

Summary Abstract: Kinetics and mechanism of the oxygen induced surface reconstruction on Ni(110)

R. J. Behm, G. Ertl, V. Penka, and R. Schwankner

Institut für Physikalische Chemie, Universität München, Federal Republic of Germany

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From the extensive literature dealing with the adsorption of oxygen on the low indexed Ni planes,¹ it is well known that adsorption and annealing temperatures are of particular importance for adsorption kinetics and the formation of ordered structures. The relatively open (110) plane is especially sensitive to temperature effects, since there is now good evidence that the (2×1) and (3×1) structures, formed at $T = 300$ K involve a reconstruction of the surface.² We present here results of a study on possible correlations between oxygen adsorption and oxygen induced reconstruction of this plane. Experimental details will be described elsewhere,³ the methods applied include AES, LEED, and work function measurements.

Oxygen adsorption on Ni(110) at $T = 150$ K leads to the formation of an ordered $c(2 \times 4)$ structure.³ Its coverage as derived from AES is slightly smaller than that of the (2×1) ($\theta = 0.3$) and is assigned as $\theta = 0.25$, which would be the coverage of a $c(2 \times 4)$ with two atoms per unit cell. The difference in work function between the two structures and the behavior of the LEED $I-V$ curves are the basis on which we attribute the $c(2 \times 4)$ to atomic oxygen adsorbed on the non-reconstructed Ni(110) surface. The transition from $c(2 \times 4)$ to (2×1) structure thus can serve to monitor the progress of the reconstruction process. In the present experiment, oxygen was adsorbed at temperatures between 90 and 300 K, and we have monitored the effects of adsorption temperature and subsequent annealing.

Annealing the $c(2 \times 4)$ to $T = 450$ K always leads to the disappearance of this structure and to the formation of the reconstructed phases, a (2×1) or (3×1) depending on the oxygen coverage. Subsequent cooling does not restore the initial situation, but causes an increase in the intensity of the LEED beams related to the reconstructed structures because of reduced thermal damping. The reconstructed phases are therefore thermodynamically more stable. During annealing from the adsorption temperature (140 K), three stages can be distinguished by their LEED patterns: Initially the intensity in the $c(2 \times 4)$ related beam stays relatively constant, with only slight changes due to thermal damping and better ordering at higher coverages, and the

(2×1) is not observed. In the next stage, at $T = 250$ K, the $c(2 \times 4)$ related intensity steadily decays and simultaneously the $(\frac{1}{2}, 0)$ beam of the (2×1) emerges. Once this beam has reached its maximum intensity, the $c(2 \times 4)$ has completely disappeared. In the third stage, at $T = 450$ K, the $(\frac{1}{2}, 0)$ intensity decreases again due to thermal damping.

This general pattern holds for the different coverages, although the transformation phases occur at different temperatures: The brighter the $c(2 \times 4)$ related intensity, i.e., the more perfect this structure, the more stable it is, and the higher the transition temperature. Correspondingly at too low or too high coverages, it is shifted to lower temperature. These trends as well as the respective temperatures are confirmed by measurements of the work function in similar experiments, which exhibit, after an initial work function increase, a decrease by up to 200 mV during formation of the (2×1) , a result of the surface reconstruction. In all of these runs, AES did not indicate any loss of oxygen from the surface.

These data allow the following interpretation: The formation of an ordered O_{ad} structure already at 90 K demonstrates the mobility of the adsorbing oxygen, either a molecular precursor or an atomic species and its ability to form an ordered structure. An intensity increase in the $(\frac{1}{2}, \frac{3}{4})$ beam at $T = 200$ K and at exposures of 0.65 L indicates that diffusion barriers do exist, but presumably are more important for the ordering of small domains rather than for single particle diffusion. Consequently, the formation of the reconstructed (2×1) and (3×1) at lower temperatures must be inhibited by an activation barrier for the reconstruction process itself. This inhibition cannot result from a too low mobility of the O_{ad} and an only local, nonordered reconstruction of the lattice at low temperatures. The barrier for reconstruction must be high enough to inhibit the reconstruction process at $T = 250-300$ K, depending on the oxygen coverage.

The decay of the $c(2 \times 4)$ and the simultaneous, but slower formation of the (2×1) structure in the second stage indicates that the ordered $c(2 \times 4)$ stabilizes the unreconstructed surface and that the reconstruction process proceeds via a disordered O_{ad} layer:



The stabilization of the unreconstructed surface by an ordered adlayer can be rationalized on energetic grounds. Assuming a constant energy level for the transition state for reconstruction and using Ni(110) — O_{ad} as the initial state, the activation barrier increases for a more stable initial state, i.e., the ordered $c(2\times 4)$, which is energetically more favorable. In addition the $c(2\times 4)$ may prevent the occupation of certain adsorption sites required for the reconstruction.⁴

The coverage dependence in the activation barrier for reconstruction and the close proximity of the transition point to 300 K directly affects the adsorption at room temperature. Although there is still intensity in the $c(2\times 4)$ related LEED beams during annealing experiments, this structure cannot form at these temperatures. If the adsorption rate is faster than the rate for reconstruction, however, oxygen adsorbed on the nonreconstructed surface can build up, which under these conditions is disordered. Despite disagreement in details of the interpretation and exact peak positions, the authors of two recent EELS studies^{4,5} correspondingly report one loss around 500 cm^{-1} at lower oxygen coverage. This coexists with a species exhibiting a loss around 400 cm^{-1} and is converted into it at higher coverages or temperatures. The latter one is related to O_{ad} on the reconstruct-

ed surface, i.e., in the (2×1) , while in one of the studies,⁴ the former one is attributed to disordered oxygen adsorbed on the unreconstructed surface. This assignment provides direct evidence for our above statement that the reconstruction proceeds via a disordered oxygen species adsorbed on the nonreconstructed surface.

In summary we have shown that the oxygen induced reconstruction of Ni(110) is activated and that this activation barrier, rather than reduced mobility of the adsorbed oxygen inhibits the formation of the reconstructed (2×1) phase at $T \leq 250\text{ K}$. For room temperature adsorption it also leads to a (time dependent) coexistence of O_{ad} adsorbed on the reconstructed and on the nonreconstructed surfaces.

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