Evolution of surface stress during oxygen exposure of clean Si(111), Si(100), and amorphous Si surfaces

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The evolutions of the surface stress of Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces upon oxygen exposure at $p_{\text{O}_2} = 1 \times 10^{-4}$ Pa and room temperature have been investigated in a comparative manner using a specimen-curvature based technique. To this end, a generally applicable, dedicated set of experiments has been devised and performed to deduce and correct for the surface stress change owing to oxygen reaction(s) at the (poorly-defined) back face of the specimen only. On this basis, it could be demonstrated that exposure of clean Si(111)- 7×7 , Si(100)- 2×1 and a-Si surfaces to pure oxygen gas results in compressive surface stress changes for all three surfaces due to the incorporation of oxygen into Si backbonds. The measured surface stress change decreases with decreasing atomic packing density at the clean Si surfaces, which complies well with the less-densely packed Si surface regions containing more free volume for the accommodation of adsorbed O atoms.

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I. INTRODUCTION

The lack of bonding partners at a free solid surface results in a significant redistribution of the electronic charge density within the (sub)surface region, and correspondingly, a modification of the (strived for) equilibrium interatomic distances at the (sub)surface as compared to those in the bulk. As a consequence, the forces then experienced by the surface atoms to assure their registry with the bulk lattice give rise to a surface stress.¹ Evidently, surface stresses play a dominant role in many surface-related phenomena, such as surface reconstructions,² surface diffusion, and surface morphological transitions.³ Surface stresses can even influence the development of “bulk” intrinsic stresses in thin films during growth.^{4,5}

Adsorption of foreign species on a solid surface modifies the local chemical environment at the surface, which typically results in a change of the surface stress.⁶ Such adsorption-induced surface stress changes are nowadays employed in, e.g., nano-mechanical sensing applications.^{7–9} Most studies of adsorbate-induced surface stress change have been conducted by measuring the change in specimen curvature.^{10–14}

Consider a thin metal, semiconductor or alloy specimen which is mounted in a sample holder such that it is free to bend. Exposure of the clean specimen surfaces to oxygen gas gives rise to the simultaneous reaction of oxygen (i.e., physisorption, chemisorption, and/or oxide formation) with the front face *and* the back face of the parent specimen. The *difference* of the resulting O-exposure-induced surface stress changes at the front face and the back face of the parent specimen leads to a measurable change of the specimen

curvature as a function of the oxygen-exposure time. Evidently, the magnitude of the surface stress changes at one face (e.g., the front face) of the specimen can be determined from such experiments only if either (i) the O-exposure-induced stress change at the opposite face (e.g., the back face) of the specimen can either be totally neglected (i.e., the specimen back face is fully inert to the oxygen exposure treatment) or (ii) the measurement can be corrected for the “back face effect”.

The front face specimen surface should be well-defined and free of contaminants at the onset of the experiment, which can only be realized by careful preparation of the specimen surface under ultrahigh vacuum (UHV) conditions. Conventional sputter-cleaning of the specimen surface by noble gas ion bombardment is often applied but this method creates a high density of surface defects, which not only alters the surface stress¹⁵ but also enhances the surface reactivity upon subsequent oxygen exposure. Hence, then a post-annealing treatment of the sputter-cleaned specimen under UHV conditions is generally required to restore the crystallinity of the ion-bombarded surface. However, such a post-annealing treatment may destroy the desired (see above) chemical inertness of the back face surface upon oxygen exposure, e.g., by partial or complete removal of the (native) oxide layer on the non-sputtered back face specimen surface.

In this work, a general applicable, dedicated set of experiments has been designed and performed, which allows resolving the “back face effect”, i.e., the surface stress change due to the undesired but unavoidable (see above) oxygen reaction(s) at the unpolished rough (poorly defined) back face of the specimen only. The thus obtained “back face effect” can be used to determine (by subtraction) precisely the surface stress change at the “front face” specimen surface. The developed experimental procedure has been utilized here for a direct determination and comparison of the surface stress evolutions during

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O-exposure of Si(111)-7 × 7, Si(100)-2 × 1, and a-Si surfaces at room temperature and $p_{O_2} = 1 \times 10^{-4}$ Pa.

II. EXPERIMENTAL SETUP

The experiments were carried out in a customized multi-chamber UHV system (base pressure $< 3 \times 10^{-8}$ Pa) for thin film deposition by thermal evaporation, in-vacuo angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and in-vacuo scanning tunneling microscopy (STM). Square-shaped (13.9×13.9 mm²), one side polished, 100 μm thin Si(111), and Si(100) wafers were loosely mounted in the specimen holder, introduced into the UHV system and then thoroughly degassed and cleaned by a programmed laser heat treatment up to a maximum temperature of 1100 °C for 1 min in UHV. After subsequent cooling to room temperature, STM and XPS measurements revealed contamination-free, well ordered Si(111)-7 × 7 and Si(100)-2 × 1 specimen surfaces, respectively. Next, the Si wafer specimens were exposed to pure oxygen gas at $p_{O_2} = 1 \times 10^{-4}$ Pa for $t = 1800$ s at room temperature. The adsorption-induced (net) change of surface stress, $\Delta\tau$ (i.e., due to physisorption, chemisorption, and/or oxide formation) was determined from the *in situ* measured specimen-curvature change, $\Delta\kappa$, as monitored in real time by a multi-optical stress sensor (MOS; k-space Associates),¹⁶ with a 3 × 3 array of parallel laser beams aligned at normal incidence to the specimen front face. According to Stoney's equation¹⁷

$$\Delta\tau = \frac{M_S h_S^2}{6} \Delta\kappa, \quad (1)$$

where M_S and h_S denote the biaxial modulus and the thickness of the specimen, respectively. The measured (net) specimen-curvature change, $\Delta\kappa$, is given by the sum of the curvature change, $\Delta\kappa_{front\ face}$, resulting from a surface stress change due to the reaction of oxygen at the front face of the specimen and the curvature change, $\Delta\kappa_{back\ face}$, resulting from a surface stress change due to the reaction of oxygen at the back face of the specimen.

In order to determine the contribution to the measured specimen-curvature change owing to the reaction of oxygen with the unpolished (rougher) back face of the specimen only, a set of experiments was designed and performed, as described below.

Step 1 (see Fig. 1(a)): First, a 15 nm thick, amorphous Si film (a-Si) was deposited by thermal evaporation of pure Si (99.999 at. %) from a Ta/W crucible at room temperature on the Si(111)-7 × 7 and Si(100)-2 × 1 reconstructed (front) surfaces of the Si(111) and Si(100) specimens (as obtained according to the preparation procedures described above).

Step 2 (see Fig. 1(b)): The specimens were then exposed to pure oxygen gas at $p_{O_2} = 1 \times 10^{-4}$ Pa for $t = 1800$ s at room temperature, while recording the (net) change of specimen curvature due to the simultaneous reaction of oxygen with both specimen surfaces (i.e., with the clean, a-Si front surface and with the clean, unpolished Si back surface).

Step 3 (see Fig. 1(c)): Next, a “fresh” 15 nm thick a-Si film was deposited on the front surfaces of the O-exposed

FIG. 1. Schematic illustration of the experimental steps for the *in situ*, accurate determination of the substrate-curvature changes due to adsorption on the rough (unpolished) Si(111) and Si(100) substrate back faces. (a) After the preparation (by thorough degassing and heating the specimen up to 1100 °C) of a Si(111) or Si(100) substrate with contamination-free front face and back face, an a-Si film is deposited onto the surface front face. (b) During subsequent oxygen exposure, oxygen is adsorbed at both the a-Si surface and the rough Si specimen back face. (c) Deposition of a second a-Si film on top of the oxidized a-Si surfaces under exactly the same growth conditions as in step (a). (d) During a second oxygen exposure, oxygen is only adsorbed at the freshly grown a-Si layer at the specimen front face, whereas no oxygen is adsorbed at the inert, passivated specimen back face, already covered with an oxide layer.

specimens, employing the same growth conditions as in step 1. Noteworthy, for both specimens, the front surface exhibits the same RMS roughness of 2.4 Å after step 1 and after step 3 (as determined by *in vacuo* STM).

Step 4 (see Fig. 1(d)): Finally, the specimens as obtained after step 3 were exposed for a second time to pure oxygen gas at $p_{O_2} = 1 \times 10^{-4}$ Pa for $t = 1800$ s at room temperature. The back surfaces of the Si(111) and the Si(100) specimens had already been passivated (saturated) during the first O exposure (see step 2).¹⁸ Hence, the specimen curvature, as measured during step 4, is only due to the reaction of oxygen with the newly deposited a-Si film at the front face surfaces of the specimens.

The amount (coverage) of reacted oxygen on the O-exposed Si(111)-7 × 7, Si(100)-2 × 1, and a-Si surfaces (after $t = 1800$ s; see above) was determined by *in-vacuo* AR-XPS analysis using a Thermo VG Thetaprobe system employing monochromatic Al-K α radiation. To this end, the O 1s and Si 2p core level spectra before and after oxygen exposure were recorded in the so-called parallel data acquisition mode by simultaneously collecting the photoelectrons over the angle detection range α (with respect to the sample surface normal) of 23°–75° in seven ranges of 7.5° each with a step size of 0.1 eV and a constant pass energy of 50 eV.¹⁹ The total O 1s and Si 2p primary zero loss (PZL; see Ref. 20) intensities were obtained from the integrated area of the Shirley-background-corrected O 1s and Si 2p main peaks. The amount of adsorbed oxygen on the O-exposed Si surfaces was determined from the PZL intensity ratio $I_{O\ 1s}/I_{Si\ 2p}$ by

adopting a model for non-attenuating adsorption layer systems which neglects any inelastic scattering in the oxygen overlayer.²¹ The values for the inelastic mean free path of the detected Si 2p photoelectrons for crystalline and amorphous Si, as required for the calculation were determined according to Ref. 22 and equal to 3.09 nm and 3.15 nm, respectively (taking into account that the density of an a-Si film is only 95% of that of a bulk Si crystal²³). Furthermore, a constant ratio of the O 1s and Si 2p total photoionization cross-sections of $\sigma_{O1s}/\sigma_{Si2p} = 3.21$ was used.²⁴

III. RESULTS

A. Determination of the “back face effect”

The measured curvature changes of the Si(111) and Si(100) specimens during the oxygen exposure steps 2 and 4, as described in Sec. II (see also Figs. 1(b) and 1(d)), have been plotted as function of the oxygen exposure time in Figs. 2(a) and 2(b), respectively. Oxygen exposure of the Si(111) and Si(100) specimens with clean (unpolished) back faces and freshly deposited a-Si films at their (polished) front faces (see step 2 in Sec. II and Fig. 1(b)), resulted in abrupt changes in specimen curvature of 2.7 km^{-1} and 0.9 km^{-1} , respectively (see *black curves* in Fig. 2). After these instantaneous *positive* changes in specimen curvature, no further changes in curvature occurred, neither with increasing oxygen exposure, nor after closing the oxygen valve after $t = 1800 \text{ s}$. Next “fresh” 15 nm thick a-Si films were

deposited on the oxidized front surfaces of the Si(111) and Si(100) specimens (see step 3 in Sec. II and Fig. 1(c)). During subsequent O-exposure of the thus prepared specimens (see step 4 in Sec. II and Fig. 1(d)) the specimen-curvature change asymptotically approached *negative* values of -0.8 km^{-1} and -1.2 km^{-1} for the Si(111) and Si(100) specimens, respectively (see *red curves* in Fig. 2). These measured curvature changes during the second oxygen exposure correspond to an equivalent change in surface stress of -0.3 N/m for both specimens, which only result from the reaction of oxygen with the freshly deposited a-Si film at the front surfaces of the Si(111) and Si(100) specimens, because the back surfaces of both specimens were already passivated with oxygen during the first oxygen exposure (see step 2 in Sec. II and Fig. 1(b)).

Subtraction of the measured curvature change, $\Delta\kappa_2$, as recorded during the second O exposure (see step 4 in Sec. II and Fig. 1(d)), from the corresponding curvature change, $\Delta\kappa_1$, as measured during the first O exposure (see step 2 in Sec. II and Fig. 1(b)) yields the curvature change, $\Delta\kappa_{\text{back face}}$, due to the reaction of oxygen at the clean (unpolished) back surfaces of the Si(111) and Si(100) specimens only. The thus obtained $\Delta\kappa_{\text{back face}}$ curves for the Si(111) and Si(100) specimens can be employed to resolve the surface stress evolutions induced by oxygen exposure of only the Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces at $p_{O_2} = 1 \times 10^{-4} \text{ Pa}$ and at room temperature (see Sec. II), by subtraction of the specimen curvature due to the “back face effect” from the measured curvature change (see what follows).

FIG. 2. The specimen-curvature changes, $\Delta\kappa$, as well as the corresponding (net) change of surface stress, $\Delta\tau$, measured during the, in Fig. 1 sketched, successively performed oxygen exposure experiments at $p_{O_2} = 10^{-4} \text{ Pa}$ and 300 K (a) for Si(111) and (b) for Si(100) substrates, respectively. Black, filled squares represent the measured substrate-curvature change, $\Delta\kappa_1$, during the first exposure, i.e., due to oxygen adsorption at an a-Si film surface and at the rough Si(111) and Si(100) specimen back faces (“step 2,” Fig. 1(b)). Red dots represent the measured substrate-curvature change, $\Delta\kappa_2$, during the second exposure, i.e., due to oxygen adsorption at only the a-Si film surface, since at this stage the back face is passivated by the oxide layer formed during the first oxygen exposure step (“step 4,” Fig. 1(d)). Finally, subtraction of $\Delta\kappa_2$ from $\Delta\kappa_1$ yields the substrate-curvature change, $\Delta\kappa_{\text{back face}}$, due to oxygen adsorption at the rough Si(111) and Si(100) wafer back face only (open squares).

B. Evolution of surface stress during oxygen exposure of Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces

The surface stress changes upon O exposure of the Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces (at $T = 300 \text{ K}$ and $p_{O_2} = 1 \times 10^{-4} \text{ Pa}$), as obtained after correcting for (i.e., subtracting) the back face effect, have been plotted as function of oxygen-exposure time in Fig. 3. For the Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces oxygen exposure results in

FIG. 3. The surface stress change due to oxygen adsorption at only the clean Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces at $p_{O_2} = 10^{-4} \text{ Pa}$ and 300 K, i.e., after correcting for the back face effect (cf. Fig. 2), as function of oxygen-exposure time.

the development of a compressive surface stress of -1.9 N/m, -0.3 N/m, and -0.4 N/m after $t = 1800$ s, respectively. Strikingly, an instantaneous compressive surface stress change occurs at the onset of O exposure for the Si(111)- 7×7 and the a-Si surfaces, whereas a relatively minor tensile surface stress change (up to 0.1 N/m after 80 s of oxygen exposure) arises at the onset of O exposure of the Si(100)- 2×1 surface, which gradually becomes compressive with increasing O exposure. Due to the fast saturation of O-adsorption sites on the exposed Si surfaces (i.e., the fast passivation of the Si surfaces; see Sec. III C and Ref. 18), no distinct changes of the developed surface stresses occur upon prolonged oxygen exposure for times $t > 1800$ s. Furthermore, also after closing the oxygen valve after $t = 1800$ s no changes of surface stress occur.

C. Fractional oxygen surface coverage

The surface stress changes of the Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces after O exposure of 1800 s can be related to the fractional oxygen coverage of the then O-passivated Si surfaces (i.e., the ratio of the atomic surface density of adsorbed oxygen and the atomic surface density of the *unreconstructed* Si(111), Si(100), and a-Si surfaces), as determined by AR-XPS. The resolved PZL intensity ratio of the measured O 1s and Si 2p core-level peaks, $I_{O\,1s}/I_{Si\,2p}$, (after correction for the asymmetry factor; see Ref. 19) is shown in Fig. 4 as function of the photoelectron detection angle α (with respect to the sample surface normal) for the O-exposed Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces (after 1800 s). For all three O-exposed Si surfaces, the resolved $I_{O\,1s}/I_{Si\,2p}$ intensity ratio is proportional to the inverse of $\cos(\alpha)$ (see inset of Fig. 4), which complies with the behavior of a non-attenuating adsorption layer on an infinitely thick substrate.²¹ In this case, the atomic surface density, s_o , of adsorbed oxygen on a Si substrate satisfies

$$\frac{I_{O\,1s}(\alpha)}{I_{Si\,2p}(\alpha)} = \frac{s_o}{\rho_{Si}} \frac{(d\sigma_O/d\Omega)}{(d\sigma_{Si}/d\Omega)A_{Si}\cos(\alpha)}, \quad (2)$$

where ρ_{Si} is the atomic volume density of the Si substrate (either crystalline or amorphous), $(d\sigma_O/d\Omega)/(d\sigma_{Si}/d\Omega)$ is the ratio of the photoionization cross sections of O 1s and Si 2p, and A_{Si} denotes the inelastic mean free path of the Si 2p photoelectrons in the substrate. The thus calculated atomic surface densities of oxygen on the O-exposed Si(111), Si(100), and a-Si surfaces after $t = 1800$ s equal to 1.3×10^{15} atoms·cm⁻², 1.5×10^{15} atoms·cm⁻², and 6.46×10^{14} atoms·cm⁻², respectively. The atomic surface densities of the clean, non-reconstructed Si(111) and Si(100) surfaces can be given as 7.83×10^{14} atoms·cm⁻² and 6.78×10^{14} atoms·cm⁻², respectively, and the atomic surface density of the clean a-Si surface is estimated (on the basis of the macroscopic atom approach²⁵) at 7.38×10^{14} atoms·cm⁻². This results in estimates of 1.7, 2.2, and 0.9 for the fractional O coverage of the O-exposed Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces after $t = 1800$ s, respectively.

IV. DISCUSSION

The results shown in Figs. 2 and 3 indicate that the surface stress changes (i.e., curvature changes) due to O reaction with the front and the back surfaces are of the same order of magnitude; i.e., the back face effect cannot be neglected! This implies that the O-exposure-induced surface stress changes of only the well-prepared Si surfaces can only be extracted from specimen-curvature measurements if the back face effects can be determined accurately.

The clean, reconstructed Si(111)- 7×7 surface has an intrinsic (tensile) surface stress of $\tau_{Si(111)-7 \times 7} \approx 2.3$ N/m.^{26,27} Combining, for the Si(111)- 7×7 surface, the determined fractional O-coverage of 1.7 after 1800 s (Sec. III C; Fig. 4) with the measured (compressive) change in surface stress of -1.9 N/m (Fig. 3), it follows that O exposure induces a decrease of the (initial, tensile) surface stress of -1.1 N/m per unit fractional coverage of O. This result complies well with the previously reported (partial) relaxation of the intrinsic tensile surface stress of clean Si(111)- 7×7 surfaces upon O exposure at room temperature due to the incorporation of O atoms between a first-layer Si atom and a second-layer Si atom of the reconstructed surface; i.e., into Si backbonds,²⁸ associated with a tendency to lateral volume expansion of the surface.^{10,12} The value of -1.1 N/m for the surface stress change per unit coverage of O, as determined in the present study, is comparable to that reported in Ref. 12 (-0.82 ± 0.25 N/m), but is inconsistent with that reported in Ref. 10 (-7.2 N/m), but this last result is flawed because the back face effect was neglected.

The clean, reconstructed Si(100)- 2×1 surface has an intrinsic tensile surface stress along the Si dimer-bonds and an intrinsic compressive surface stress along the Si dimer-rows.^{29,30} Combining, for the Si(100)- 2×1 surface with orthogonal equivalent (2×1) domains, the determined fractional O-coverage of 2.2 after 1800 s (Sec. III C; Fig. 4) with the measured (compressive) change in surface stress of

FIG. 4. The ratio of the asymmetry-factor-corrected intensities of the O 1s and Si 2p photoelectron peaks, $I_{O\,1s}/I_{Si\,2p}$, as function of the detection angle α after oxygen exposure of Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces at $p_{O_2} = 10^{-4}$ Pa and 300 K for 1800 s. For all three surfaces, the ratio increases proportionally to $1/\cos(\alpha)$ (see the dashed lines and the inset).

-0.3 N/m (Fig. 3), it follows that O exposure induces a decrease of the surface stress of about -0.1 N/m per unit coverage of O. The adsorbed O species are incorporated into Si backbonds of the Si(100)- 2×1 surface,^{31,32} which also (i.e., as for the Si(111)- 7×7 surface) induces a compressive surface stress contribution due to the tendency to (lateral) volume expansion of the surface. Such O-adsorption-induced compressive surface stress can even lead to “push-out” (emittance) of Si atoms from the surface, forming isolated Si dimer bonds at the O-exposed Si(100)- 2×1 surface.^{33,34}

For the Si(100)- 2×1 surface, the initially small tensile and then gradually becoming compressive surface stress change can represent a transition of preferred oxygen adsorption site:^{35,36} from O occupying the bridging sites in between adjacent Si dimer bonds to O insertion into Si backbonds. The formation of an oxygen-bridged structure leads to a distinct contraction of the Si(100)- 2×1 surface parallel to the Si dimer-bonds,¹⁴ and thus induces a tensile surface stress contribution at the very initial stage of oxygen exposure of the Si(100)- 2×1 surface.

The observation of an exclusively tensile surface stress change of 0.2 N/m per unit coverage of O, as reported in Ref. 10, is in sharp contrast with the tensile-compressive surface stress evolution as measured in the present study, which can be the consequence of different oxygen exposures or, likely, the consequence of the unjustified neglect of a back face effect correction in Ref. 10.

The clean a-Si surface has an intrinsic (tensile) surface stress of $\tau_{\text{a-Si}} \approx 1.5 \pm 1.2\text{ N/m}$.³⁷ Combining, for the a-Si surface, the determined fractional O-coverage of 0.9 (Sec. III C; Fig. 4) after 1800 s with the measured (compressive) change in surface stress of -0.4 N/m (Fig. 3), it follows that O exposure induces a decrease of the (initial, tensile) surface stress by 0.5 N/m per unit coverage of O. The reduction of the tensile surface stress upon O exposure is again attributed to the (partial) incorporation of adsorbed O atoms into Si backbonds (i.e., subsurface sites) of the a-Si surface,³⁸ which induces a compressive surface stress contribution due to the tendency to (lateral) volume expansion of the surface adjacent layer(s).

The value for the surface stress change (per unit coverage of O) for the 1800 s O-exposed a-Si surface is in-between the corresponding values for the 1800 s O-exposed Si(100)- 2×1 and Si(111)- 7×7 surfaces. It can therefore be concluded that the surface stress change upon O exposure decreases with decreasing atomic packing density of the clean Si surfaces (i.e., it decreases from Si(111), over a-Si to Si(100)). This result reflects that the less-densely packed Si surface regions contain more free volume for the accommodation (incorporation) of adsorbed O atoms and suggests that the detailed Si-O subsurface bonding geometry (bonding length and bonding angles) is of minor importance for the compressive surface stress change occurring upon oxygen exposure of Si surfaces.

V. CONCLUSION

Specimen-curvature based measurements of adsorption induced surface stress changes are largely affected by the

undesired but unavoidable reaction(s) of the gaseous species at the back face of the specimen.

As demonstrated by a generally applicable, dedicated set of experiments, the oxygen-adsorption induced specimen curvature change at the (well-defined) atomically smooth front surfaces and the (poorly defined) unpolished rough back surfaces of a Si specimen are of the same order of magnitude, and thus such “back face effect” cannot simply be neglected.

After subtraction of the “back face effect,” using the developed procedure, it is revealed that exposure of clean Si(111)- 7×7 , Si(100)- 2×1 , and a-Si surfaces to pure oxygen gas at $p_{\text{O}_2} = 1 \times 10^{-4}\text{ Pa}$ and room temperature results in compressive surface stress changes for all three surfaces due to the incorporation of O atoms between a first-layer Si atom and a second-layer Si atom, i.e., into Si backbonds.

The measured surface stress change decreases with decreasing atomic packing density of the clean Si surfaces (i.e., from Si(111), a-Si to Si(100)), in correspondence with the less-densely packed Si surface regions containing more free volume for the accommodation of adsorbed O atoms.

¹W. Haiss, *Rep. Prog. Phys.* **64**, 591 (2001).

²H. Ibach, *Surf. Sci. Rep.* **29**, 195 (1997).

³A. J. Schell-Sorokin and R. M. Tromp, *Phys. Rev. Lett.* **64**, 1039 (1990).

⁴R. C. Cammarata, *Prog. Surf. Sci.* **46**, 1 (1994).

⁵J. A. Floro, P. G. Kotula, S. C. Seel, and D. J. Srolovitz, *Phys. Rev. Lett.* **91**, 096101 (2003).

⁶R. D. Meade and D. Vanderbilt, *Phys. Rev. Lett.* **63**, 1404 (1989).

⁷A. M. Moulin, S. J. O'Shea, and M. E. Welland, *Ultramicroscopy* **82**, 23 (2000).

⁸R. Berger, E. Delamarche, H. P. Lang, C. Gerber, J. K. Gimzewski, E. Meyer, and H.-J. Güntherodt, *Science* **276**, 2021 (1997).

⁹J. Fritz, M. K. Baller, H. P. Lang, H. Rothuizen, P. Vettiger, E. Meyer, H.-J. Güntherodt, C. Gerber, and J. K. Gimzewski, *Science* **288**, 316 (2000).

¹⁰D. Sander and H. Ibach, *Phys. Rev. B* **43**, 4263 (1991).

¹¹D. Sander and H. Ibach, in *4.4 Surface Free Energy and Surface Stress* (SpringerMaterials-The Landolt-Börnstein Database, Springer-Verlag Berlin Heidelberg, 2002), Vol. 42A2 pp. 303–312.

¹²N. T. Kinahan, D. E. Meehan, T. Narushima, S. Sachert, J. J. Boland, and K. Miki, *Phys. Rev. Lett.* **104**, 146101 (2010).

¹³D. Flötotto, Z. M. Wang, L. P. H. Jeurgens, and E. J. Mittemeijer, “Intrinsic stress evolution during amorphous oxide film growth on Al surfaces” *Appl. Phys. Lett.* (submitted).

¹⁴M. Kitajima, T. Narushima, T. Kurashima, A. Itakura, S. Takami, A. Yamada, K. Teraishi, and A. Miyamoto, *J. Phys.: Condens. Matter* **25**, 355007 (2013).

¹⁵T. Narushima, A. N. Itakura, T. Kurashima, T. Kawabe, and M. Kitajima, *Appl. Surf. Sci.* **159–160**, 25 (2000).

¹⁶E. Chason and B. W. Sheldon, *Surf. Eng.* **19**, 387 (2003).

¹⁷G. G. Stoney, *Proc. R. Soc. London, Ser. A* **82**, 172 (1909).

¹⁸G. Hollinger and F. J. Himpsel, *J. Vac. Sci. Technol. A* **1**, 640 (1983).

¹⁹M. S. Vinodh and L. P. H. Jeurgens, *Surf. Interface Anal.* **36**, 1629 (2004).

²⁰L. P. H. Jeurgens, W. G. Sloof, C. G. Borsboom, F. D. Tichelaar, and E. J. Mittemeijer, *Appl. Surf. Sci.* **161**, 139 (2000).

²¹C. S. Fadley, *Prog. Surf. Sci.* **16**, 275 (1984).

²²A. Jablonski and C. J. Powell, *Surf. Sci. Rep.* **47**, 33 (2002).

²³O. Renner and J. Zemek, *Czech. J. Phys.* **23**, 1273 (1973).

²⁴M. B. Trzhaskovskaya, V. I. Nefedov, and V. G. Yarzhevsky, *At. Data Nucl. Data Tables* **77**, 97 (2001).

²⁵F. R. de Boer, R. Boom, W. C. M. Mattens, and A. R. Miedema, *Cohesion in Metals: Transition Metals Alloys* (Elsevier Science, Amsterdam, North Holland, 1989).

²⁶R. D. Meade and D. Vanderbilt, *Phys. Rev. B* **40**, 3905 (1989).

²⁷D. Vanderbilt, *Phys. Rev. Lett.* **59**, 1456 (1987).

²⁸Y. T. A. Yoshigoe, *Jpn. J. Appl. Phys., Part 1* **49**, 115704 (2010).

- ²⁹M. C. Payne, N. Roberts, R. J. Needs, M. Needels, and J. D. Joannopoulos, *Surf. Sci.* **211–212**, 1 (1989).
- ³⁰Y. Miyamoto, *Phys. Rev. B* **49**, 1947 (1994).
- ³¹T. Uchiyama and M. Tsukada, *Phys. Rev. B* **53**, 7917 (1996).
- ³²M. Wasekura, M. Higashi, H. Ikeda, A. Sakai, S. Zaima, and Y. Yasuda, *Appl. Surf. Sci.* **159–160**, 35 (2000).
- ³³H. Kageshima and K. Shiraishi, *Phys. Rev. Lett.* **81**, 5936 (1998).
- ³⁴D. G. Cahill and P. Avouris, *Appl. Phys. Lett.* **60**, 326 (1992).
- ³⁵M. N. Y. Harada, T. Nagatomi, and R. Shimizu, *Jpn. J. Appl. Phys., Part 1* **39**, 560 (2000).
- ³⁶Y. Miyamoto and A. Oshiyama, *Phys. Rev. B* **41**, 12680 (1990).
- ³⁷S. Hara, S. Izumi, T. Kumagai, and S. Sakai, *Surf. Sci.* **585**, 17 (2005).
- ³⁸T. Nagatomi, Y. Harada, M. Niwa, Y. Takai, and R. Shimizu, *Surf. Interface Anal.* **27**, 776 (1999).