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M. Khachane [ab]; P. Nowakowski [b]; S. Villain [b]; J. R. Gavarri [b]; Ch. Muller [b]; I. Luk'Yanchuk [c]; M. Elaatmani [a]; A. Outzourhit [d]; A. Zegzouti [a]

[a] Laboratoire de Chimie du Solide Minéral, Département de Chimie, Faculté des Sciences Semlalia, Université Cadi Ayyad BP, Marrakech, Maroc [b] Laboratoire Matériaux & Microélectronique de Provence, - UMR CNRS 6137, Université du Sud Toulon Var-BP 20132, La Garde, France [c] Laboratoire de Physique de la Matière Condensée, Université Picardie Jules Vernes Amiens, France [d] Laboratoire de Physique du Solide et Couches Minces, Département de Physique, Faculté des Sciences Semlalia, Université Cadi Ayyad BP, Marrakech, Maroc

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M. KHACHANE,[1,2] P. NOWAKOWSKI,[2] S. VILLAIN,[2]
J. R. GAVARRI,[2] CH. MULLER,[2] I. LUK'YANCHUK,[4]
M. ELAATMANI,[1,*] A. OUTZOURHIT,[3] AND A. ZEGZOUTI[1]

[1]Laboratoire de Chimie du Solide Minéral, Département de Chimie, Faculté des Sciences Semlalia, Université Cadi Ayyad BP: 2390, Marrakech, Maroc
[2]Laboratoire Matériaux & Microélectronique de Provence, –UMR CNRS 6137, Université du Sud Toulon Var–BP 20132, F-83957 La Garde, France
[3]Laboratoire de Physique du Solide et Couches Minces, Département de Physique, Faculté des Sciences Semlalia, Université Cadi Ayyad BP : 2390, Marrakech, Maroc
[4]Laboratoire de Physique de la Matière Condensée, Université Picardie Jules Vernes Amiens, France

Films of a catalytic compound (RuO$_2$) were deposited by spin- coating process on ferroelectric films mainly constituted of SrBi$_2$Ta$_2$O$_9$ (SBT) and Ba$_2$NaNb$_5$O$_{15}$ (BNN) phases. SBT films were deposited by MOCVD method, and BNN films were deposited by sputtering. After thermal treatment under air, these ferroelectric-catalytic systems were characterized by X-ray diffraction and scanning electron microscopy (SEM). SEM images showed that RuO$_2$ film morphology depended on substrate nature. A study of CH$_4$ conversion into CO$_2$ and H$_2$O was carried out using these catalytic-ferroelectric multilayers: the conversion was analyzed from Fourier Transform Infrared (FT-IR) spectroscopy, at various temperatures. Improved catalytic properties were observed for RuO$_2$ films deposited on BNN oxide layer.

Keywords Catalysis; infrared spectroscopy; ruthenium dioxide; ferroelectrics coating; multilayers; spin coating

1. Introduction

In a series of surface science studies it has been demonstrated that Ru turns into a very efficient oxidation catalyst under high pressures of the reactants and oxidizing conditions [1, 2]. To a first approximation the high activity of RuO$_2$ was traced back to the relatively low adsorption energy of surface O* atoms together with the high adsorption energy of CO [3]. Even though RuO$_2$ has a great advantage in terms of via a wide potential range of highly reversible redox reactions with high specific capacitance, it is somewath expensive for commercial electrodes in bulk-like electrochemical capacitors. Several strategies have been pursued in this regard [4].

Ruthenium dioxide (RuO_2) crystallizes in a tetragonal rutile-type structure (space group $P4_2/m\,n\,m$, cell parameters: $a = 450.9$, $c = 310.87$ pm) and presents a metallic conductivity in a wide temperature range, arising from the partially filled Ru 4d states [5, 6]. In addition, it presents a high thermal stability under air, namely up to 700°C, with a low electron resistivity. The high interest of this oxide resides in the fact that it might be involved in many attractive applications [7]. Recently, polycrystalline RuO_2 thin films were envisaged as promising electrodes, instead of classical metal platinum electrodes, for the fabrication of ferroelectric capacitor stacks (electrode/ferroelectric/electrode) to be used as dynamic random access memory (DRAM) and non-volatile random access memory (NVRAM). RuO_2 films can be prepared via diversified chemical or physical routes: Metal-Organic Chemical Vapor Deposition (MOCVD) [8], spray pyrolysis [9], sputtering [10, 11], pulsed laser deposition (PLD) [12] and sol-gel approach [13] associated with spin coating process.

In the present work, we deal with a potential application of ferroelectric-catalytic thin layer associations, in the general field of gas sensor technologies. As a first step, we have elaborated multilayer systems and studied the catalytic properties of RuO_2 films deposited on $Ba_2NaNb_5O_{15}$ (BNN) ferroelectric films, in presence of methane gas. The BNN oxide presents an orthorhombic structure (with space group Pba2, cell parameters $a = 1242$, $b = 1248$, $c = 397.7$ pm). In this work, RuO_2 films were deposited from sol gel and spin coating approaches, on three different substrates: (1) metal platinum deposited on silicium (Pt/Si) and (2) ferroelectric oxide BNN deposited on Si substrate (BNN/Si). The conversion of methane gas (in air-methane mixtures) was studied as a function of temperature, making use of homemade device and infrared spectroscopy.

2. Experimental

2.1. *Preparation of Solution*

The following starting materials and reagents were used: ruthenium chloride ($RuCl_3$, xH_2O STREM CHEMICALS), absolute ethanol (C_2H_5OH). $RuCl_3$, xH_2O was dissolved in absolute ethanol with agitation. The obtained solution was maintained under agitation during 24 hours. After 7 days of ageing, the solution was used for thin film preparation. A half of obtained solution was made to obtain RuO_2 powder.

2.2. *Powder Preparation*

For preparation of RuO_2 powder, the obtained solution was oven dried at 120°C in order to evaporate the solvent. After, the powder is annealed at tree temperatures 400, 450 and 500°C during tow hours for each.

2.3. *Films Deposition*

RuO_2 films were deposited using spin coating method. Before applying the sol-gel coating, substrates were washed in acetone and ethanol using an ultrasound bath during 1h, rinsed with pure water and dried. All the substrates were washed except BNN/substrate. A unique spin coating process was applied to deposit RuO_2 precursor solution on Pt/Si and BNN/Si substrates. The optimized spin coating parameters were as follows: rate of 2000 revolutions per minute (rpm), acceleration of 1000 rpm/s, time of 10s.

Ferroelectric BNN films were deposited by Radio Frequency sputtering making use of a specific equipment. Before RuO_2 deposition, BNN films were annealed at 400°C during 1 hour. This procedure was repeated several times until we obtained 6 layers of RuO_2 on the substrate. After each deposition, each multilayer system was subsequently heated in a hotplate for 2 min, in order to evaporate solvents. A final thermal treatment, aiming to promote stabilization and densification of the films and to remove unreacted organic residues, was carried out in a furnace at 450°C for 2 h. The obtained films were characterized by X-ray diffraction and scanning electron microscopy.

2.4. X-ray Diffraction and Scanning Electron Microscopy Analyses

X-Ray Diffraction (XRD) patterns were recorded on Siemens-Brucker D5000 equipment, with copper X-Ray source (154.06 pm), Soller slides, a secondary monochromator for powder and thin films. To analyze our thin films, it was necessary to use a grazing-incidence X-ray configuration for films, with an X-ray beam irradiating the thin film plane with a fixed angle of 0.5 degree, a 2 step of 0.05 degree and a counting time of 300 seconds.

Scanning electron microscopy (JEOL JSM- 5500) was used to characterize the surfaces of RuO_2 films deposited on the various substrates and obtained powder.

2.5. Fourier Transform Infrared Spectroscopy (FTIR) and catalysis.

A homemade device coupling a specific reactor with FTIR spectrometer was used to study the catalytic efficiency of these systems [RuO_2 /ferroelectrics/Si] in presence of air-CH_4 mixture [14, 15]. The catalytic efficiency is relative to the proportion of CO_2 (and H_2O) resulting from classical reaction: $CH_4 + O_2 \rightarrow CO_2 + H_2O$. The reactor was constituted of a cylindrical cell in which the sample could be subjected to reactive air-methane flow. The cell was heated in a furnace at temperatures ranging between room temperature and 450°C. Figure 1 represents the reactor. The emitted gases resulting from conversion of methane into CO_2 and H_2O were then led up to a FTIR spectrometer (UNICAM-MATTSON) allowing analyzing the intensity variations of vibration adsorption bands of CH_4, CO_2 and H_2O molecules. The intensities of these bands (surfaces of peaks) were assumed to directly give the conversion rates.

The gas flow-rate was constant (flow rate: 10 cm³/mn; gas composition: 12 700 ppm CH_4 in air). The catalytic conversion was analyzed at various fixed temperatures (T = 100, 200, 250, 300, 350, 400 and 450°C). For a given temperature, Tree FTIR spectra were
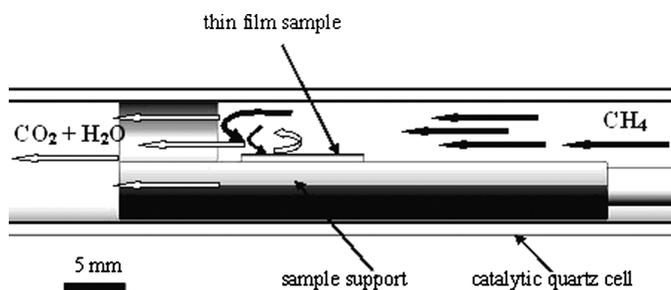

Figure 1. Catalytic cell for gas solid interaction: air methane flow interacting with thin film.

recorded during one hour, in order to observe time dependent fluctuations of conversion. The FTIR records were then statistically treated to give one unique average for each temperature.

3. Results and Discussion

3.1. *Structural and Microstructural Characterizations*

Figure 2 represents the XRD patterns of RuO_2 powder after annealing at various temperatures (450, 475 and 500°C) show that RuO_2 single phase was obtained at 450°C°C but at 500°C the cristallinity is better.

Due to the small amounts of analyzed phases in thin films, XRD data only allowed identification of phases and evaluation of cell parameters. The RuO_2 phase was easily identified in each sample. The BNN phase was observed only as traces because of weak thickness of the BNN layer. The Pt phase was detected. In the case of RuO_2/Pt sample, all phases were clearly identified. We report the XRD pattern of RuO_2/Pt sample on Fig. 3. Bragg peaks of RuO_2, Pt phase of substrate is visible. Despite strong experimental errors due to the analysis, estimated elemental cell parameters were found in good agreement with standard parameters (see introduction) : RuO_2 : a = 451, c = 311 pm ; BNN : a = 1242, b = 1248, c = 398 pm.

A microstructural study was performed by Scanning Electron Microscopy (SEM). Figure 4 (a) show the SEM images obtained for RuO_2 powder after annealing at 450°C. It shows that the RuO_2 grains size was small than 0.5 μm and the morphology was homogenous. Figures 4 b,c show the SEM images obtained for the RuO_2 films deposited on Pt and BNN layers. In sample (b) the surfaces are uniform and a continuous layer of small grains having dimensions ranging between 0.5 and 1 μm is observable. Figure 4c represents the surface of RuO_2/BNN sample: grain dimensions also range from 0.5 to 1 μm, frequent discontinuities having 10 to 30 micron of length are clearly observed.
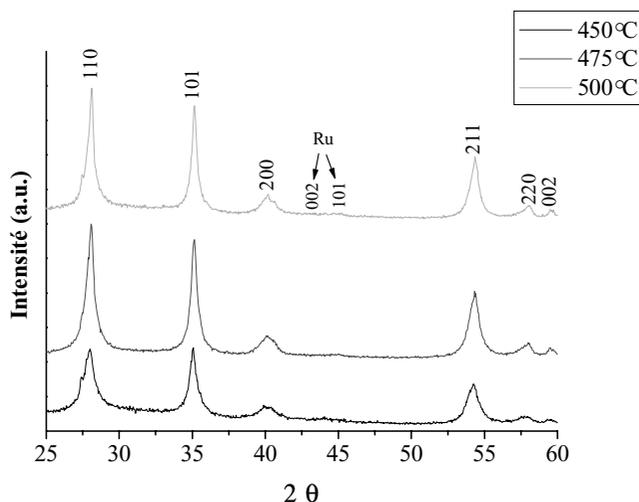

Figure 2. XRD patterns of RuO_2 powder after heating at 450, 475 and 500°C/2 h. (See Color Plate VII)
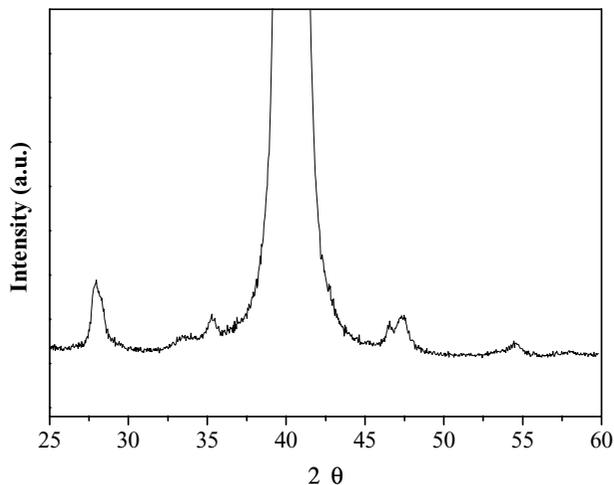
Figure 3. XRD patterns of RuO_2/Pt/substrate after heating at $450°C/2$ h.

3.2. FTIR Analysis of Catalytic Efficiency.

The typical absorption bands of CH_4, CO_2 and H_2O molecules are shown on Fig. 5 a,b, respectively for thermally treated RuO_2 on Pt (4a) and BNN (4b) substrates. The evolution of the CO_2 peak surface can give a relative estimation of conversion rate and catalytic efficiency.
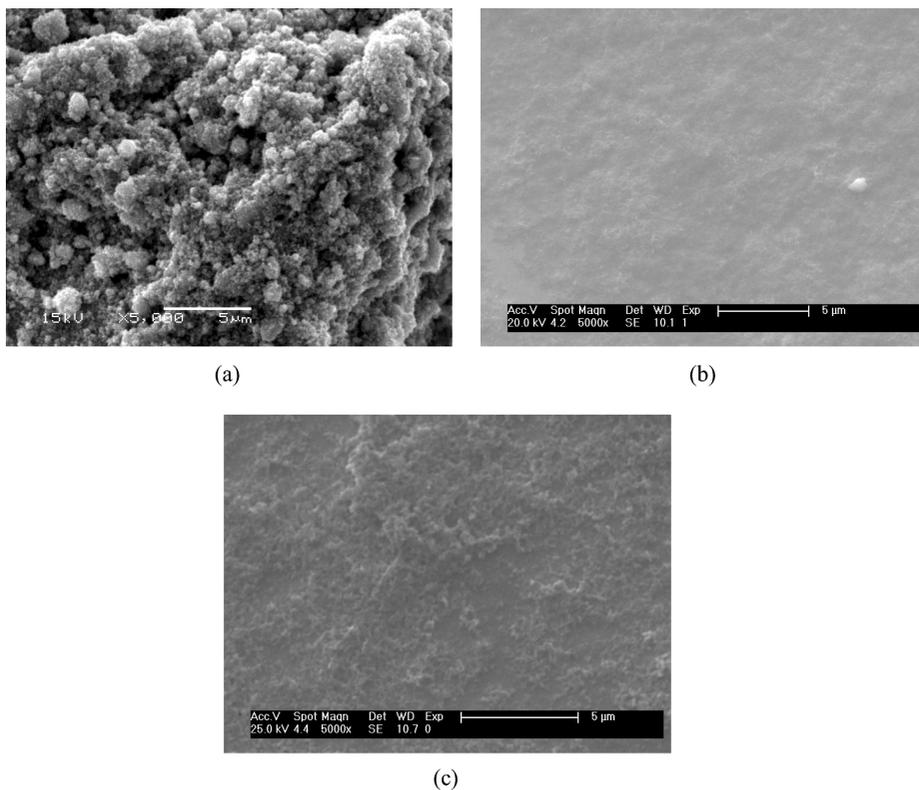

(a)

(b)

(c)

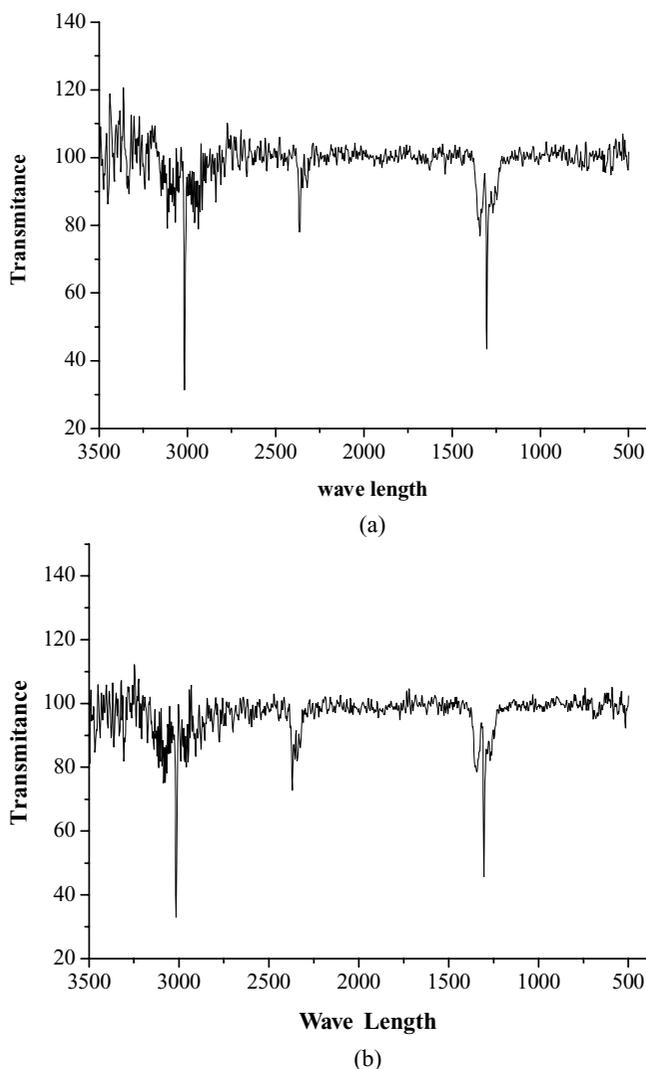**Figure 4.** SEM images of RuO_2 powder (a) and films deposited on Pt (b) and BNN (c).

(a)

(b)

Figure 5. (a). FTIR spectra obtained for RuO₂/Pt sample at 400°C. (b): FTIR spectra obtained for RuO₂/BNN sample at 400°C.

In fact, the ratio CO_2 over CH_4 peaks surfaces should better represent the conversion efficiency. All surface measurements were normalized to the CH_4 band surface. Table 1 reports the numerical values of FTIR CO_2 band intensities due to catalytic conversion by each film, for 7 temperatures 100, 200, 250, 300, 350, 400 and 450°C. These data were obtained after subtracting the residual CO_2 background, systematically observed at low temperatures in such experimental configuration, because of environmental conditions. Figure 6 reports these results. Let us recall that on abscissa (temperature axis), we have reported averaged data for a given temperature. The thermal evolution shows increasing catalytic activation up to an optimal temperature that we established as being close to 400°C for RuO_2 catalyst. At low temperature, no significant conversion occurred, despite the fact that residual environmental CO_2 traces were observed. From 200–250°C, CH_4 conversion

Table 1
Conversion of CH_4 into CO_2: intensity I of CO_2 vibrational
bands from FTIR analyses (in arbitrary units)

Temperature (°C)	I (RuO_2/Pt)	I (RuO_2/BNN)
100	0	0
200	0.901	0.122
250	0.156	0.427
300	0.702	0.732
350	0.975	1.281
400	2.535	3.355
450	2.613	3.721

into CO_2 started. Above 400°C, catalytic efficiency was not improved in a significant way. The experiment at 450°C shows that catalytic activation reached a limit.

The observed thermal evolution of catalytic activity can be interpreted in terms of elemental Arrhenius model as follows: I $(CO_2) = A . \exp(-E/RT)$, where E is activation energy of catalytic mechanism for each sample. As a first approximation, we have obtained, for the Pt and BNN based samples, the following activation energies in $J.mol^{-1}$: 43 295, 39190. In other terms, we observe a decreasing energetic barrier respectively for Pt and BNN based multilayers, which agrees well with a better capacity of BNN based samples to convert CH_4 into CO_2.

The main difficulty of such measurements resides in the fact that our system presents some fluctuations in flow rate, in catalytic interactions between gas and film, mainly because of gas convection occurring in the reactor cell. Other fluctuations might be caused by gas circulation in the spectrometer, and during evacuation of this gas out of the spectrometer.
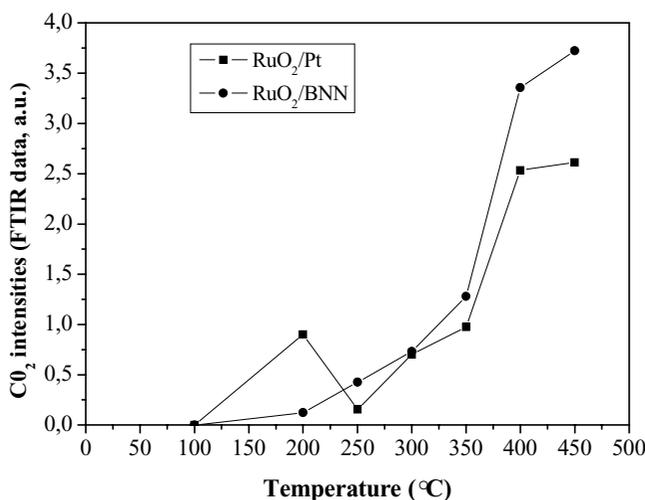

Figure 6. Catalytic efficiency of RuO_2 films from FTIR data. CO_2 intensities of adsorption bands. Each data is obtained from statistical analysis if CO_2 intensity during one hour at a fixed temperature.

It is the reason why FTIR data were recorded during delays of one hour for each fixed temperature. Finally, the general relative incertitude on I/I_0 values was estimated to be close to $\Delta \ln I/I_0 = 0.10$ at $400°C$. This incertitude increases with decreasing catalytic temperature ($I(CO_2)$ decreases). Despite these experimental incertitudes, we might admit that the catalytic efficiency of RuO_2/BNN samples was higher than that of the two other samples.

These differences in catalytic behaviors might be interpreted in terms of surface roughness of RuO_2 film. In the case of Pt substrate, a good adhesion of initial RuO_2 precursor on Pt film should have allowed a homogeneous growth of RuO_2 film, giving rise to a relatively smooth surface, which is not in favor of optimal catalysis. In the case of BNN substrate, the deposition process was fully different (RF sputtering), and probably because of nature of BNN surface, adhesion of initial precursor film should have been insufficient, and cracks were generated during crystal growth and thermal treatment.

4. Conclusion

In the present work, catalytic multilayers involving RuO_2 catalyst deposited on ferroelectric films were successfully synthesized. The various phases constituting catalyst and ferroelectrics were unambiguously identified from X-ray diffraction. SEM analyses allowed characterizing the surface qualities. Making use of a homemade device, FTIR analyses of CH_4/RuO_2 catalytic interactions under air-methane flows were performed at variable temperatures up to $450°C$. The RuO_2/BNN multilayers presented interesting catalytic efficiencies that appeared as being significantly improved in comparison with that of the RuO_2/Pt multilayer. These differences in catalytic activities might be due first to the two different deposition processes of ferroelectric layers, and secondly to the nature of adhesion between each Pt or BNN film and the RuO_2 layer. The observed performances of RuO_2/BNN multilayer might be connected with the existence of cracks, or with increased specific surface. Now, electrical measurements are planned in order to test these catalytic-ferroelectric multilayers and to better understand the influence of ferroelectric undercoating on catalytic responses.

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