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Characterisation of Pt deposition on clean and oxidised Ni(1 1 0) surfaces

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Abstract

Coaxial impact collision ion scattering spectroscopy (CAICISS), X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) have been used to investigate the initial stages of Pt deposition on clean and oxidised Ni(1 1 0) surfaces. Pt deposition on the clean surface led to the formation of a Ni–Pt alloy in the surface region. During the oxidation of Ni(1 1 0), (2×1), (3×1) and (9×5) reconstructions were observed. Further oxidation led to the formation of a thick NiO film with a disordered surface. Subsequent Pt deposition led to the formation of a thin Pt film on top of the NiO substrate.

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1. Introduction

Platinum is one of the most widely used materials in modern catalytic processes and therefore many recent experiments have focussed on the formation and characterisation of thin Pt films on a number of different substrates [1–4]. The deposition of Pt on Ni surfaces has been studied using a range of techniques [3–6]. Previous reports indicate that Pt grows in a disordered layer-by-layer fashion on top of both the Ni(1 0 0) and Ni(1 1 1) surfaces. On the Ni(1 1 0) surface, however, Pt atoms were observed to replace Ni atoms, leading to the formation of an alloy at the surface [4].

The oxidation of transition metal surfaces, such as Ni [3,7–10] and Pt [11], have also received attention in recent years. Adsorption of oxygen on to Ni surfaces initially leads to the formation of a (2×1), a (3×1) and finally a (9×5) reconstruction [9]. Further O adsorption leads to a thick NiO film in the surface region [10]. In the Pt case, oxidation of the surface with O_2 is restricted. However, a higher degree of oxidation has been obtained using atomic oxygen, with a saturation coverage in the region of 1.3 ML on the Pt(1 1 1) surface [11].

In this paper we report the results of a series of coaxial impact collision ion scattering spectroscopy (CAICISS), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) investigations on the deposition of Pt on to clean and oxidised Ni(1 1 0) surfaces. LEED and XPS have also been used to investigate the oxidation of the clean surface.

2. Experimental details

The experiments were carried out using the Warwick modular CAICISS system, described in detail elsewhere [11,12]. The Ni(1 1 0) surface was prepared using cycles of bombarding the surface using an incident 3 keV Ar^+ beam for 30 min, followed by annealing at 700 °C for 1 h until

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the observation of a sharp (1×1) LEED pattern and contaminant-free XPS spectra. CAICISS experiments were carried out using a 3 keV He^+ beam, with the data taken in the $\langle 1\,0\,0 \rangle$ azimuth and analysed using the FAN simulation package [13]. In all cases CAICISS data is shown in the polar angle range 0–90° only, as in this azimuth the structure is symmetric about the surface normal. Atomic oxygen adsorption was achieved using a TC-50 thermal gas cracker (Oxford Applied Research, UK), with an O_2 cracking efficiency of ~60%.

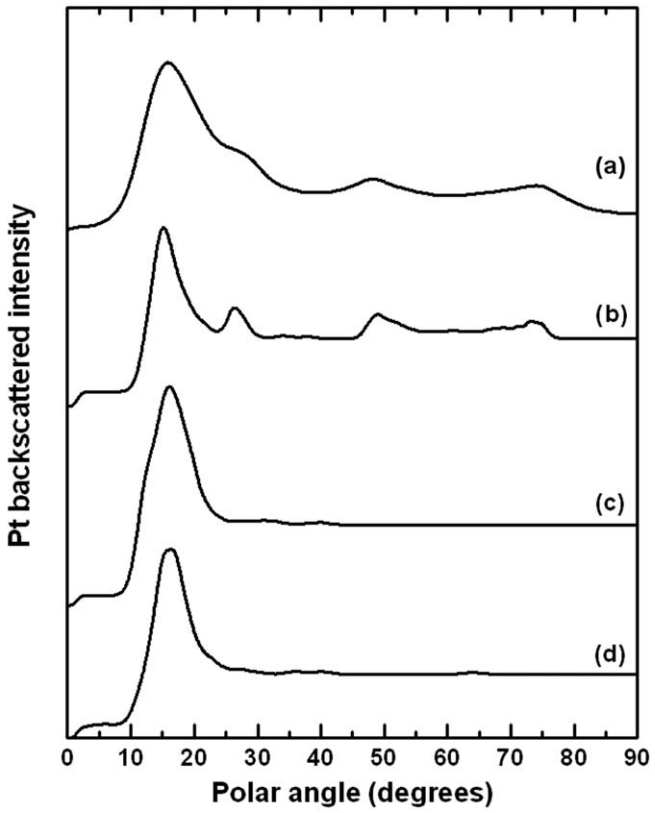

Fig. 1. (a) The Pt backscattered intensity as a function of polar angle following the deposition of 0.22 ML of Pt on the clean Ni(1 1 0) surface. Also shown are FAN simulation results for three possible Pt growth modes; (b) three-layer Ni–Pt alloy; (c) layer-by-layer growth and (d) Pt island formation.

3. Results and discussion

3.1. Pt deposition on clean Ni(1 1 0)

To investigate the initial growth characteristics, approximately 0.22 ML of Pt was deposited on to the clean Ni(1 1 0) surface (coverage determined by XPS and CAICISS). No LEED pattern was observed, indicating Pt-induced disorder at the surface. The Pt backscattered profile extracted from the CAICISS data is shown in Fig. 1, along with FAN simulations of three of the possible scenarios (layer-by-layer growth, the growth of Pt islands and the formation of a Ni–Pt random alloy structure). Considering the simulation results, the features observed at 27°, 48° and 74° in the experimental data are indicative of alloy formation in the surface region. The interlayer spacings in the surface region were observed to have expanded by approximately 10% due to the incorporation of larger Pt atoms in to the Ni(1 1 0) lattice.

3.2. Oxidation of the clean Ni(1 1 0) surface

The clean Ni(1 1 0) surface was exposed to a series of room temperature atomic oxygen doses, with LEED patterns recorded after each exposure, as shown in Fig. 2. A (2×1) LEED pattern was observed following a 1.5 L oxygen exposure (quoted dosage is of O_2 prior to being cracked). A 3.0 L exposure yielded a (3×1) reconstruction, whilst a 5.0 L exposure yielded a weak (9×5)-like reconstruction, although the high background intensity prevented verification of this. Previous work, based on the exposure of Ni(1 1 0) to molecular oxygen (O_2), indicates that these reconstructions correspond to O coverages of 0.5, 0.66 and 1.0 ML respectively [9,14]. Further exposure of our sample to atomic oxygen led to the loss of the LEED pattern behind an increased background intensity, indicating the formation of a disordered surface.

The Ni 2p region was recorded from the clean surface and following a total cracked O_2 exposure of 1800 L, as shown in Fig. 3. All three features in the spectrum were observed to have shifted relative to the clean surface data as a result of the inclusion of highly electronegative O atoms in the Ni structure. No indication of metallic Ni

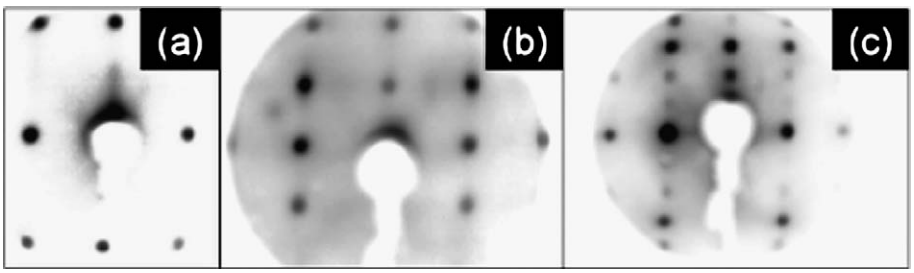

Fig. 2. LEED patterns observed during the oxidation of the Ni(1 1 0) surface: (a) shows the (1×1) reconstruction of the clean surface at 70 eV; (b) shows the 0.9 L atomic O exposure which led to the formation of a (2×1) reconstruction at 92 eV, whilst in (c) a 1.8 L exposure led to a (3×1) reconstruction at 92 eV.

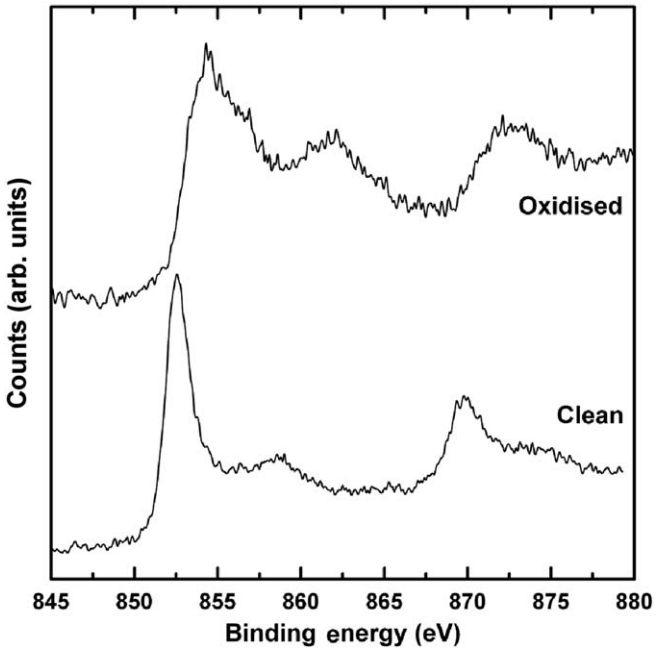

Fig. 3. The Ni 2p region of the XPS spectra recorded prior to and following exposure of the surface to 1800 L of thermally cracked O_2.

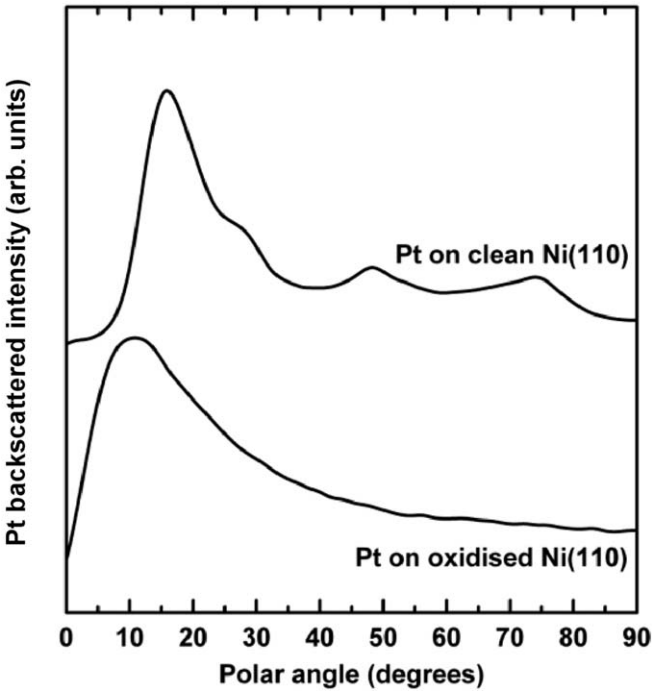

Fig. 4. A comparison of the Pt backscattered CAICISS profiles obtained following Pt deposition on the clean and oxidised Ni(1 1 0) surfaces, with coverages of 0.22 ML and 0.31 ML respectively.

peaks were observed following the oxidation process, demonstrating the formation of a thick NiO film.

3.3. Pt deposition on the oxidised Ni(1 1 0) surface

A coverage of approximately 0.31 ML of Pt was deposited on to the oxidised Ni(1 1 0) surface to investigate oxidation-induced changes to the Pt growth mode. The Pt backscattered profile from this surface is shown in Fig. 4. Comparing this profile to that obtained from the Pt-covered clean surface shows several interesting differences. Oxidation of the Ni(1 1 0) surface prior to deposition led to a 6° shift in the Pt surface peak towards a more grazing angle, indicating a large increase in the inter-atomic spacing in the layer in which the Pt atoms reside. The broadness of the peak at 10° also indicates a wide range of inter-atomic spacings in this layer. No features were observed at higher polar angles, indicating that all of the Pt atoms reside in the same layer. All of these observations suggest the formation of a partial Pt overlayer on the NiO film and indicate the layer-by-layer growth of Pt on the oxidised Ni(1 1 0) surface.

Further evidence to support this is presented in the XPS spectra shown in Fig. 5. In spectra 5(a) and 5(c), only the bulk Pt 4f peaks are observed. Spectrum 5(b) was obtained following the oxidation of a Pt(1 1 1) surface [11], and exhibits an additional feature at 76.8 eV which corresponds to Pt atoms incorporated in a Pt-oxide film. The lack of this feature in spectrum (c) indicates very little interaction between the deposited Pt atoms and the O atoms within the NiO film.

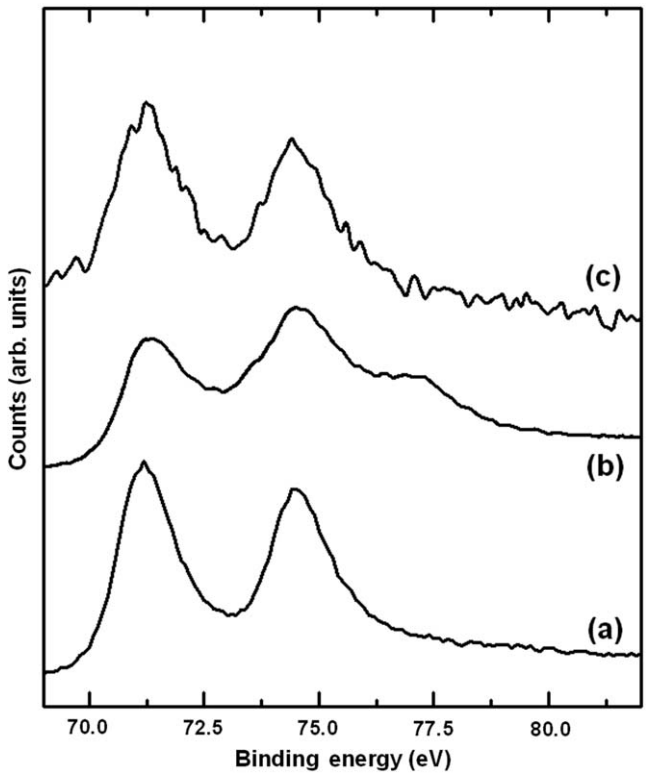

Fig. 5. The Pt 4f region of the XPS spectrum recorded from (a) the clean Pt(1 1 1) surface [11]; (b) an oxidised Pt(1 1 1) surface and (c) following the deposition of Pt on to the oxidised Ni(1 1 0) surface. The feature at 76.8 eV was only observed following the oxidation of Pt(1 1 1).

4. Conclusions

The deposition of Pt on to clean and oxidised Ni(1 1 0) surfaces has been investigated using CAICISS, XPS and LEED. On the clean surface, the deposition of Pt led to the formation of a Ni–Pt alloy structure in the surface region. However, data obtained following Pt deposition on the oxidised surface indicated the formation of a partial Pt overlayer on top of a NiO film. We suggest that this indicates the layer-by-layer growth of Pt on the oxidised surface. The formation of the NiO film has also been investigated, with LEED showing three low oxygen coverage reconstructions and XPS showing the formation of a thick NiO film following an exposure of 1800 L of thermally cracked molecular oxygen.

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