Surface & Coatings Technology xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Growth of ruthenium dioxide nanostructures by micro-afterglow oxidation at atmospheric pressure

D. Kuete Saa [a,b], R.P. Cardoso [c], F. Kosior [a], A. Al Taweel [a], T. Gries [a,d], S. Laminsi [b], T. Belmonte [a,d,*]

[a] Université de Lorraine, Institut Jean Lamour, UMR CNRS 7198, NANCY, F-54042, France
[b] Université de Yaoundé 1, Laboratoire de Chimie Minérale, 812 Yaoundé, Cameroun
[c] Universidade Federal do Paraná, 81531-990-Curitiba, PR, Brasil
[d] CNRS, Institut Jean Lamour, UMR CNRS 7198, NANCY, F-54042, France

ARTICLE INFO

Available online xxxx

Keywords:
RuO_2
Nanostructuration
Localized growth
Micro-plasma
Afterglow

ABSTRACT

Various ruthenium dioxide nanostructures were grown locally by the oxidation of ruthenium samples with an Ar-O_2 microwave micro-afterglow operated at atmospheric pressure. A special attention was paid to the distribution of the surface temperature of the sample which evolves between 530 K and 820 K. Whatever the treatment time, the temperature and the gas composition set within the studied ranges, a general nanostructure, made of lamellae separated by 20–50 nm, is found. When the temperature rises, localized nano-sea urchins, nanotubes with square sections, nano-needles, and more complex structures are found spread over the surface. Treated surfaces were characterized by different surface diagnostics (SEM, XRD, SIMS, etc.) Finally, a growth mechanism is proposed emphasizing the role of emerging defects and stress on the appearance of localized nanostructures.
© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The synthesis of metallic oxides is a field of extensive research owing to the widespread applications of these materials. Ruthenium dioxide (RuO_2) as single crystal is among the most conductive oxides for it has a very low (35 μΩ cm^{-1}) electrical resistivity [1]. It belongs to the family of transition-metal oxide compounds, and it is usually classified as a metal because its Fermi level lies in the middle of a conduction-band density-of-states curve that is comprised primarily of Ru-4d orbitals. It has a tetragonal rutile structure with a crystalline density of 7.026 g/cm^3 [2], a large work function (~5 eV) [3]. It is characterized by a high thermal and chemical stability [4,5], and it behaves as a diffusion barrier [6]. This combination of properties makes RuO_2 an excellent candidate in many devices like thin film resistors [7], supercapacitors [8], sensors for measurement of pH and dissolved oxygen [9], electrodes for high-k materials in dynamic random access memories [10] and non-volatile random access memories [11]. It is also a good candidate for catalyst [12], field emission [13] and charge storage materials [14].

Numerous synthesis methods were employed to produce RuO_2 in different forms. RuO_2 crystals were grown from the decomposition of volatile oxides of Ru [15]. Thin films of RuO_2 were deposited by chemical vapor deposition from organic compounds of Ru as precursors [16], by pulsed laser ablation of pure RuO_2 target [17], and by electrostatic spray deposition of $RuCl_3$ [18,19]. RuO_2 nanorods were synthesized by reducing $RuCl_3$ over carbon nanotube templates [20], by reactive sputtering of pure Ru in an O_2 environment [21], and by CVD of Ru-containing compounds mixed with O_2 as carrier gas [22]. Thermal decomposition of Ru-containing compounds in a continuous flow of carrier gas also led to the growth of RuO_2 nanorods [23].

Little information is available on low-temperature oxidation mechanisms of ruthenium, although many studies investigated surface processes for catalyst [24,25]. By heating ruthenium in the air, a thin film of RuO_2 forms on the surface above 400 °C and becomes visible as a brown coloration [26]. It is the only solid oxide that exists in equilibrium with the metal and with oxygen, and it transforms only at very high temperature (1405 °C in the air). The formation of solid RuO_2 is driven by n-type bulk diffusion at sufficiently high temperature. However, this is only an intermediate stage in the oxidation of ruthenium metal. Weight losses measured when ruthenium is heated are not the result of volatilisation of the solid oxide but it is due to the formation of new volatile species by its further oxidation. At sufficiently high temperature (900 K after [27]), RuO_2 reacts with the surrounding oxygen and forms gaseous RuO_3 and RuO_4. Combining XPS microscopy and TDS, Blume et al. [28] demonstrated that the formation of a crystalline rutile RuO_2 phase starting from an ordered Ru(0001) surface is kinetically hindered at temperatures lower than 500 K. The main reason for this is the limited incorporation of oxygen, which does not reach the critical coverage of 4 monolayers (two rutile layers). Sharma and Hines [29] found that for temperatures up to 473 K, Ru oxidizes to produce a thin film of a lower oxide of Ru (probably RuO), which causes high contact resistance. For temperatures above 573 K, Ru forms RuO_2, which has low contact resistance.

In this paper, we report the growth of RuO_2 nanostructures by a versatile process, a microwave micro-afterglow [30,31], which produces

* Corresponding author at: Université de Lorraine, Institut Jean Lamour, UMR CNRS 7198, NANCY, F-54042, France. Tel.: +33 383584091; fax: +33 383534764.
E-mail address: thierry.belmonte@univ-lorraine.fr (T. Belmonte).

0257-8972/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.surfcoat.2013.10.040

ARTICLE IN PRESS

nanostructures nicely controlled in size and shape. Experiments were carried out in order to study the influence of treatment time and gas composition on the growth of various RuO_2 nanostructures. Structure and surface morphology of as-grown RuO_2 nanostructures were investigated thoroughly.

2. Experimental setup

2.1. General procedure

The experimental setup is shown in Fig. 1. Briefly, the atmospheric microwave plasma is created in a fused silica tube (27 mm inner diameter) located in a 2.45-GHz resonant cavity. The power supply delivers 100 W in present conditions. A rotating fan is used to center the plasma on the tube axis. Minimizing the reflected power from the power supply is ensured by two Teflon rungs mounted on screws located on two opposite sides of the cavity. Flow rates of gases are controlled by two mass flow controllers, and the total flow rate is 825 sccm (standard cubic centimeter per minute). The partial pressure of oxygen in the gas mixture (Ar-O_2) varies from 2.5 to 10 vol.%. Extracting a micro-afterglow from such a source is possible by drilling a tiny hole on a brass plate screwed on one wall of the cavity. The size of the hole is 600 μm. The flow escapes through this aperture and forms a kind of flame outside. This flame is clearly an afterglow [30]. Once the afterglow is created, a laminar beam of excited neutral species exit the nozzle and the treatment starts. This beam is mainly composed of O, $O_2(X)$, $O_2(a)$, and Ar species because it is too hot to produce O_3 (typically, the gas temperature is 1200 K at the nozzle exit). However, far enough from the beam (and then from the treated spot on the substrate surface), O_3 can be detected.

Samples are cuboids ($5 \times 5 \times 3$ and $2 \times 2 \times 2$ mm^3) of high purity metallic ruthenium (99.99%). They were polished mechanically (final stage 1 μm diamond paste), ultrasonically cleaned in acetone and rinsed with ethanol before treatment. The sample-nozzle distance was 4.5 mm. By changing time and gas composition, different oxide nano-objects could be grown. They were characterized by several surface diagnostics (Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), and Secondary Ion Mass Spectrometry (SIMS)).

2.2. Surface temperature

An important aspect of micro-afterglow treatments deals with the sample surface temperature distribution. The temperature of the micro-afterglow is determined from the OH rotational spectrum resolved spatially with a CCD camera. The heat flux transferred to the ruthenium substrate coated by a thin RuO_2 layer can thus be determined, and a heat transfer model is used to estimate the surface temperature (for a complete description of the model, see reference [32]). Because of the short distance between the substrate and the resonant cavity, direct infrared measurements are impossible to perform. Only the temperature on the sample backside can be used to validate the model. Furthermore, by lack of available data, the emissivity of the surface of a passivated ruthenium sample was determined in the range [300 K–900 K] at wavelengths between 8 and 14 μm: $\varepsilon(T)_{8-14\,\mu m} \approx 0.20 + 1.2 \times 10^{-4}\,T$.

Specific data required for this model and corresponding results are given in Table 1. Relatively good agreement is obtained between experimental and simulated data. For the smaller sample, the simulated temperature is slightly higher, probably because of a greater importance of the heat flux at the walls in heat transfer mechanisms. The temperature gradient along the surface is very limited (3 K–4 K) and almost null (1 K) for the smaller sample (Fig. 2). From simulation results, we observe that the temperature of the sample side submitted to the plasma flux is only about 4 K higher than the corresponding backside. The oxide layer is too thin to limit the heat flux from the afterglow and to impose a strong thermal gradient between the opposite sides of the sample. Then, we shall consider hereafter that the temperature is constant at steady state.

The plasma temperature goes through a maximum when the oxygen amount is between 0% and 2.5%. Above this content, it decreases. Typically, changing the gas composition from 2.5% to 10% induces a temperature variation of about 40 K. Let's mention finally that the steady state is reached after a couple of minutes, typically.

3. Results and discussion

The afterglow oxidation of ruthenium samples ($5 \times 5 \times 3$ mm^3) produces an oxidized circular spot on the surface of about 1100 μm in radius (approximately four times the radius of the hole of the resonant cavity from which the atoms beam flows). The general aspect of the surface is depicted in Fig. 3a. It does not depend markedly on the surface temperature reached by the sample. When the surface is observed carefully at high magnification (Fig. 3b and c), a specific nanostructure is found over a distance along the surface of approximately 800 μm. It corresponds to lamellae, separated by approximately 20–50 nm and aggregated into domains of about 1 μm in length. On the other hand,

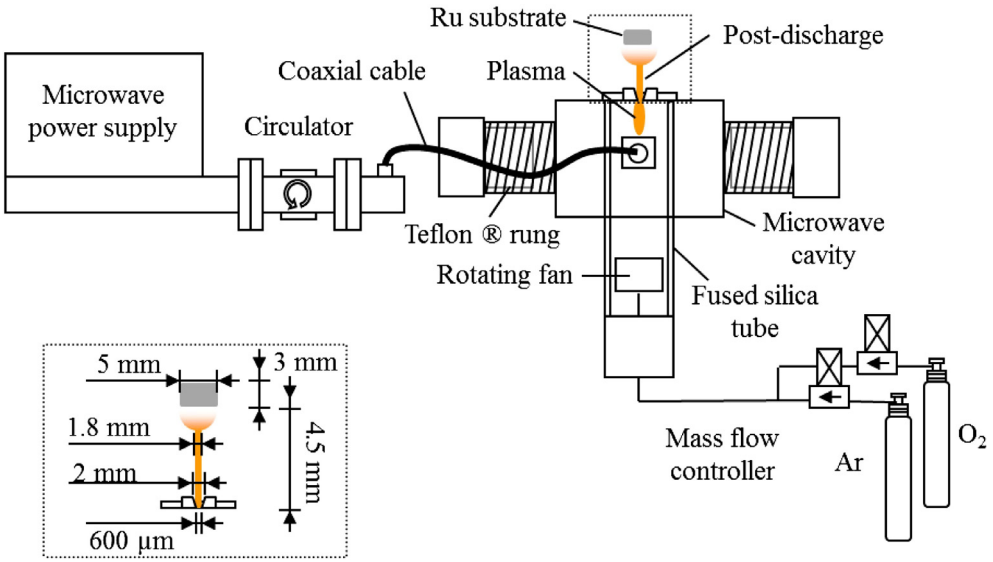

Fig. 1. Experimental device.

Please cite this article as: D. Kuete Saa, et al., Surf. Coat. Technol. (2013), http://dx.doi.org/10.1016/j.surfcoat.2013.10.040

Download English Version:

https://daneshyari.com/en/article/8027467

Download Persian Version:

https://daneshyari.com/article/8027467

Daneshyari.com