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Preparation of nanostructured Al_2O_3–TiO_2 composite films by MOCVD

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ABSTRACT

Nanostructured Al_2O_3–TiO_2 composite films were prepared on glass substrates by metalorganic chemical vapor deposition (MOCVD) using aluminum acetylacetonate and titanium tetraisopropoxide precursors. Oxygen and argon were used as the reactive and carrier gases, respectively. Deposition temperature (T_{dep}) was varied from 723 to 873 K and total pressure was kept constant at 133–266 Pa. The formation of composite films was achieved by mixing the precursor vapors, which were obtained by heating the aluminum and titanium precursors at 403 and 323–353 K, respectively. The films were characterized by XRD, SEM, EPMA and TEM. The crystalline structure and the surface morphology of the nanostructured Al_2O_3–TiO_2 composite films were strongly dependent on the precursor and deposition temperatures.

1. Introduction

For long time, Al_2O_3 and TiO_2 have been highly recognized for their effectiveness in a wide variety of practical applications. As a consequence, many efforts have been undertaken to combine their extraordinary properties such as in Al_2O_3–TiO_2 composite coatings [1–3], Al_2O_3–TiO_2 composite powders [4–5] or TiO_2 deposition on Al_2O_3 [6–8]. In recent years, additional efforts have been devoted to the synthesis of Al_2O_3–TiO_2 nanocomposite architectures. Thus, various synthesis methods have been employed to attempt well-dispersed nanostructured composites. Plasma spraying has been the most common preparation method to attain thick-enough Al_2O_3–TiO_2 composite coatings, which have been improved by supplying the individual components in nanometric sizes [9–10]. The deposition of TiO_2 on nanozised powders of Al_2O_3 or alternatively, the formation of Al_2O_3–TiO_2 nanocomposite powders have been investigated by the sol–gel method over the last decade [11–12]. The synthesis of Al_2O_3–TiO_2 composite films by using the chemical vapor deposition (CVD) method has been more recent [13–14]. So far, the CVD Al_2O_3–TiO_2 composite films have been prepared by using traditional Al and Ti chloride precursors and the resulting films have been amorphous in nature [14]. Here, we report the preparation of nanostructured Al_2O_3–TiO_2 composite films by CVD using metalorganic precursors (MOCVD) that allow deposition temperatures as low as 723 K. The nanostructured composite films consist of crystalline TiO_2 in an amorphous Al_2O_3 matrix.

2. Experimental

The nanostructured Al_2O_3–TiO_2 composite films were prepared on amorphous glass slides (25 mm × 30 mm × 1 mm) in a horizontal hot-wall MOCVD type reactor, which is depicted in Fig. 1. Titanium tetraisopropoxide, $Ti[OCH(CH_3)_2]_4$ (abbr. TTIP) and aluminum acetylacetonate, $Al(CH_3–COCHCO–CH_3)_3$ (abbr. $Al(acac)_3$) were used as precursors. The MOCVD apparatus consists of: (1) quartz tube reactor, (2) electrical furnace, (3) substrate, (4) TTIP precursor, (5) $Al(acac)_3$ precursor, (6) $Al(acac)_3$ thermocouple, (7) substrate thermocouple, (8) thermal bath, and (9) vacuum pump. The liquid TTIP precursor was evaporated in a thermal bath at 323–353 K (T^{Ti}_{prec}) and carried by O_2 gas (FR_{O2} = 25 sccm) into the tube reactor, while the powdered $Al(acac)_3$ precursor was evaporated inside the reactor at 403 K. Both precursor vapors were mixed with Ar (FR_{Ar} = 25 sccm) and then carried to the deposition zone. The deposition temperature (T_{dep}) was varied from 723 to 873 K and the total pressure (P_{tot}) was controlled at 133–266 Pa. The crystal structure and morphology of the composite films were investigated by X-ray diffraction (XRD) using Cu Kα radiation, scanning (SEM) and transmission (TEM) electron microscopies, respectively. Chemical composition of the films was analyzed by electron-probe microanalysis (EPMA).

3. Results and discussion

Fig. 2 shows the effect of deposition temperature on the XRD patterns of Al_2O_3–TiO_2 composite films prepared at P_{tot} = 133–266 Pa, T^{Ti}_{prec} = 323 K and T^{Al}_{prec} = 403 K on amorphous glass substrates. No observable XRD reflections were obtained at T_{dep} = 723 K suggesting the formation of a significant amorphous film, thick enough to hide the amorphous signal from the substrate. Previous results have shown that crystalline TiO_2 films can be obtained by CVD at temperatures as low as 623 K using the TTIP precursor [15]. In addition, the simultaneous growth of amorphous alumina and crystalline titania has been reported by using the sol–gel method [16]. Therefore, the present results may imply the formation of films consisting of amorphous alumina in coexistence with crystalline titania. As

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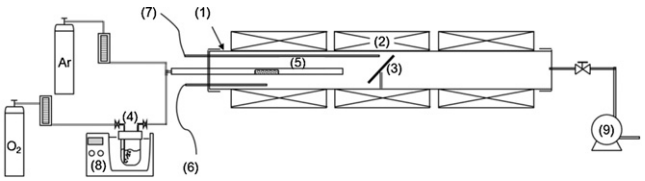

Fig. 1. Schematic representation of the MOCVD apparatus.

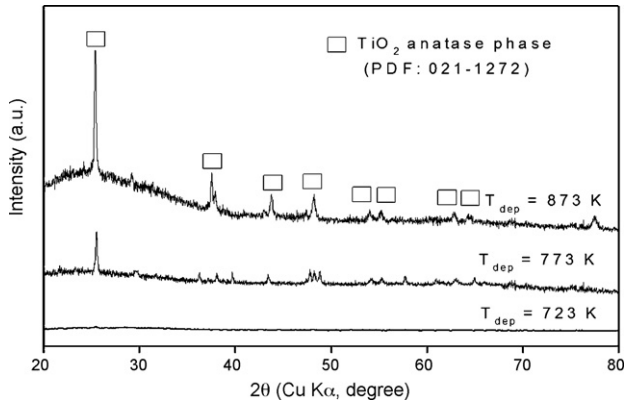

Fig. 2. Effect of the deposition temperature on the XRD patterns of Al_2O_3–TiO_2 composite films.

deposition temperature increases, the crystalline nature of films is more evident. At T_{dep} = 873 K, most of the reflections correspond to those of the TiO_2 anatase phase, while at T_{dep} = 773 K only a few of them are present. This suggests that the films obtained a T_{dep} = 873 K mainly consist of anatase phase and amorphous alumina, most likely. In fact, the semi-quantitative EPMA analysis indicated an Al/O ratio consistent with that of the Al_2O_3 stoichio-

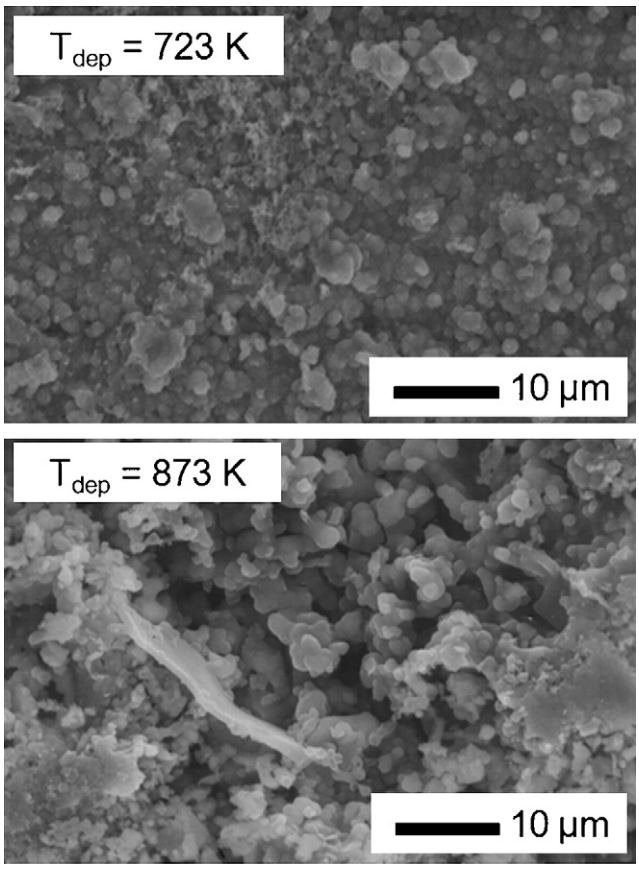

Fig. 3. Influence of the deposition temperature (T_{dep}) on the film surface morphology.

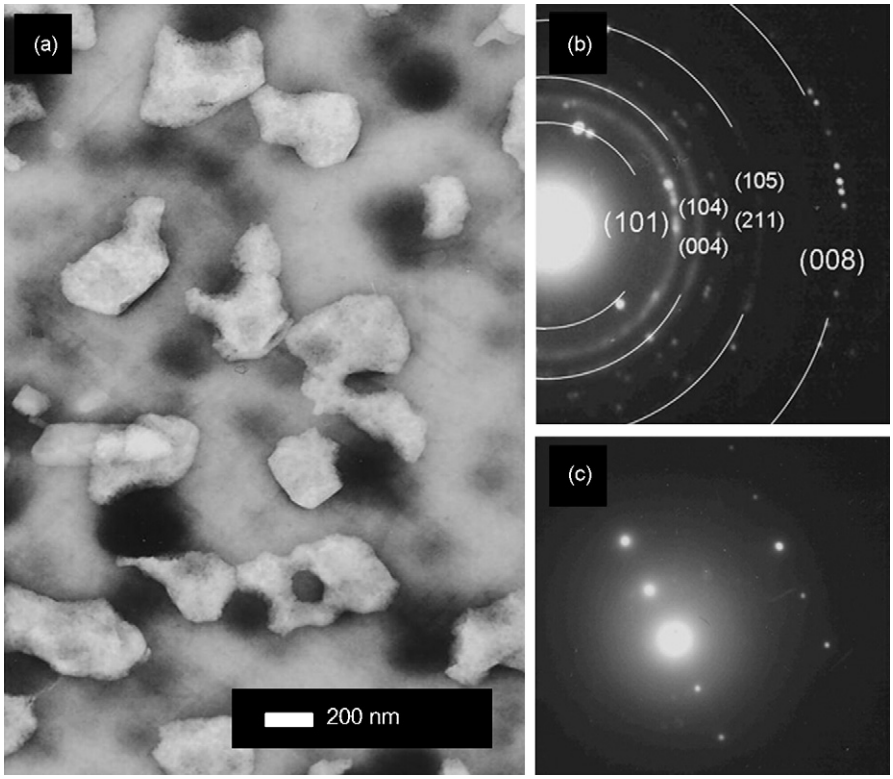

Fig. 4. Bright field TEM image and SAED patterns of the composite films prepared at T_{dep} = 773 K, T^{Ti}_{prec} = 323 K and T^{Al}_{prec} = 403 K.

metric ratio. In contrast, films prepared at T_{dep} = 773 K may consist of various crystalline Ti–O phases (e.g. TiO, Ti_4O_{10} and Ti_7O_{13}) which are not necessarily TiO_2 anatase or rutile.

Fig. 3 illustrates the influence of the deposition temperature (T_{dep}) on the film surface morphology. At T_{dep} = 723 K, the films exhibit a rough surface resulting from agglomerated particles (~1 μm in size) probably consisting of smaller primary particles, which may cause the broad reflections in Fig. 2. As the deposition temperature increases (T_{dep} = 873 K), the composite films show rougher surfaces characterized by a more open porous morphology. This increase in surface area could be the result of higher deposition rates promoted by the raise in precursor vapor concentrations. The kinetic studies on the formation of TiO_2 and Al_2O_3 films using the individual precursors TTIP or $Al(acac)_3$, respectively report a surface reaction regime controlling the growth of the films in the deposition temperature range of 523–873 K [18–19]. As the Al_2O_3–TiO_2 composite films were prepared at T_{dep} = 723–873 K, a considerable increment in the deposition rate for this temperature range could be expected. On the other hand, it was observed that Al_2O_3–TiO_2 composite films showed notable rough surface morphologies at $T^{Ti}_{prec} = 333–363$ K. These results are consistent with those previously reported for the deposition of titania using the TTIP precursor under similar deposition conditions [17].

A typical bright field TEM image of the composite films prepared at T_{dep} = 773 K, $T^{Ti}_{prec} = 323$ K and $T^{Al}_{prec} = 403$ K is shown in Fig. 4a. This image reveals a homogeneous mixture of two phases. One is a continuous matrix (white areas) basically consisting of nanocrystalline TiO_2 in anatase phase as suggested by the characteristic ring pattern of Fig. 4b. The EPMA analysis further suggests that Al_2O_3 is also a component of this continuous matrix. This implies that the continuous matrix is essentially amorphous Al_2O_3 with incorporated crystalline TiO_2 anatase particles. Higher magnification observations indicated that the TiO_2 anatase particles are about 20 nm in size. The second phase (dark areas) was attributed to crystalline Ti–O phases such as TiO, Ti_4O_{10} or Ti_7O_{13}, which display the spot pattern of Fig. 4c.

4. Conclusions

Nanostructured Al_2O_3–TiO_2 composite films were prepared by MOCVD. The composite films consist of a continuous matrix of nanocrystalline TiO_2 anatase particles (~20 nm in size) embedded in amorphous Al_2O_3 and crystalline areas of Ti–O phases different from anatase or rutile. The crystalline structure and the surface morphology of the nanostructured Al_2O_3–TiO_2 composite films were strongly dependent on the precursor and deposition temperatures.

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