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Surface and interface structures of epitaxial silicon nitride on Si(111)

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Surface and interface structures of an ultrathin silicon nitride film grown epitaxially on the Si(111) surface are investigated by core-level and valence-band photoelectron spectroscopy using synchrotron radiation. The Si $2p$ photoelectron spectra reveal a characteristic series of components for the Si species not only in stoichiometric Si_3N_4 (Si^{4+}) but also in the intermediate nitridation states with one (Si^{+}) or three (Si^{3+}) nitrogen nearest neighbors. The Si $2p$ core-level shifts for the Si^{+}, Si^{3+}, and Si^{4+} components are determined to be 0.64, 2.21, and 2.74 eV, respectively. In sharp contrast to the well-known SiO_2/Si(111) case, no trace of the Si^{2+} species is observed, indicating an atomically abrupt and defect-free interface in accordance with a recent interface model of β-Si_3N_4/Si(111). In addition, the origin of the characteristic N $1s$ spectra and a strong surface-state emission observed in the valence-band spectra are discussed.

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I. INTRODUCTION

The growth of high-quality thin silicon nitride (Si_3N_4) films on Si substrates is very important in frontier microelectronic devices due to its dielectric properties and chemical stability. Despite such technological interests, a highly ordered Si_3N_4 film cannot easily be formed on a Si(100) substrate by direct thermal reaction because of a large lattice mismatch and the side reaction, such as etching, leading to an ill-defined interface. However, recently, an epitaxial β-Si_3N_4(0001) film was successfully formed on a Si(111) substrate using a thermal nitridation process.[1] This success is understood from the fact that the specific nitride phase of β-Si_3N_4(0001) ($a_0 = 7.61$ Å) is lattice matched to the Si(111)2×2 unit cell ($2a_0 = 7.68$ Å) to within 1%.[1]

For thermal nitridation of a Si substrate, various nitrogen-containing reagents such as NO, NH_3, and N_2 (or N_2^+ ion) gases have been used. This thermal reaction was characterized by a self-limited growth kinetics: the fast initial nitride formation and a very slow further reaction due probably to the blocking of N diffusion by the initial nitride film.[2] Another characteristic feature of the initial nitridation on Si(111) is the appearance of an 8×8 surface structure in low-energy electron diffraction (LEED).[1,3–8] A few scanning-tunneling microscopy studies suggested that the surface structure has actually a local "$\frac{8}{3}\times\frac{8}{3}$" reconstruction.[1,6–11] Morita and Tokumoto further suggested a structure model for the "$\frac{8}{3}\times\frac{8}{3}$" reconstruction based on a *single planar Si-N layer* on top of a bulk-terminated Si(111) surface.[9] On the contrary, a combined experimental and theoretical study recently showed that the 8×8 structure is, in fact, a *complex multilayer surface reconstruction of an ultrathin stoichiometric* Si_3N_4 *film grown epitaxially on Si(111)*.[11] This structure is composed mainly of nine N adatoms in an 8×8 unit cell, which are arranged in local $\frac{8}{3}\times\frac{8}{3}$ unit cells. However, the above structure models have not been tested thereafter and especially the atomic structure and bonding configuration at the interface between the Si_3N_4 film and the Si(111) substrate are largely unknown.

In the present study, the chemical bonding configurations of the surface and interface of an ultrathin epitaxial Si_3N_4 film formed by thermal reaction of NH_3 onto Si(111) are investigated using photoelectron spectroscopy (PES) based on a synchrotron-radiation source. The Si $2p$, N $1s$, and valence-band spectra are measured systematically and analyzed for an ultrathin Si_3N_4 film with a clear 8×8 surface structure. The Si $2p$ core-level spectra reveal the distinct components for the nitrided Si species not only in stoichiometric Si_3N_4 but also in the intermediate nitridation states of Si^{+} and Si^{3+}. This result strongly indicates an abrupt and defect-free β-Si_3N_4(0001)/Si(111) interface in accordance with a recent interface model.

II. EXPERIMENT

The NH_3 gas was introduced onto the clean Si(111)7×7 surface held at 1123–1223 K by back-filling the chamber. After this nitridation with a dose of typically 100-L NH_3, a characteristic 8×8 phase appears in LEED, where the "$\frac{8}{3}$" order spots are more intense over the others. We could not observe any quadruplet LEED spots that had been suspected to be due to contamination.[1] In order to obtain such a clear 8×8 LEED pattern, a sufficient gas dose and a substrate temperature higher than 1073 K were necessary. Before and after the NH_3 exposure, no trace of contaminants such as C or O was detected in PES spectra. The PES measurements were performed on a soft-x-ray beam line (8A1) connected to an undulator at Pohang Accelerator Laboratory in Korea, which is equipped with a high-performance photoelectron analyzer (SES-200, Gammadata, Sweden). The overall instrumental resolution was better than 0.35 for N $1s$, 0.10 for Si $2p$, and 0.15 eV for valence-band spectra. Each core-level spectrum was analyzed by a standard curve-fitting procedure using Voight functions and an integral background.

III. RESULTS AND DISCUSSION

Figure 1 shows an atomic force microscopy (AFM) image of an ultrathin Si_3N_4 film grown on Si(111), which was taken *ex situ* after the photoemission measurement. The recent

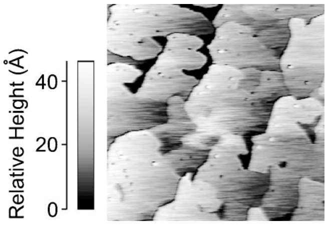

FIG. 1. AFM image (3×3 μm in area) of a Si(111) surface exposed to NH_3 (100 L) at 1123 K.

growth studies showed that the thermal nitridation of the Si(111) surface produces a β-Si_3N_4(0001) film with a thickness less than 2 nm.[1,2] The surface morphology is atomically flat with the wide domains separated by the step boundaries, which is very similar to the previous report.[12] The pits or particles (the dark and bright spots in the image, respectively) may be due to the possible etching reaction. However the area covered by these ‘‘defects’’ are less than 3% of the total surface area making the following PES analyses insensitive to them.

Before providing a detailed description of the photoemission results, it is helpful to introduce a simple atomic structure model of the present system. Figure 2 shows the side and top views of a thin β-Si_3N_4(0001) film connected ideally with the bulk-terminated (111) surface of a Si substrate.[13] As shown in Fig. 2(a), the interfacial layer between Si_3N_4 and Si(111) has *no unsaturated bonds*, which requires some of the Si atoms in the interfacial layer to be nitrided partially in the Si^+ or Si^{3+} valence state, that is, three among four Si atoms in the interfacial layer on the Si_3N_4 side bond to three N and one Si atom (the Si^{3+} state), while one among four Si atoms in the interfacial layer on the Si side bonds to three Si and one N atom (Si^+).[13] In the top view of Fig. 2(b), a 1×1 unit cell of the unreconstructed β-Si_3N_4(0001) surface is drawn with dashed lines (7.61×7.61 Å), which nearly coincides with a 2×2 unit cell of the Si(111) surface. Within that 1×1 surface unit cell, three Si and three N atoms of the topmost layer have a single dangling bond on each as indicated by the black dots located along a characteristic 12-membered ring structure (the solid line) in the figure. This ideal surface reconstructs into an 8×8 structure, for which the recent structure model features only four dangling bonds within the unit cell.[11] The reduction in dangling-bond density is achieved through the extra N adatoms and the N-N dimerization.[11]

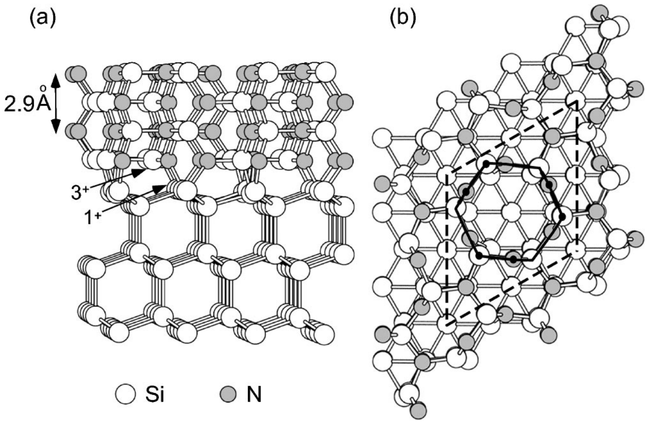

FIG. 2. (a) Side and (b) top views of the structure model of an ideal β-Si_3N_4/Si(111) system. The larger and open circles denote Si atoms and the smaller and shaded ones N atoms. The dashed line is a guide for the 1×1 surface unit cell of β-Si_3N_4(0001) and the dots point out the surface atoms with an unsaturated bond at the topmost layer.

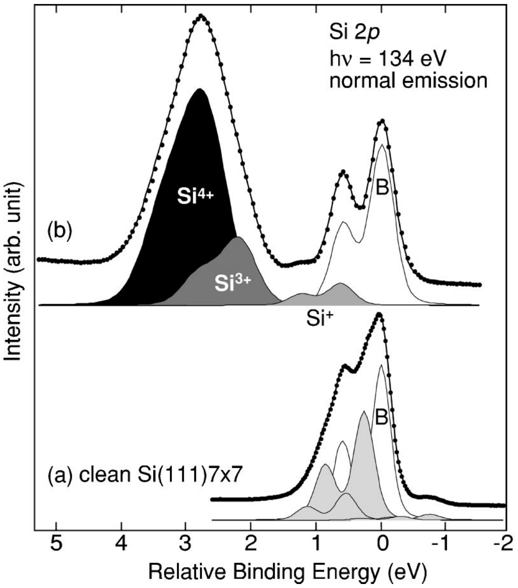

FIG. 3. Si $2p$ core-level spectra of (a) a clean Si(111)7×7 and (b) a β-Si_3N_4/Si(111) surface (made by a 100-L NH_3 dose at 1123 K) taken at $h\nu=134$ eV along the normal emission. The corresponding decompositions by least-squares fitting are given together. The higher-binding-energy components in (b) are located at $+0.64$, $+2.21$, and $+2.74$ eV relative to the bulk component B. The parameters used in the curve fitting are a spin-orbit splitting of 0.602 eV, a branching ratio of 0.50; a Lorentzian width of 0.085 eV, and Gaussian widths of 0.39, 0.58, and 0.75 eV for B (Si^+), Si^{3+}, and Si^{4+}, respectively.

As explained above, the proposed structure models for the interface and the surface of the present system features characteristic bonding configurations, which can be probed by PES. Figure 3 shows the Si $2p$ core-level spectra and the corresponding decomposition for a clean Si(111)7×7 surface and an 8×8-reconstructed surface after reaction with NH_3 (100 L) at 1123 K. The Si $2p$ spectrum of the clean Si(111)7×7 surface consists of at least four different surface components shifted from the main bulk component (B) by -0.75, -0.30, $+0.27$, and $+0.54$ eV [Fig. 3(a)]. These values and their relative intensities are fully consistent with those reported previously.[14] Such surface components of the clean Si(111)7×7 surface are completely removed after nitride formation as shown in Fig. 3(b). Instead, three higher-binding peaks appear with the binding-energy (E_b) shifts of $+0.64$, 2.21, and 2.74 eV accompanying the broadening of the bulk component B. Previous PES studies of the nitrided Si surfaces reported similar components but with E_b shifts of 0.6 and 2.59 eV on Si(111); 0.72, 1.5, and 2.58 eV on Si(100),[15] or 0.77, 1.47, 2.49, and 3.29 eV on Si(100) (Ref. 16). In contrast to the case of the SiO_2/Si interface,[17,18] the interpretation of these Si $2p$ components of the nitride interface has not been established; the former work on the Si(100) substrate assigned the peaks at 0.72, 1.5, and 2.58 eV as the intermediate nitridation species of Si^{+} and Si^{2+} and the stoichiometric nitride of Si^{4+}, respectively,[15] but the latter work assigned the peaks at 0.77, 1.47, 2.49, and 3.29 eV to Si^{+}, Si^{2+}, Si^{3+}, and Si^{4+}, respectively.[16] That is, the previous studies agreed on the E_b shifts of the Si^{+} and Si^{2+} species as ~0.7 and ~1.5 eV but not on those of Si^{3+} and Si^{4+}. On the other hand, an *ab initio* calculation showed that each Si-N bond gives an E_b shift of ~0.7 eV, which increases linearly with the number of Si-N bonds.[19] This is consistent with the previous experimental results for Si^{+} and Si^{2+} and one can further expect the shifts for Si^{3+} and Si^{4+} to be about 2.1 and 2.8 eV, respectively. Combining all the above information and in full consistency with the theory, we can assign the Si $2p$ components observed presently as due to the Si^{+} (0.64), Si^{3+} (2.21), and Si^{4+} (2.74 eV) species as shown in Fig. 3(b). Supporting the present assignment further, the Si $2p$ peak positions for the ideal β-Si_3N_4/Si(111) model (Fig. 2) were calculated to be ~2.0 eV for Si^{3+} at the interface and ~3.0 eV for Si^{4+} in Si_3N_4.[13] The occasional observations of a higher E_b for the Si^{4+} component (3.0–3.5 eV) than for the present one[16,20] could be explained by the core-hole screening effect, which increases with the film thickness or local band-bending difference on an inhomogeneous surface.[21,22] From the intensity of the Si^{4+} component the thickness of the stoichiometric Si_3N_4 film formed on Si(111) is roughly estimated to be ~3 Å taking the electron mean free path within Si_3N_4 as ~5.6 Å at the kinetic energy used (35 eV).[23] This thickness corresponds to only a single unit cell of β-Si_3N_4(0001) along the c axis [see Fig. 2(a)].

An important qualitative feature of the Si $2p$ spectra of β-Si_3N_4/Si(111) shown in Fig. 3(b) is the presence of the Si^{3+} emission, which was not observed before for a furnace-grown film[20] and for the thermal reaction of NH_3 on Si(111).[15] The presence of the Si^{3+} component is, however, clearly verified from the asymmetric line shape of the highest-E_b peak of the raw spectrum. What is more important is that no Si^{2+} species is identified in the spectrum, which is expected to be at around +1.5 eV as explained above; the maximum allowed intensity of the Si^{2+} component, if put intentionally, was less than 1% of the total intensity of the interfacial components of Si^{1+}-Si^{3+}. This behavior is in clear contrast to the oxidation of Si(111) and also to the oxidation or nitridation of Si(100), where the Si^{2+} component is observed with a significant intensity.[15–18,22,24] Since the interfacial Si atoms can have only Si^{+} or Si^{3+} valence states in the ideal SiO_2Si(111) interface[24] as well as in the ideal β-SiN_4(0001)/Si(111) interface (see Fig. 2), the Si^{2+} emission, if any, is regarded as due to defect structures at the interface. Thus, the present result clearly indicates that *the thermally grown* Si_3N_4 *film on Si(111) has an atomically abrupt and defect-free interface* as far as the present PES measurement can tell. The intensity ratio of the Si^{3+} and Si^{+} component is roughly 3:1 in further agreement with the interface model of Fig. 2.

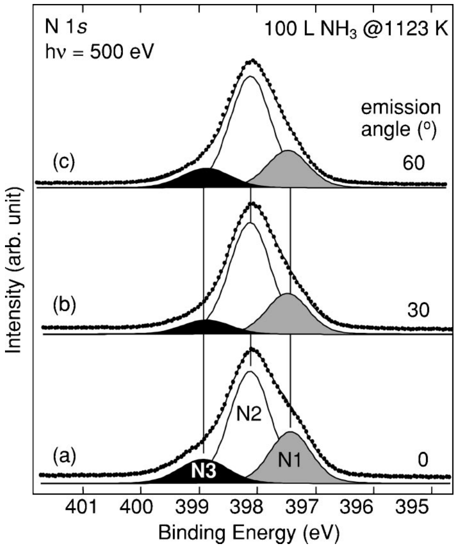

FIG. 4. N $1s$ core-level spectra and the corresponding decompositions of β-Si_3N_4/Si(111) taken at $h\nu = 500$ eV along the emission angles of (a) 0, (b) 30, and (c) 60° from the surface normal. The parameters used in the curve fitting are a Lorentzian width of 0.15 eV, and Gaussian widths of 0.75 and 0.90 for (N1 N2) and N3, respectively. See text for the explanation of the N1, N2, and N3 components.

Figure 4 shows N $1s$ core-level spectra and their decompositions for the same β-Si_3N_4(0001)/Si(111) sample as in Fig. 3(b). From the raw data, one can find a dominant peak at the center, and the obvious shoulders at both sides. These spectra are straightforwardly decomposed into three components: the main peak (N2) is located at $E_b = 398.1$ eV and the others (N1 and N3) shifted relatively by -0.66 ± 0.05 and $+0.76 \pm 0.1$ eV. In the fitting procedure, we used the same Lorentzian width of 0.20 eV, but different Gaussian widths of 0.75 for N1 or N2, and 0.90 eV for N3. A recent photoemission experiment observed very similar N $1s$ spectra for a Si(111)7×7 surface dosed with 5-L NH_3 at room temperature and annealed subsequently at 1200 K. This study seemed to not intend to produce any nitride films on the surface, and the reaction products after the annealing were not characterized al all.[25] We guess that a similar Si_3N_4 film to the present study was formed at least locally on that particular surface.

Among the three N components, the major species N2 is naturally ascribed to N atoms in the stoichiometric Si_3N_4 layer. This assignment is consistent with the observation of a dominant Si^{4+} component in the Si $2p$ spectrum of Fig. 3(b) and is corroborated by the binding energy of N2, which is in good agreement with that reported for an amorphous Si_3N_4 film.[26] The present observation is an identification of the N $1s$ binding energy of an *epitaxial* Si_3N_4 film, which can serve as a good standard free from possible artifacts due to roughness or inhomogeneity.[27,28]

Although not too evident in Fig. 4, the N1 component is shown to be more bulk sensitive and N3 more surface sensitive than N2 by comparing the N $1s$ spectra taken at many different photon energies and emission angles. The most bulk-sensitive species represented by N1 could be related to the N species at the Si_3N_4/Si(111) interface. It has the same

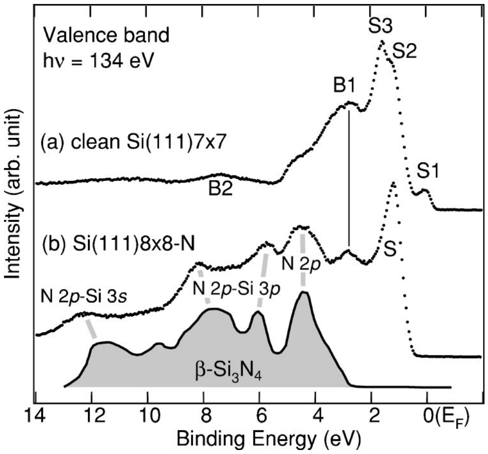

FIG. 5. Valence-band photoemission spectra of (a) a clean Si(111)7×7 and (b) a β-Si$_3$N$_4$/Si(111) surface taken at $h\nu=134$ eV. The bottom curve is the density of states calculated for β-Si$_3$N$_4$ (Ref. 31).

binding energy of 397.4 eV as that in the N-rich Si layer on the Si(100) surface[29] and as that of the interfacial N atoms of various oxynitride films on Si(100).[25–27] On the other hand, N3 is thought to come from an N species specific to the 8×8 surface structure. We do not consider any N-O or N-H bonding on the surface since no trace of oxygen atom is found in the O 1s PES and the reaction temperature is high enough to desorb any hydrogen species from the surface. The N bonding configurations specific to the recent 8×8 structure model are the N-N dimers, N adatoms, and N surface atoms with dangling bonds (see Fig. 2).[13] These configurations yield less of a charge transfer to electronegative N atoms than does the N-Si$_3$ configuration, making the N 1s binding energy higher. The calculated N 1s binding energies for Si$_2$=N-N=Si$_2$ (a N-N pair) species are ~0.6 eV higher than that of the stoichiometric Si$_3$N$_4$, in agreement with the experimental results for N3 in Fig. 4.[19] However, a more detailed assignment of the N3 component is not possible at present.

Another characteristic surface-related spectral feature is observed in the valence-band photoemission spectra as shown in Fig. 5. After nitridation, a few characteristic valence states appear as shown in Fig. 5(b) while the Si(111)7×7 surface states[30] [denoted as S1, S2, and S3 in Fig. 5(a)] disappear completely. Through a comparison with the density of states calculated for β-Si$_3$N$_4$ (the bottom curve in Fig. 5),[31] the three peaks between 5.5 and 12.5 eV are identified as N 2p-Si 3s and N 2p-Si 3p bonding states, respectively, as indicated in the figure. The feature at $E_b=4.5$ eV is a nonbonding lone-pair state of N and is considered as the valence-band maximum of Si$_3$N$_4$.[15,31] A striking feature is the lowest-binding-energy peak at 1.1 eV (denoted as S) since this energy corresponds to the band gap of Si$_3$N$_4$ and no Si substrate peak is expected either. This feature is clearly distinguished from the Si(111)7×7 surface state and of course no Si surface state is expected since the present film is a homogeneous one covering the whole surface as shown in Fig. 1. The state S is sensitive to residual gas adsorption and is recovered by flash annealing. Thus, we conclude that S is a unique surface state of the 8×8 surface originating possibly from the Si or N dangling bonds (see Fig. 2). A further theoretical calculation of the electronic states of the 8×8 structure proposed is desirable.

IV. SUMMARY

We have performed a photoelectron spectroscopy study for a Si(111) surface nitrided by NH$_3$ at high temperature, on which a flat and homogeneous β-Si$_3$N$_4$(0001) film was formed with an 8×8 surface reconstruction. The clear Si 2p emission features for the interfacial Si^{+} and Si^{3+} states are observed with core-level shifts of 0.64 and 2.21 eV, respectively, and those for the stoichiometric Si$_3$N$_4$ layer are observed with a core-level shift of 2.72 eV. These values are in good agreement with a recent *ab initio* calculation. No Si^{2+} species is observed in the Si 2p spectra indicating an abrupt and defect-free (less than 1%) interface due possibly to the nearly perfect lattice matching between crystalline β-Si$_3$N$_4$ and Si(111). On the other hand, three different N chemical bonding configurations are identified from the N 1s core-level spectra, which are identified as due to the N species within the β-Si$_3$N$_4$(0001) film, at the interface and on the 8×8 surface layer, respectively. This is generally consistent with the Si 2p results and the interface and surface structural models proposed recently. In the valence-band photoemission spectra, an intense and characteristic surface-state emission is observed at a binding energy of 1.1 eV, which is well above the valence-band maximum of Si$_3$N$_4$.

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[1] X. Wang, G. Zhai, J. Yang, and N. Cue, Phys. Rev. B **60**, R2146 (1999); Thin Solid Films **366**, 121 (2001); X.-S. Wang, G. Zhai, J. Yang, L. Wang, Y. Hu, Z. Li, J. C. Tang, X. Wang, K. K. Fung, and N. Cue, Surf. Sci. **494**, 83 (2001).

[2] I. J. R. Baumvol, Surf. Sci. Rep. **36**, 1 (1999); R. M. C. de Almeida and I. J. R. Baumvol, Phys. Rev. B **62**, R16 255 (2000).

[3] A. G. Schrott and S. C. Fain, Jr., Surf. Sci. **111**, 39 (1981); **123**, 204 (1982).

[4] M. Nishijima, H. Kobayashi, K. Edamoto, and M. Onchi, Surf. Sci. **137**, 473 (1984).

[5] E. A. Khramtsova, A. A. Saranin, and V. G. Lifshits, Surf. Sci. **280**, L257 (1993).

[6] E. Bauer, Y. Wei, T. Müller, A. Pavlovska, and I. S. T. Tsong, Phys. Rev. B **51**, 17 891 (1995).

[7] B. Röttger, R. Kliese, and H. Neddermeyer, J. Vac. Sci. Technol. B **14**, 1051 (1996).

[8] J. S. Ha, K.-H. Park, W. S. Yun, E.-H. Lee, and S.-J. Park, J. Vac. Sci. Technol. B **15**, 1893 (1997); Appl. Phys. A: Mater. Sci. Process. **66**, S495 (1998).

[9] Y. Morita and H. Tokumoto, Surf. Sci. **443**, L1037 (1999).

[10] C.-L. Wu, J.-L. Hsieh, H.-D. Hsueh, and S. Gwo, Phys. Rev. B **65**, 045309 (2002).

[11] H. Ahn, C.-L. Wu, S. Gwo, C. M. Wei, and Y. C. Chou, Phys. Rev. Lett. **86**, 2818 (2001).

[12] Y. Morita and H. Tokumoto, Surf. Sci. **486**, L524 (2001); Jpn. J. Appl. Phys., Part 1 **40**, 4357 (2001).

[13] G. L. Zhao and M. E. Bachlechner, Phys. Rev. B **58**, 1887 (1998).

[14] C. J. Karlsson, E. Landemark, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. B **50**, R5767 (1994).

[15] G. Dufour, F. Rochet, H. Roulet, and F. Sirotti, Surf. Sci. **304**, 33 (1994).

[16] J. Stober, B. Eisenhut, G. Rangelov, and Th. Fauster, Surf. Sci. **321**, 111 (1994).

[17] F. J. Himpsel, F. R. McFeely, A. Taled-Ibrahimi, J. A. Yarmoff, and G. Hollinger, Phys. Rev. B **38**, 6084 (1988).

[18] H. W. Yeom, H. Hamamtsu, T. Ohta, and R. I. G. Uhrberg, Phys. Rev. B **59**, R10 413 (1999); H. W. Yeom and R. I. G. Uhrberg, Jpn. J. Appl. Phys., Part 1 **39**, 4460 (2000).

[19] G.-M. Rignanese and A. Pasquarello, Appl. Phys. Lett. **76**, 553 (2000); Phys. Rev. B **63**, 075307 (2001).

[20] A. Stesmans and G. Van Gorp, Phys. Rev. B **52**, 8904 (1995).

[21] S. Iwata and A. Ishizuka, J. Appl. Phys. **79**, 6653 (1996).

[22] Y. D. Chung, J. W. Kim, C. N. Whang, and H. W. Yeom, Phys. Rev. B **65**, 155310 (2002).

[23] C. J. Powell and A. Jablonski, Computer code NIST Electron Inelastic-Mean-Free-Path Database Version 1.1 (National Institute of Standard and Technology, Gaithersburg, MD, 2000).

[24] D.-A. Luh, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **79**, 3014 (1997).

[25] M. Björkqvist, M. Göthelid, T. M. Grehk, and U. O. Karlsson, Phys. Rev. B **57**, 2327 (1999).

[26] G. M. Ingo, N. Zacchetti, D. Della Sala, and C. Coluzza, J. Vac. Sci. Technol. A **7**, 3048 (1989); R. Kärcher, L. Ley, and R. L. Johnson, Phys. Rev. B **30**, 1896 (1994).

[27] J. W. Kim, H. W. Yeom, Y. D. Chung, K. Jeong, C. N. Whang, M. K. Lee, and H. J. Shin, Phys. Rev. B **66**, 035312 (2002).

[28] G.-M. Rignanese, A. Pasquarello, J.-C. Charlier, X. Gonze, and R. Car, Phys. Rev. Lett. **79**, 5174 (1997).

[29] C. H. F. Peden, J. W. Rogers, Jr., N. D. Shinn, K. B. Kidd, and K. L. Tsang, Phys. Rev. B **47**, 15 622 (1993).

[30] P. Martensson, A. Cricenti, L. S. O. Johansson, and G. V. Hansson, Phys. Rev. B **34**, 3015 (1986).

[31] Y.-N. Xu and W. Y. Ching, Phys. Rev. B **51**, 17 379 (1995).