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**Abstract.**   High-resolution scanning tunnelling microscopy images show that low-coverage room temperature coadsorption of potassium on the Ni(100)(2 × 2)p4g–N surface occurs at step edges aligned preferentially along the $\langle 011 \rangle$ directions. The data indicate that the potassium atoms sit at the step edges a distance of $5.0 \pm 0.05$ Å apart. A model is presented for the coadsorbed step structure.

## 1. Introduction

Steps on metal surfaces are a form of line defect that can dramatically influence surface properties. In a simple picture the electrostatic potential of a metal surface is altered at a step, with a positive potential at the upper edge and a negative potential at the lower step landings [1]. This asymmetry is the cause of step–step ordering (due to repulsion of these dipoles) [2], of Ehrlich–Schwoebel barriers in growth processes (see e.g. [3]), and of step-site adsorption which is commonly found for many adsorbate systems, including alkalis [4, 5], where the adsorbates at the steps can be considered to smooth out the electronic perturbation caused by the step edges.

When one attempts to understand 'real' systems, for example systems which might mimic chemical behaviour under catalytic or reaction conditions, then more complex conditions obtain than those on clean metal surfaces. One important consideration is whether the step sites still exert an influence on adsorption behaviour in the case of a *coadsorption* system, where the metal surface has already been 'passivated' with an overlayer of an electronegative species.

The system described here is the Ni(100)(2 × 2)p4g–N overlayer with coadsorbed potassium. On the clean Ni(100) surface, the nitrogen atoms penetrate into the fourfold site so as to lie almost coplanar with the surface metal layer, and in doing so introduce a large compressive stress [6]. This stress is relieved through an expansion of the hollow sites which is achieved by tangential movements of the surrounding Ni atoms resulting in alternate clockwise and anticlockwise rotations of the Ni atoms with a longer nearest-neighbour distance. This substrate distortion turns the otherwise c(2 × 2) overlayer structure into an overall p(2 × 2) phase with p4g space group symmetry [7].

In previous work, we have characterized this coadsorption system using low-energy electron diffraction (LEED) and angle-resolved photoemission spectroscopy (ARPES) [8], surface x-ray diffraction (SXRD) [9], and scanning tunnelling microscopy (STM) [10]. LEED studies revealed a change from a (2 × 2)p4g pattern to a c(2 × 2) pattern at a potassium coverage of ~0.16 monolayers (ML) and the ARPES work focused on the differences in electronic

structure between the p4g and c(2 × 2) systems [8]. The SXRD measurements addressed the structural changes that take place when a relatively large amount of potassium ($\geqslant 0.16$ ML) is coadsorbed [9]. We found that the reconstruction is removed and the nickel atoms revert to their bulk-like positions. In the previous STM work we focused on the mechanism for the removal of the reconstruction, finding that the reconstruction is lifted locally around isolated potassium atoms; and that initial adsorption of potassium takes place at step edges [10].

In the previous STM paper the resolution achieved was not sufficient to determine the adsorption sites of the potassium atoms. In this paper we present previously unreported higher-resolution images with atomic resolution of the coadsorbate system. The higher resolution achieved allows us to ascertain that at low coverages, bonding of potassium on the Ni(100)(2 × 2)p4g–N surface occurs preferentially at steps running along the $\langle 011 \rangle$ rather than to the $\langle 001 \rangle$ directions. We offer an interpretation of these results in terms of the more open architecture of the $\langle 011 \rangle$ steps and present a model of the coadsorbed step structure based on these results. Finally we compare these results with those from similar systems and discuss the generality of the processes found here.

## 2. Experimental details

Sample preparation was carried out using well-established procedures [8]. A clean, well-ordered Ni(100) crystal was prepared by cycles of argon-ion bombardment and annealing to 600 K until a sharp (1 × 1) LEED pattern was observed and no surface contaminants were detectable by Auger electron spectroscopy (AES). The Ni(100)(2 × 2)p4g–N structure was formed by sputtering the sample with 500 eV nitrogen ions followed by gentle annealing for several minutes at approximately 600 K. Potassium was gradually coadsorbed in small dose increments onto the Ni(100)(2 × 2)p4g–N structure by means of an SAES getter source.

The potassium coverage was ascertained via AES by comparing the ratio of the potassium LVV (252 eV) peak to that of the nickel LVV (848 eV) feature with a previous calibration for potassium adsorption on clean Ni(100) [11]. To be consistent with previous work, we use units of monolayers (ML) to describe the coverage, where a monolayer is the substrate atom density in the surface layer. Thus because of the size of the potassium atoms, one complete potassium layer is formed at a coverage corresponding to 0.38 ML.

STM experiments were carried out using an Omicron instrument in the Chemistry Department at Manchester University. The measurements used constant-current mode, with a grounded tungsten tip. The sample bias was typically $\sim -0.3$ eV, with tunnelling currents of typically 1 nA. Where appropriate, images have been corrected for thermal drift and calibrated using the known dimensions of the surface unit cell. All measurements presented were taken at room temperature.

## 3. Results and analysis

Figure 1 shows a 100 × 100 Å$^2$ area of the Ni(100)(2 × 2)p4g–N surface with a single step in the centre of the image running predominantly along the [0$\bar{1}$1] direction and some more jagged steps in the upper and lower sections of the image (here and elsewhere we have labelled the specific directions shown as [010] and [001] for clarity). Under the tunnelling conditions used here (see the figure caption for details), the underlying metal atoms are not imaged, and the nitrogen atoms can clearly be seen on the terraces [10]. The surface has been dosed with a potassium coverage of 0.10 ± 0.05 ML. It is clear that preferential adsorption has taken place along the straight step edge; the step is decorated with protrusions of diameter ∼5 Å. There
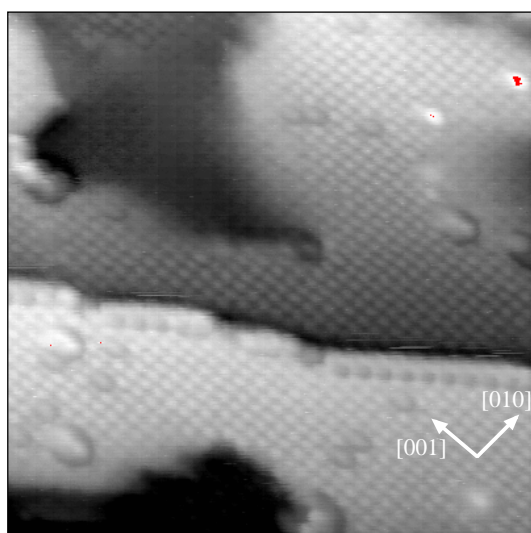
**Figure 1.** A $100 \times 100$ Å$^2$ image of the Ni(100)($2 \times 2$)p4g–N surface after dosing with $0.10 \pm 0.05$ ML of potassium. ($I_t = 1.39$ nA, $V_t = -0.29$ V.)

is no evidence of potassium-induced step restructuring as the morphology of the steps on the clean surface looks similar to that on the dosed surface. Residual potassium has adsorbed on the terraces evidenced by large protrusions of diameter $\sim$5–10 Å. Closer inspection of figure 1 shows that the straight step along the [0$\bar{1}$1] direction becomes saturated with potassium atoms. However where the steps are jagged with a high density of kinks it appears that potassium adsorption has not occurred.

Figure 2 shows a $50 \times 50$ Å$^2$ area of the surface with a step running along the [010] direction. The square pattern of protrusions on the terraces are the nitrogen atoms (as stated
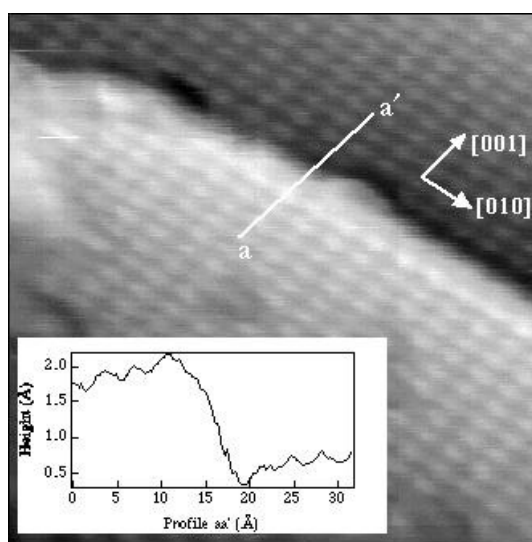


**Figure 2.** A $50 \times 50$ Å$^2$ image obtained from a similar surface to that in figure 1. This image shows a step running along the [010] direction. Inset: line profile aa'. ($\theta_K = 0.10 \pm 0.05$ ML, $I_t = 2.64$ nA, $V_t = -0.29$ V.)

above, the underlying nickel substrate atoms which have undergone the clock reconstruction are not visible under these conditions of bias and tunnelling current). The nitrogen–nitrogen spacing is 3.51 Å (equal to the nickel lattice constant) and we have used this known distance to calibrate subsequent distance measurements. A line profile aa′ running across the step edge (shown as an inset) shows the nitrogen–nitrogen spacing between protrusions on the terraces (3.51 Å) and a fairly broad featureless step structure. This step structure is similar to that of steps on Ni(100)(2 × 2)p4g–N surfaces before potassium adsorption.

Figure 3 shows a 40 × 50 Å$^2$ section of the surface, again with a step edge present, this time however running in the [011] direction. A line profile along aa′ is shown as an inset at the top of figure 3. This indicates that the step height is consistent with a single-atom-height step. The line profile shows the characteristic N–N spacing between protrusions on the terraces; it also shows a large protrusion (∼5 Å in diameter) at the step edge. The second inset at the bottom right of the figure shows the result of taking the line profile bb′ along the step edge chosen to originate and end on nitrogen atoms. The maxima in these protrusions are located *between* the rows of N atoms running towards the step on the upper terrace. The distance between these maxima is $5.0 \pm 0.5$ Å, which is double the nearest-neighbour distance on the surface. The most likely explanation for this is that the protrusions along the profile bb′ in figure 3 are due to potassium atoms adsorbing along the step edges at every second twofold site. We infer that the ⟨011⟩ step edge sites are preferential sites for potassium adsorption and that ⟨010⟩ sites are not favoured for adsorption.
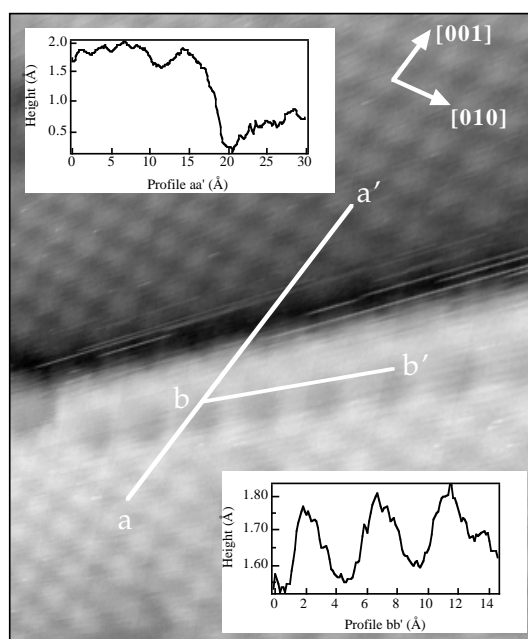


**Figure 3.** A 40 × 50 Å$^2$ image of the same surface showing a step oriented along the [011] direction. The insets correspond to the line profiles along aa′ and bb′. ($\theta_K = 0.10 \pm 0.05$, $I_t = 1.39$ nA, $V_t = -0.29$ V.)

Figure 4 shows plan and side views of a possible adsorption site for potassium atoms which is consistent with the STM data. The line bb′ in this schematic diagram corresponds to the line bb′ in the image shown in figure 3. In this model the potassium atoms sit on the top edge of the steps a distance of 4.96 Å apart in a bridge-like site with bonding to nickel surface atoms.
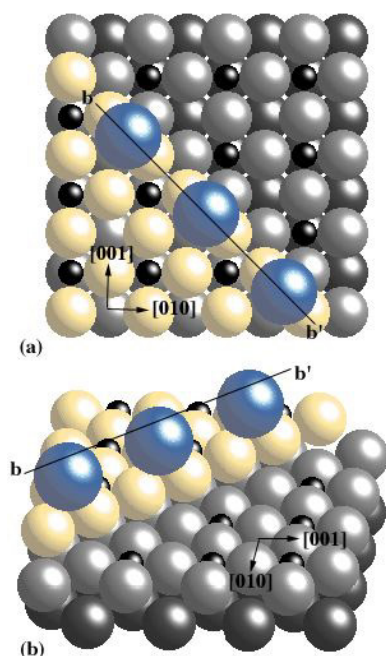
**Figure 4.** (a) Top and (b) side views of a model of the coadsorbed structure along a ⟨011⟩ step. Key: large grey spheres: potassium; small dark spheres: nitrogen; light grey spheres: top Ni layer; medium grey spheres: second Ni layer; dark grey spheres: third Ni layer.

This top-edge adsorption is inferred by the protrusion observed in the line profile aa′ across the step edge shown as an inset in figure 3. This is not of course a definitive site identification; STM cannot be used for this purpose without corroborating evidence from other techniques. Indeed, if the charge distribution across the step edge in the coadsorbed system remains the same as on the clean surface (i.e. a more negative potential at the lower edges as discussed in the introduction), then the more favoured site for the alkali could well be at the lower edges of the steps. It is equally possible that nitrogen atoms are adsorbed along the steps, and that the potassium atoms sit above the nitrogen atoms; again, it is not possible with STM to distinguish these possibilities.

## 4. Discussion and summary

In alkali systems, step-site adsorption has been observed in a number of previous studies. Step adsorption followed by island nucleation was found for sodium adsorption on an Al(111) surface at low coverages [4] using STM, and caesium atoms were found to be adsorbed at step edges on the heavily stepped Cu(211) and Cu(511) surfaces using spot-profile-analysis low-energy electron diffraction (SPA-LEED) [5]. It is thought that intercalation of alkalis on graphite surfaces proceeds via migration to step edges [12, 13]. Indeed, step-edge adsorption may be more ubiquitous for alkali systems than is generally assumed; dipole–dipole repulsion leads to a dispersed overlayer, but it may be that the higher reactivity of step sites overcomes the dipole repulsion in many systems. In general there is a paucity of structural information due to the difficulties encountered in imaging alkalis on metal surfaces.

Here we have demonstrated preferential step-site adsorption in a coadsorbed system. The results clearly indicate that at low coverages step-site adsorption is favoured energetically, but only on ⟨011⟩-type steps. We can conclude that some of the electronic asymmetry in the surface potential corrugation due to steps therefore persists after 'passivation' by a nitrogen adlayer.

This conclusion, based on our STM study, is echoed in other studies of alkali coadsorption systems using spectroscopic techniques. For coadsorption of $H_2O$ and sodium on a stepped Ni(111) surface, it was found that preferential adsorption of sodium at step edges led to a reduction in the number of $H_2O$ molecules which could be considered to be bonded at step edges [14]. For coadsorption of CO with a potassium-promoted Cu(332) surface, it was found that the CO molecules bonded at step sites are the first to be influenced by the coadsorbed potassium [15]. Thus it appears that even in the presence of coadsorbates, the step sites remain more reactive for alkali adsorption.

Our conclusion concerning preferential adsorption on the ⟨011⟩ rather than the ⟨001⟩ steps demonstrates the power of STM is studying such localized phenomena, and also its limitations for adsorption site determination. Although we have presented a plausible model for the adsorption site based on our observations, analysis with a quantitative structural technique is necessary to locate the exact adsorption site.

In summary, we have presented a study of the early stages of coadsorption of potassium on the Ni(100)(2 × 2)p4g–N surface. Adsorption of potassium takes place initially at step edges. A preference is shown for adsorption on ⟨011⟩-type steps rather than steps running along the ⟨001⟩ directions. A model for the potassium coadsorption site at step edges based on these results has been presented.

## Acknowledgments

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