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Core-level electronic properties of nanostructured NiO coatings

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Abstract

Nanostructured NiO films with different thicknesses were grown on nanoporous alumina membrane substrates by reactive evaporation of Ni in an oxygen atmosphere. The reactive deposition process was assisted by a low energy oxygen ion-beam in order to increase the NiO input into the pores. Surface morphology and structure of the films were analyzed by SEM and XPS. SEM observations reveal a well adhered film of NiO on the substrate. This film appears to be uniform and presents a rather irregular nanostructured morphology, built of NiO clusters with sizes ranging between 5 and 30 nm. The core-level electronic properties of this nanostructured NiO film result to be similar to those of an ultrathin film about one monolayer thick. This behaviour can be explained by the large surface to volume ratio of both systems.

Keywords: Alumina membrane substrates; Core-level electronic properties; NiO films

1. Introduction

One of the effects of growing porous materials at the nanoscale is that the effective surface is dramatically increased. This is especially important in applications that involve an interaction between gases or liquids and the material surface, like in catalysis, gas sensing devices, or electrochemical devices [1–4]. Recent advances in nanotechnology have enabled the fabrication of nanostructured materials by deposition onto nanostructured templates of the material of interest. Since the development of anodic alumina membranes with highly ordered nanopores by Masuda and Fukuda [5], many efforts have been devoted to functionalize these membranes by introducing materials into the pores, both by physical [6,7] and chemical methods [8,9]. This kind of approach can lead to nanostructured materials with high surface to volume rate [10].

Transition metal oxides are very interesting materials, both from the fundamental and technological points of view. In particular, NiO has remarkable catalytic and magnetic properties, as well as a good sensitivity in gas sensing applications [11–14]. On the other hand, we have recently reported on changes in the electronic properties of nanostructured NiO with respect to macroscopic NiO, which are directly associated with its large surface to volume ratio [15]. These changes could help to explain the larger activity of NiO in catalytic applications when it is nanostructured.

In this work, we report on the growth of nanostructured NiO on nanoporous alumina membranes by ion-beam assisted thermal evaporation of Ni. The reason to use ion-beam assistance was to optimize the material input into the pores. NiO coatings with nominal thickness between one-monolayer and 20 nm were grown and characterized by XPS and SEM. Additionally, some NiO coatings grown without ion-beam assistance were also analyzed for comparison.

2. Experimental

Nanoporous alumina membranes with a thickness of 0.5 μm have been grown by anodic oxidation of aluminum in oxalic acid, as reported elsewhere [16]. The pore diameter and the distance between pores were approximately 35 nm and 100 nm, respectively. Nickel was then thermally evaporated on these templates at room temperature in a partial oxygen atmosphere of 1×10^{-5} mbar. Under these experimental conditions, the growth

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rate of NiO was, approximately, 0.1 Å/min. With the aim of optimizing the material input into the pores, ion beam assistance was used. A low energy (100 eV) ionic oxygen beam was directed onto the substrate at an angle normal to the surface. The ionic current on the sample was approximately 1 μA.

Surface morphology and electronic properties of the films were analyzed by SEM and XPS, respectively. XPS measurements were carried out in a conventional surface analysis chamber equipped with a Mg-anode X-ray source, and a VG-CLAM4 hemispherical electron analyzer. The base pressure in the analysis chamber was in the 10^{-10} mbar range. The morphology of the film was observed using a field emission scanning electron microscopy (JEOL JSM6500f).

3. Results and discussion

In Fig. 1 we show Ni-2p XPS spectra of NiO coatings with different thickness. Fig. 1a corresponds to bulk, polycrystalline NiO and is included as a reference. As it can be seen, the photoemission spectral line shape of Ni-2p states in NiO is rather complex. The spectrum can be divided in two regions that correspond to the spin orbit splitting into $2p_{1/2}$ and $2p_{3/2}$ final states. We will focus on the $2p_{3/2}$ states, between 850 and 870 eV. Assuming a description of this system in terms of a charge transfer insulator, the spectrum reflects the three possible final states: the main peak, at ~855 eV, assigned to $\underline{c}3d^9\underline{L}$ final states, (where $\underline{c}$ means a hole in the core, and $\underline{L}$ means a hole in the ligand, i.e., in the oxygen ions), a second, broad peak, at ~863 eV, assigned $\underline{c}3d^{10}\underline{L}^2$ final states, and a third peak, much weaker, at ~867 eV, assigned to $\underline{c}3d^8$ final states [17–19]. The origin of the satellite observed at 1.5 eV from the main peak is more controversial. Traditionally, it has been explained in terms of non-local screening effects, originated in second oxygen neighboring ions [20], but a very recent experimental and theoretical study shows clear evidences that point towards strong surface effects associated with this satellite [21]. Both main peak and satellite will be taken as a characteristic of bulk NiO. The vertical dashed lines in Fig. 1 are plotted to serve as an eye-guide to compare these two features among all spectra shown in the figure.

Fig. 1b shows a Ni-2p XPS spectrum of a very thin coating (of the order of one monolayer) of NiO on an Al_2O_3 substrate. As it can be seen, all features remain approximately constant with respect to the spectrum of bulk NiO, except the main peak and its satellite. In this case, the double peak observed in Fig. 1a transforms into an asymmetric single peak at the energy position of the satellite. The fact that the rest of the spectrum remains the same as that of bulk NiO, as well as previous experimental evidences on NiO monolayers grown by the same method [15], allow us to discard non-stochiometric NiO

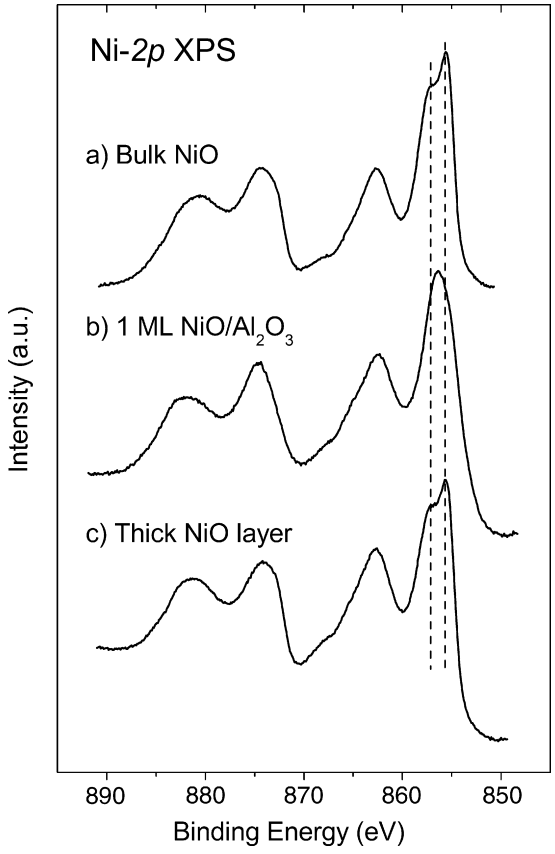

Fig. 1. Ni-2p XPS spectra of (a) polycristalline bulk NiO (b) one equivalent monolayer of NiO grown on an alumina substrate, and (c) a thick NiO layer grown on the same substrate. Both samples (b) and (c) were grown without ion beam assistance.

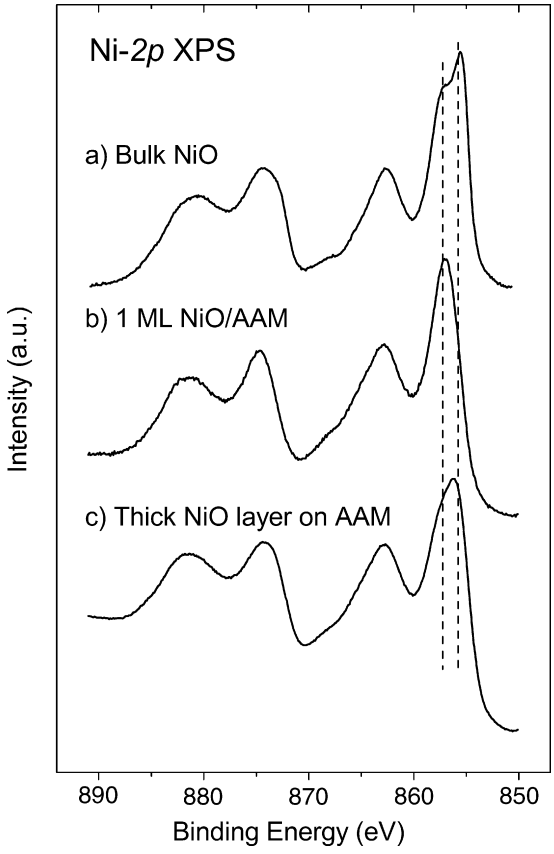

Fig. 2. Ni-2p XPS spectra of (a) polycristalline bulk NiO (b) one equivalent monolayer of NiO grown on an anodic alumina membrane, and (c) a thick NiO layer grown on the same substrate. Both samples (b) and (c) were grown with ion beam assistance.

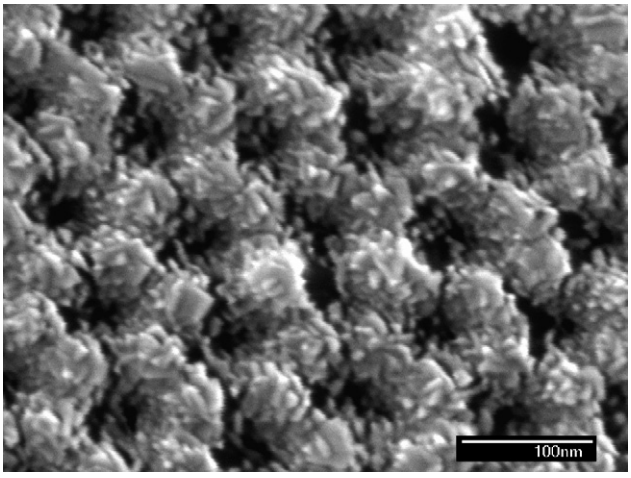

Fig. 3. SEM image of a thick NiO layer grown on an anodic alumina membrane with ion beam assistance. The equivalent thickness of the NiO film is 20 nm. The acceleration voltage of the electrons was 15 kV.

growth, and to conclude that the Ni cations of the NiO monolayer are in the form of high-spin Ni^{2+}. Fig. 1c shows the Ni-2p XPS spectrum of a thicker NiO layer (∼6 nm thick) on the same substrate as that of Fig. 1b. In this case the original double peak observed in Fig. 1a is again present. One can conclude that the anomalous line shape observed in Fig. 1b is associated with the low coverage, whereas for larger coverages the line shape evolves towards that of bulk NiO.

In Fig. 2a we again show the Ni-2p spectrum of bulk NiO as a reference. Fig. 2b and c correspond to a NiO monolayer and a thicker NiO coating, respectively, deposited on an alumina anodic membrane (AAM). The parameters for NiO deposition were the same as those of Fig. 1, but in this case, ion beam assistance was used, as described in Section 2. The spectrum for the NiO monolayer is very similar to that of Fig. 1b; a single peak is observed, at the same energy position as the satellite. In this case of an alumina nanoporous membrane substrate, however, the peak width is slightly smaller. The situation for the thicker layer with respect to the former case is completely different. Instead of an evolution of the spectral line shape towards that of bulk NiO, a single asymmetric peak is observed, with an energy position between those of the main peak and the satellite in bulk NiO. From this picture it seems clear that when using AAM as substrates and ion beam assistance, the thicker NiO layer does not have the same electronic properties as bulk NiO. Rather, the spectrum of Fig. 2c can be seen as a mixture between low-dimensional NiO and bulk NiO.

To put more light and try to explain the anomalous spectral behaviour of ion assisted NiO grown on AAM, the structure and morphology of these films were observed by SEM. Fig. 3 shows a SEM image, taken with an accelerating voltage of 15 keV, of a NiO film grown with ion beam assistance on a nanoporous alumina membrane. Although the film has a nominal thickness of 20 nm, the rather irregular morphology of the film appreciated in the figure suggests to take this value just as an equivalent thickness, i.e., as the amount of NiO equivalent to a continuous film 20 nm thick. As it can be seen in Fig. 3, NiO grows as nanometric whiskers and flakes both at the walls and inside the pores of the alumina membranes. The typical shape of the observed nanostructures is oblong, approximately 5–10 nm wide and 15–30 nm long. This nanostructured mode of growing NiO is probably the result of using ion beam assistance during growth. Also the fact that the substrate is nanostructured might have an influence on the final result. One can correlate the morphology of the NiO film observed in Fig. 3 with the spectrum shown in Fig. 2c. In that case, the spectral shape of a thick, nanostructured NiO layer resembled that of a NiO monolayer. A single NiO monolayer has an enhanced surface to volume ratio, as compared with bulk NiO. On the other hand, a nanostructured morphology, as that shown in Fig. 3, can also be regarded as a system with enhanced surface to volume ratio.

4. Conclusions

We were able to grow nanostructured NiO on nanoporous alumina membranes by ion-beam assisted reactive thermal evaporation of Ni. The morphology of the NiO films grown in this way consists of tiny whiskers and flakes with oblong shape, and typical dimensions of 5 nm × 20 nm. The core-level electronic properties of these nanostructured NiO film grown with ion-beam assistance are different to those of bulk NiO, and resemble those of an ultrathin (∼1 nm) standard NiO film. The differences of these nanostructured NiO systems could be related to their high surface to volume rate.

References

[1] C.J. Martínez, B. Hockey, C.B. Montgomery, S. Semancik, Langmuir 21 (2005) 7937.
[2] A.A. Tomchenko, G.P. Harmer, B.T. Marquis, Sens. Actuators B: Chem. 1080 (2005) 41.
[3] G. Sedmak, S. Hocevar, J. Levec, J. Catal. 222 (2004) 87.
[4] W.Y. Li, L.N. Xu, J. Chen, Adv. Funct. Mater. 15 (2005) 851.
[5] H. Masuda, K. Fukuda, Science 268 (1995) 1466.
[6] S.M. Park, C.H. Bae, W. Nam, S.C. Park, J.S. Ha, Appl. Phys. Lett. 86 (2005) 023104.
[7] E.D. Mishina, V.I. Stadnichuk, A.S. Sigov, Y.I. Golovko, V.M. Muckhorotov, S. Nakabayashi, H. Masuda, D. Hashizume, A. Nakao, Physica E 25 (2004) 35.
[8] Y. Li, W. Meng, L.D. Zhang, F. Phillipp, Appl. Phys. Lett. 76 (2000) 2011.
[9] J. Oh, Y. Tak, J. Lee, Electrochem. Solid State Lett. 7 (2004) C27.
[10] M. Harada, F. Matsumoto, K. Nishio, H. Masuda, Electrochem. Solid State Lett. 8 (2005) E27.
[11] R. de Masi, D. Reinicke, F. Müller, P. Steiner, S. Hüfner, Surf. Sci. 516 (2002) L515.
[12] I. Hotovy, J. Huran, P. Siciliano, S. Capone, L. Spiess, V. Rehacek, Sens. Actuators B: Chem. 103 (2004) 300.
[13] W. Shin, M. Matsumiya, F. Qiu, N. Izu, N. Murayama, Sens. Actuators B: Chem. 97 (2004) 344.
[14] C.-B. Wang, G.-Y. Gau, S.-J. Gau, C.-W. Tang, J.-L. Bi, Catal. Lett. 101 (2005) 241.
[15] L. Soriano, A. Gutiérrez, I. Preda, S. Palacín, J.M. Sanz, M. Abbate, J.F. Trigo, A. Vollmer, P.R. Bressler, Phys. Rev. B 74 (2006) 193402.
[16] M. Hernández-Velez, Thin Solid Films 495 (2006) 51.
[17] A. Fujimori, F. Minami, S. Sugano, Phys. Rev. B 29 (1984) 5225.
[18] G.A. Sawatzky, J.W. Allen, Phys. Rev. Lett. 53 (1984) 2339.
[19] S. Hüfner, Solid State Commun. 52 (1984) 793.
[20] M.A. van Veenendaal, G.A. Sawatzky, Phys. Rev. Lett. 70 (1993) 2459.
[21] L. Soriano, A. Gutiérrez, I. Preda, S. Palacín, M. Abbate, A. Vollmer, Phys. Rev. B 75 (2007) 233417.