Supplementary Material

Adlayer growth versus spontaneous (near-) surface alloy formation: Zn growth on Au(111)

*Konstantin M. Schüttler, Joachim Bansmann, Albert K. Engstfeld and R. Jürgen Behm**

Institute of Surface Chemistry and Catalysis, Ulm University,

Albert-Einstein-Allee 47, D-89081 Ulm, Germany

Prof. R.J. Behm
Universität Ulm
Institut für Oberflächenchemie und Katalyse
Albert Einstein Allee 47
D–89069 Ulm, Germany
Phone: +49 (0)731-50–25451
Fax: +49 (0)731-50–25452
E–Mail: juergen.behm@uni-ulm.de

Fig. S1 shows XP spectra recorded after deposition of increasing amounts of Zn onto a Au(111) surface at RT. The gain in Zn 2p and loss in Au 4f intensity with increasing coverage is clearly evident. Furthermore, the spectra resolve a clear shift of the Au 4f peaks to higher BE

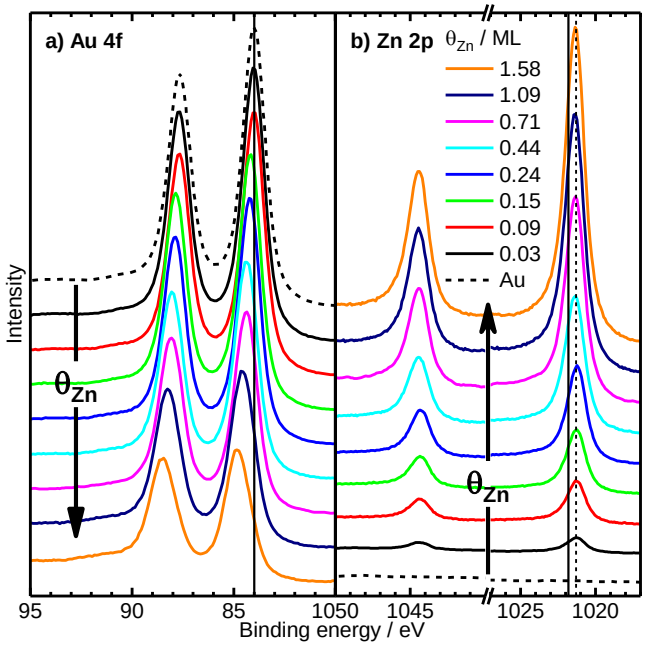

Fig. S1 a) Au 4f and b) Zn 2p XP spectra recorded after deposition of increasing amounts of Zn onto a Au(111) surface at RT. Solid vertical lines denote the bulk binding energies of the Au $4f_{7/2}$ and the Zn $2p_{3/2}$ peaks, the dashed vertical line illustrates the invariance of the Zn 2p peak position with coverage.

Structures obtained after annealing a higher Zn coverage of 0.6 ML Zn deposited at RT on Au(111) to 400 K for 1 min are depicted in Fig. S2. The large vacancy island in Fig. S2a (indicated by the dashed black circle) is attributed to partial coalescence of the finger-like structures grown off the ascending Au steps after Zn deposition at RT. Furthermore, the image resolves a larger island on the terrace (see dashed green line).

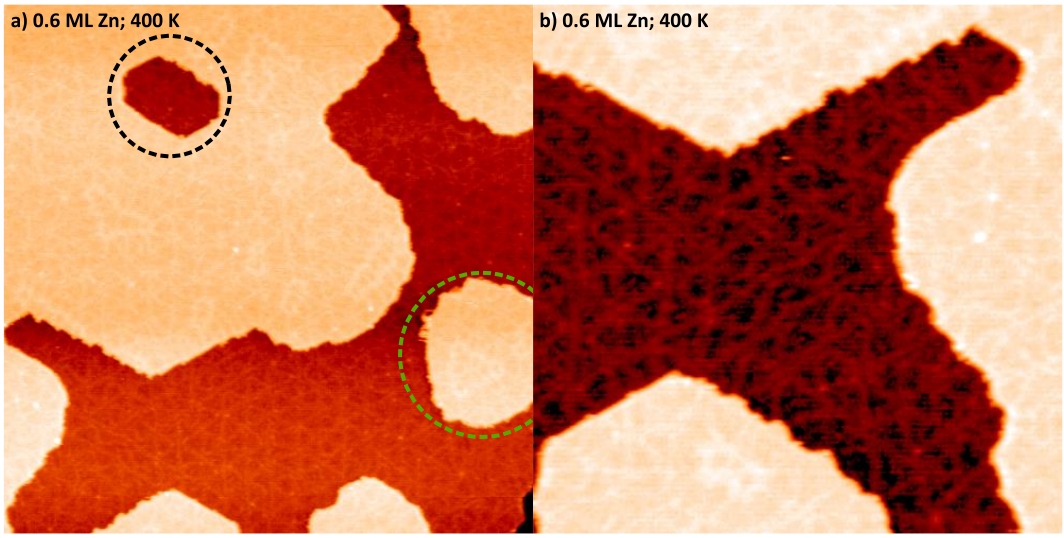

Fig. S2 STM images of a Au(111) surface after 0.6 ML Zn deposition at RT and annealing to 400 K: (a) 100 nm × 100 nm, b) 50 nm × 50 nm). In a), the vacancy island is indicated by a dashed black circle and islands on the terrace are indicated by dashed green lines.

On a much larger scale, the structural irregularities remaining after annealing of a surface obtained after Zn deposition at RT are seen more clearly. Fig. S3a shows a surface after RT deposition of 0.3 ML Zn and subsequent annealing at 400 K. Besides the irregular shape of the step edges, we find several vacancy islands in the terraces close to the step edges, which are indicated by dashed black circles. We assume that these structures were created by coalescence of the finger-like structures at the Au step edges formed during RT Zn deposition. Furthermore, this image shows a compact island on the middle terrace (dashed green line). After 500 K annealing (cf. Fig. S3b) two very large remaining islands are observed on both large terraces.

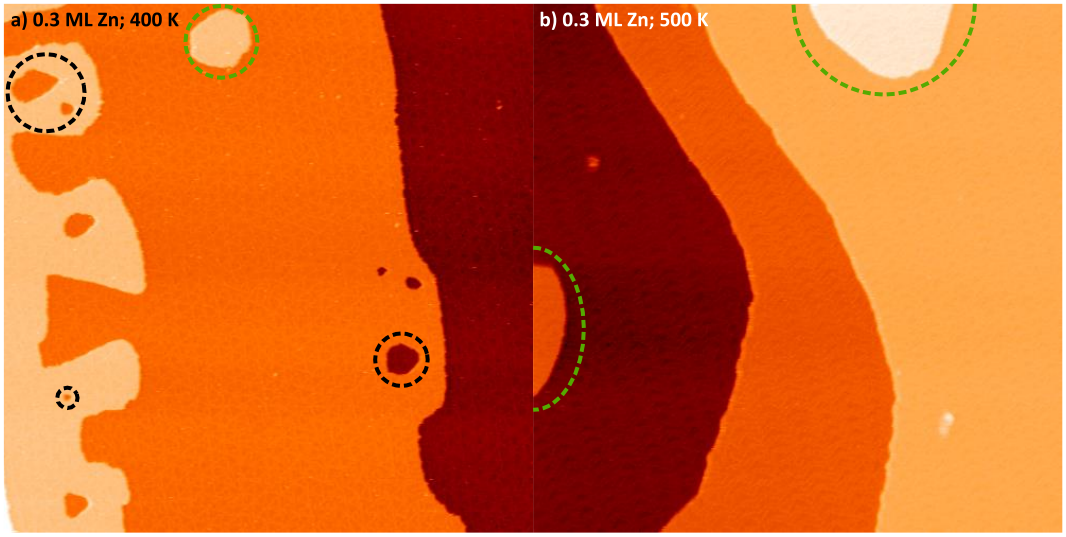

Fig. S3 Large scale STM images of 0.3 ML Zn deposited on Au(111) at RT after annealing. a) 400 K (200 nm × 200 nm) and b) 500 K (250 nm × 250 nm). Vacancy islands are indicated by dashed black circles and islands on terraces by dashed green lines.

Fig. S4 shows series of Au 4f and Zn 2p XP spectra recorded upon annealing the AuZn near-surface alloys formed during RT deposition of different amounts of Zn. The gain in Au 4f and loss in Zn 2p intensity upon annealing to different temperatures as well as the gradually back-shift of the Au 4f peaks to their original position are clearly evident.

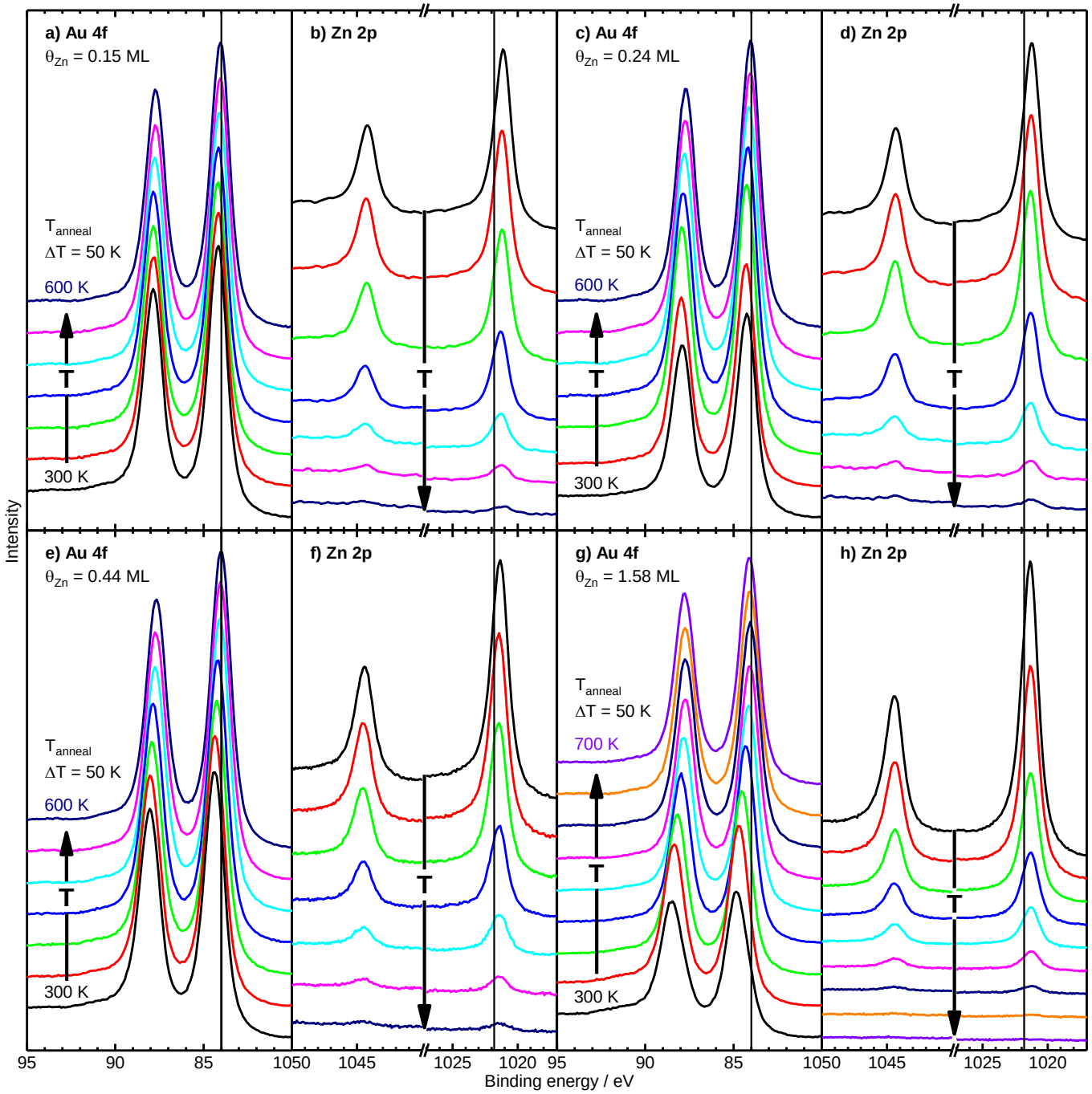

Fig. S4 Series of XP spectra recorded after successive annealing of Au(111) surface covered by different amounts of Zn (RT deposition, coverage given in each panel).

Fig. S5 shows the complete evaluation of the XP spectra recorded after successive annealing of the RT Zn deposited surfaces (spectra shown in Fig. S4).

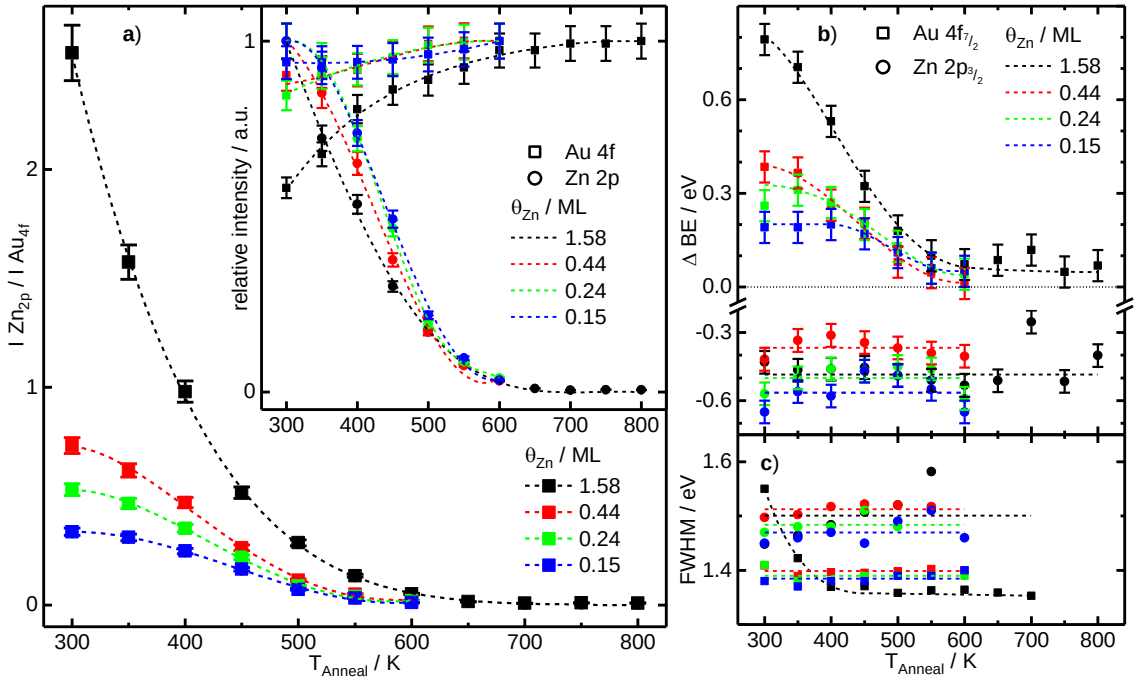

Fig. S5 Full set of XPS results for Zn deposition at RT on Au(111), followed by successive annealing to the temperatures indicated by the symbols. a) Zn 2p / Au 4f intensity ratio for subsequent annealing steps, the initial Zn coverages are given in the panel. Inset: Relative Au 4f and Zn 2p XPS intensities. b) Binding energy shifts ΔBE and c) FWHM of the Au $4f_{7/2}$ and Zn $2p_{3/2}$ peaks upon annealing. Note that for the 750 and 800 K annealing steps the spectrometer settings (pass energy) were changed, to obtain a reasonable intensity. Therefore, the FWHMs are not comparable to the other measurements. Dashed lines are guides to the eye.

Table SI: Literature overview of admetal nucleation and growth on the herringbone reconstructed Au(111) surface. Note that in some cases, which are marked with a *, the literature results or conclusions are inconsistent. In these cases we provide the values found most frequently or appearing most plausible to us. Note also, that literature investigations do not necessarily comment and/or conclude on all aspects addressed in Table S1. T_{alloy} indicates the temperature where alloy formation has been observed. If possible, partial or complete alloy formation is distinguished (n.a.: not available).

Metal	**T_{Alloy}**	**Reconstruction**	**Refs**
Ti	above 350 K	distorted above 0.25 ML	1-3
Cr	n.a.	distorted above 0.25 ML at RT	4,5
Mn	above RT	distorted above 0.2 ML	6,7
Fe	above 323 K	intact after 323 K deposition*	8-16
Co	450 K (partial), 600 K (complete)	intact after RT deposition, beginning distortion at 450 K, distorted at 600 K	17-27
Ni	450 K (partial), 550 K (complete)	intact after RT deposition, beginning distortion at 450 K, distorted at 550 K	28-33
Mo	above 307K*	na*	34,35
Ce	n.a.	intact after RT deposition	36
Ru	above RT	intact after RT deposition*	37-39
Rh	673 K	intact after RT deposition, beginning distortion at 673 K, distorted at 798K	40,41
Pd	above RT*	distorted above 0.25 ML at RT	42-47
Pt	below RT	distorted at RT	48,49

Cu	below RT*	distorted at RT	50-56
Ag	below RT*	distorted at RT*	57-62
Au	-	-	29,63
Al	230 K	intact below 230 K, distorted above	64,65
Sn	below 373 K	distorted after 373 K deposition	66
Na	200K	distorted at RT	67-69
K	below RT	distorted at RT	68,70
Ba	below RT	n.a.	71

References

1. J. Biener, E. Farfan-Arribas, M. Biener, C. M. Friend, and R. J. Madix, J. Chem. Phys. **123**, 094705 (2005).
2. D. V. Potapenko and R. M. Osgood, Nano Lett. **9**, 2378 (2009).
3. P. Carrozzo, F. Tumino, M. Passoni, C. E. Bottani, C. S. Casari, and A. L. Bassi, Surf. Sci. **619**, 77 (2014).
4. C. Boeglin, P. Ohresser, R. Decker, H. Bulou, F. Scheurer, I. Chado, S. S. Dhesi, E. Gaudry, and B. Lazarovits, Phys. Stat. Sol. B **242**, 1775 (2005).
5. A. Rai, J. Nayak, and S. R. Barman, E-J. Surf. Sci. Nanotechnol **12**, 49 (2014).
6. M. Fonin, Y. Dedkov, U. Rudiger, and G. Guntherodt, Surf. Sci. **529**, L275 (2003).
7. S. Shiraki, H. Fujisawa, M. Nantoh, and M. Kawai, Surf. Sci. **552**, 243 (2004).
8. B. Voigtländer, G. Meyer, and N. M. Amer, Surf. Sci. **255**, L529 (1991).
9. J. A. Stroscio, D. T. Pierce, and R. A. Dragoset, J. Vac. Sci. Technol. A **10**, 1981 (1992).
10. N. A. Khan and C. Matranga, Surf. Sci. **602**, 932 (2008).
11. W. C. Lin, H. Y. Chang, Y. T. Hu, and C. C. Kuo, Jap. J. Appl. Phys. **48**, 08JB07 (2009).
12. T. Allmers and M. Donath, New J. Phys. **11**, 103049 (2009).
13. W. C. Lin, H. Y. Chang, Y. C. Hu, Y. Y. Lin, C. H. Hsu, and C. C. Kuo, Nanotechnol. **21**, 015606 (2009).
14. A. Delga, J. Lagoute, V. Repain, C. Chacon, Y. Girard, M. Marathe, S. Narasimhan, and S. Rousset, Phys. Rev. B **84**, 035416 (2011).
15. F. Donati, G. Fratesi, M. Passoni, C. S. Casari, A. Mairov, C. E. Bottani, M. I. Trioni, and A. L. Bassi, Phys. Rev. B **83**, 153404 (2011).
16. F. Donati, A. Mairov, C. S. Casari, M. Passoni, and A. L. Bassi, Surf. Sci. **606**, 702 (2012).
17. B. Voigtländer, G. Meyer, and N. M. Amer, Phys. Rev. B **44**, 10354 (1991).
18. J. Wollschläger and N. M. Amer, Surf. Sci. **277**, 1 (1992).
19. S. Padovani, F. Scheurer, and J. P. Bucher, Eur. Phys. Lett. **45**, 327 (1999).
20. S. Padovani, F. Scheurer, I. Chado, and J. P. Bucher, Phys. Rev. B **61**, 72 (2000).
21. I. Chado, S. Padovani, F. Scheurer, and J. P. Bucher, Appl. Surf. Sci. **164**, 42 (2000).

22. V. Repain, G. Baudot, H. Ellmer, and S. Rousset, Eur. Phys. Lett. **58**, 730 (2002).

23. I. Chado, C. Goyhenex, H. Bulou, and J. P. Bucher, Phys. Rev. B **69**, 085413 (2004).

24. H. Bulou and J. P. Bucher, Phys. Rev. Lett. **96**, 076102 (2006).

25. K. Morgenstern, J. Kibsgaard, J. V. Lauritsen, E. Laesgaard, and F. Besenbacher, Surf. Sci. **601**, 1967 (2007).

26. J. Kibsgaard, K. Morgenstern, E. Lægsgaard, J. V. Lauritsen, and F. Besenbacher, Phys. Rev. Lett. **100**, 116104 (2008).

27. P. Campiglio, V. Repain, C. Chacon, O. Fruchart, J. Lagoute, Y. Girard, and S. Rousset, Surf. Sci. **605**, 1165 (2011).

28. D. D. Chambliss, R. J. Wilson, and S. Chiang, Phys. Rev. Lett. **66**, 1721 (1991).

29. D. D. Chambliss, R. J. Wilson, and S. Chiang, J. Vac. Sci. Technol. B **9**, 933 (1991).

30. J. A. Meyer, I. D. Baikie, E. Kopatzki, and R. J. Behm, Surf. Sci. **365**, L647 (1996).

31. W. G. Cullen and P. N. First, Surf. Sci. **420**, 53 (1999).

32. S. Jensen and C. J. Baddeley, J. Phys. Chem. C **112**, 15439 (2008).

33. A. G. Trant, T. E. Jones, J. Gustafson, T. C. Q. Noakes, P. Bailey, and C. Baddeley, Surf. Sci. **603**, 571 (2009).

34. M. M. Biener, J. Biener, R. Schalek, and C. M. Friend, Surf. Sci. **594**, 221 (2005).

35. S. Helveg, J. V. Lauritsen, E. Laegsgaard, I. Stensgaard, J. K. Nørskov, B. S. Clausen, H. Topsøe, and F. Besenbacher, Phys. Rev. Lett. **84**, 951 (2000).

36. X. Ma, X. Zhao, J. A. Rodriguez, and J. Hrbek, J. Phys. Chem. C **111**, 3685 (2008).

37. T. Cai, Z. Song, Z. Chang, G. Liu, J. A. Rodriguez, and J. Hrbek, Surf. Sci. **538**, 76 (2003).

38. T. Cai, Z. Song, J. A. Rodriguez, and J. Hrbek, J. Am. Chem. Soc. **126**, 8886 (2004).

39. B. Herd, D. Langsdorf, C. Sack, Y. He, and H. Over, Langmuir **32**, 5291 (2016).

40. E. I. Altman and R. J. Colton, Surf. Sci. **304**, L400 (1994).

41. I. Chado, F. Scheurer, and J. P. Bucher, Phys. Rev. B **64**, 094410 (2001).

42. C. J. Baddeley, R. M. Ormerod, A. W. Stephenson, and R. M. Lambert, J. Phys. Chem. **99**, 5146 (1995).

43. A. W. Stephenson, C. J. Baddeley, M. S. Tikhov, and R. M. Lambert, Surf. Sci. **398**, 172 (1998).

44. C. S. Casari, S. Foglio, F. Siviero, A. Li Bassi, M. Passoni, and C. E. Bottani, Phys. Rev. B **79**, 195402 (2009).

45. A. E. Baber, H. L. Tierney, and E. C. Sykes, ACS Nano **4**, 1637 (2010).

46. A. E. Baber, H. L. Tierney, T. J. Lawton, and E. C. Sykes, ChemCatChem **3**, 607 (2011).

47. C. S. Casari, S. Foglio, M. Passoni, F. Siviero, C. E. Bottani, and A. L. Bassi, Phys. Rev. B **84**, 155441 (2011).

48. M. Ø. Pedersen, S. Helveg, A. Ruban, I. Stensgaard, E. Lægsgaard, J. K. Nørskov, and F. Besenbacher, Surf. Sci. **426**, 395 (1999).

49. Y. Nahas, V. Repain, C. Chacon, Y. Girard, and S. Rousset, Surf. Sci. **604**, 829 (2010).

50. M. Ruff, Diploma thesis, Ulm University, 1995.

51. O. M. Magnussen and R. J. Behm, J. Electroanal. Chem. **467**, 258 (1999).

52. F. Grillo, H. Früchtl, S. M. Francis, and N. V. Richardson, New J. Phys. **13**, 013044 (2011).

53. W. Wang, H. Shi, L. Wang, Z. Li, H. Shi, K. Wu, and X. Shao, J. Phys. Chem. C **122**, 19551 (2018).

54. Q. Liu, Y. Ning, W. Huang, Q. Fu, F. Yang, and X. Bao, J. Phys. Chem. C **122**, 8364 (2018).

55. F. Grillo, R. Megginson, J. Christie, M. Francis, N. V. Richardson, and J. Baddeley, e-J. Surf. Sci. Nanotechnol. **16**, 163 (2018).

56. F. Grillo, R. Megginson, D. Batchelor, M. Muntwiler, and C. J. Baddeley, Jap. J. Appl. Phys. **58**, SII B09 (2019).

57. M. M. Dovek, C. A. Lang, J. Nogami, and C. F. Quate, Phys. Rev. B **40**, 11973 (1989).

58. D. D. Chambliss and R. J. Wilson, J. Vac. Sci. Technol. B **9**, 928 (1991).

59. D. D. Chambliss, K. E. Johnson, R. J. Wilson, and S. Chiang, J. Magn. Magn. Mater. **121**, 1 (1993).

60. H. Cercellier, Y. Fagot-Revurat, B. Kierren, D. Malterre, and F. Reinert, Surf. Sci. **566**, 520 (2004).

61. C. Didiot, S. Pons, B. Kierren, Y. Fagot-Revurat, and D. Malterre, Surf. Sci. **600**, 3917 (2005).

62. H. Cercellier, C. Didiot, Y. Fagot-Revurat, B. Kierren, L. Moreau, and D. Malterre, Phys. Rev. B **73**, 195413 (2006).

63. C. A. Lang, M. M. Dovek, J. Nogami, and C. F. Quate, Surf. Sci. **224**, L947 (1989).

64. B. Fischer, J. V. Barth, A. Fricke, L. Nedelmann, and K. Kern, Surf. Sci. **389**, 366 (1997).

65. B. Fischer, H. Brune, J. Barth, A. Fricke, and K. Kern, Phys. Rev. Lett. **82**, 1732 (1999).

66. P. Sadhukhan, V. K. Singh, A. Rai, K. Bhattacharya, and S. R. Barman, AIP Conference Proceedings **1942,** 080073 (2018).

67. J. V. Barth, H. Brune, R. Schuster, G. Ertl, and R. J. Behm, Surf. Sci. **292**, L769 (1993).

68. J. V. Barth, R. J. Behm, and G. Ertl, Surf. Sci. **302**, L319 (1994).

69. J. V. Barth, R. J. Behm, and G. Ertl, Surf. Sci. **341**, 62 (1995).

70. J. V. Barth, R. Schuster, R. J. Behm, and G. Ertl, Surf. Sci. **348**, 280 (1996).

71. C. Wu and M. R. Castell, Surf. Sci. **606**, 181 (2012).