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Oxidation of nickel surfaces by low energy ion bombardment

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ABSTRACT

We have studied formation of oxides on Ni surfaces by low energy oxygen bombardment using X-ray photoemission spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). Different oxidation states of Ni ions have been identified in XPS spectra measured around Ni 2*p* and O 1*s* core-levels. We have compared our results with thermal oxidation of Ni and shown that ion bombardment is more efficient in creating thin oxide films on Ni surfaces. The dominant Ni-oxide in both oxidation processes is NiO (Ni^{2+} oxidation state), while some Ni_2O_3 contributions (Ni^{3+} oxidation state) are still present in all oxidised samples. The oxide thickness of bombarded Ni samples, as determined by SIMS, was shown to be related to the penetration depth of oxygen ions in Ni.

1. Introduction

Nickel oxide (NiO), as a p-type semiconductor, is used in a wide range of applications, from electrochromic devices or chemical sensors to antiferromagnetic layers in spin valve structures, due to its excellent durability and chemical stability as well as favourable optical, electrical, and magnetic properties [1–3]. The quality of final devices depends critically on the electrical properties of NiO films, thus it is important to fully understand the oxidation mechanisms of nickel that seem to be quite complex [4].

Thin NiO films have been grown using many different methods, including sputtering, vacuum evaporation, electron beam evaporation, spray pyrolysis, chemical deposition, sol–gel processes or electrochemical methods [5]. However, in most of these techniques, it is difficult to control the amount of oxidation, while relatively high temperatures are required for an efficient oxidation process. The low-energy oxygen implantation may represent an alternative method for thin oxide-film formation on Ni surfaces. It has been shown previously that ion-bombardment represent an attractive and feasible alternative for oxidation of different metallic and semiconductor surfaces with controlled amount of oxidation and oxide thickness, even at room temperature (RT) [6–9]. Indeed, in our previous study, we have shown that oxygen bombardment is more efficient in creating thin NiO films on Ni surfaces than oxidation by electrochemical methods [6]. In the present paper, we provide a detailed characterisation of nickel oxidation by low-energy oxygen ion bombardment at low temperatures using X-ray photoemission spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). In addition, we show some results of thermal oxidation of Ni in order to compare thermal with ion-induced oxidation processes.

2. Experimental

The 1 mm-thick nickel foil (Alfa Aesar, 99.945 wt.% Ni) was abraded with SiC papers of 800–1200 grit and was cleaned with ethanol and redistilled water. Before any oxidation step, the surface of nickel foil was cleaned within the analytical ultrahigh vacuum (UHV) chamber by cycles of low energy Ar^+ bombardment at room temperature (these samples are referred to as clean samples). For the ion-beam oxidation we have used a broad beam of O_2^+ ions in the energy range of 1–5 keV and with the typical current density of 2 μA cm^{-2}. Cleaned and oxidised Ni surfaces were characterised by XPS and SIMS. The XPS spectra were recorded with a SPECS XPS spectrometer equipped with the Phoibos MCD 100 electron analyser and a monochromatized source of Al K_α X-rays of 1486.74 eV. The typical pressure in the UHV chamber was in the 10^{-7} Pa range. For the electron pass energy of the hemispherical electron energy analyser of 10 eV used in the present study, the overall energy resolution was around 0.8 eV. The photoemission spectra were simulated with several sets of mixed Gaussian–Lorentzian functions with Shirley background subtraction. SIMS in-depth profiles were obtained by a quadrupole-type instrument (Hiden SIMS Workstation) using a 3 keV Ar^+ primary beam at

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impact angle of 45° and rastered over an area of 1500 × 1500 $(\mu m)^2$, while collecting positive secondary ions. The depth scale of SIMS craters was determined by Dektak XT stylus surface profiler.

3. Results and discussion

The thermal oxidation of Ni is well documented in the literature, thus we have started our study by examining the effect of oxygen dose on thermal oxidation of cleaned Ni surfaces. In Fig. 1 we show a set of typical Ni $2p_{3/2}$ core-level photoemission spectra from clean and oxidised Ni surfaces. Oxidation was done *in situ* in the main chamber of the XPS instrument by supplying the pure oxygen gas into the chamber to the pressure of 5×10^{-6} torr. The oxidation dose is expressed in units of Langmuir, connected to the gas pressure and the exposure time ($1\ L = 1 \times 10^{-6}$ torr s). The spectrum from a cleaned Ni reveals one dominant, asymmetric line shape at 852.5 eV and two broad, less intensive satellite lines (plasmon loss peaks) with binding energies (BE) about 3.0 eV and 6.0 eV above the main line. The same XPS spectra have been previously reported from cleaned Ni surfaces in the literature [7,10], supporting our assumption of efficient cleaning of Ni surfaces within the UHV chamber. After oxidation, the XPS spectra become more complex with several new and well-distinguished peaks. In Fig. 1 we only show the spectra taken after oxidation with 10^3 and 10^4 L of oxygen at RT and 100 °C, respectively.

We note here that our measurements revealed that Ni $2p_{3/2}$ core-level photoemission spectra for the RT oxidation are only slightly affected by the oxygen dose and remain almost unchanged up to the highest oxygen dose of 10^4 L used in our experiments. On the other hand, oxidation at elevated temperature is dose dependent, showing a gradual increase in intensity of additional peaks in Ni $2p_{3/2}$ spectra with the oxygen dose. A strong metallic Ni peak at BE of 852.5 eV is still present after thermal oxidation at both RT and 100 °C which indicates the formation of a very thin or nonuniform oxide film on the surface. In such case, the XPS signal includes a contribution from the underlying metallic nickel.

It is generally accepted that at low temperatures the oxidation of Ni is driven by the creation of negative O ions due to the tunnelling of electrons from Ni to O atoms adsorbed at the surface. This produces an electric field, which attracts positive Ni ions to the surface, resulting in the thickening of the oxide with time. In this process oxidation is terminated when the electric field is no longer strong enough to support ion migration [10]. This is in agreement with our measurements at RT that are only slightly affected by oxygen dose.

On the other hand, at elevated temperatures the oxidation of Ni is driven by Ni^{2+} diffusion through the oxide film. Ni^{2+} cations diffuse through lattice defect sites (such as vacancies created within the oxide) to the surface where they react with adsorbed oxygen [4]. When a Ni^{2+} vacancy is created, two neighbouring Ni^{2+} atoms, in order to balance charge, each lose an electron forming two Ni^{3+} ions [4,11]. Therefore, one expects not only a dose dependence of the oxidation process of Ni at elevated temperature but also several new peaks in Ni 2*p* XPS, characteristic of NiO (Ni^{2+} oxidation state) and Ni_2O_3 (Ni^{3+} oxidation state). This assumption is consistent with our measurements shown in Fig. 1, where, in addition to metallic Ni components from a cleaned surface, we have fitted the 10^4 L, 100 °C spectrum with several new peaks: peaks at 854.2 eV and 855.9 eV are attributed to NiO multiple-splitting lines while peaks at 861.1 eV, 864.1 eV and 866.5 eV represent satellite lines associated with Ni^{2+} [11–13]. On the other hand, small contributions at 856.2 eV and 861.5 eV (thick curves in fitted spectrum) are related to emission from Ni_2O_3 [11,14].

The presence of both NiO and Ni_2O_3 on surfaces of thermally oxidised Ni is clearly visible from the O 1*s* core-level spectra shown in Fig. 2. Both RT and 100 °C spectra are characterised with a sharp resonance at 529.5 eV, associated with Ni^{2+} (i.e. NiO) and an additional line at BE of 531.5 eV, assigned in the literature to the Ni^{3+} oxidation state of Ni (i.e. Ni_2O_3) [3,11,14].

We can turn now to the ion-bombardment induced oxidation of Ni. In Fig. 3 we show Ni $2p_{3/2}$ core-level photoemission spectra from Ni surfaces exposed to 1 keV O_2^+ ions at RT and 100 °C for 10 and 20 min, corresponding to the estimated ion doses of

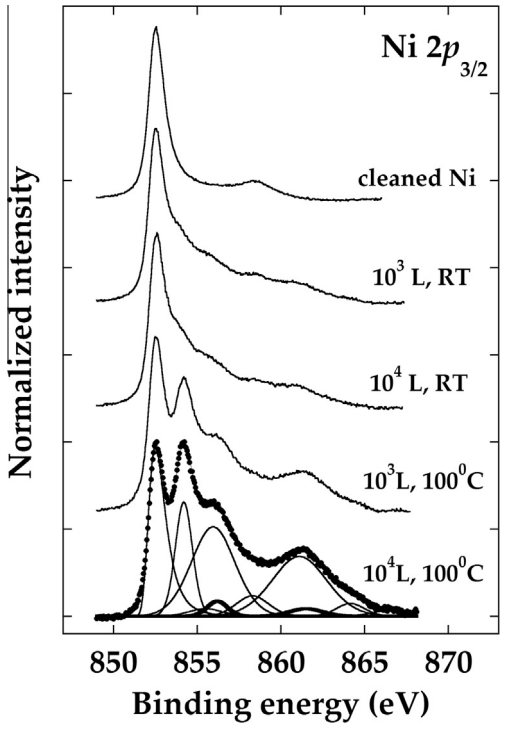

Fig. 1. Ni $2p_{3/2}$ core-level photoemission spectrum from a clean nickel surface and spectra from nickel surfaces after oxidation at room temperature (RT) and 100 °C with oxygen doses up to 10^4 L. Solid lines of spectrum for 10^4 L, 100 °C represent convolution of Gaussians and Lorentzians.

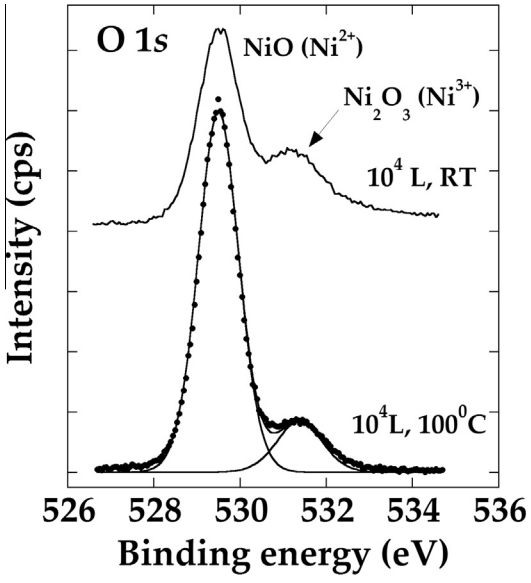

Fig. 2. XPS spectra around O 1*s* atomic level from nickel surfaces after oxidation at room temperature (RT) and 100 °C with an oxygen dose of 10^4 L. The 100 °C curve is fitted with two mixed Gaussian–Lorentzian functions.