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Study of the morphology of NiO nanostructures grown on highly ordered pyrolytic graphite, by the Tougaard method and atomic force microscopy: a comparative study[†]

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We studied the morphology of the deposits of NiO grown on highly ordered pyrolytic graphite (HOPG), by means of inelastic peak shape analysis and atomic force microscopy. The results obtained by both techniques show an excellent agreement. The results indicate that NiO grows on HOPG by following the Stransky–Krastanov type of growth. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: NiO/HOPG; AFM; XPS quantitative

Introduction

The main purpose of this work is to study the morphology of the deposits of NiO grown on highly ordered pyrolytic graphite (HOPG). To achieve this, we have performed a comparative study by using two different techniques. One is an indirect technique based on the analysis of the inelastic peak shape of photoemission and Auger spectra and is known as Tougaard method.[1,2] This technique is specially suited for the study of the morphology of the deposits of materials grown *in situ* in systems, where no probe microscopes are available. The other technique is atomic force microscopy (AFM) that can give direct quantitative information on the topography of the surface of the film. Oxide thin films have become key materials in many technological applications such as catalysis, magnetic supports, materials with unique mechanical and thermal properties, sensors, etc. In all these applications, the control of the growth of thin films is of extreme importance. In particular, the knowledge of the mechanisms influencing the growth at the interface could lead to the control of the final properties of the thin film.

NiO is a very interesting material whose electronic structure has been controversial for years. Its complex electronic configuration gives rise to unusual properties making it a catalytic and antiferromagnetic material. We have already studied the growth of NiO on HOPG by AFM.[3] Preliminary results showed that NiO grows on graphite by forming interesting small nanostructures at the early stages of growth; however, the Ni 2p x-ray photoemission spectra (XPS) of these stages showed a strange shape similar to that shown by 3–5 nm NiO nanoparticles with extraordinary catalytic and magnetic properties studied elsewhere.[4] This motivated us to perform a detailed quantitative analysis of the morphology of the deposits of NiO during the growth process.

In spite of the impact of oxide thin films in current technologies, studies on oxide/metal and oxide/oxide interfaces have been scarce in the literature until the early 1990s when several studies focused on oxide surfaces.[5–8] In these studies, the authors suggested the growth of thin oxide films on conductive supports in order to avoid charging problems during the characterization of the oxide layers. Since then, many studies on oxide thin films have been carried out using different characterization techniques.[9] The growth of NiO on different supports has been extensively studied, but most of these studies are mainly related to the preparation of supported catalysts. In particular, the growth of thin NiO films on Cu (100)[10] and MgO[11–15] has been studied in more detail. It has been found that whereas NiO grows by following a Stranski–Krastanov growth mode on Cu (100), it grows epitaxially on the MgO (001) and (100) substrates. Structural studies show that, initially, the overlayer NiO lattice grows coherently on MgO until a critical thickness of 60 nm is reached, at which relaxation of the NiO lattice occurs.[14] Also, a comparative study of the growth

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of NiO on a selected set of oxides (SiO_2, Al_2O_3 and MgO) has been performed by us.[16] In this study, interface effects have been observed as a consequence of the relative covalent character of the substrate. The formation of cross-linking bonds Ni–O–M (M = Si, Al, Mg) at the interface has been suggested.

In this study, we have found an excellent agreement between the results obtained in both the techniques.

Experimental

Clean surfaces of HOPG were prepared by cleavage in air before being inserted in a ultra high vacuum (UHV) system, with a base pressure of 5×10^{-9} mbar, where the NiO deposition was performed. NiO was grown by reactive thermal evaporation of Ni at room temperature in an oxygen atmosphere of 1×10^{-5} mbar. Ni evaporation was performed by resistive heating of a W wire surrounded by a Ni filament. In order to enhance the oxygen local pressure at the surroundings of the substrate, oxygen of 99.995% purity was introduced through a metal tube directed to the sample. The evaporation rate was kept constant and low enough to allow the study of the early stages of growth in detail. The samples were prepared according to progressive evaporation time to obtain different coverages along with the growth process. Once the samples were prepared and characterized by XPS, they were taken out of vacuum in order to proceed with the AFM measurements in air.

The XPS measurements were performed using a CLAM4 electron energy analyzer and a Mg K_α x-ray source from Thermo-Scientific. The pass energy was set to 20 eV. The survey and core level spectra from the NiO deposits have been measured for chemical and quantitative analysis. AFM images were measured in dynamic mode (tapping) using Nanotec's microscope and software.[17]

Results and Discussion

Inelastic peak shape analysis

The Ni 2p and Ni LVV Auger energy regions of the XPS spectra of the different stages of growth analyzed are shown in Fig. 1. It can be clearly seen that the background at lower kinetic energies from the main peaks varies according to the amount of the deposited material. It can be seen from the spectra shown in Fig. 1 that not only the background of the spectra progressively changes as a function of the deposited material but also the line-shape of both series of spectra changes. Although this is not the subject of this study, this effect can be explained in terms of surface effects as reported elsewhere.[18] Both Ni 2p and Ni LVV Auger energy regions were submitted to inelastic peak shape analysis using the well known QUASES software.[2] We have used the inelastic mean free paths (IMFP) for NiO, as given by the Tanuma–Penn and Powell formula,[19] as 9.21 Å for the Ni 2p XPS spectra and 15.35 Å for the Ni LVV Auger spectra.

Te results obtained in the above analysis are depicted in Fig.2 where the height of the islands of the NiO deposits is represented as a function of the graphite surface coverage. Dashed lines represent the amount of equivalent material deposited on the substrate in monolayers (ML). It is clearly seen that there is a good agreement of the results obtained with both, Ni 2p and Ni LVV Auger energy regions. Since the IMFPs of these energy regions are significantly different, this agreement gives consistency to the calculations. Figure 2 shows that the growth of NiO on the graphite substrates is through the Stransky–Krastanov-like mode, i.e. growth of small islands of a determined height at the early stages of growth. For coverages of about 1 ML of equivalent material, only 10% of the surface has been covered forming the NiO deposits of islands of about 2–3 nm in height. Further evaporation produces a progressive slight increase of the islands' height up to about 4 nm, covering approximately 50% of the substrate surface at this stage. Finally, evaporation of more material produces a rapid increase of the island height, having the island heights of 10 nm when the substrate has been covered about 80% of its surface. An important parameter for this type of way of growth is to determine the thickness at which coalescence, i.e. complete coverage of the substrate surface, is reached. In this case, coalescence must be produced at a thickness close to the limit of the technique, taking into account the relative short IMFP of the photoelectrons of the Ni 2p states.

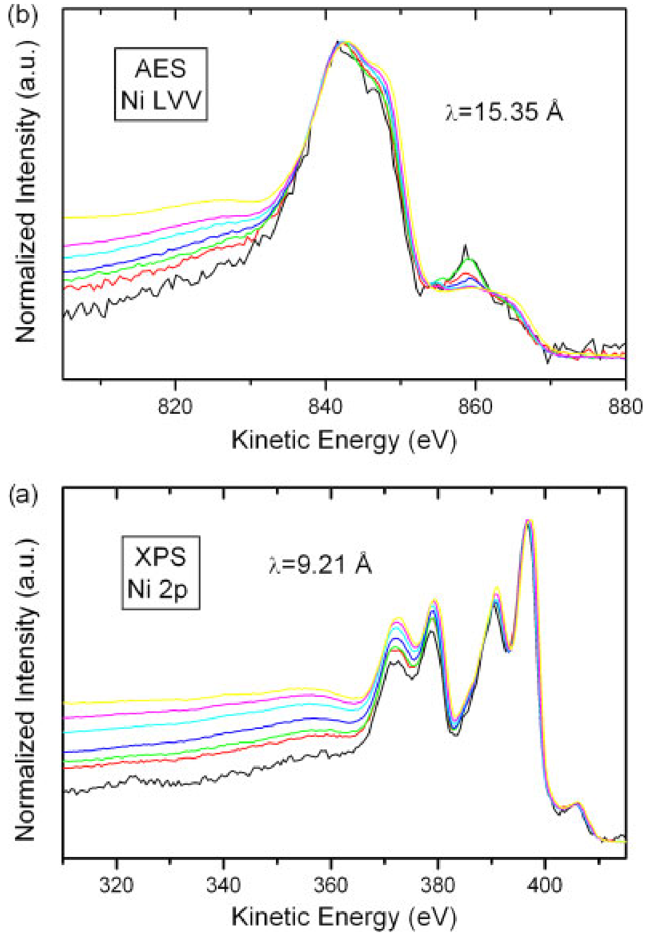


Figure 1. (a) Ni 2p and (b) Ni LVV energy regions of the XPS spectra used for the inelastic peak shape analysis. The background at the higher kinetic energy side of the regions has been set to zero.

Atomic force microscopy

It is well known that AFM can provide direct images of the topography of the sample. However, one of the most difficult problems in this type of microscopy is to know the effect of the tip on the sample, especially for wet materials and weakly bounded deposits. To avoid this problem, new measurement techniques in AFM have been developed to prevent the contact of the tip

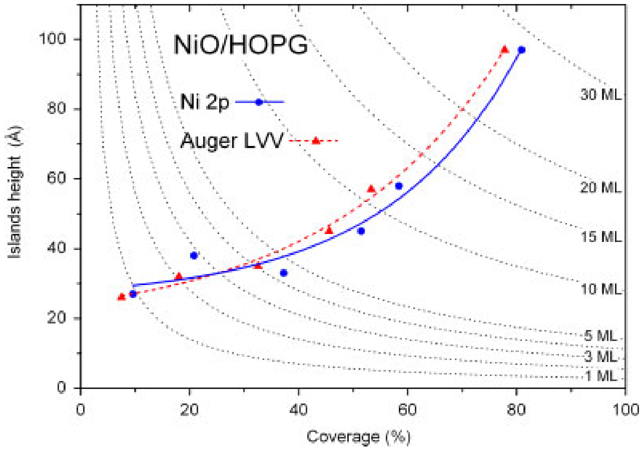


Figure 2. Results of the inelastic peak shape analysis. Dashed lines represent the amount of equivalent NiO material.

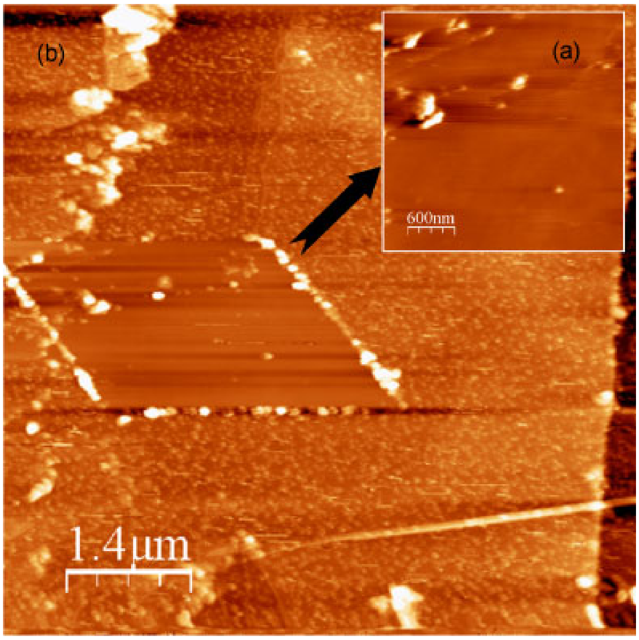


Figure 3. Tip effect on the contact imaging mode of NiO on HOPG. The 7 × 7 µm^2 AFM image measured in noncontact (dynamic) mode image of 0.8 Å of NiO/HOPG; (inset) the 3 × 3 µm^2 AFM image measured in contact mode.

with the sample. This study is a very clear case in which the weak interaction of the deposits with the graphite substrate makes these measurements very difficult to perform. As an example, in Fig. 3, a 7 × 7 µm^2 AFM image taken in dynamic (tapping) mode of NiO deposits on the HOPG substrate is shown. This sample had been previously measured in contact mode with an area of 3 × 3 µm^2, as it is clearly observed in the AFM image. The NiO deposits have been swept by the tip during the measurement of the contact mode image. This makes the deposits to accumulate at the end of the scanned area and at the steps, keeping the HOPG terraces free of deposits, as it is seen in the inset of Fig. 3.

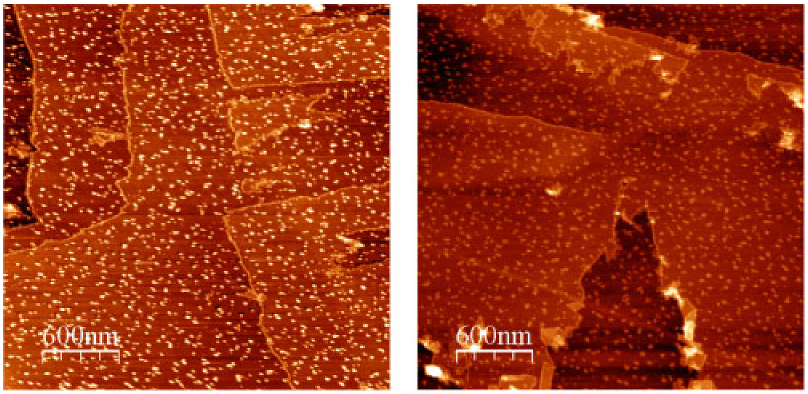
According to the previous results, all images presented below have been taken in dynamic mode (tapping) and using small amplitudes since large oscillating amplitudes also produced the displacement of the deposits throughout the substrate surface.

The 3 × 3 µm^2 AFM images corresponding to six different stages of growth of NiO on the graphite substrate are presented in Fig. 4. The equivalent thickness of the NiO deposits at these stages, as given by the QUASES software, is also indicated in each image. The images were submitted to profiling and flood analysis using Nanotec's software.[17] It is worthy to note that images of the clean HOPG substrate (not shown) showed steps of heights between two and ten graphite planes (7–33.5 Å). Fig. 4(a) shows the image corresponding to the very early stage of growth of an equivalent thickness of 0.7 Å of NiO. It is seen that the NiO deposits form nucleation centers which are spread throughout the graphite terraces and also fill the steps. Flooding analysis of this stage gives values of 5.1% of the graphite surface covered with NiO islands of to a height of 1.4 nm. The lateral size of the NiO nanostructures is about 25 nm. For an equivalent thickness of 1.7 Å, the image shown in Fig. 4(b) is rather similar to that of the previous stage, although the width of the islands has increased slightly. In this case the flood analysis gives values of 10.3% for the area covered by islands with averaged height of 1.6 and 40 nm in lateral size. At this stage all steps appear to be completely filled with NiO islands. Figure 4(c) shows the image corresponding to an equivalent thickness of 18 Å of NiO. The islands have now increased both their height and lateral sizes being 6 nm in height and about 80 nm in lateral size. In fact, these islands consist of aggregation of several nucleation centers as those obtained in the first stages, forming bunch-like islands. They cover up to 55% of the graphite surface. The image corresponding to the next stage studied is shown in Fig. 4(d) and corresponds to an equivalent NiO thickness of 35 Å. The image clearly shows that the bunch-like islands are formed by aggregation of new nucleation centers and their lateral size has increased with respect to that of the previous stage. However, coalescence has not been produced yet since the graphite substrate has been detected in the AFM images. Flood analysis of the image gives a lateral size of 90–100 nm covering 70% of the substrate surface. Profiling analysis of this stage could determine the islands' height with respect to the graphite substrate as 7 nm. The AFM image corresponding to the next stage analyzed is shown in 4(e) and it corresponds to an equivalent thickness of 60 Å. It is clearly seen that coalescence has already been produced although the NiO layer is not homogeneous yet. The image in Fig. 4(f) shows that at this stage a homogeneous NiO thin film of an equivalent thickness of 400 Å has been obtained.

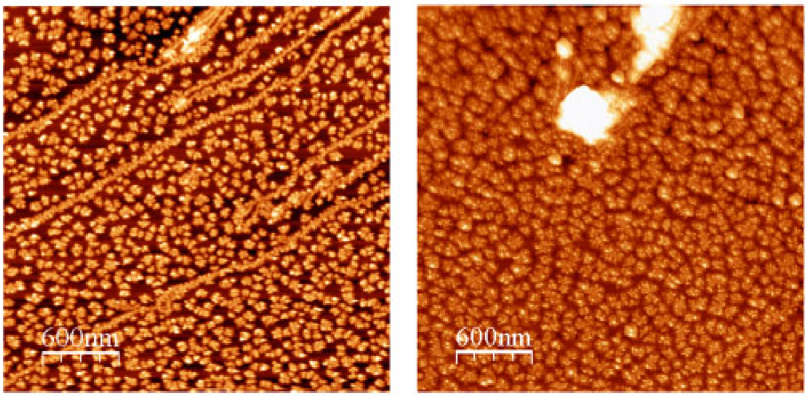
Comparison of AFM *versus* inelastic peak shape analysis

To compare the results obtained with both techniques, they have been depicted in Fig. 5 in terms of the islands' height *versus* coverage curves. The agreement is excellent since both techniques predict the same behavior of the way of growth and give similar values. However, for very small coverages it is observed that the intensities predicted by inelastic peak shape analysis are slightly larger than those obtained by AFM topography images. This small discrepancy can be due to the difference in height of the islands grown at certain steps with respect to those grown at the terraces, being higher those grown at the steps formed by many graphite planes.

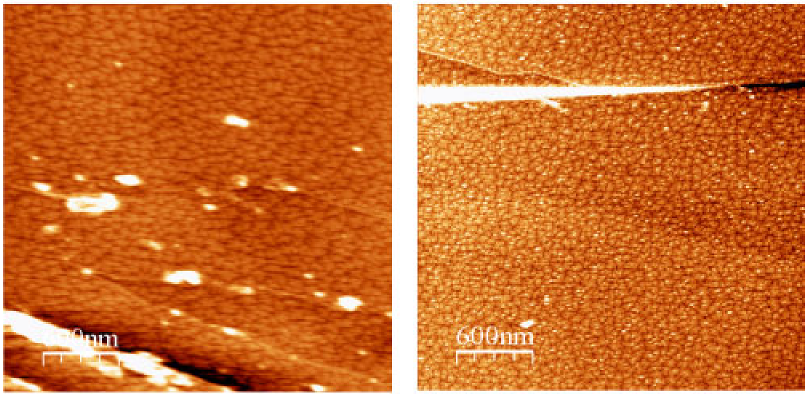
On the other hand, inelastic peak shape analysis has not been able to detect coalescence, whereas AFM detects it for an equivalent thickness of approx. 30 ML. One possible reason for this disagreement is that, although our AFM analysis has been performed on several images obtained from different regions of the substrate surface at the same stage, small



(a) *0.8 Å of NiO on HOPG* (b) *1.7 Å of NiO on HOPG*



(c) *18 Å of NiO on HOPG* (d) *35 Å of NiO on HOPG*



(e) *60 Å of NiO on HOPG* (f) *400 Å of NiO on HOPG*

Figure 4. $3 \times 3\ \mu m^2$ AFM images of various stages (as labeled) of the NiO growth on HOPG.

nonexplored uncovered regions might exist. This would result in an overestimation of the coverage obtained by AFM.

Conclusions

We found an excellent agreement between both inelastic peak shape analysis and AFM in the determination of the way of growth of NiO on HOPG. From the values obtained from these two techniques we can conclude that NiO grows on HOPG by following the Stransky–Krastanov-like mode of growth. The nucleation centers spread through the graphite terraces and steps forming nanometric islands. These islands consist of small bunches of the former nucleation centers which keep on rapidly growing in lateral size, whereas their height increases slowly. The graphite steps are rapidly filled while the islands on the terraces keep on growing. Coalescence seems to be produced when the NiO film reaches a thickness of about 6 nm.

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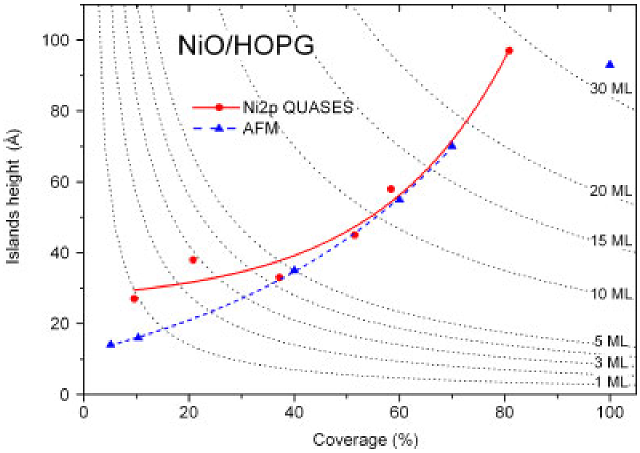

Figure 5. Comparison of the values obtained in inelastic peak shape analysis and AFM methods.

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