

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Peter Dowben Publications

Research Papers in Physics and Astronomy

May 1988

Summary Abstract: Formation of Cr₂N overlayers on a Fe/Cr{110} crystal

H. Ruppender
University of Maine

M. Grunze
University of Maine

Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

Follow this and additional works at: <https://digitalcommons.unl.edu/physicsdowben>



Part of the [Physics Commons](#)

Ruppender, H.; Grunze, M.; and Dowben, Peter A., "Summary Abstract: Formation of Cr₂N overlayers on a Fe/Cr{110} crystal" (1988). *Peter Dowben Publications*. 132.

<https://digitalcommons.unl.edu/physicsdowben/132>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Peter Dowben Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

tional modes due to impact scattering in off-specular measurements for both the nitro and the chelating isomers implies that the ONO asymmetric stretching frequencies may be very close to their respective symmetric stretching frequencies.

The NO₂ surface chelate found on Au(111) is capable of reacting with NO at 100 K to form a stable N₂O₃ species in an upright configuration on the Au(111) surface.⁸ The reaction can be reversed by warming the surface to 170 K. This implies that the N–N bond energy is 10 kcal/mol. Similarly to N₂O₃ in a CH₂Cl₂ solution,⁹ the vibrational frequencies in the molecule are essentially the summation of the vibrational frequencies of the NO₂ and the NO components with the addition of an ON–NO₂ stretching frequency at 250 cm⁻¹. The formation of N₂O₃ lends chemical support to the identification of the Au(111) O,O'-nitrito surface chelate.

The sticking coefficient of NO₂ is unity and is essentially independent of coverage over a large temperature range on each of the surfaces reported here. This indicates that there is a dramatic precursor effect on the adsorption kinetics. Though not stable on the HREELS time scale, the existence of a variety of short-lived adsorption intermediates that are analogous to the numerous linkage isomers of NO₂ found in transition metal complexes and that interact favorably with the surface may explain the origin of the high sticking coefficient for NO₂.

Each of the surfaces in this paper adsorbs NO₂ in a preferential bonding geometry, providing an example of the characteristic vibrational spectrum for each adsorption isomer. Since the heat of adsorption for NO₂ in each case is relatively small, these vibrational spectra may serve as reference spectra from which the linkage isomers of NO₂ adsorbed on other surfaces may be identified.

Acknowledgments: Financial support for this work from the National Science Foundation through a grant given to Sievers Research Inc. as a part of the SBIR program Contract No. IFI-8521288 and the National Acid Precipitation Assessment Program is gratefully acknowledged.

¹M. A. Hitchman and G. L. Rowbottom, *Coord. Chem. Rev.* **42**, 55 (1982).

²M. E. Bartram, R. G. Windham, and B. E. Koel, *Surf. Sci.* **184**, 57 (1987).

³M. E. Bartram, R. G. Windham, and B. E. Koel, *Langmuir* (accepted for publication).

⁴D. H. Parker, M. E. Bartram, D. T. Wickham, and B. E. Koel, *Surf. Sci.* (submitted).

⁵M. E. Bartram, R. G. Windham, and B. E. Koel, *Surf. Sci.* (submitted).

⁶C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.* **1960**, 613.

⁷D. A. Cutka, R. J. Madix, G. B. Fisher, and C. Dimaggio, *Surf. Sci.* **179**, 1 (1987).

⁸M. E. Bartram and B. E. Koel, *Surf. Sci.* (submitted).

⁹I. C. Hisatsune and J. P. Devlin, *Spectr. Acta* **16**, 401 (1960).

Summary Abstract: Formation of Cr₂N overlayers on a Fe/Cr{110} crystal

H. Ruppender and M. Grunze

Laboratory for Surface Science and Technology and Department of Physics and Astronomy, University of Maine, Orono, Maine 04469

P. A. Dowben

Department of Physics, Syracuse University, Syracuse, New York 13244-1130

(Received 19 October 1987; accepted 2 November 1987)

In this communication we summarize our experiments related to the formation of chromium surface nitride layers on a Fe₇₂Cr₂₈{110} surface. These surface nitrides were produced by (i) exposure to molecular nitrogen, (ii) exposure to ammonia, and (iii) segregation of nitrogen to the crystal surface. It was found in all cases that the nitrogen concentration in the selvedge scales linearly with the chromium concentration and that chromium segregation is the rate determining step for the formation of a surface nitride.

The dissociative adsorption of molecular nitrogen on Cr{110} and FeCr(110) surfaces of varying surface composition has been described previously.¹ By comparing the nitrogen dissociation probability on Fe/Cr surfaces of varying compositions prepared by different sputtering/annealing procedures, it was found that small concentrations of iron at the surface have a drastic effect on the activity of chromium with respect to N₂ dissociation. Since geometrical arguments

considering the distribution of chromium clusters of sufficient size to dissociate N₂ cannot explain the decrease in dissociation probability, it was concluded that the presence of iron alters the activity of chromium in a subtle way, probably through electronic effects.

In the following we address the segregation of chromium during nitrogen and ammonia exposure to the crystal and compare these results with chromium segregation following nitrogen segregation from the bulk of the crystal. It should be noted that all experiments described here were performed on surfaces contaminated in the 5%–10% range by oxygen and carbon. We were unable to produce an atomically clean alloy surface during the 12-month period of these measurements.

On iron-rich surfaces (i.e., having the bulk composition of the crystal Fe₇₂Cr₂₈) it was found that at $T < 550$ K saturation with atomic nitrogen is obtained after a N₂ exposure of

$\sim 10^6$ L. However, at $T > 550$ K a continuous increase of nitrogen coverage is paralleled by chromium segregation from the bulk of the crystal, eventually leading to the formation of a Cr₂N surface nitride layer.¹ The surface enrichment of chromium by segregation thus leads to additional nitrogen dissociation, and chromium segregation rather than nitrogen dissociation itself must be the rate determining step in the formation of the chromium surface nitride. The structure of the chromium nitride phase has been reported in Ref. 1.

The same conclusions were derived by experiments using NH₃ as a nitriding agent. As with N₂, it was found that NH₃ dissociation to atomic nitrogen depends on the chromium concentration of the surface. The ratios for dissociative adsorption of NH₃ to atomic nitrogen (which was the reaction product monitored by Auger electron spectroscopy) on Cr{110}, Fe₇₂Cr₂₈(110) with a surface concentration of chromium at 65%, and polycrystalline iron² is 1:0.3:10⁻², respectively. As with our results on N₂ dissociation at temperatures below 550 K, the surface was saturated with atomic nitrogen, and chromium segregation was too slow to be detected over reasonable time periods (~ 10 min). At $T > 550$ K, however, chromium segregation to the surface was observed leading to an increase in atomic nitrogen produced by NH₃ exposure.

The third method of producing a chromium nitride surface was by nitrogen diffusion from the bulk. The Fe/Cr alloys were saturated with nitrogen by extensive N₂ exposures and subsequently sputtered at room temperature resulting in a nitrogen-free surface close to the bulk composition Fe₇₂Cr₂₈. The crystal was then heated and nitrogen started to segregate to the surface. No change in Fe/Cr surface composition was detectable below 550 K. At temperatures of 645 and 785 K, however, chromium segregated to the surface, as was found in the N₂ and NH₃ experiments. A short delay between nitrogen diffusion and chromium segregation was observed. As with gas exposure, formation of the surface nitride low-energy electron diffraction (LEED) structure was observed at a relative nitrogen coverage of $\Theta = 0.7$.

The relationship between relative nitrogen coverage and chromium enrichment obtained from the segregation and NH₃ exposure experiments are shown in Fig. 1. In both cases the relative nitrogen coverage scales linearly with chromium segregation, although the rates for N segregation and NH₃ dissociation differ by orders of magnitude, emphasizing that chromium segregation to the surface determines the rate of surface nitride formation.

At this point, we have not measured carefully enough the rate of chromium segregation as a function of nitrogen coverage for the gas phase exposure methods used to produce a nitride layer. Only for the segregation experiments have the rates been determined to obtain the activation energies for nitrogen segregation in the Fe/Cr alloy. The activation energy for nitrogen segregation in the Fe/Cr alloy was determined to be 57 ± 10 kJ/mol for $\Theta_N \rightarrow 0$. This value is slightly lower than the activation energies reported for nitrogen diffusion in α -Fe which range between 68 and 77 kJ/mol.³⁻⁶ The activation energy for chromium segregation to the sur-

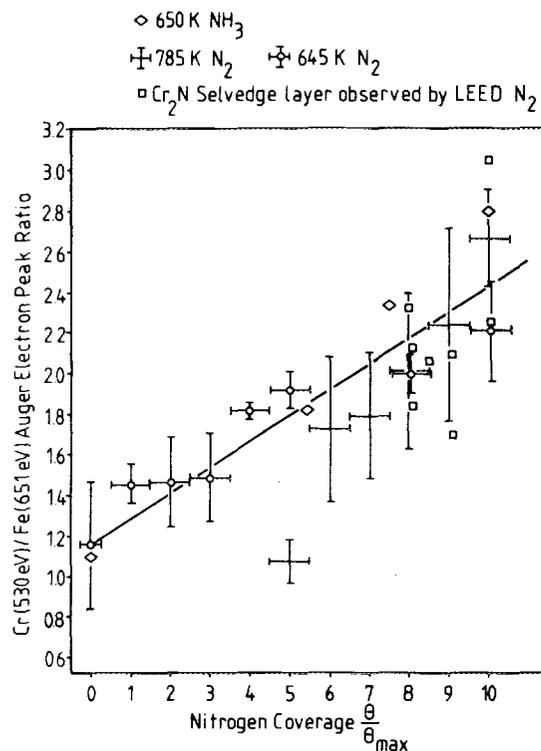


FIG. 1. The relation between chromium enrichment on a Fe₇₂Cr₂₈{110} crystal surface and relative nitrogen coverage for segregation of nitrogen from the bulk and ammonia decomposition. Substrate temperature: 785, 645, and 650 K. Cr₂N surface nitride observed by LEED.

face in our experiments was found to be 97 ± 15 kJ/mol. This value is considerably smaller than the activation energy for self-diffusion of chromium in α -iron of 240 kJ/mol.⁷ Unfortunately, data for the diffusion of chromium on a clean Fe/Cr alloy surface are not available, because of the severe problems in completely suppressing bulk diffusion of nitrogen and other impurities (O,C) and maintaining a clean surface even in ultrahigh vacuum for a sufficiently long time period. An explanation for the low value of the activation energy of segregation is therefore not possible due to the unknown segregation behavior for an atomically clean surface.

The main conclusion of this work is that independent of the method by which atomic nitrogen is produced on a Fe/Cr alloy surface, the rate of surface nitride formation is determined by segregation of chromium from the bulk and therefore depends on the sample temperature only. The initial excess in nitrogen concentration on the surface produced by NH₃ exposure does not lead to a different segregation behavior of chromium within the accuracy of our experiments.

Acknowledgments: This work was performed at the Fritz-Haber-Institut of the Max-Planck-Gesellschaft and was supported through the Sonderforschungsbereich 6 of the Deutsche Forschungsgemeinschaft with additional partial support provided by U.S. DOE Grant No. DE-FG02-87ER-45319.