alm).
[1] Also at Research Group on Laser Physics of the Hungarian Academy of Sciences, University of Szeged, P.O. Box 406, H-6701 Szeged, Hungary.

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gas sensors have proved to be very promising since they represent a low-cost option to the methods used today.

The active medium of a semiconductor gas sensor is typically a metal oxide film such as SnO_2, TiO_2, ZnO, Cr_2O_3, Mn_2O_3, WO_3. Nanocrystalline tungsten oxide is promising also as a catalytic and photo-catalytic purifier for air and water [5,6] and as a component of electrochromic ''smart windows'' capable of controlling of the transmittance of windows providing indoor comfort with large energy efficiency [7,8].

The thermodynamically stable crystal structure of WO_3 is perovskite. This structure is, however, easily distorted thus resulting in various polymorphs at different temperatures. There are four polymorphs in the temperature region from −189 to 900 °C. A large number of sub-stoichiometric phases, WO_{3-x} ($0 < x \leq 0.4$), so called Magnéli phases, also exists.

WO_3 nanoparticles can be produced by a wide range of methods, such as sol–gel synthesis [9], self-propagating high temperature synthesis (SHS) [10] and gas-phase methods such as advanced gas deposition (ADG) [11]. Recently, it has been shown that tungsten nanoparticles can be deposited by laser assisted chemical vapor deposition (LCVD) using ultraviolet laser excitation of a $WF_6/H_2/Ar$ gas mixture [12–16]. Importantly, the size distribution of the particles can also be controlled by tuning the laser parameters and the partial pressures of the reactants [13–15]. In addition, narrow size-distribution of the particles can be achieved by avoiding agglomeration [14], which can be important for several applications.

In this paper, we present results from our extended investigations on producing tungsten oxide nanoparticles by adding O_2 to the $WF_6/H_2/Ar$ gas mixture and using the LCVD technique.

2. Experimental

The LCVD set-up applied for photolytic synthesis of WO_3 was the same as that employed for the generation of tungsten nanoparticles [12–16]. Argon gas was used to purge the laser entrance window and the reactants WF_6, H_2 and O_2 were introduced at a distance from it. The gases traveled parallel to the laser beam for 14 cm before reaching the deposition zone. Linear flow of the gas mixture in the reactor was 5 cm/s. The reactor was brought to 50 °C in order to avoid condensation of WF_6 on the walls. The laser source was an excimer laser (ArF) operated at 50 Hz and 193 nm (nominal pulse duration: 15 ns [FWHM]). The laser beam was focused in order to achieve the desired laser fluences by a cylindrical lens with a focal length of 38 cm, which resulted in a laser spot area of about 0.5 cm^2 at the deposition zone. The fluence was varied from 70 to 220 mJ/cm^2, the total pressure in the experiments was kept at 2000 Pa, while the partial pressure of WF_6 was fixed at 24 Pa. The effect of the oxygen partial pressure was examined up to 900 Pa, keeping the linear gas velocity constant by adjusting the Ar partial pressure while the H_2 pressure was maintained at 60 Pa. The effect of the H_2 partial pressure on the deposition rate was also examined in the zero to 120 Pa region.

Particle films were deposited onto Si(1 0 0) substrates placed 1.5–2 mm below the laser beam. The deposition time for all samples was 10 min. The structure of the layers were characterized by X-ray diffraction (XRD) in a parallel beam setup using a Cu Kα radiation.

For determination of particle size distributions, samples were deposited onto carbon covered copper grids at laser fluences of 70, 130 and 170 mJ/cm^2. Deposition time varied from 10 to 40 s to avoid thick deposits that would have been unsuitable for the transmission electron microscopy (TEM) analysis. TEM bright field pictures and scanning electron microscopy (SEM) pictures were taken on the samples. At least 1500 particles for each sample were used to construct the particle distributions.

The chemical composition of the films was examined by X-ray photoelectron spectroscopy (XPS) for different laser fluences (70, 90 and 220 mJ/cm^2) and O_2 partial pressures (0, 60 and 900 Pa). The porous structure of the deposits did not make it possible to perform depth profiling.

The relative deposition rate for different laser fluences and partial pressures of H_2 and O_2 was determined by X-ray fluorescence spectroscopy (XRF) by monitoring the area of the tungsten Lα peak in the fluorescence spectrum. It should be noted that this measurement only could yield data for the relative amount of the elemental tungsten in the deposits.