Nanoparticulated hydrophobic CdO coatings deposited by microwave procedure

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A novel and inexpensive way to deposit nanostructured cadmium oxide (CdO) coatings is described. Metallic Cd is evaporated by heating a silicon carbide crucible, via microwave radiation at standard atmosphere conditions. The Cd vapour rises from the crucible and reacts with the atmospheric oxygen depositing on a glass substrate. CdO coating is homogeneously distributed above the glass surface and it presents a well-defined cubic-shaped nanostructure. The as-deposited CdO coatings showed good hydrophobic properties and achieved symmetric contact angles of 112°. The hydrophobic behaviour was lost after a 75 min of heat treatment at 723 K.

1. Introduction: Cadmium oxide (CdO) is a very interesting material because it presents properties that can be useful in a wide variety of applications. Some prominent uses of this material include catalytic applications as gas sensors [1–3], transparent conductors [4, 5] and hydrophobic coatings [6]. The multiplicity of applications of this oxide are due to its properties, having a forbidden band-gap that can be engineered from 1.44 eV up to 3.1 eV, an electric conductivity as high as 42,000 S/cm, and has exhibited a non-linear refractive index that varies one order of magnitude depending on the wavelength of the incident radiation. It crystallises in a cubic rocksalt structure with lattice parameter $a = 4.69$ Å [7]. There has been a continuous increase in the number of articles published relating CdO since 1990, and 2007 was the year when the number of articles increased in significant way [7]. The main techniques used to obtain CdO thin films can be basically divided in vapour phase techniques and solution phase techniques. The former involves the condensation of a gas made of Cd or CdO onto the surface of the substrate and the later is based on the chemical or electrochemical deposition or growth of the CdO on the surface of the substrate. Depending on the particulars of each technique, both methods could lead to the formation of a monocrystalline CdO thin film but in most cases the formation of a nanostructured thin film is achieved [7].

Microwave heating is a novel technique for physical evaporation of metals to obtain thin solid films. It presents the advantages of short deposition times and that it can be done at atmosphere pressure. It works by heating a microwave-absorbing ceramic crucible that can be heated up to hundreds of Kelvin in a short period of time, then making possible the evaporation of certain materials including metals.

Deposition of a nanostructured thin solid film on the surface of a substrate is an effective way to obtain hydrophobic properties on a non-hydrophobic base material. Hydrophobicity is the property of a surface of being water repellent; the term is now related to surfaces that can repel liquids due to the difference of surface energies between the solid and the liquid, even though the liquid is not water. Basically, there are three models that describe hydrophobicity [8]: the Young equation describes a sessile drop on the surface of an ideal flat, homogeneous and rigid surface; the Wenzel model that includes the surface roughness and assumes that the liquid wets the whole surface; and the Cassie–Baxter model that assumes that the liquid does not penetrate into the cavities formed by the surface roughness (Fig. 1). All the models relate the hydrophobicity of the surface to the inner angle formed by a drop of the liquid and the surface. Depending on the value of this angle, the material could be classified as hydrophilic ($\theta_C \leq 90^\circ$), hydrophobic ($90 < \theta_C \leq 150^\circ$) or super-hydrophobic ($\theta_C > 150^\circ$).

The Wenzel and Cassie–Baxter models are based on the Young model, adding only terms related to the roughness of the surface, making clear that changing the fine topography of the surface could modify the hydrophobic properties of a surface.

In this Letter, a preliminary study on a non-expensive procedure to deposit metal oxide coatings is presented, along with results for CdO as an example of the potential of this very simple technique in depositing nanoparticulated hydrophobic materials.

2. Experimental procedure: The crucible was made by mixing silicon carbide (SiC), iron oxide (Fe_2O_3) and aluminium oxide (Al_2O_3) powders (all commercial grades) with water added in a quantity that produced a manageable paste, able to be easily moulded. The mixture was cold pressed to a cylindrical shape. A hole was dug on the top of the cylinder and the crucible was heat treated at 723 K in a conventional electric oven, until the crucible was hardened. SiC was chosen as a heater and refractory material due to its microwave power absorption properties [9, 10].

The CdO coatings were deposited by evaporating high-purity cadmium metal (up to 99.99%) in an ambient atmosphere. The metallic Cd was left into the crucible and subject to microwave radiation for 2 min. The microwave oven is a commercial model (brand: LG, model: LF 5700S. 900 W output power at 2.4 GHz).

The topology of the coatings was analysed by field-emission scanning electron microscopy in a TESCAN VEGA II electron microscope and the crystal structure was determined by X-ray diffraction (XRD) analysis performed in a PHILIPS PW3040 X-ray diffractometer with a CuKα source.

The contact angles were measured by taking a picture of a drop of water on the surface of the samples; the images were processed with ImageJ [11] and the plug-in was developed by Stalder *et al.* [12]. The snake-based approach method was employed to determine the value of the contact angles that can be seen at both sides of the droplet image.

3. Results and discussion

3.1. Deposition system: The full deposition system consisted of two refractory bricks that were placed inside the microwave oven at the opposite sides of the SiC crucible with the Cd granules inside

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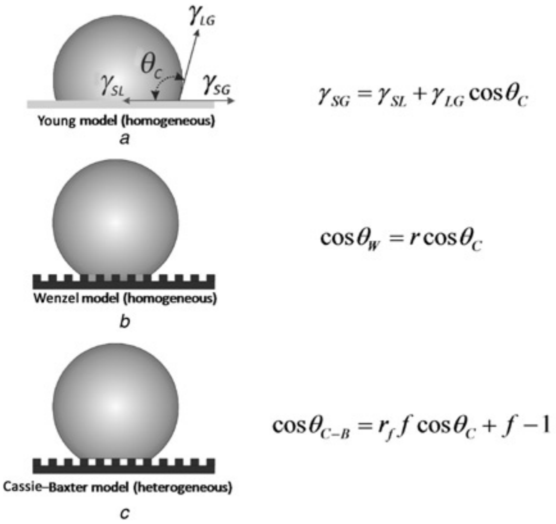

Fig. 1 *Hydrophobic models*
a Young model: the wetting depends on the free energies (γ) of the system
b Wenzel model: the liquid penetrates into the micro/nano features composing the roughness (r) of the surface
c Cassie–Baxter model: the liquid does not penetrate into the roughness and the contact angle also depends on the ratio of the surface in contact with the liquid with respect to the total area under the liquid

(Fig. 2). A soda-lime glass slide was placed on the top of the bricks 5 cm above the crucible (Fig. 3).

The microwave oven was programmed to run at a maximum power for 2 min. After 30 s, a purple glow appears on the top of the crucible (Fig. 4*a*) indicating that the cadmium started to evaporate. At 60 s a column of high radiant energy appeared coming from the crucible (Fig. 4*b*).

3.2. Composition and crystalline structure: Deposited coatings were found to be pure CdO (Fig. 5) with an face centered cube (FCC) structure (S.G. 225: Fm-3m [13]), meaning that the evaporated metallic cadmium reacted with the atmospheric oxygen, depositing on the surface as CdO. Scherrer's formula was used to calculate the average crystallite size [14] and was found to be 52 nm by measuring the six indexed peaks shown in the diffractogram.

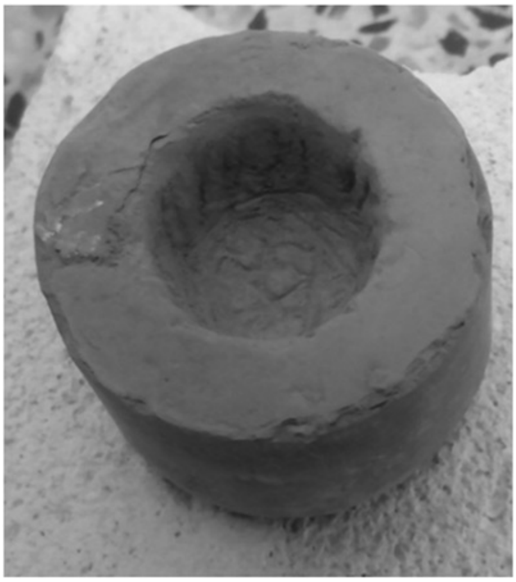

Fig. 2 *SiC crucible made by cold pressing a paste composed by SiC, Fe_2O_3, Al_2O_3 and water. Hole was dug before the heat treatment at 723 K*

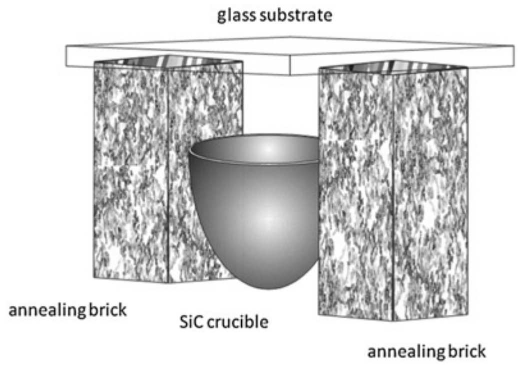

Fig. 3 *Scheme of the deposition system. Cold-pressed SiC crucible was placed between two refractory bricks and a soda-lime glass was placed on the top of the bricks at 5 cm of the crucible*

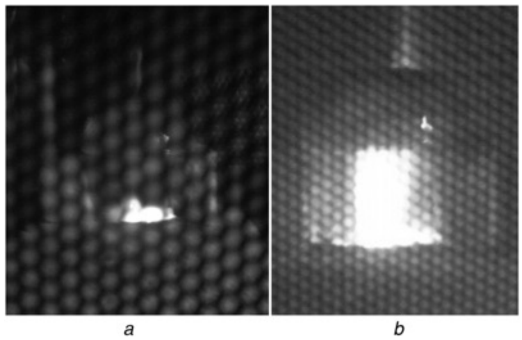

Fig. 4 *View of the crucible at 30 s and 60 s after the process has started*
a View of the crucible at 30 s after the process has started. Purple glow appears on the top of the crucible, above an incandescent radiation
b View of the crucible at 60 s after the process has started. Incandescent radiation forms a column rising from the crucible to the glass substrate. Purple glow is still present

3.3. Nanostructure of the surface: As-deposited coatings showed a cube-shaped nanostructure (Fig. 6) with features ranging from <100 up to 500 nm. Most of these nanostructures, larger than the crystallite size, are composed by the stacking of crystallites of smaller size; some of the particles with large size present coalescence of two or more particles that are not fitted by the flat sides. To evaluate the effect of a heat treatment, some samples were heated at 723 K for 75 min, resulting in the loss of the cube-shaped structures by necking and Ostwald ripening process (Fig. 7).

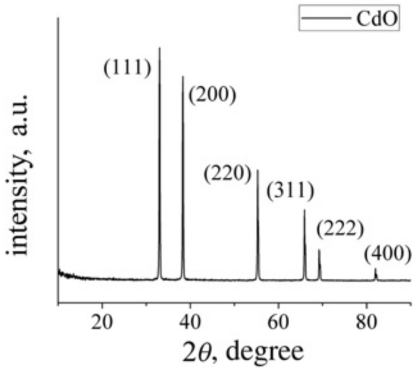

Fig. 5 *XRD plot of a CdO sample deposited on glass. Diffractogram is indexed as pure CdO with FCC structure and lattice parameter a = 4.69 Å [13]*

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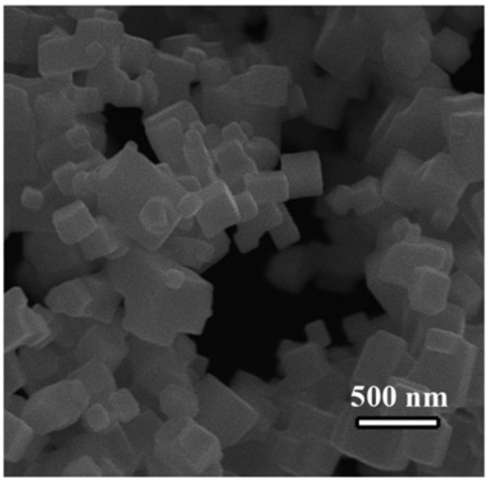

Fig. 6 *As-deposited CdO sample. Coating presents a nanostructured surface conformed by cubic-shaped nanoparticles*

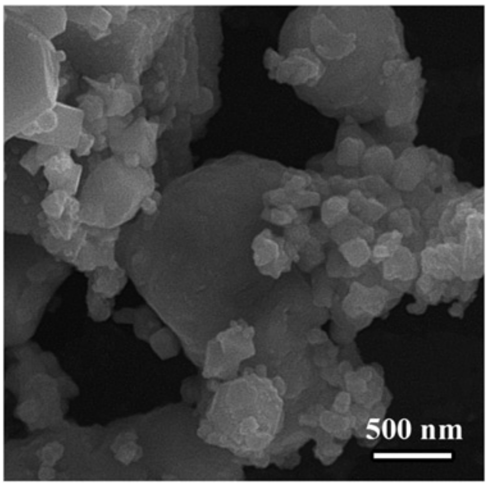

Fig. 7 *CdO sample after a 75 min heat treatment at 723 K. Nanoparticles lost its cubic shape due to solid-state material migration that presents rounded edges as main characteristic as shown in this sample*

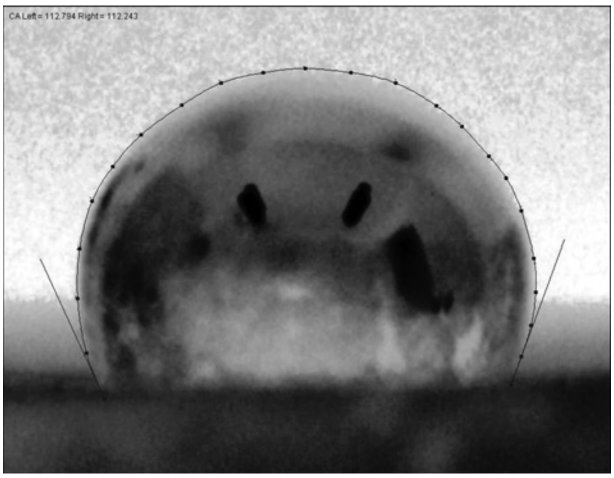

Fig. 8 *Contact angles of an as-deposited sample. Both contact angles are 112° ranking this surface as hydrophobic*

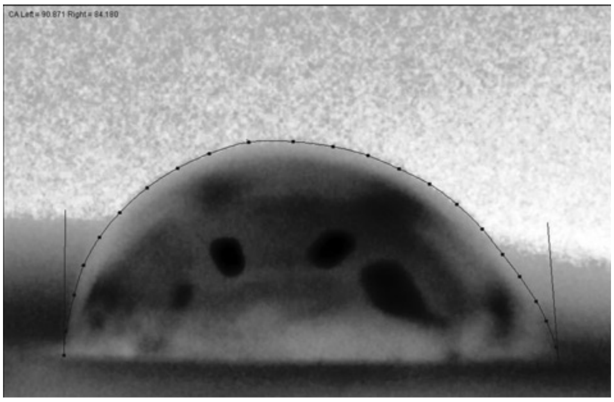

Fig. 9 *Contact angles of a sample heat treated for 75 min at 423 K. Left angle: 90°, right angle: 84°. Non-symmetrical values could be due to the non-homogeneous loss of cubic-shaped nanostructure and the solid-state migration of the material*

3.4. Hydrophobicity: Symmetric contact angles of 112° were found on as-deposited samples (Fig. 8), which indicate that the coating exhibit a hydrophobic behaviour. The contact angles of the sample after heat treatment are ≤90° (Fig. 9). This loss of hydrophobic properties are related to the shape and amount of nanoparticles present on the coating. In Fig. 7, the reduction in the amount of nanoparticles, being predominant (by mass) particles with size above 500 nm is evident.

Further studies are underway to correlate the microstructural properties to the hydrophobicity of the coatings, and will be presented in a forthcoming paper.

4. Conclusions: Cubic-shaped nanostructured CdO coatings were obtained via microwave heating of metallic Cd at standard atmospheric conditions. A custom-made microwave deposition system was used, with a cold pressed SiC crucible, which has demonstrated to be effective to perform the evaporation of metals and deposit nanostructured coatings of metallic oxides due to the reaction of the metallic vapour with the atmospheric oxygen. Deposited coatings show to act as a hydrophobic coating on glass, behaviour that is lost after a heat treatment for 75 min at 723 K.

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