

Sulfur chemisorption on Ni(111): The clock structure of the $(5\sqrt{3}\times 2)S$ phase

M. Foss

Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

R. Feidenhans'l, M. Nielsen, and E. Findeisen
Risø National Laboratory, DK-4000 Roskilde, Denmark

R. L. Johnson and T. Buslaps

II Institute for Experimental Physics, University of Hamburg, D-2000 Hamburg 50, Germany

I. Stensgaard and F. Besenbacher

Center for Atomic-Scale Materials Physics (CAMP) and Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

(Received 28 March 1994)

From an interplay between x-ray diffraction and scanning tunneling microscopy the atomic structure of the $(5\sqrt{3}\times 2)S$ reconstruction on Ni(111) has been revealed. It consists of four squarelike tetramers of Ni atoms, rotated in pairs $\sim 14^\circ$ clockwise and counterclockwise, onto which eight fourfold-coordinated S atoms are chemisorbed. The results have a significant bearing on the understanding of the detailed structure of postulated pseudo-(100) reconstructions of fcc(111) surfaces and support a general principle of increased adsorbate coordination as being decisive for the reconstruction.

Recently, adsorbate-induced reconstructions of the close-packed fcc(111) surfaces have received increased attention, especially in the case of Ni(111). Scanning-tunneling-microscopy (STM) investigations of the S-induced $(5\sqrt{3}\times 2)$ reconstruction¹ were interpreted as giving evidence of a missing-row reconstruction of an fcc(111) surface, and the positions of the S atoms in the topmost layer, as imaged with STM, were found to be consistent with adsorption in the threefold hollow sites if only a small lateral relaxation of the Ni atoms was assumed. However, a comparison of the surface-extended x-ray-absorption fine-structure (SEXAFS) amplitudes calculated for this model² with measured amplitudes^{3,4} did not support the threefold coordination of the S atoms, a fact that has been used as an argument against the missing-row model.² The measured SEXAFS amplitudes, on the other hand, were consistent with those calculated for S adsorption in fourfold-coordinated sites on a surface which has reconstructed into a pseudo-(100) structure.⁵ Adsorbate-induced reconstruction to form a Ni surface with pseudo-(100) orientation has also been inferred from low-energy electron-diffraction (LEED) data for C and N adsorption on Ni(111).⁶ A strong similarity of the I - V curves for the Ni(111)- $c(5\sqrt{3}\times 9)C$ and Ni(111)- $c(5\sqrt{3}\times 9)N$ structures to those from the Ni(100)- $(2\times 2)2C$ phase was taken as support for a reconstruction of the (111) surface to an almost square (100) Ni superstructure. In the same study, a similar reconstruction, again with the adsorbate in fourfold-coordinated hollows, was believed to exist for the Ni(111)- $(5\sqrt{3}\times 2)S$ and Ni(111)- $(2\times 6)N$ structures.⁶

In this paper, we present an unequivocal structural model for the Ni(111)- $(5\sqrt{3}\times 2)S$ phase which reconciles the discrepancy between the missing-row model and the pseudo-

(100) model. Based on grazing-incidence surface x-ray diffraction (SXRD), we derive a surface structure consistent with the missing-row picture, but in which the remaining top-layer Ni atoms have relaxed considerably to form a clock reconstruction, consisting of pairs of squares, rotated alternately clockwise and counterclockwise, onto which fourfold-coordinated S atoms are chemisorbed. These results have general implications in two ways: The first pertains to the nature of pseudo-(100) reconstructions on fcc(111) surfaces. Obviously, the SEXAFS-amplitude measurements^{3,4} on the reconstructed (111) surface can only be taken as evidence for fourfold adsorbate coordination. As shown in the present case, strong lateral relaxations of the substrate atoms can remove the similarity with an extended (100)-surface layer. Based on the present results it is likely that the C- and N-induced reconstructions of the Ni(111) surface mentioned above are not simple pseudo-(100) structures but clock reconstructions as well. The second implication is related to the coordination of the adsorbates. Based on an analysis of SXRD measurements,⁷ we propose that also the two S-induced reconstructions of the Cu(111) surface⁸ are formed primarily of rotated quadratic Cu units with fourfold-coordinated sulfur, in spite of the fact that the formation dynamics of the two phases is quite different.^{1,8} It appears therefore that a general principle of increased adsorbate coordination is decisive for the final structure, as has been suggested for the C-induced clock reconstruction of Ni(100),⁹ and, furthermore, that the clock reconstruction observed here on an fcc(111) surface may be much more common than previously anticipated.

The $(5\sqrt{3}\times 2)S$ reconstruction is not describable in Wood's notation¹⁰ since it is rectangular on a hexagonal substrate. The unit cell has its primitive vectors along $\langle 112 \rangle$ and $\langle 110 \rangle$ surface directions and has the more correct matrix no-

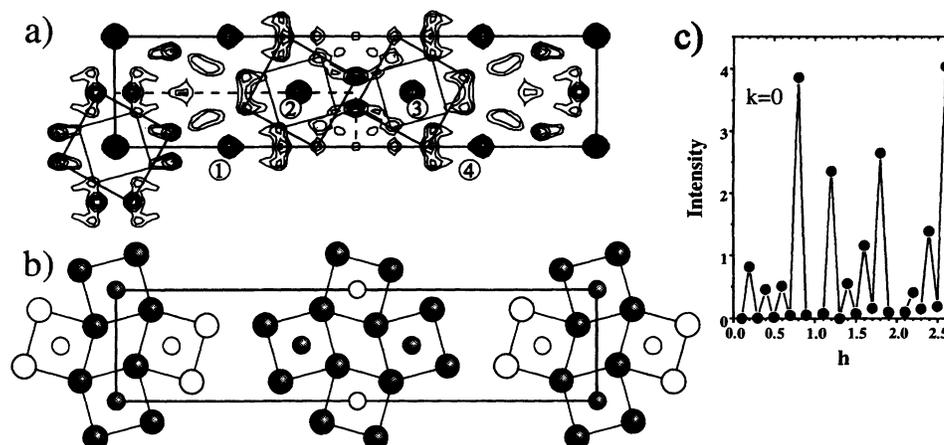


FIG. 1. (a) Patterson contour map of the Ni(111) structure created by the in-plane fractional-order intensities; the irreducible unit is indicated by dashed lines. The peak at the origin rises 20 contour levels and only positive contours are shown. The peaks around the origin reproduce themselves at positions 2 and 3. The vectors from the origin to the corners of the large square near the origin correspond to the Ni-Ni interatomic vectors in (b) and the corners of the small square represent Ni-S interatomic vectors. (b) Filled circles: atomic positions derived from the Patterson map. Open circles: atomic positions found by imposing the glide-line symmetry. Small circles are S atoms, large circles Ni atoms. (c) Measured in-plane intensities along the $(h0)$ direction. The systematic near-extinction of every second intensity (observed only for $k=0$) indicates a glide-line symmetry along the $\langle 112 \rangle$ surface direction.

tation $[\frac{2}{-5} \frac{0}{10}]$. From the STM measurements of the relative area of islands formed by Ni atoms ejected from terraces during the formation,¹ this structure is known to consist of a reconstructed Ni layer, with a coverage of $\Theta_{\text{Ni}}=0.8$ ML. The S coverage Θ_{S} has been judged by Auger electron spectroscopy⁴ to be 0.3–0.4 ML, and a radioactive tracer measurement using ^{35}S yielded 0.40 ML.¹¹ A basic requirement to a structural model is therefore that it comprises 16 Ni atoms and, most probably, 8 S atoms per unit cell. Note that these coverages are compatible with both the missing-row and the pseudo-(100) models.

The SXRD experiments were performed at the Hamburger Synchrotronstrahlungslabor (HASYLAB). The crystal was cleaned at the FLIPPER II beam line using standard procedures and then exposed to 10 L ($1 \text{ L} = 10^{-6} \text{ torr sec}$) of H_2S followed by 240 sec of annealing at 470 K. This treatment produced a good-quality $(5\sqrt{3} \times 2)$ LEED pattern. The sample was then moved to a portable UHV chamber and transferred to the wiggler beam line BW2. The wavelength was chosen to be $\lambda = 1.52 \text{ \AA}$, the optical surface of the crystal was aligned by total reflection, and the angle of incidence was set to the critical angle $\alpha_c = 0.415^\circ$.

A total of 302 fractional-order and 8 integer-order in-plane intensities were measured, out of which 136 and 6, respectively, were nonequivalent. The intensities were corrected for the Lorentz factor and the change in active area.¹² Since the reconstruction is expected to involve a major rearrangement of Ni atoms,¹ an extensive out-of-plane data set consisting of 26 fractional-order and 5 integer-order Bragg rods was measured.

Since the reflections from the three different domain orientations of the $(5\sqrt{3} \times 2)\text{S}$ structure do not overlap, it is possible to record data from only one of them. The intensities of the (hk) reflections¹³ are proportional to the square of the structure factors F_{hk} and can be used to create the Patterson (autocorrelation) function $P(x,y)$ of the electron density.¹²

$$P(x,y) = \sum_{h,k} |F_{hk}|^2 \cos[2\pi(hx + ky)].$$

A contour plot of $P(x,y)$ depicting the in-plane projection of the interatomic vectors in the reconstructed unit cell is shown in Fig. 1(a). It is worth noting that the Patterson function always has inversion symmetry, so additional symmetries not present in the structure may be introduced as in this case of an fcc(111) surface.¹² Apart from the origin, the Patterson function has four very distinct peaks labeled 1, 2, 3, and 4, where 4 is equivalent to 1 and 3 to 2. The existence of three (including the origin) nonequivalent peaks means that the building block of the reconstruction must reproduce itself in at least three positions. The internal structure of this building block is revealed by investigating the peaks in the Patterson plot near the origin. Clearly, there are eight strong peaks which can be arranged in two squares with small peaks centered at the middle of the sides. This is the signature of a rotated square of Ni atoms with a S atom placed in the fourfold-coordinated position, as indicated in Fig. 1(b). The strong peaks in the corners of the large square around the origin in Fig. 1(a) are the Ni-Ni nearest-neighbor interatomic vectors whereas the weak peaks in the corners of the small square represent Ni-S interatomic vectors. The high-symmetry S position is similar to that found on the Ni(100) surface.¹⁴ The set of peaks near the origin repeats itself around the positions of the strong peaks called 2 and 3 in the Patterson map. The peaks labeled 1 and 4 correspond to the vectors between the complexes at positions 2 and 3. We therefore arrive at a model with three quadratic units as shown in Fig. 1(b) with filled circles. Note that this structure breaks the bulk mirror line along the $\langle 112 \rangle$ direction.

The models were compared with the experimental data by a conventional least-square (χ^2) analysis, with the systematic errors judged to be 10%.¹² The model with three quadratic units yielded the relatively poor agreement of

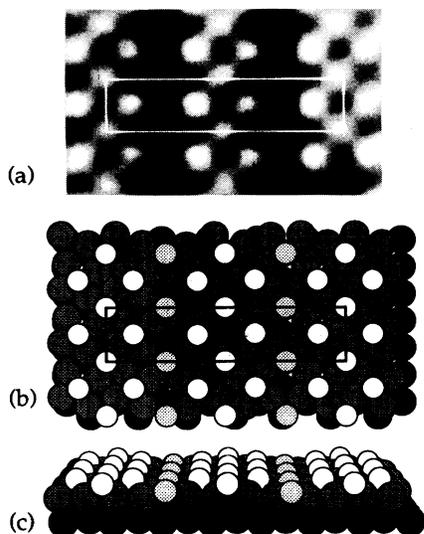


FIG. 2. (a) An STM image ($18 \times 29 \text{ \AA}^2$) of the $(5\sqrt{3} \times 2)$ S structure with a unit cell indicated. The vertical “troughs” are along a $\langle 110 \rangle$ direction. The six strong and two weak bright features per unit cell correspond to S atoms. (b) Top view of the final clock structure as derived by SXRD. The unit cell is indicated. The small circles are S atoms and the large circles Ni atoms. (c) Perspective view of the model along a $\langle 110 \rangle$ surface direction.

$\chi^2 = 30.0$. However, this structure is incomplete, since it accounts for only three of the protrusions associated with S atoms in the STM images [see Fig. 2(a)] and only 12 out of 16 Ni atoms. Further insight into the structure can be gained by investigating the fractional-order in-plane intensities along the $(h0)$ direction, see Fig. 1(c), where every second intensity is almost vanishing (only for $k=0$). This indicates the existence of a glide-line symmetry along the $\langle 112 \rangle$ direction and the model can therefore be further completed by imposing this requirement of glide-line symmetry. The resulting structure shown in Fig. 1(b) has $p2mg$ symmetry and consists of 16 Ni atoms in agreement with the Ni coverage found by STM, and all the S atoms have local coordinations corresponding to pseudo-Ni(100)-S sites. This model also explains the six major protrusions in each unit cell in the STM picture, cf. Fig. 2(a). Another refinement of the atomic positions results in $\chi^2 = 9.8$, which is acceptable. However, the model incorporates only six S atoms, while both the radioactive tracer data¹¹ and the STM image [Fig. 2(a)] suggest eight S atoms. It is natural to place the two extra S atoms in the positions suggested by the STM image since this prevents the distance between the S atoms from being too small, compared to S-S distances in Ni-S compounds ($\sim 3.3 \text{ \AA}$). Furthermore, the two new S positions also have a coordination of four as suggested by photoemission and high-resolution electron energy-loss spectroscopy (HREELS).¹⁵ With this model having 44 free parameters, a good agreement is obtained, giving $\chi^2 = 5.4$, considering the inherent contributions from relaxations in the top layers of the underlying substrate. The registry of the reconstructed unit cell relative to the substrate has been determined by a χ^2 analysis of the in-plane integer-order reflections.¹² The final in-plane model with relaxations is shown in Fig. 2(b).

Having solved the in-plane structure, the heights of the

atoms have to be found from the intensities in the fractional-order rods. Unfortunately, there are too many (24) height parameters to allow a systematic derivation, even with the large amount of out-of-plane data acquired. Instead, the heights of the atoms are deduced by assuming Ni-S bond lengths close to 2.25 \AA , as the two SEXAFS studies indicate.^{3,4} The final, three-dimensional model shown in Figs. 2(b) and 2(c) has Ni-Ni bond lengths down to 2.35 \AA and S-Ni distances between 2.10 and 2.41 \AA . Part of this variation in bond lengths is due to the uncertainties (0.1 – 0.2 \AA) of the in-plane positions. This model produces a good agreement with the measured out-of-plane intensities.⁷

We now discuss the present structure in relation to the missing-row and the pseudo-(100) models. The missing-row model was derived on the basis of a measured surface Ni density and the observation by STM of deep (~ 0.5 – 1 \AA) $\langle 110 \rangle$ -directed surface troughs.¹ As argued previously,¹⁶ this depth exceeds significantly the depth (0.3 – 0.4 \AA) of the apparent troughs which can be created^{2,17} by systematic fluctuations in the Ni-Ni distances along the $\langle 112 \rangle$ direction of a pseudo-(100) structure. In the present model, the S atoms in the troughs are located $\sim 0.8 \text{ \AA}$ below the S atoms in the topmost layer, in good agreement with the STM data. The results therefore further corroborate the missing-row description of the reconstruction which is suggested to be driven in the following way:¹ The Ni atoms on the clean surface have coordination number $N_c = 9$ and are therefore undercoordinated relative to the bulk atoms ($N_c = 12$). Adsorption of sulfur atoms donates so much charge to the surface that the Ni surface atoms become “overcoordinated,” resulting in a compressive stress in the surface. This stress is relieved by a periodic ejection of entire Ni $\langle 110 \rangle$ surface rows which energetically is the cheapest way to reduce the Ni density.

The squeezeout of surface rows is followed by a lateral restructuring of the remaining Ni atoms which adopt a geometry that locally is identical to the C-induced clock reconstruction on Ni(100).⁹ In the final structure, the S atoms have lowered their energy by increasing their coordination to the Ni atoms from three to four. Locally, this is similar to S on Ni(100),¹⁴ but the resemblance to a (100) surface, i.e., a pseudo-(100) reconstruction, is partly lost due to the rotations of the squarelike units and to lateral relaxations. The main argument against the missing-row model has been the proposed threefold coordination of the S atoms.^{2,17} The present model finds fourfold coordination and is, furthermore, in good agreement with still unpublished results from a S $2p$ photoemission and HREELS study,¹⁵ indicating the presence of two different S states at high coverage, neither of which is the same as the low coverage threefold hollow S site.

The restructuring of surfaces to gain energy by increasing the adsorbate coordination number appears to be a more general phenomenon. The C atoms in the $c(2 \times 2)p4g$ clock reconstruction on Ni(100), for example, have increased their coordination number N_c from four to five after reconstruction.⁹ In the present case, N_c increases from three to four for the S atoms. Another reconstruction, which also includes the breaking of Ni-Ni bonds to increase the number of highly coordinated positions, is the Ni(110)-(4 \times 1)S structure.¹⁸ There is thus increasing evidence that S atoms, which are fourfold coordinated to a squarelike structure of

metal atoms, constitute the basic element in S-induced reconstructions of metal surfaces. A similar local structure has been identified in the analysis of SXRD data from the $(\sqrt{7} \times \sqrt{7})R19^\circ$ and $[\begin{smallmatrix} 4 & 1 \\ -1 & 4 \end{smallmatrix}]$ S structures on Cu(111) (Ref. 7) and is proposed for the $(\sqrt{17} \times \sqrt{17})R14^\circ$ S structure on Cu(100), based on an STM study.¹⁹

In summary, an atomic model of the Ni(111)- $(5\sqrt{3} \times 2)$ S structure has been deduced from an interplay between SXRD and STM. The unit cell, which has $p2mg$ symmetry, consists of two pairs of squarelike tetramers of Ni atoms, rotated $\sim 14^\circ$ alternately clockwise and counterclockwise relative to the $\langle 112 \rangle$ direction, with six chemisorbed, fourfold-coordinated S atoms. Two additional S atoms are placed in the remaining two (strongly distorted) fourfold-coordinated positions, making a nearly quadratic S

layer. This clock model incorporates all the existing experimental evidence. The results have at least two general implications, one concerning the nature of the postulated pseudo-(100) reconstructions, the other related to a principle of increased coordination of the adsorbates governing the reconstructions.

We would like to thank L. Ruan for very helpful discussions. We gratefully acknowledge the financial support from the Danish Natural Science Research Council (DNSRC), from the DNSRC through the Center for Surface Reactivity, from the Center for Atomic-Scale Materials Physics (CAMP) funded by the Danish National Research Foundation, and from the Bundesministerium für Forschung und Technologie (BMFT) under Project No. 055GUABI. We also thank the staff of HASYLAB for their help and assistance.

¹L. Ruan, I. Stensgaard, F. Besenbacher, and E. Laegsgaard, *Phys. Rev. Lett.* **71**, 2963 (1993).

²D. P. Woodruff, *Phys. Rev. Lett.* **72**, 2499 (1994).

³D. R. Warburton, P. L. Wincott, G. Thornton, F. M. Quinn, and D. Norman, *Surf. Sci.* **211/212**, 71 (1989).

⁴Y. Kitajima, T. Yokoyama, T. Ohta, M. Funabashi, N. Kosugi, and H. Kuroda, *Surf. Sci.* **214**, L261 (1989).

⁵T. Edmonds, J. J. McCarroll, and R. C. Pitkethly, *J. Vac. Sci. Technol.* **8**, 68 (1971).

⁶D. E. Gardin, J. D. Batteas, M. A. Van Hove, and G. A. Somorjai, *Surf. Sci.* **296**, 25 (1993).

⁷M. Foss, R. Feidenhans'l, M. Nielsen, E. Findeisen, R. L. Johnson, T. Buslaps, I. Stensgaard, and F. Besenbacher (unpublished).

⁸L. Ruan, I. Stensgaard, F. Besenbacher, and E. Laegsgaard, *Ultramicroscopy* **42-44**, 498 (1992).

⁹C. Klink, L. Olsen, F. Besenbacher, I. Stensgaard, and E. Laegs-

gaard, *Phys. Rev. Lett.* **71**, 4350 (1993).

¹⁰E. A. Wood, *J. Appl. Phys.* **38**, 1306 (1964).

¹¹M. Perdureau and J. Oudar, *Surf. Sci.* **20**, 80 (1970).

¹²R. Feidenhans'l, *Surf. Sci. Rep.* **10**, 105 (1989).

¹³The reflections are labeled according to the usual convention in LEED, i.e., based on a surface (real space) unit cell with 120° between the primitive vectors.

¹⁴W. Oed, U. Starke, K. Heinz, K. Müller, and J. B. Pendry, *Surf. Sci.* **251/252**, 488 (1991).

¹⁵D. Mullins and S. H. Overbury (private communication).

¹⁶L. Ruan, I. Stensgaard, F. Besenbacher, and E. Laegsgaard, *Phys. Rev. Lett.* **72**, 2500 (1994).

¹⁷G. Thornton (private communication).

¹⁸M. Foss, R. Feidenhans'l, M. Nielsen, E. Findeisen, T. Buslaps, R. L. Johnson, F. Besenbacher, and I. Stensgaard, *Surf. Sci.* **296**, 283 (1993).

¹⁹M. L. Colaianni and I. Chorkendorff, *Phys. Rev. B* **50**, 8798 (1994).

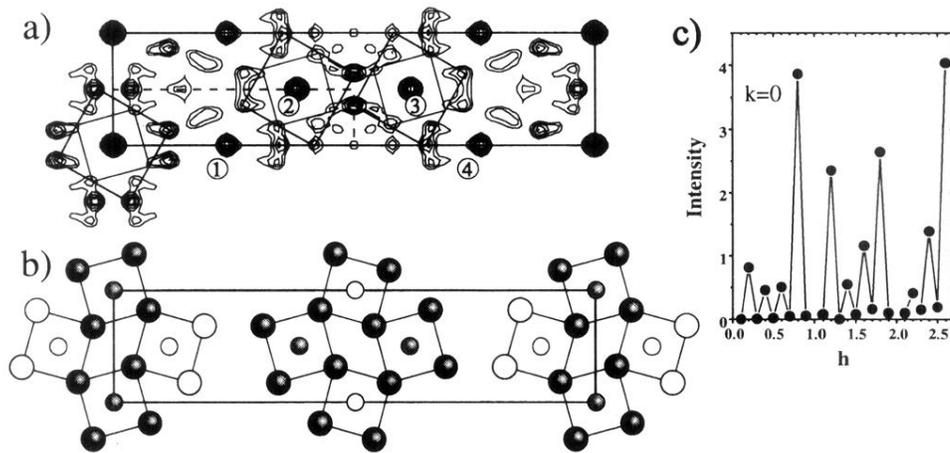


FIG. 1. (a) Patterson contour map of the Ni(111) structure created by the in-plane fractional-order intensities; the irreducible unit is indicated by dashed lines. The peak at the origin rises 20 contour levels and only positive contours are shown. The peaks around the origin reproduce themselves at positions 2 and 3. The vectors from the origin to the corners of the large square near the origin correspond to the Ni-Ni interatomic vectors in (b) and the corners of the small square represent Ni-S interatomic vectors. (b) Filled circles: atomic positions derived from the Patterson map. Open circles: atomic positions found by imposing the glide-line symmetry. Small circles are S atoms, large circles Ni atoms. (c) Measured in-plane intensities along the $(h0)$ direction. The systematic near-extinction of every second intensity (observed only for $k=0$) indicates a glide-line symmetry along the $\langle 112 \rangle$ surface direction.

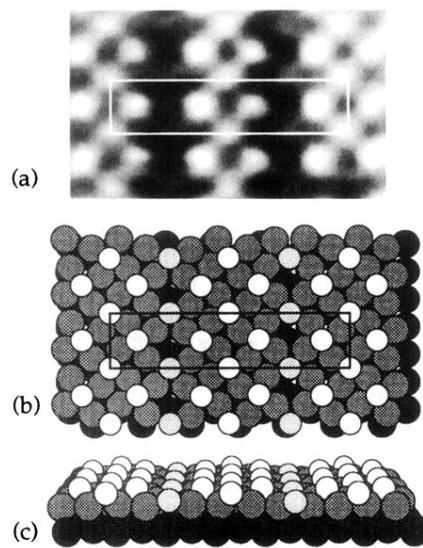


FIG. 2. (a) An STM image ($18 \times 29 \text{ \AA}^2$) of the $(5\sqrt{3} \times 2)\text{S}$ structure with a unit cell indicated. The vertical “troughs” are along a $\langle 110 \rangle$ direction. The six strong and two weak bright features per unit cell correspond to S atoms. (b) Top view of the final clock structure as derived by SXRD. The unit cell is indicated. The small circles are S atoms and the large circles Ni atoms. (c) Perspective view of the model along a $\langle 110 \rangle$ surface direction.