Theory and experiments on the structure of 7 Å alumina films grown on Ni₃Al[☆]

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Abstract

Recently, X-ray diffraction (XRD) and scanning tunneling microscopy (STM) experiments confirmed a theoretical prediction that the surface of the two O-layer, or 5 Å, alumina film on NiAl(1 1 0) has 50% tetrahedral and 50% octahedral Al-site occupancy, a distorted A-plane of κ-alumina. Now density functional theory (DFT) calculations for a 7 Å (i.e., three oxygen layer) alumina film are compared with experiments on Ni₃Al(1 1 0). To minimize the surface energy, we assume that the first two planes of the thicker film are the A- and B- planes of the κ-phase. As with the thinner film, significant distortions occur from the crystalline form. However, a 2 × 1 unit cell occurs with rows separated by ~1 nm. STM of this film confirms this structure. Finally, an earlier theoretical conjecture is confirmed using low energy electron diffraction (LEED) on the same film: the bottom oxygen layer is chemisorbed on a plane of Al(1 1 1), and these are rotated against the substrate to produce the observed domain structures. Thus this system is tri-layered as κ-alumina (A–B planes)/O(1 1 1) on Al(1 1 1)/Ni₃Al.
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1. Introduction

Recently, Qin, Magtoto, and Kelber [1] made a remarkable and unanticipated observation during the 300 K exposure of a 7 Å film of alumina, grown on two faces of Ni₃Al, at 10^{-4}–10^{-5} Torr of H_2O. While the lower pressure exposure had no effect, the higher pressure induced a severe topographical reconstructing and roughening that completely consumed the surface over a period of ~1 h, as observed by STM. No OH was visible to x-ray photoelectron spectroscopy (XPS) upon sample reintroduction to ultra-high vacuum (UHV; $P < \sim 10^{-8}$ Torr), in contrast to observations made on other alumina surfaces at >1 Torr H_2O (see below). Upon heating to 1100 K in UHV, the ordered oxide surface was completely restored.

Since interactions between H_2O and heterogeneous catalysts are potentially important for understanding a multitude of reactions, many papers have probed H_2O interactions with alumina, a common support material [2–9]. Several studies involved the basal plane of α-Al₂O₃ or sapphire(0 0 0 1) [2–6,8–9]. Though not a cleavage plane, it can be prepared for UHV studies. It is known that the sticking probability of H_2O to this surface at 300 K is essentially zero in UHV [2]. If the partial pressure of H_2O is raised to ≥1 Torr, however, the surface changes to one that is OH terminated [6]. This only minimally disturbs the deeper crystal because the old surface layer with three O-ions and one Al-ion per unit cell has a charge of 3−, just the same as the new OH-ion terminated surface. Indeed, all alumina exposed to ambient conditions is OH-terminated, with the clean surface 1/3 ML of Al-ions removed [6].

It has been shown that annealing the sapphire(0 0 0 1) surface in UHV to 1200 K [4,5] or even 1400 K [3] does not remove all OH. We conjecture that this is because OH-ions are electrostatically bound and hence immobile, so nearest neighbor OH-ions are needed to react and release H_2O. In-

deed, XPS shows about 1/3 ML of OH remains since below this coverage, OH groups have no nearest neighbor hydroxyls with which to react.

In order to study alumina supports without charging and to use all surface science tools such as STM, ultrathin (<1 nm) films have been grown on nickel aluminides such as NiAl [10] and Ni$_3$Al [11,12] by high temperature oxidation, which draws Al out of the substrate but not Ni.

The most studied film is the 5 Å (or two O-layer) film on NiAl(1 1 0) [13]. As with sapphire, H$_2$O does not chemisorb on Al$_2$O$_3$/NiAl(1 1 0) in UHV at 300 K, and only one experiment created OH on this film by using a small deposition of Al metal, which formed islands to adsorb and dissociate water [7].

Since the earliest work on ultrathin alumina films on NiAl(1 1 0) [10], it was known that a domain structure results because of a lattice mismatch between the overlaying alumina and the substrate. The exact structure of the film, however, was elusive in spite of many experiments that used it as a model for a heterogeneous catalyst support [13]. Crystalline metal nanoclusters were produced and chemical activities were determined as a function of cluster size [13].

While the structural details of the film were unknown, STM was able to show a hexagonal array of surface O-ions [14]. However, this is not definitive as several alumina phases have similar O-lattice structures and the vertical relief (buckling) could be mitigated by film thinness. In this early study, the Al-ions were invisible.

Finally, STM was used to determine the adhesion between a Pd crystalline nanocluster and the film [15]. Indeed, the latter experimental breakthrough, made in a collaboration between the Freund and Besenbacher groups, also stimulated theoretical work concerning surface energy determination [16], which resulted in considerable recognition [17]. Theory and experiment now agree on the work of adhesion; however, sapphire (α-alumina) was used in the theoretical work to model the oxide surface. The agreement between theory [sapphire(0 0 0 1)] and experiment [5 Å Al$_2$O$_3$/NiAl(1 1 0)] suggests that these thinnest films (5 Å) [10] are either sapphire-like or indeed buckle less and thus behave (relax) differently than thicker films grown on other substrates.

Very recently, crystal truncation rod (CTR) XRD by Stierle, et al. [18] provided definitive information on the Al-sublattice structure of the 5 Å film on NiAl(1 1 0). By having equal amounts of tetrahedral and octahedral site Al-ions, the film resembles the A-plane of κ-alumina [19]. Improved STM experiments were also able to show the characteristic zig-zag rows of Al-ions in alternating sites [20]. These results were predicted by theory several years earlier by Jennison and Bogicevic [21], where DFT showed that distributing the Al-ions in this manner in the first layer was favored energetically over having all ions occupying the same type of site.

In order to understand the results of Ref. [1], and the interactions of oxide surfaces with the complex reaction environments relevant to catalysis, we must know the atomic structure of this film both on the surface and with depth, and

how the film interacts with H$_2$O as the latter produces both of the remarkable effects mentioned above, the reactions at 10^{-4} Torr and the restoration upon heating to 1100 K.

In this paper, we address structural issues: (1) does the preference for κ-alumina extend to thicker films, such as those with three O-layers? (2) What is the nature of the interface with the underlying nickel aluminide metals? (3) To what extent are these films accurate models for catalyst support materials? In order to probe these questions, we combine DFT calculations with STM, Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) experiments done on a 7 Å (three O-layer) film.

It has been known for some time that films thicker than 5 Å can be grown, either on NiAl(1 0 0) [22] or on facets of Ni$_3$Al [1,11,23,24]. Here, using both STM and LEED, we examine one such film, on Ni$_3$Al(1 1 0). We compare it to our first DFT calculation on a three O-layer film on a substrate of Al(1 1 1) and to the earlier prediction of phase [21] and to a conjecture concerning the oxide/metal interface [25].

2. Results

The DFT [26] calculations were made with the Vienna Ab initio Simulations Package (VASP) [27] in the local density approximation (LDA) [28] and in the generalized gradient approximation (GGA) known as PW91 [29]. Because the former yields a slightly more accurate geometry for this system, it was used here. The ultrasoft pseudopotentials of Vanderbilt [30] describe this system to high accuracy with a plane wave cutoff of 396 eV. Because of the long-range electrostatic forces in oxide as opposed to metallic systems, we used a large vacuum gap between the slabs, which repeats along the **c**-axis due to the plane wave basis set. We found ~15 Å or greater to be adequate.

Ambient temperature scanning tunneling microscopy (STM) studies were carried out using a commercial instrument (Omicron) in an ion-pumped system (base pressure, 5 × 10^{-11} Torr) equipped for Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). Details of this system, and the preparation of W tips, have been described previously [23]. H$_2$O exposures were carried out in a turbo-pumped introduction chamber (base pressure, 1 × 10^{-9} Torr) followed by transfer to UHV. Total contaminant coverage after exposures was <0.05 monolayer, as determined by AES. X-ray photoelectron spectroscopy (XPS) spectra were acquired in a separate system equipped with a dual anode X-ray source (Physical Electronics), hemispherical analyzer (VSW) operated at 22 eV constant pass energy, reverse view LEED (Omicron), and an introduction chamber for higher pressure H$_2$O exposures. XPS and LEED data acquisition and analysis procedures were as described previously [4,24].

Al$_2$O$_3$ films were grown on Ni$_3$Al(1 1 0) by exposure to 500 L O$_2$ (saturation level) at 900 K followed by annealing to 1100 K for 60 min in UHV. High temperature oxidation of

$Ni_3Al(1\,1\,0)$ was necessary since oxidation at room temperature followed by annealing to ~1100 K resulted in the disappearance of the O_{503} signal or the O(1s) XPS signal as previously reported [12,24]. $Al_2O_3/Ni_3Al(1\,1\,1)$ films were grown by exposure to 700 L O_2 (saturation level) at 300 K followed by annealing to 1100 K for 60 min. Constant current STM and LEED images of the $Al_2O_3/Ni_3Al(1\,1\,0)$ film were similar to those previously reported [12], but AES spectra showed the presence of Al^{+3} species, indicative of true oxide formation. AES was also used to determine the oxide film thickness −7 Å. The surface structure of the $Al_2O_3/Ni_3Al(1\,1\,0)$ film is not known, although a model of the incommensurate interface has been proposed based on studies of chemisorbed O on $Ni_3Al(1\,1\,0)$ [12]. $Al_2O_3/Ni_3Al(1\,1\,1)$ STM, LEED and AES spectra were as previously reported [23]. The proposed structure of this oxide film is γ'-$Al_2O_3(1\,1\,1)$, based on annealing temperature and the observation of a hexagonal oxygen lattice symmetry [23]. The stoichiometries of the two films are similar, as manifested by O/Al AES peak-to-peak height ratios that are equal to within experimental error, and equal average thicknesses (7 Å) [1]. No changes in STM, LEED or AES spectra were observed for either film after >6 h exposures to H_2O at pressures $<10^{-7}$ Torr, 300 K.

The κ-phase of alumina is the CVD phase. Since the A-plane results in a maximal spread of Al-ions in a monolayer, it is natural to suspect that this might serve as a template for further growth. Therefore, we computed a 7 Å (three O-layer) film. Because of the rotation of the film with respect to the underlying material (to relieve interfacial stress caused by a lattice mismatch), the unit cell is too large for computational study at present. Thus, we placed the film on a four layer Al(1 1 1) substrate, which has a minimal lattice mismatch. Because two studies (one on a film [21] and one on the sapphire/Al(1 1 1) interface [31]) showed that a true Al metal substrate would result in Al atoms crossing the interface and becoming chemisorbed on the oxide, the Al-metal substrate was frozen on the z-axis. Because the A-plane has maximal

Al-ion separation and minimal buckling, it should have the lowest surface energy. Therefore, the theory calculation was A/B/O(1 1 1)/Al(1 1 1) where the O(1 1 1) was chemisorbed on the Al(1 1 1) surface (see below concerning structure with depth).

Fig. 1 shows the top and side view of the relaxed film. More distortion is found than Stierle, et al. [18] found for the thinner film, as is logical since the freedom to relax is less for the thinner film.

Fig. 2 shows a near atomic-resolution constant current STM image obtained for $Al_2O_3/Ni_3Al(1\,1\,0)$. Clear rows are seen and the distance between the rows, ~1 nm, is the same as in Fig. 1. Both Figs. 1 and 2 have a 2 × 1 surface unit cell. As shown nicely in a figure in Ref. [18], only the κ-phase has this cell. Thus we conclude that the 7 Å films are κ-like; i.e., are distorted versions of this phase.

In Fig. 3 we see a conjecture made several years ago concerning the interface between alumina films and nickel aluminide substrates. It was proposed [25] that there would be chemisorbed oxygen (1 ML) on Al(1 1 1), which has been drawn out of the substrate. The logic was that less energy would be needed to rotate Al(1 1 1) on a nickel aluminide substrate (metal on metal) than oxide on metal in order to relieve the lattice mismatch.

In Fig. 4, we see LEED from the film. The pattern is a clear superposition of three structures. Having the most atoms per unit cell (forty) is the small κ-alumina signature. There is also the larger Ni_3Al substrate pattern. Finally, having the largest LEED pattern is the octahedral O(1 1 1)/Al(1 1 1) pattern. This supports the previous conjecture [25].

The films discussed here are κ-like, but other transitional phase films can be grown by variations in oxidation procedure or annealing temperature [32]. A question of considerable importance is the extent to which the κ-like or other transitional phase thin alumina films grown on single crystal aluminide substrates are actual models for the amorphous gamma-like alumina generally used as a catalyst support. Experimental
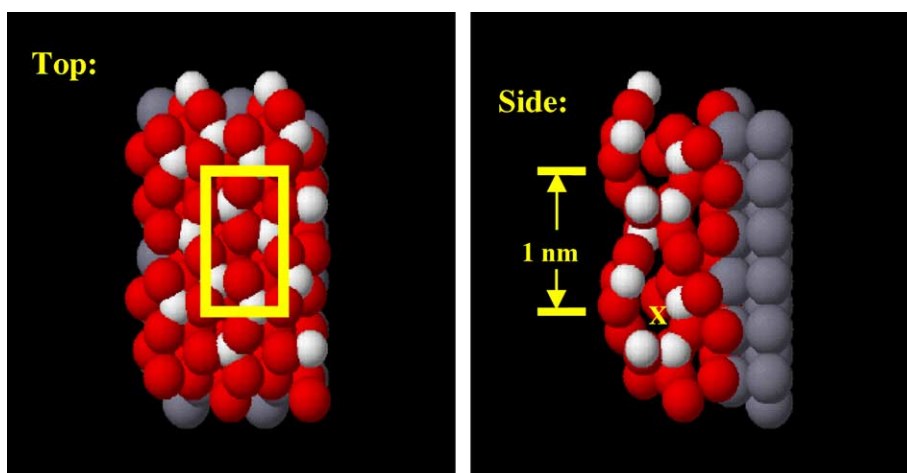

Fig. 1. Top and side views of the relaxed slab computed using DFT. The 2 × 1 unit cell (left) has its edges at the row tops, explicitly shown on the right. "X" marks the largest interstitial sites, which can contain atomic H (Ref. [33]) upon exposure to water at sufficient pressures (suggested as a possibility by Ref. [1]). O-ions are red, Al-ions are white, and Al-metal atoms in the model substrate, necessitated by a lattice mismatch at the interface, are gray.
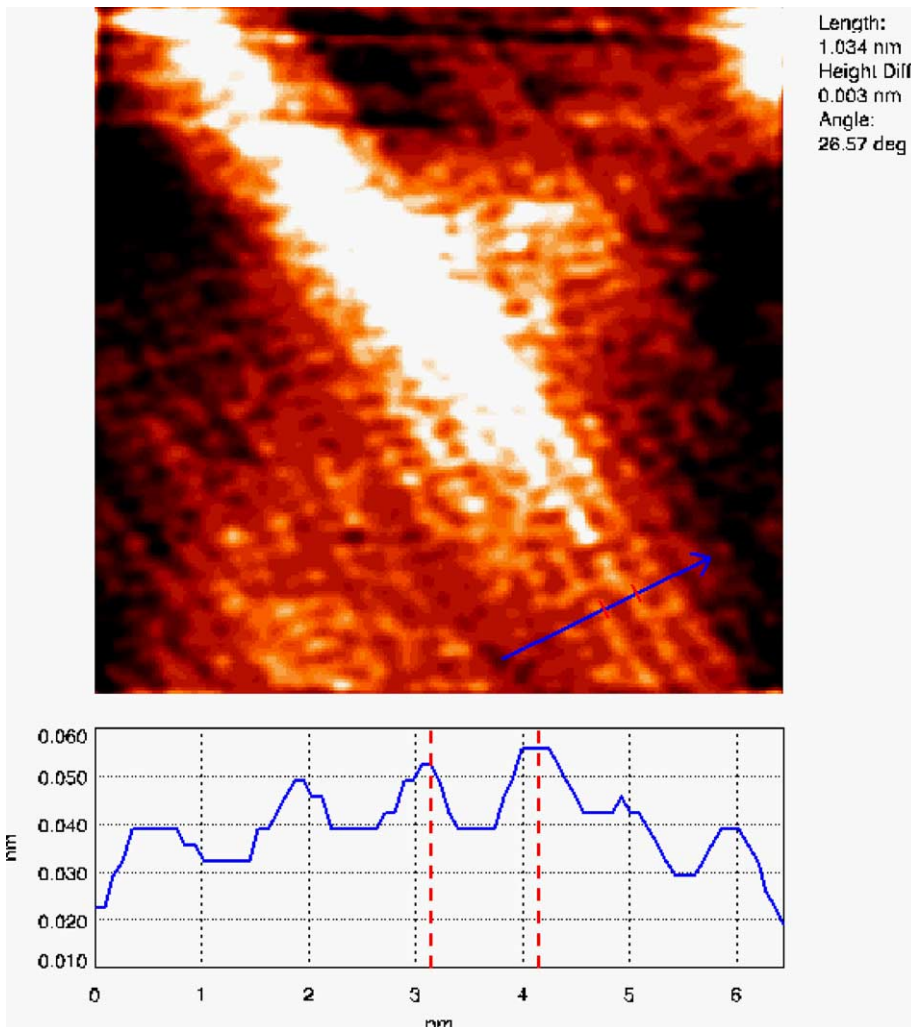
Fig. 2. Near atomic resolution, constant current STM image of the $Al_2O_3/Ni_3Al(1 1 0)$.film, showing the row structure and a row separation in agreement with the prediction of the calculation shown in Fig. 1.

[32] and theoretical studies indicate that the various transitional (non-α) phases differ from each other only in terms of relative octahedral vs. tetrahedral site occupancy and share many common characteristics regarding density and structure. In addition, recent agreements between electrochem-
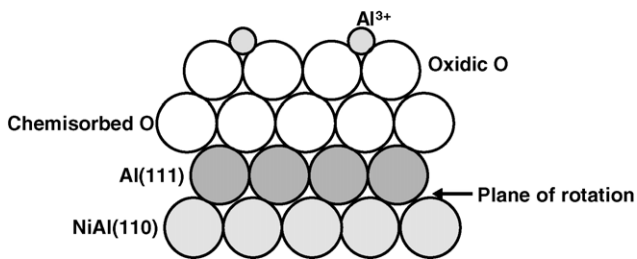

Fig. 3. The original conjecture of a structure having alumina and chemisorbed O on Al(1 1 1), rotated on nickel aluminide substrates, from Ref. [25].

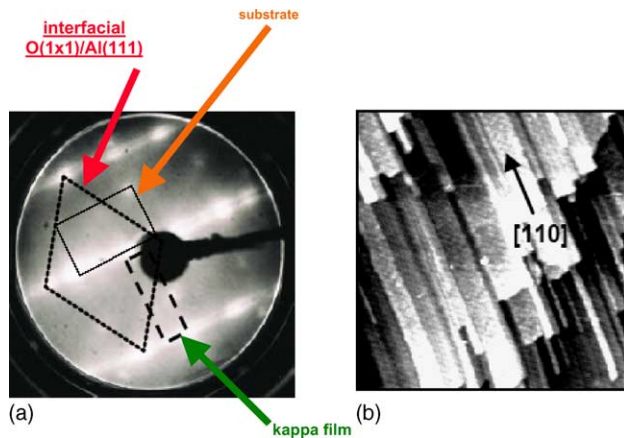Fig. 4. The LEED pattern of $Al_2O_3/Ni_3Al(1 1 0)$, supporting the trilayer conjecture of Ref. [25].

istry results for amorphous alumina films grown on Al(1 1 1) and DFT calculations on a κ-phase model indicate that the kappa film is an excellent model for amorphous alumina [33]. In contrast, vibrational studies of probe molecules at various oxide surfaces under UHV conditions indicate systematic variation in acid/base surface properties with annealing temperature and the transitional phase produced [32]. A recent study of high resolution electron energy loss spectroscopy (HREELS) study of a thin, amorphous γ-like alumina film indicated only two different types of surface hydroxyl sites on the thin film surface (i.e., different pK_a values), as opposed to five observed for amorphous alumina powders. The preponderance of evidence therefore seems to be that all transitional phase alumina films manifest strong similarities in reactivity, electronic properties and structure, but that differences in surface acid/base properties are revealed by detailed measurements under UHV conditions [34]. The extent to which differences in UHV-stable surface structures result in differences in reactivity and supported metal particle behavior under complex catalytic environments is an outstanding challenge for modern surface science.

3. Conclusion

First steps have been taken that to understand the structure and behavior [1] of 7 Å films of κ-like alumina on Ni₃Al. An earlier theoretical prediction [21], a film which is kappa-like, and a conjecture [25], 1 ML of $O_{(a)}$ on Al(1 1 1) at the interface, are now both supported by experiment. With this knowledge of atomic structure, it is now possible to turn to the questions involving the interactions with H_2O, adsorption, dissociation, possible penetration of neutral H atoms into the film, and finally recombination and dissociation. Transitional phase alumina thin films grown on single crystal aluminides share many common structural, electronic and chemical characteristics with each other and with actual support materials. Despite systematic differences in surface acid/base properties revealed under UHV conditions, these alumina films appear sufficiently similar to amorphous catalyst supports to serve as tractable models for bridging the pressure gap between UHV surface science and realistic catalytic environments.

References

[1] F. Qin, N.P. Magtoto, J.A. Kelber, Surf. Sci. 565 (2004) L277.

[2] J.W. Elam, C.E. Nelson, M.A. Cameron, M.A. Tolbert, S.M. George, J. Phys. Chem. B 102 (1998) 7008.

[3] J. Ahn, J.W. Rabalais, Surf. Sci. 388 (1997) 121.

[4] J.A. Kelber, C. Niu, K. Shepherd, D.R. Jennison, A. Bogicevic, Surf. Sci. 446 (2000) 76.

[5] C. Niu, K. Shepherd, D. Martini, J. Tong, J.A. Kelber, D.R. Jennison, A. Bogicevic, Surf. Sci. 465 (2000) 163.

[6] P.J. Eng, T.P. Trainor, G.E. Brown Jr., G.A. Waychunas, M. Neville, S.R. Sutton, M.L. Rivers, Science 288 (2000) 1029, references therein.

[7] J. Libuda, M. Frank, A. Sandell, S. Andersson, P.A. Brühwiler, M. Bäumer, N. Mårtensson, H.-J. Freund, Surf. Sci. 384 (1997) 106.

[8] S.A. Chambers, T. Droubay, D.R. Jennison, T.R. Mattsson, Science 297 (2002) 837.

[9] D.R. Jennison, T.R. Mattsson, Surf. Sci. 544 (2003) 689.

[10] J. Libuda, F. Winkelmann, M. Bäumer, H.-J. Freund, Th. Bertrams, H. Neddermeyer, K. Müller, Surf. Sci. 318 (1994) 61.

[11] A. Rosenhahn, J. Schneider, C. Becker, K. Wandelt, Appl. Surf. Sci. 142 (1999) 169.

[12] G.F. Cotterill, H. Niehus, D.J. O'Connor, Surf. Rev. Lett. 3 (1996) 1355.

[13] M. Baumer, H.-J. Freund, Prog. Surf. Sci. 61 (1999) 127.

[14] G. Ceballos, Z. Song, J.I. Pascual, H.P. Rust, H. Conrad, M. Baumer, H.-J. Freund, Chem. Phys. Lett. 359 (2002) 41.

[15] K.H. Hansen, T. Worren, S. Stempel, E. Lægsgaard, M. Bäumer, H.-J. Freund, F. Besenbacher, I. Stensgaard, Phys. Rev. Letts. 83 (1999) 4120.

[16] A.E. Mattsson, D.R. Jennison, Surf. Sci. 520 (2002) 611; A.E. Mattsson, D.R. Jennison, Surf. Sci. 520 (2002) 3–5.

[17] M. Jacoby, C & E News 80 (4 November, 2002); S. Borman C & E News 80 (16 December, 2002).

[18] A. Stierle, F. Renner, R. Streitel, H. Dosch, W. Drube, B.C. Cowie, Science 303 (2004) 1652.

[19] Y. Yourdshahyan, C. Ruberto, M. Halvarsson, L. Bengtsson, V. Langer, B.I. Lundqvist, S. Ruppi, U. Rolander, J. Am. Ceram. Soc. 82 (1999) 8265.

[20] M. Kulawik, N. Nilius, H.P. Rust, H.J. Freund, Phys. Rev. Lett. 91 (2003) 256101.

[21] D.R. Jennison, A. Bogicevic, Surf. Sci. 464 (2000) 108.

[22] R.-P. Blum, D. Ahlbehrendt, H. Niehus, Surf. Sci. 396 (1998) 176.

[23] S.G. Addepalli, B. Ekstrom, N.P. Magtoto, J.-S. Lin, J.A. Kelber, Surf. Sci. 442 (1999) 385–399.

[24] M. Garza, N.P. Magtoto, J.A. Kelber, Surf. Sci. 519 (2002) 259.

[25] D.R. Jennison, C. Verdozzi, P.A. Schultz, M.P. Sears, Phys. Rev. B 59 (1999) 15605; A. Bogicevic, D.R. Jennison, Phys. Rev. Lett. 82 (1999) 4050.

[26] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864; W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133.

[27] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558; G. Kresse, J. Hafner, Phys. Rev. 49 (1994) 14251; G. Kresse, J. Hafner, Phys. Rev. 54 (1996) 11169.

[28] J. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048; D.M. Ceperley, B.J. Alder, Phys. Rev. Lett. 45 (1980) 566.

[29] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.

[30] D. Vanderbilt, Phys. Rev. B 32 (1985) 8412; D. Vanderbilt, Phys. Rev. 41 (1990) 7892.

[31] D.J. Siegel, L.G. Hector Jr., J.B. Adams, Mat. Res. Soc. Symp. Proc. 654 (2001) AA 4.2.1; D.J. Siegel, L.G. Hector Jr., J.B. Adams, Phys. Rev. B 65 (2002) 85415.

[32] R. Gassman, R. Franchy, H. Ibach, Surf. Sci. 319 (1994) 95–109; M.B. Lee, J.H. Lee, B.G. Grederick, N.V. Richardson, Surf. Sci. 448 (2000) 207.

[33] D.R. Jennison, P.A. Schultz, J.P. Sullivan, Phys. Rev. B 69 (2004) 041405.

[34] K.A. Layman, J.C. Hemminger, J. Catalysis 222 (2004) 207.