

Oxygen plasma preparation of nickel oxide layers[†]

N. Bellakhal^{a,b} and J. L. Brisset^{b*}

a Département de Chimie et de Biologie Appliquées, Institut National des Sciences Appliquées et de Technologie (INSAT), B.P.N°676, 1080 Tunis Cedex, Tunisie

b Laboratoire d'Electrochimie (LEICA), UFR des Sciences et Techniques de Rouen, F-76821 Mont Saint Aignan Cedex, France

Nickel oxide thin films form and grow when Nickel foils are exposed to an inductively coupled low pressure oxygen plasma. The resulting oxide (NiO) is identified by near-grazing X-ray diffraction and by FTIR specular reflectance spectroscopy methods. The thickness of the NiO layer increases with exposure time.

Keywords: oxygen plasma preparation, nickel oxide layers

Introduction

Chemical surface modification of metallic films is typically performed by means of solution based treatments or via electrochemical processes. However, for the last few years, the plasma processes have found increasing application for surface modification. The required processes induced by electric discharges, such as etching, nitriding or deposition, result from poorly understood physical and chemical processes, which occur in the gas phase and at the gas/solid interface. They depend on the energy transfer from the plasma to the metal surface.¹ The chemical reactions between the reactive gas and the material (*i.e.*, oxidation, carbiding and nitriding) lead to an evolution of the material composition. The particles present in an RF oxygen plasma (*i.e.*, excited molecules, atomic oxygen, molecular ions and atomic ions) result from a number of processes, such as ionisation, dissociation by electron impact and attachment phenomena. Previous emission spectroscopy studies² of an oxygen RF plasma show the occurrence of oxygen atoms in the discharge, with a dissociation degree around 10%. There are literature reports on the oxidising properties of oxygen plasmas, and, for example, oxygen atoms are implied in the plasma treatment of YBaCuO thin films.³ The use of an oxygen plasma to prepare copper and zinc oxides is also widely described.^{2,4,5}

Nickel hydroxide has been a subject of many exhaustive studies because of its application as an electrode material in nickel–cadmium batteries.⁶ On account of its commercial importance, several methods have been developed for the synthesis of nickel hydroxide. It is prepared by electrodeless methods^{7,8} or by chemical synthesis. The latter method involves the slow addition of 0.1M Ni(NO₃)₂ solution to trisodium citrate (one equivalent of trisodium citrate per equivalent of Ni²⁺). KOH (0.1 M) was added in drops with vigorous stirring and the pH was raised⁸ to 11.6. A few hours later, a voluminous floating precipitate formed. Nickel oxide NiO is also prepared by thermal oxidation of nickel foils.⁹

The IR reflectance spectrum of NiO thin (< 0.2 μm) films laid down on metal substrate exhibits a single band at 580 cm⁻¹, which can be attributed to the longitudinal optical mode (LO).⁹ This band is shifted to longer wavenumbers, *e.g.*, from 580 to 620 cm⁻¹, for increased layer thicknesses (0.5 – 1 μm)⁹; NiO is then easily identified⁹ by its transversal optical band (TO) in the range 380–400 cm⁻¹.

The IR spectrum of the chemically synthesised β-Ni(OH)₂ exhibits many peaks. In the OH stretching region (3700–3300

cm⁻¹) β-Ni(OH)₂ shows a sharp peak in agreement with the characteristic of a highly ordered brucite structure which does not permit hydrogen bonding between the hydroxyl groups.¹⁰ At lower frequencies (*i.e.*, in the range 1000–200 cm⁻¹) chemically prepared β-Ni(OH)₂ shows two strong peaks at 530 and 345 cm⁻¹, due to the in-plane and out-of-plane OH deformations respectively, and a peak at 460 cm⁻¹ due to the Ni-O stretch.⁸

In this paper, we focus on the nickel oxide phase. We used the low pressure oxygen RF plasma method to prepare the samples, and FTIR spectroscopy and grazing incidence X-ray diffraction to characterise nickel oxide. An interpretation of the resulting experimental data and the growing of the oxide layer for various exposure times at fixed working conditions is presented in terms of oxide film growth theory.

Materials and experimental procedures

The system used for processing has already been detailed.^{2,4,5,11} Briefly, the nickel target was treated in a quartz tube reactor (10 cm in diameter and 30 cm long) which was connected to an oil diffusion primary pump. The luminescent electric discharge was created by a 13.56 MHz generator, which was inductively coupled to the reactor by a 7-turn coil. The oxygen gas was injected into the reactor at a fixed flow rate (0.25 NI/ min⁻¹) in standard conditions. The sample was positioned normally to the gas flow on a stainless steel quenching head. A thermocouple was used to continuously monitor the sample temperature during exposure to the plasma.

Nickel was supplied as hot-rolled strip of 1 mm thickness (Goodfellow). Its analysis was: Co, 8; Cr, 8; Cu, 10; Fe, 10; Mg, 10; Mn, 10; Si, 8; Ti, 10; C, 70; S, 10 ppm. The samples (≅ 1 cm² surface area) were mechanically polished with different grinding papers (400, 800, 1000 and 1200 grade) rinsed in absolute ethanol and dried immediately with nitrogen gas before being exposed to the oxygen plasma.

The specular infrared spectra were recorded on a Nicolet FTIR 710 (analysed range: 225 to 5000 cm⁻¹, incidence angle: 80°). The X-ray diffraction patterns were recorded at a near grazing incidence (α ~ 5°) with a cobalt anticathode (λκα1 = 0.1789 nm).

Results and discussion

The basic key parameters to vary the plasma treatment conditions are the exposure duration *t*, the injected electric power *P* and the distance between the nickel sample and the first coil (HT). For given distance (*d* = 5 cm), pressure (*p* = 2300 Pa) and electric power (*P* = 1100 W), the oxidation kinetics of nickel sample depends only on the time of exposure which was varied between 15 and 120 minutes. In these working

* To receive any correspondence. E-mail: jean-louis.brisset@univ-rouen.fr

[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

conditions, the samples temperature was 605 K during the oxygen plasma treatment.

Figure 1 reports the spectra of nickel samples treated for 15 min or longer, which were recorded under an incidence angle of 80 degrees. They present two bands near 610 cm^{-1} and 385 cm^{-1} , which are respectively attributed to the longitudinal and transverse optical vibrations of NiO. The positions of these two bands move to higher energies when the treatment time increases (Table 1).

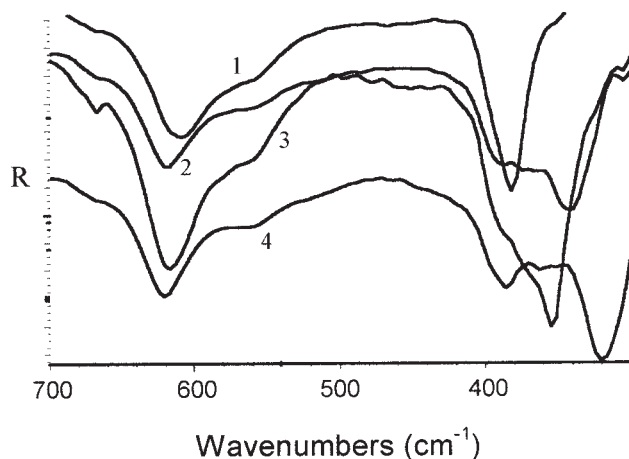


Fig. 1 IR reflectance spectra of nickel oxidised in oxygen plasma. Working conditions ($p = 2300\text{ Pa}$, $P = 1100\text{ W}$, $d = 5\text{ cm}$)

Table 1 The specular reflectance IR bands positions of NiO oxide layers for different exposure time ($P=1100\text{ W}$, $d=5\text{ cm}$, $p=2300\text{ Pa}$).

t (min)	15	30	60	120
LO mode	609	618	617	622
TO mode	382	387*	388*	385*

*Shoulder due to the presence of an interference fringe.

The occurrence of NiO on the metal surface after various oxygen plasma treatments was confirmed by the X-ray diffraction method. All the spectra of the treated samples present three intense peaks at $\theta = 21.79^\circ$, $\theta = 25.37^\circ$ and $\theta = 37.31^\circ$. They respectively correspond to NiO [111], NiO [200] and NiO [220].

The thickness of the oxide film was measured by interferometry. Most of the spectra present extremums, which result from interference phenomena between light and the thin oxide layers. The interference effect was thus used to determine the oxide thickness, which is given by:

$$e = \frac{\lambda_{m+1}\lambda_m}{2n(\lambda_m - \lambda_{m+1})}$$

where λ_m and λ_{m+1} are two successive wavelengths at which the emission spectrum presents an interference maximum; $n = 2.2$ is the refractive index of NiO.⁹ Figure 2 shows that the measured layer thickness e is an increasing function of the exposure time for fixed working parameters.

The reported results show that oxygen RF plasma treatment, which was found to be efficient^{2,4,5} in the case of the

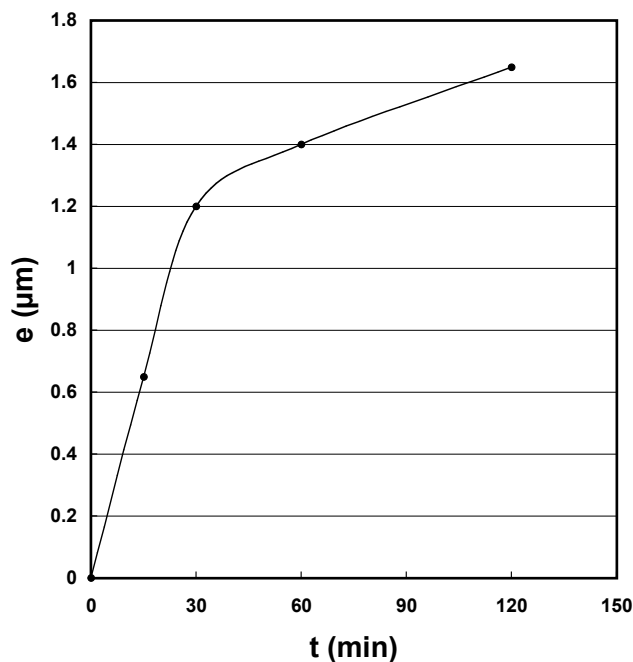


Fig. 2 Variations of the thickness $e(\mu\text{m})$ of the oxide layer with the exposure time $t(\text{min})$. Working conditions ($p = 2300\text{ Pa}$, $P = 1100\text{ W}$, $d = 5\text{ cm}$)

metal copper and zinc, can also be used to prepare nickel oxide on a nickel substrate. NiO was identified by means of FTIR spectroscopy and X-ray diffraction with an excellent agreement with other studies.⁹ The mechanism of oxygen plasma oxidation is complex and remains to be detailed. However, the reaction product, NiO, was identified, as were the basic reagents (*i.e.*, oxygen atoms and ions O and O⁺, through their emission lines²), which are likely involved in the metal oxidation process.

The authors thank Professor Lenglet for help in recording the IR spectra.

Received 18 January 2001, accepted 8 April 2001
Paper 01/711

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