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Controlled growth of copper oxide nanostructures by atmospheric pressure micro-afterglow

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ABSTRACT

A large variety of copper oxide nanostructures encompassing nanodots, nanowires and nanowalls, sometimes organized in “cabbage-like” architectures, are grown locally by direct oxidation of copper thin films using the micro-afterglow of an Ar–O_2 microwave plasma operating at atmospheric pressure. Morphology, structure and composition of the oxidized copper thin films are characterized by X-ray diffraction, secondary ion mass spectrometry and scanning electron microscopy. The concentric areas where each kind of nanostructures is found are defined by both their radial position with respect to the afterglow centre and by experimental conditions. A growth mechanism is proposed, based on stress-induced outward migration of copper ions. The development of stress gradients is caused by the formation of a copper oxide scale layer. If copper oxide nanowires can be grown as in thermal oxidation processes, micro-afterglow conditions offer novel nanostructures and nano-architectures.

1. Introduction

Metal oxide nanostructures with controlled shapes and size distribution have stimulated great interest in fundamental scientific research owing to their morphology-dependent properties that offer potential wide-ranging applications. Metal oxide nanomaterials are expected to exhibit specific properties compared to their bulk counterparts, because surface processes dominate bulk processes as far as their surface-to-volume ratio is sufficiently high. In this context, copper oxide is a promising material because of its non-toxicity, its abundance and its relatively low cost. Copper oxide nanostructures have been widely studied recently in various application domains: solar cells [1], gas sensors [2], catalysis [3], supercapacitors [4], field emission devices [5], photoelectrochemistry [6], batteries [7], etc.

Consequently, various methods for the synthesis of copper oxide nanostructures have been reported in the literature. Among them, we shall present only self-assembly methods where no templates or surfactants are needed. Various copper oxide nanostructures (nanorods, nanowires, nanowalls, urchin-like structures) can be synthesized by solution-based methods such as thermal decomposition of liquid copper precursors [8,9], hydrothermal decomposition methods [10,11] or electrochemical methods [12,13]. Copper oxide nanostructures can also be easily synthesized in gas phase by thermal oxidation methods [14]. For example, Jiang et al. [15] reported the possibility to grow copper oxide nanowires by simple heating of copper substrates between 300 and 800 °C in air at atmospheric pressure. Thermal oxidation is a very attractive method to produce copper oxide nanostructures because of its ease of implementation, but only one-dimensional nanostructures could be obtained so far: nanowires or whiskers.

Plasma-assisted processing is one of the emerging processes used for the production of various metal oxide nanostructures [16–18]. For example, Cvelbar et al. [19] demonstrated the ability to control the morphology and nucleation density of single-crystalline α-Fe_2O_3 nanowires and nanoneedles by varying the electrical potential of iron surfaces directly exposed to low-pressure oxygen plasmas. Kumar et al. [20] synthesized various metal oxide nanowires (SnO_2, ZnO, TiO_2, Al_2O_3) in gas-phase using direct oxidation of metal microparticles in a high-throughput atmospheric pressure microwave plasma jet reactor. Mariotti et al. [21] proposed a method based on the utilization of atmospheric microplasmas where complex nanoarchitectures composed of spherical nanoparticles and nanosheets of molybdenum oxide could be controlled by adjusting the gap distance between a

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molybdenum wire and the substrate used for deposition. Amazingly, only few studies report the possibility to fabricate copper oxide nanostructures by using plasma-assisted methods. Among them, Koh et al. [22] proposed a micro-plasma assisted chemical vapour deposition process to synthesize a large variety of vertically-aligned, anisotropic copper oxide nanostructures (wires, needles, trees, leaves and fans). A directed flux of active copper species, coming from the dissociation of a copper precursor, is mixed with a supersonic microplasma jet operating in an oxidizing background gas at moderate pressure (∼50 Torr).

In this work, we present an innovative strategy based on plasma oxidation, to form different copper oxide nanoarchitectures: "cabbage-like" structures (3D), and various nanostructures like nanowalls (2D), nanowires (1D) and nanodots (0D). This very simple process consists in exposing a copper film directly to the afterglow of an argon–oxygen micro-plasma at atmospheric pressure. This afterglow oxidation method seems to be close to the thermal oxidation method but in the former medium, molecular oxygen is strongly dissociated into atomic oxygen, leading to a substantial gain in oxidation rates at very low temperature. This opens a window of experimental conditions where novel copper oxide nanostructures can be grown by a gas-phase process at atmospheric pressure.

2. Experimental section

2.1. Copper thin film deposition

Nanostructured copper oxide samples are obtained by atmospheric pressure micro-afterglow oxidation of thin copper films beforehand deposited on soda lime glass substrates using DC magnetron sputtering. The base vacuum in the sputtering chamber is 5×10^{-6} mbar. The distance between the sample and the copper target (50 mm in diameter, 6 mm thick and >99.99% purity) is 100 mm. The substrate-holder rotates at 28 revolutions per minute during deposition to ensure homogeneity. The copper thin films are deposited at a pressure of 6×10^{-3} mbar in a 10 vol% H_2–90 vol% Ar mixture. The power applied to the copper target is 80 W. Before deposition, a shutter is placed in front of the target to isolate the substrate during 5 min in order to remove the native oxide layer. Thin films are deposited without external heating and the deposition temperatures are below 50 °C. Half an hour is needed to obtain a 1 μm-thick coating.

2.2. Micro-afterglow oxidation

The experimental set-up is shown in Fig. 1(a). A detailed description is reported in Ref. [23]. It consists of a fused silica tube, crossing a resonant cavity connected to a microwave generator operating at 2.45 GHz. The applied power is 100 W in this study. The atmospheric pressure plasma (Ar – 10 vol% O_2) is centred on the tube axis by a rotating fan and neutral species exit the reactor through a hole (400 μm in diameter). A total flow rate of 275 standard cubic centimetre per minute (sccm) is injected in the plasma, which produces a laminar post-discharge (Fig. 1(b)), containing atomic oxygen and various neutral excited species of oxygen [23]. The diameter of the beam is about twice as large as the diameter of the hole (∼800 μm). The axial profile of the gas temperature was previously studied [24]; under the present experimental conditions, a relatively flat profile is observed in the centre of the beam with a mean temperature close to 1200 K. The temperature decreases sharply at the edge of the beam with strong thermal gradients (∼1000 K/mm). The evolution of the surface temperature of the substrate was previously determined by heat transfer simulation from time-resolved infra-red measurements on the sample backside [25,26]. The surface temperature reaches a steady state after about 3 min with a maximum temperature of approximately 300 °C under the present experimental conditions. The hole–substrate distance is 2 mm and the treatment is performed in a confined environment to prevent air contamination. Fig. 1(c) shows a copper thin film after the afterglow oxidation process. Coloured rings appear on the substrate area hit by the afterglow over a diameter between 1 and 2 cm, depending on the treatment duration. The afterglow exposure varies between 2 min and 8 h. At the end of the treatment, the sample is removed from the beam and cools down to room temperature in a few seconds. Next, it is stored in a bell jar under primary vacuum.

2.3. Sample characterization

The sample morphology is imaged with a Philips XL 30 Scanning Electron Microscope (SEM). Film thicknesses are also measured by SEM from cross-section views. Film structures are studied by X-ray diffraction in Grazing Incidence Geometry (GIXRD) using Co-Kα radiation (0.178897 nm) on a Brüker D8 Discover diffractometer, at an incidence angle of 4°. In this configuration, the analysed surface is limited to about 300 μm × 3000 μm by using a beam collimator and the depth of the sample probed by X-rays is estimated to be 2 μm. Secondary Ion Mass Spectrometry (SIMS) analyses are performed on

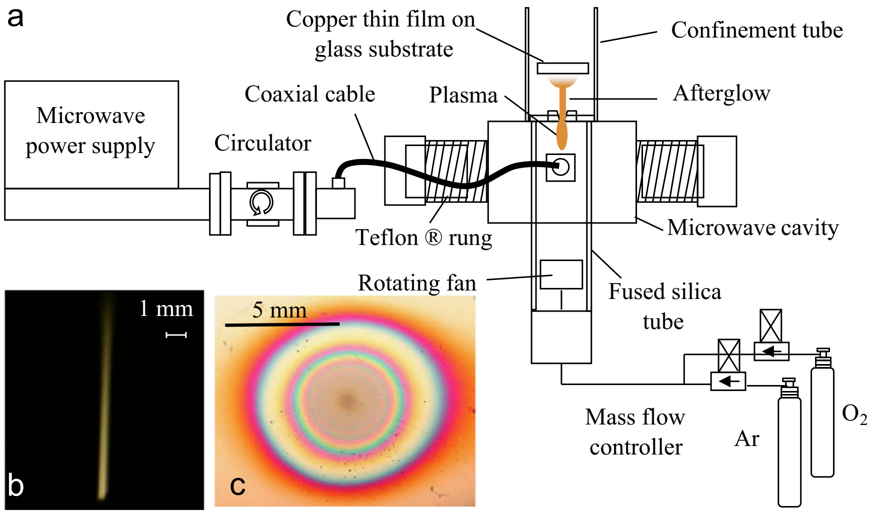

Fig. 1. (a) Schematic of the atmospheric pressure oxidation process, (b) photograph of the micro-afterglow through a 400-μm diameter hole for a total flow rate of 275 sccm (Ar – 10 vol% O_2), and (c) photograph of copper thin film after afterglow oxidation (2 h).