

Step-induced optical anisotropy of Si(111):H surfaces

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(Received 27 September 1999)

The step-induced optical anisotropy of the hydrogenated Si(111) surface has been calculated using a real-space multigrid method together with *ab initio* pseudopotentials. The investigated step configurations give rise to relatively similar anisotropy spectra with maxima close to the E_1 and E_2 critical points of the silicon bulk band structure. The spectrum for $\langle 11\bar{2} \rangle$ steps resembles the reflectance anisotropy for Si(110):H and is in good agreement with measurements for Si(111):H vicinally cut toward $[11\bar{2}]$. Our results for $\langle \bar{1}\bar{1}2 \rangle$ steps, however, are qualitatively different from the corresponding measurements for surfaces miscut toward $[\bar{1}\bar{1}2]$. This apparent discrepancy can be resolved if the formation of staircaselike structures of monohydride terminated steps is assumed.

I. INTRODUCTION

The optical spectroscopy of surfaces, in particular, reflectance anisotropy/difference spectroscopy (RAS/RDS), is becoming popular as a nondestructive and versatile tool of surface analysis.^{1,2} However, the anisotropy spectra are difficult to interpret and provide only indirect information. Only a strong interaction between experimental and theoretical efforts allows for a full exploitation of the potential of RAS. The theoretical progress has been hampered, however, by the large numerical expense required for converged calculations of surface optical properties. Most existing calculations have been carried out using tight-binding schemes, which in spite of their successes (see, e.g., Refs. 3,4), are often not sufficiently accurate. Recently, it has become possible to study surface optical properties by means of *ab initio* methods. In particular these methods have been applied to Si(001) surfaces,⁵⁻⁸ due to their technological importance and their model character for semiconductor surface science. Si(113) (Ref. 7) and Si(110):H surfaces⁹ were recently studied with tight-binding methods. However, realistic surfaces, and growth structures in particular, are characterized by defects such as surface steps. The latter have been shown experimentally to give rise to distinct optical anisotropies,¹⁰⁻¹² the origin of which is presently under debate (see, e.g., Ref. 13). The theoretical description of these step-related optical anisotropies is therefore not only important in the context of the correct interpretation of RAS spectra measured during growth, but also for more fundamental reasons.

In the present study we investigate the optical anisotropy of the hydrogenated Si(111) surface induced by the formation of bilayer steps. For the (111) surface, the two principal directions of miscut are $\langle 11\bar{2} \rangle$ and $\langle \bar{1}\bar{1}2 \rangle$. Assuming straight steps and barring any reconstruction, the first miscut gives step atoms with one dangling bond each [Fig. 1(a)] and the second with two dangling bonds each. In the latter case two different atomic structures are possible: a dihydride structure forms that either lies in a plane parallel [Fig. 1(b)] or perpendicular to the step edge [Fig. 1(c)]. The optical response of these three configurations is investigated in the present work. More precisely, adapting the accepted nomenclature for vicinal samples, the Si[3(111)-(11 $\bar{2}$)] and Si[2(111)-($\bar{1}\bar{1}2$)] surfaces are studied, which consist of regularly

spaced terraces that are three/two Si atoms wide along the $[11\bar{2}]/[\bar{1}\bar{1}2]$ direction, separated by single bilayer steps. In the following we refer to these structures as $\langle 11\bar{2} \rangle$ and $\langle \bar{1}\bar{1}2 \rangle$ steps.

II. METHOD

The calculations have been carried out using the same method as in our recent studies of the optical properties of III-V(001) growth planes.^{14,15} In short, we use density-functional theory in the local-density approximation (DFT-LDA) together with nonlocal norm-conserving pseudopotentials¹⁶ to determine the structurally relaxed ground state of the system. A massively parallel, real-space finite-difference method¹⁷ is used to deal efficiently with the large surface unit cell and the many states required for the calculation of the dielectric function. A multigrid technique is employed for convergence acceleration. The spacing of the finest grid used to represent the electronic wave functions and charge density was determined through a series of bulk calculations. We find that structural and electronic properties are converged for a spacing of 0.238 Å. This corresponds to an energy cutoff in plane-wave calculations of about 24 Ry. The calculations yield a bulk equilibrium lattice constant of 5.378 Å and a bulk modulus of 0.979 Mbar (experiment:¹⁸ 5.43 Å and 0.96–0.99 Mbar). The calculated excitation energies suffer from the neglect of self-energy effects in DFT-LDA and are smaller than the measured values: the calculated indirect band gap is 0.58 eV (room temperature experiment:¹⁸ 1.11 eV). A similar underestimation of about 0.5 eV occurs for the E_1 and E_2 critical points (CP's) of the bulk band structure, for which we obtain 3.0 and 3.8 eV, respectively. The slab polarizability calculated in the independent-particle approximation is used to determine the reflectance anisotropy following the scheme devised by Del Sole¹⁹ and Manghi *et al.*²⁰ We neglect the contributions to the optical transition operator from the spatially nonlocal pseudopotentials. Although these effects contribute of order 5–10 % to the transition matrix elements,²¹ their influence on the RAS spectra is negligible due to the normalization of the slab polarizability with respect to the bulk dielectric

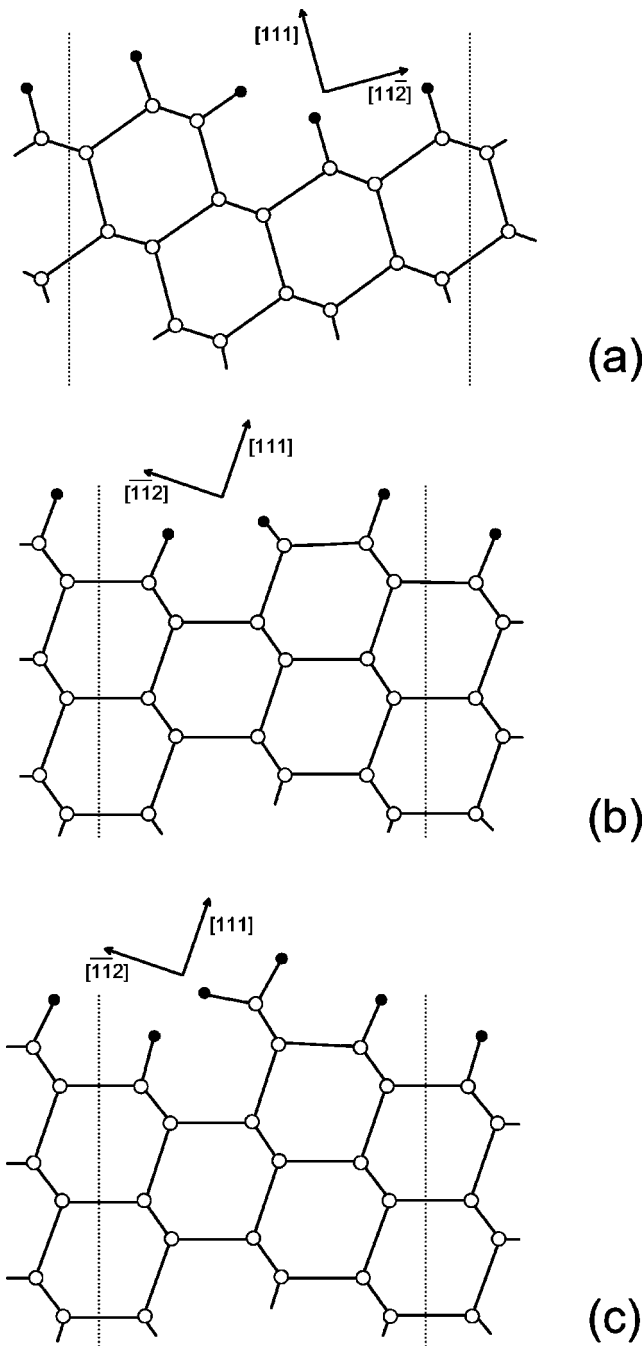


FIG. 1. Side view of the relaxed step configurations studied in this work. Empty (filled) circles represent Si (H) atoms. The lateral dimension of the periodic supercell perpendicular to the step direction is indicated by dashed lines.

function.²² In order to compare the theoretical spectra with experiment we apply an upward rigid shift of 0.5 eV to the conduction bands and renormalize the momentum matrix elements accordingly.²³ This is in agreement with *GW* calculations on Si surfaces.^{24,25} Our study is thus on the same level as other recent *ab initio* studies on the optical properties of Si surfaces.^{5,8}

To model the step configurations we consider periodic supercells along the surface normal. They contain slabs about 48 Å thick, separated by 14 Å of vacuum. All surface dangling bonds are saturated with hydrogen. The atomic configurations used to study the $\langle 11\bar{2} \rangle$ and $\langle \bar{1}\bar{1}2 \rangle$ steps con-

tained 102 and 90 atoms, respectively. The investigated geometries were carefully relaxed until all calculated forces were below 10 meV/Å. The atoms in the innermost 13 Å of the material layers were kept frozen in the ideal bulk configuration. Integrations in the surface Brillouin zone (SBZ) for calculating the atomic and electronic ground state of the system were performed using two special \mathbf{k} points in the irreducible part. In the calculation of the dielectric function all conduction bands within 9 eV of the top of the valence bands were included, using 48/40 uniformly distributed \mathbf{k} points in the irreducible parts of the SBZ for the $\langle 11\bar{2} \rangle/\langle \bar{1}\bar{1}2 \rangle$ steps. For comparison we also performed calculations for the hydrogenated Si(110) surface, using a slab containing 23 atomic Si layers and 88 \mathbf{k} points. The \mathbf{k} space integration was thus performed with a sampling point density corresponding to 665, 452, and 575 \mathbf{k} points in the full (1×1) SBZ of the (111) surface for the $\langle 11\bar{2} \rangle$ steps, the $\langle \bar{1}\bar{1}2 \rangle$ steps, and the (110) surface, respectively.

III. RESULTS AND DISCUSSION

The side views of the relaxed step geometries are shown in Fig. 1. All surface bonds are saturated. The Si atoms thus remain in bulklike configurations and the relaxations are rather small and local. For $\langle 11\bar{2} \rangle$ steps [Fig. 1(a)] the largest shifts occur for the actual step atoms: the uppermost atom moves about 0.08 Å along the surface normal and a similar relaxation of about 0.07 Å occurs for the second step atom. For $\langle \bar{1}\bar{1}2 \rangle$ steps, two different configurations, shown in Figs. 1(b) and 1(c), were investigated. We find that the formation of a vertical dihydride structure in a plane perpendicular to the step edge [Fig. 1(c)] is energetically preferred by 0.19 eV per step atom. The formation of vertical rather than in-plane dihydride structures on $\langle \bar{1}\bar{1}2 \rangle$ steps is in agreement with infrared^{26–28} and Raman spectroscopy.²⁹ The atomic structure of the dihydride-terminated step edge is dominated by steric interaction between the lower hydrogen atom of the dihydride group and the H on the step below. If the dihydride group were placed in the bulk-terminated position, these two hydrogens would be only 1.4 Å apart—significantly less than twice the van der Waals radius of H (2.4 Å). The repulsion between the two hydrogens, however, causes the dihydride species to rotate away from the lower terrace. We calculate a rotation angle of 6.7°, increasing the H-H distance to 1.91 Å. These relaxations are considerably smaller than the ones predicted earlier by a Hartree-Fock cluster calculation,³⁰ which determined a rotation of 20°, thus increasing the H-H distance to 2.3 Å. Our results are, however, in good agreement with a DFT-LDA calculation by Li, Vanderbilt, and King-Smith³¹ for Si[5(111)- $\langle \bar{1}\bar{1}2 \rangle$]. They determined a rotation angle of 3.5°, resulting in a H-H separation of 1.78 Å. Experimentally, rotation angles of $37^\circ \pm 4^\circ$ (Ref. 29) and 21° (Refs. 27,28) were obtained. The discrepancies between the relatively small relaxations determined with DFT-LDA in Ref. 31 and the present work and the much larger shifts obtained from cluster calculations³⁰ may be related either to the insufficient description of the H-H interaction in LDA or to the limited cluster size in the latter study. However, while we cannot provide a satisfactory explanation for the apparent discrepancies between our results for the rotation angle and

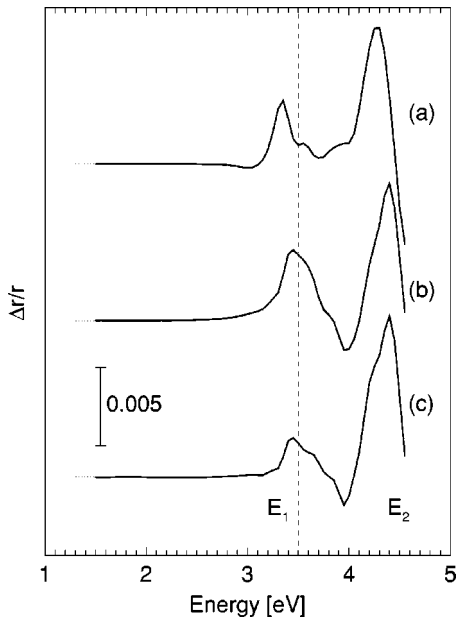


FIG. 2. Calculated RAS [$\text{Re}\{(r_\alpha - r_\beta)/\langle r \rangle\}$] for Si step geometries. The α and β principal axes lie in the surface plane and are parallel and perpendicular to the respective step edge. The labels of the curves refer to the atomic structures of Fig. 1. Bulk CP energies are indicated.

the spectroscopic experiments, it will be shown below that the optical spectra do not depend crucially on these structural details.

The calculated RAS spectra for the three investigated step geometries are presented in Fig. 2. All steps give rise to strong anisotropy features close to the bulk CP energies. The main differences between the spectrum calculated for $\langle 11\bar{2} \rangle$ steps [Fig. 2(a)] and $\langle \bar{1}\bar{1}2 \rangle$ steps [Figs. 2(b) and 2(c)] are a blueshift of about 0.1 eV and the occurrence of negative anisotropies at around 3 eV for the former and at around 4 eV for the latter two spectra. Based on the striking similarity of the measured step-induced RAS to that of Si(110):H it was suggested in Ref. 10 that the optical response of $\langle 11\bar{2} \rangle$ steps arises from the (110)-like regions of the stepped surface. Figure 3 shows the spectrum for the Si(110):H surface,

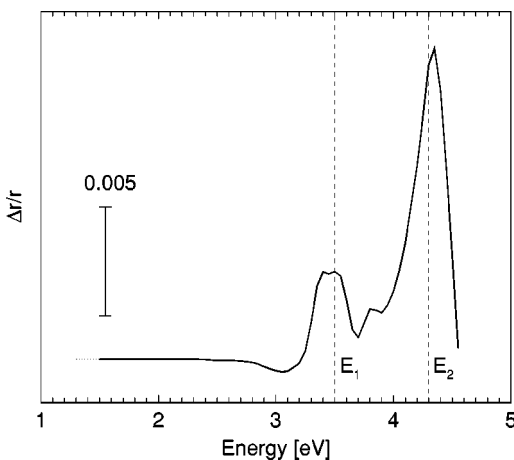


FIG. 3. Calculated RAS [$\text{Re}\{(r_{[\bar{1}10]} - r_{[001]})/\langle r \rangle\}$] for Si(110):H. Bulk CP energies are indicated.

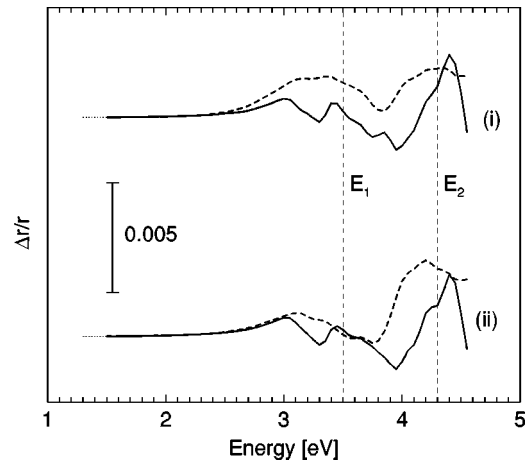


FIG. 4. Calculated RAS (same notation as Fig. 2) for the $\langle \bar{1}\bar{1}2 \rangle$ step geometries, terminated by (i) in-plane and (ii) vertical dihydride groups, corresponding to the structures shown in Fig. 1(b) and 1(c). The dashed/solid lines represent the RAS caused by electronic transitions within/below the uppermost 8 Å of the surface. Bulk CP energies are indicated.

calculated with a set of technical parameters comparable to those used for the stepped surfaces. The spectrum is at variance with the tight-binding results of Ref. 9, but agrees in its main features with experiment.¹⁰ It is indeed rather similar to the RAS induced by $\langle 11\bar{2} \rangle$ steps: Maxima appear at the CP energies and there is an additional weak minimum around 3 eV. The line shape, however, in particular around the E_1 energy, is different from that calculated for the step configuration and the relative ratio of the anisotropies at the E_1 and E_2 CP energies is smaller. Furthermore, the overall similarity of the calculated RAS for all investigated step configurations suggests that one cannot explain the optical response of the $\langle 11\bar{2} \rangle$ stepped surface solely in terms of its (110)-like regions.

The overall similarity of all calculated step spectra indicates that the reflectance anisotropy originates from the perturbation of bulk wave functions by the formation of surface steps, rather than from electronic transitions between step-localized surface states. In order to clarify this point we performed additional calculations for the two different $\langle \bar{1}\bar{1}2 \rangle$ step configurations and separated spatially the origin of the RAS contributions from surface and subsurface regions using a linear cutoff function. Figure 4 shows separately the reflectance anisotropy arising from electronic transitions within the uppermost 8 Å of the surface (with respect to the top hydrogens) and the anisotropy arising from the transitions below. As expected, the surface contribution to the RAS indeed depends on the step geometry: steps with in-plane dihydride groups cause relatively broad surface-related positive anisotropies around 3.3 and 4.3 eV. The surface contribution to the RAS from steps with vertically oriented dihydride groups is characterized by a relatively weak positive signal at 3.1 eV and a much stronger one at 4.2 eV. In contrast to that, however, are the very similar anisotropy signals for both geometries arising from the deeper layers. The surface-related features are still contained in the spectra calculated for the full systems. They cause the E_1 -related peak in the RAS of steps decorated with in-plane dihydride groups

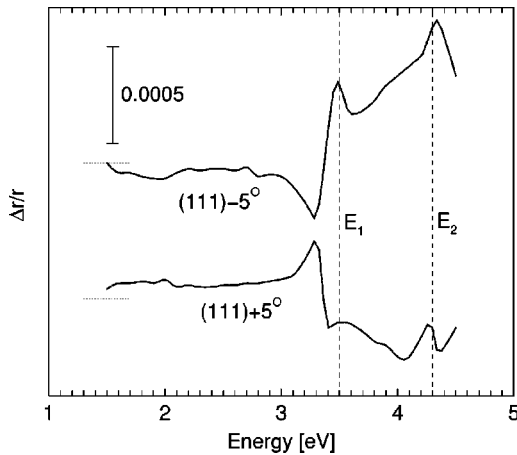


FIG. 5. Measured RAS (same notation as Fig. 2) for vicinally cut Si(111):H surfaces. (From Ref. 10.)

[curve (b) in Fig. 2] to be about 40% larger than the corresponding peak for the steps terminated by vertical dihydride groups. The latter step also has an additional surface-related shoulder at about 4.2 eV. These differences are small, however, compared with the common principal features that arise mainly from electronic transitions in subsurface layers.

A direct comparison of the calculated data with experiment is not possible, as the existing measurements¹⁰ were performed on surfaces with considerably smaller step densities. Unfortunately, the lateral periodicities needed to accommodate wider terraces are still out of reach of *ab initio* calculations of the optical response. In Ref. 10 it was noted, however, that the anisotropy signal for Si(111):H vicinally cut toward $[11\bar{2}]$ depends nearly linearly on the step density. A similar dependence was recently obtained for Si(001).¹² Furthermore, our results, as well as earlier work,³¹ show that the atomic relaxations of the step edges are rather small and local. Therefore, it can be expected that our calculations can be extrapolated to allow for a meaningful comparison with the measured data.

In Fig. 5 we show the experimental data¹⁰ for surfaces vicinally cut $\pm 5^\circ$. The upper curve in Fig. 5 shows the RAS of the surface cut toward $[11\bar{2}]$. The main characteristics of the spectrum are the pronounced anisotropy maxima near the E_1 and E_2 CP's of the bulk band structure. This is in qualitative agreement with the corresponding calculated spectrum for $\langle 11\bar{2} \rangle$ steps [Fig. 1(a)]. The measured anisotropies are about one order of magnitude smaller than the calculated values. This can be explained partially by the lower step density: a miscut angle of $\theta = 5^\circ$ corresponds to an average terrace width n of 11 rows [$\tan \theta = 2\sqrt{2}/(3n-1)$], as opposed to the width of 3 rows in our calculation. Temperature effects and sample imperfections neglected in our calculation also reduce the measured anisotropy signal. The calculated line shape, in particular around the E_1 energy, is only an approximate description of the measured signal. This is not surprising, however. The neglect of excitonic effects³² in the calculations leads to a bulk dielectric function where the E_1 peak is underestimated by about 50% and reduced to a weak shoulder of the E_2 peak. Since the step-induced reflectance anisotropy is to a large extent determined by transitions between bulklike electronic states, the problematic description

of the bulk dielectric function will cause differences in the line shape between the measured and calculated RAS spectra, in particular around the E_1 energy, even if no further approximations had been made in describing the surface. Additionally, the surface local-field effect, neglected in our study, may influence the line shape.⁹ If these limitations are borne in mind, however, the agreement between experiment and theory for the $\langle 11\bar{2} \rangle$ step-induced optical anisotropy is satisfactory.

This is seemingly not the case for $\langle \bar{1}\bar{1}2 \rangle$ steps. The lower curve in Fig. 5 shows data measured for the Si(111):H surface miscut 5° toward $[\bar{1}\bar{1}2]$. Yasuda *et al.*¹⁰ assumed that the measured anisotropy is induced by bilayer $\langle \bar{1}\bar{1}2 \rangle$ steps. This interpretation does not agree with the calculations shown in Fig. 2(c). Theory predicts positive anisotropy features at the E_1 and E_2 energies, while the measured anisotropies are negative. Even considering all the limitations discussed above, it is implausible that the calculations should yield a qualitatively wrong result. From Fig. 5 it seems as if the $(111)+5^\circ$ spectrum were an inverted and somewhat reduced version of the $(111)-5^\circ$ spectrum. This fact has already been noted in Ref. 10. By means of infrared^{33,26} and Raman spectroscopy,²⁹ as well as scanning tunneling microscopy measurements,^{34,35} it has also been demonstrated that the atomic structures of Si(111):H surfaces miscut toward $[\bar{1}\bar{1}2]$ depend strongly on the preparation conditions. In particular, a transformation of straight dihydride-terminated $\langle \bar{1}\bar{1}2 \rangle$ steps into a staircaselike arrangement of monohydride terminated $\langle 11\bar{2} \rangle$ steps was observed. These newly formed steps form angles of $60^\circ/120^\circ$ with the original step edges. Assuming a complete transformation of straight $\langle \bar{1}\bar{1}2 \rangle$ steps into zigzag chains of ideal $\langle 11\bar{2} \rangle$ steps, the optical anisotropy of the surface should from pure geometrical considerations correspond to the anisotropy measured for straight $\langle 11\bar{2} \rangle$ steps, but multiplied by $-\sqrt{3}$. In reality, the optical anisotropy of remaining, not-transformed parts of $\langle \bar{1}\bar{1}2 \rangle$ steps will partially cancel the signal from the zigzag chains. A further disturbance of the “ideal” RAS spectrum can be expected from contributions due to the edges of the staircase structures. Thus, it seems likely that the optical spectrum of a Si(111):H surface miscut toward $[\bar{1}\bar{1}2]$ is an inverted, reduced, and somewhat disturbed version of the spectrum measured for a surface miscut toward $[11\bar{2}]$. Obviously, the actual spectrum will depend on the preparation conditions. This hypothesis, if correct, gives a natural explanation of the experimental findings of Ref. 10, which are seemingly at odds with our calculations. Moreover, RAS might then be utilized to monitor quantitatively the step transformation on Si surfaces. However, further experiments are needed to verify the suggested interpretation.

IV. SUMMARY

We presented the results of *ab initio* calculations for the step-induced optical anisotropy of hydrogenated Si(111) surfaces. Bilayer steps are found to give rise to pronounced anisotropy features close to the bulk CP energies. The anisotropy arises to a large extent from subsurface transitions between surface-perturbed bulk wave functions and is rela-

tively insensitive to the step orientation and geometry. Our results for $\langle 11\bar{2} \rangle$ steps are in good agreement with experiment and resemble the anisotropy of hydrogenated Si(110) surfaces. The theoretical results for $\langle \bar{1}\bar{1}2 \rangle$ steps are seemingly at odds with the measured data. This apparent contradiction can be resolved, however, if a step transformation to $\langle 11\bar{2} \rangle$ facets is assumed.

ACKNOWLEDGMENTS

We thank Professor D. E. Aspnes for suggesting this work and useful discussions. Support by DFG (Schm 1361/1-1), ONR (N00014-96-I-0161), and DoE(DE-FG02-98ER45685) as well as grants of computer time from the DoD Challenge Program and the North Carolina Supercomputing Center are gratefully acknowledged.

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