Applied Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Chemical vapor deposition of low reflective cobalt (II) oxide films

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ARTICLE INFO

Article history:
Received 20 July 2015
Received in revised form 20 October 2015
Accepted 26 October 2015
Available online xxx

Keywords:
Optical reflectivity
MOCVD
Refractive index gradient
CoO
Cobalt oxide

ABSTRACT

Low reflective CoO coatings are processed by chemical vapor deposition from $Co_2(CO)_8$ at temperatures between 120 °C and 190 °C without additional oxygen source. The optical reflectivity in the visible and near infrared regions stems from 2 to 35% depending on deposition temperature. The combination of specific microstructural features of the coatings, namely a fractal "cauliflower" morphology and a grain size distribution more or less covering the near UV and IR wavelength ranges enhance light scattering and gives rise to a low reflectivity. In addition, the columnar morphology results in a density gradient in the vertical direction that we interpret as a refractive index gradient lowering reflectivity further down. The coating formed at 180 °C shows the lowest average reflectivity (2.9%), and presents an interesting deep black diffuse aspect.

1. Introduction

Low reflectivity films are used in optical instruments and sensors with the aim to attenuate noise, namely to reduce the effect of stray and scattered light in different spectral domains [1]. Such films find applications in military night sight for optical guidance systems [2], in space applications [3] and can also be used for heat dissipation between different components in microelectronic devices [4]. Moreover, light absorber films are used in the renewable energy domain in photothermal energy conversion [5–8], in photoelectric energy conversion [9], and in solar thermophotovoltaic conversion systems [10–12].

Black coatings are spread over a large variety of materials in the families of metals, alloys, ceramics, and polymers [5,6,13]. Among them, the cobalt (II, III) oxide Co_3O_4 exhibits high optical absorbance which is appropriate for solar absorbers for photothermal conversion [14]. Indeed, Co_3O_4 presents spectrally selective surfaces exhibiting high values of solar absorbance (α) in the visible and the near infra-red (NIR) spectrum and low values of thermal emittance (ε) in the IR spectrum which improves their thermal performance by reducing the radiative heat loss component. Moreover, in contrast to chromium based black coatings, Co-based ones maintain acceptable values of α and ε even after exposure to air (1000 h at 650 °C [15]).

Co oxide films are obtained by wet processes such as thermal decomposition, electrodeposition [14,16,17] and sol–gel [18]. Dry processes are also employed such as PVD [19,20], ALD [21–24] and metalorganic CVD (MOCVD) [25–28]. Several authors use MOCVD to grow cobalt oxide films. Fuji et al. formed Co oxide films by plasma enhanced MOCVD (PEMOCVD). They obtain CoO films at low oxygen flow rate with a surface morphology in the form of packed columnar grains. Increasing the oxygen flow rate leads to the formation of columnar Co_3O_4 films within the same temperature range (400 °C) [29]. Similar observations are mentioned by Tyezkowski et al. who show that film composition is highly correlated to the O_2 molar fraction. Films are composed essentially of Co_3O_4 with the presence of carbon and amorphous CoO_x at low O_2 flow rate [25]. Mane and Shivashankar similarly obtained by MOCVD dense and continuous Co_3O_4 films with a packed grains morphology when using O_2, but porous films composed of a mixture of Co_3O_4 and CoO while using N_2O [30]. Co_3O_4 films are grown as well by Direct Liquid Injection (DLI-) MOCVD under a working pressure of 5 Torr but at temperatures higher than ours: 350–600 °C [26]. Authors notice that while increasing deposition temperature, the film morphology varies depending on the substrate type. Film roughness increases in the case of $LaAlO_3$ substrate while it decreases in the case of sapphire and MgO; an interesting way for tailoring the microstructure of Co oxide films.

Finally, different MOCVD precursors can be used in order to obtain Co oxide films, such as tricarbonyl nitrosyl [27], dicarbonyl cyclopentadienyl cobalt [31], Cobalt (II) b-diketonate adducts [26], and Cobalt (II) acetylacetonate [30]. In particular, dicobalt octacarbonyl ($Co_2(CO)_8$) is used to process films at low temperature

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http://dx.doi.org/10.1016/j.apsusc.2015.10.188
0169-4332/

Please cite this article in press as: E. Amin-Chalhoub, et al., Chemical vapor deposition of low reflective cobalt (II) oxide films, Appl. Surf. Sci. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.10.188

Table 1
MOCVD process parameters used for the deposition of cobalt oxide films.

Deposition temperature (°C) – T_d	120–190
Precursor temperature (°C)	27
Total pressure (Torr)	5
Saturation vapor pressure of $Co_2(CO)_8$ (Torr)	0.0041
N_2 carrier gas flow rate (sccm)	30
N_2 dilution gas flow rate (sccm)	170
$Co_2(CO)_8$ flow rate (sccm)	24.6×10^{-3}
$Co_2(CO)_8$ molar fraction*	1.23×10^{-4}
Deposition duration (min)	80

* Upper limit assuming full efficiency of precursor vaporization and transport.

(<200 °C), ultimately allowing processing thermally sensitive substrates [32–36]. The present work revisits the use of $Co_2(CO)_8$ for the low temperature MOCVD of cobalt oxides, with following three peculiarities: (a) it investigates the thermolysis of the precursor in the absence of reactive gas, e.g. oxygen, (b) it aims at processing pure CoO films, (c) it focuses on the microstructure of the films. It is worth noting that such an approach has never been investigated for the MOCVD of cobalt oxides. The rationale of the work is to elaborate a process operating in a parametric window which allows processing films with stable physicochemical and microstructural characteristics and thus high performance optical properties.

The paper is organized as follows. After the experimental details section, we present and discuss the results concerning the process–structure–properties relationship. Growth rate, crystallography, composition, and morphology of the coatings are correlated with deposition temperature (T_d). Then, the optical reflectivity of the films is correlated with chemical and microstructural characteristics, namely surface roughness, grain size distribution and fractal dimension, before providing concluding remarks.

2. Experimental details

CVD experiments are performed in a vertical cold-wall reactor composed of a 46 mm diameter quartz tube. Silicon samples ($20 \times 10 \times 1\ mm^3$) are cut from 4″ Si(1 0 0) wafers and sonicated in acetone and ethanol baths for 5 min, dried in an Ar flow, and baked at 60 °C for 20 min. They are weighted and immediately positioned flat on an inductively heated stainless steel susceptor. Deposition temperature T_d is controlled by a K-type thermocouple inserted into the core of the susceptor. Surface temperature is calibrated with an additional thermocouple attached to the surface of a dummy Si sample. Pure N_2 (99.9999%, Air Products) is used as both carrier and dilution gas and is delivered through two gas lines, thermally regulated at 35 °C, and equipped with mass flow controllers. A vane pump and pressure gauges connected to the output of the quartz tube is used to regulate the reaction pressure at 5 Torr. T_d is varied from 120 to 190 °C in order to investigate its effect on the films morphology, composition and optical absorptivity. $Co_2(CO)_8$ powder (Alfa Aesar, stabilized in 5% hexane) is filled into a U shaped tube, in a glove box under 99.9997% pure Ar (Air Products) before being connected under N_2 flow with the CVD set-up. The precursor is thermally regulated at 27 °C resulting in a saturated vapor pressure of 0.0041 Torr. Its vapor is carried with N_2 leaching the surface of the powder, and then mixed with the dilution gas N_2. This gas mixture is introduced from the upper part of the reactor through an 8 mm tube facing the substrate holder. The resulting input process conditions are listed in Table 1.

Surface morphology and roughness are measured using scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM is performed on a LEO 435VP microscope. AFM is used in ambient conditions on an Agilent Technologies 5500 instrument. Scanning is performed in contact mode with tips of spring constant of about 0.292 N/m (AppNano). Scanning rate is 2 μm/s. Images are processed with the software Pico Image (Agilent Technologies). Films thicknesses are measured by SEM on cross sectional micrographs at the center of each sample. Crystallographic structures are determined by X-ray diffraction (XRD) on a SEIFERT-3000TT instrument using a Cu K_α (1.5418 Å) X-ray tube operated at 40 kV and 40 mA, a Ni filter and solid-state Lynxeye detector. EPMA is used to determine the elemental composition of the films (Cameca SXFive instrument). Calibration is performed using high purity standards. Each measurement is repeated five times at different locations to determine spatial homogeneity. Finally, the UV–vis–NIR total reflectivity spectra are measured by a Perkin-Elmer Lambda-19 spectrophotometer equipped with an integration sphere. The reflected light is collected in the directional-hemispherical geometry with an incidence angle of 8°.

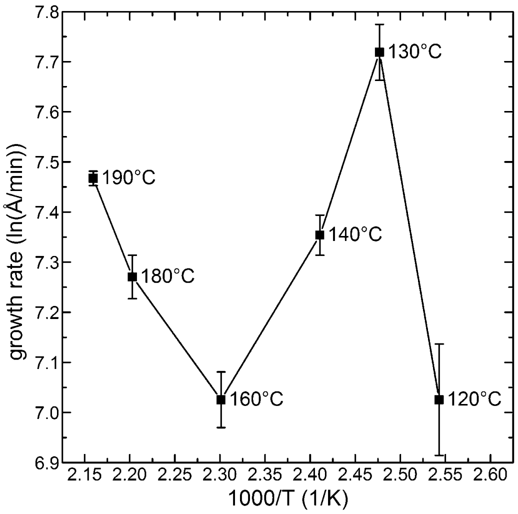

Fig. 1. Arrhenius-type plot of the growth rate of CoO films from $Co_2(CO)_8$ on Si.

3. Results and discussions

3.1. Growth kinetics

Processed films systematically present a mat aspect. The color change is visually observed on the silicon substrates during the first minutes of deposition, corresponding to the upper limit of incubation time. Visual inspection of the surface facing the feeding tube reveals that films deposited at 160 °C and 180 °C are black, while those obtained at 120 °C, 130 °C, 140 °C and 190 °C are grey. Fig. 1 presents an Arrhenius-type plot of the global deposition reaction. Lines connecting points are guide to the eye. Growth rate fluctuates as a function of T_d, increasing from 120 to 130 °C, then decreasing down to 160 °C and finally increasing up again at higher T_d. Growth rate values vary between 110 nm/min at T_d = 120 °C and 160 °C, and 225 nm/min at T_d = 130 °C, resulting in films whose thickness varies between 9 and 18 μm, as measured on cross sections by SEM.

Then, the growth rate does not show an Arrhenius-type behavior. It evolves between two maxima at 130 °C and 190 °C and one minimum at 160 °C. This behavior has already been reported for processes involving $Co_2(CO)_8$. While scanning a range of temperature from 50 °C to 250 °C at a working pressure of 0.01 Torr (which is two orders of magnitude lower than ours), Ye et al. notice two growth rate maxima at 120 °C and 220 °C. They attribute the sharp increase of the deposition rate around 120 °C to a possible increase of the sticking coefficient of the precursor at low temperature [33,37]. Then, the growth rate is likely to decrease as T_d is further increased because of homogeneous undesirable reactions [36]. In

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