Electron-Stimulated Modification of Si Surfaces

Koji Nakayama and J. H. Weaver

Department of Materials Science and Chemical Engineering, University of Minnesota, Minneapolis, Minnesota 55455

(Received 31 August 1998)

Scanning tunneling microscopy studies show significant structural modifications that involved atom desorption and displacement following mild irradiation by electrons of 90–2000 eV. For Si(111)-(7×7), adatom layer vacancies increased monotonically with incident energy. For Si(100)-(2×1), irradiation produced dimer vacancies, and ad-dimers as Si atoms transferred to the terrace. The modification processes are tied to the energy distribution of electron-hole and electron attachment states achieved by inelastic cascade scattering. Hence, beams previously believed to be benign induce surface structural modifications. [S0031-9007(99)08389-1]

PACS numbers: 81.05.Dz, 61.16.Ch, 61.80.Fe

Electron beams of 10–5000 eV have long been used to investigate the chemical and structural character of surfaces [1,2]. For ionic materials, electron stimulated desorption, ESD, is known to occur [3,4], and this implies atomic-scale structural changes. For clean metal and semiconductor surfaces, however, it is generally believed that these energetic electrons do not cause structural changes. To test the conventional wisdom, we have used scanning tunneling microscopy, STM, to study the structural consequences of irradiation by 90–2000 eV electrons of the sort routinely used in low-energy electron diffraction, LEED, and Auger-electron spectroscopy, AES.

In this Letter, we show that electron irradiation is quite effective in modifying the structures of clean Si surfaces. For Si(100), exposure produced dimer vacancies through a combination of atom desorption and atom transfer processes. For Si(111)-(7×7), the cross section for desorption increased monotonically despite Si $2s$ and $2p$ core level thresholds. We relate these structural changes to inelastic cascade scattering. Scattering excites electrons into antibonding states, as for field-emitted electrons from a tip or photons from a laser, but electrons are also captured at antibonding surface resonances. Coupling to the nuclear motion results in desorption induced by electronic transitions, DIET, and/or displacement onto the terrace. Differences for the two surfaces reflect the types of defects created and the tendency of atoms ejected onto the terraces to form stable structures. While demonstrating that surfaces are less robust than previously thought, these results suggest new opportunities to atomic scale surface engineering.

Clean Si(100)-(2×1) and Si(111)-(7×7) surfaces were prepared by thermal treatments [5,6]. They were imaged with tungsten tips at room temperature in ultrahigh vacuum (base pressure 5×10^{-11} Torr). The samples were irradiated by electron beams from a LEED gun (primary energy $E_p = 90$ eV) and an AES gun ($500 \leq E_p \leq 2000$ eV). The latter was mounted in a double-pass cylindrical mirror analyzer [7]. In each experiment, the beam profile was characterized with a Faraday cup [8]. STM images obtained within ± 0.5 mm of the center of the irradiated area spots revealed approximately uniform defect and adatom densities. These densities decreased with distance away from this central spot, consistent with the beam profile. Exposures are given by the incident current. We irradiated Si(100) samples that were B doped at 3×10^{17} and 9×10^{18} cm^{-3} and P doped at 5×10^{18} cm^{-3} but there was no significant dependence on dopant type or concentration.

Figure 1(a) shows an occupied-states image of clean Si(100)-(2×1). The surface dimers buckle dynamically and appear as oval structures [5]. Steps and defects stabilize them, and asymmetric dimers appear as bright protrusions, labeled B. Dimer vacancies (DV) and c-type defects (CD) (Refs. [9,10]) were about equal in number; their total concentration was typical for surfaces prepared by heating, $\sim 4\%$ [5,6].

The images in Figs. 1(b) and 1(c) were obtained after irradiation by 9.6×10^{16} electrons mm^{-2} at 2000 eV (exposure time 150 s). The dark features again represented single DV's and c-type defects but their concentration was much greater and there were also dimer vacancy complexes (DV_C). Though created differently, these vacancies were analogous to those produced by thermal or chemical means because removal of one atom from a dimer destabilizes the other and it transfers to the terrace, regardless of the initiation process. Annihilation of a DV requires the simultaneous capture of two diffusing Si atoms, and this is unlikely at 300 K. While single adatoms could not be imaged, the bright spots labeled A_1, A_2, and A_3 correspond to ad-dimers formed from displaced atoms (Refs. [11–14]). They were unstable with respect to tip-induced motion under typical imaging conditions [11]. Bright spots up to 2 nm in width represent Si clusters, labeled A_4 in Fig. 1(c).

Figure 2(a) shows that the total area of the DV's increased almost linearly with dose until ~ 100 s, rising from 0.02 ML for the clean surface. In this time, their density, right axis of Fig. 2(a), increased linearly from 0.14

 0031-9007/99/82(5)/980(4)$15.00

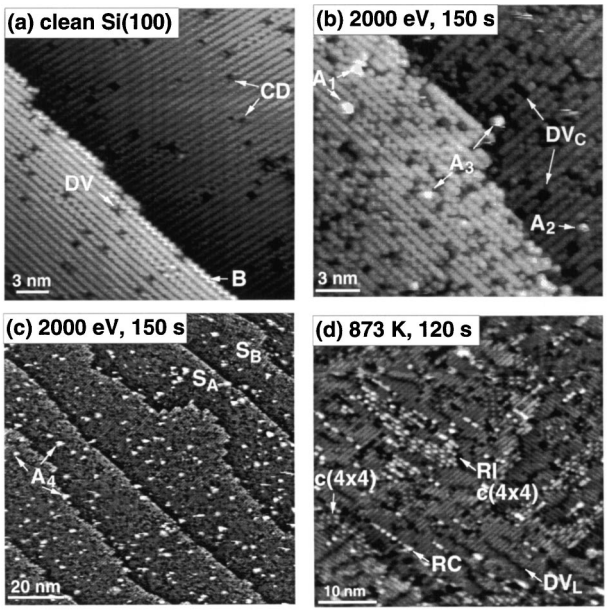

FIG. 1. (a) Filled state image of clean Si(100)-(2 × 1) showing dimer vacancies (DV) and c-type defects (CD), and a row of asymmetric buckled dimers at a step (B). (sample −2.0 V, 0.2 nA). (b) Image after 2000 eV irradiation for 150 s showing dimer vacancy complexes (DV_C). Ad-dimers are labeled A_1 if their axis is parallel to the dimer row, A_2 if they lie perpendicular to the dimer row, and A_3 if they reside between dimer rows. (c) Large scan image showing Si clusters, A_4, uniformly distributed on the surface. (d) Surface like (c) after annealing to produce dimer vacancy lines (DV_L), regrowth chains (RC), and regrowth islands (RI). $c(4 \times 4)$ structures appear near steps and in regrowth areas.

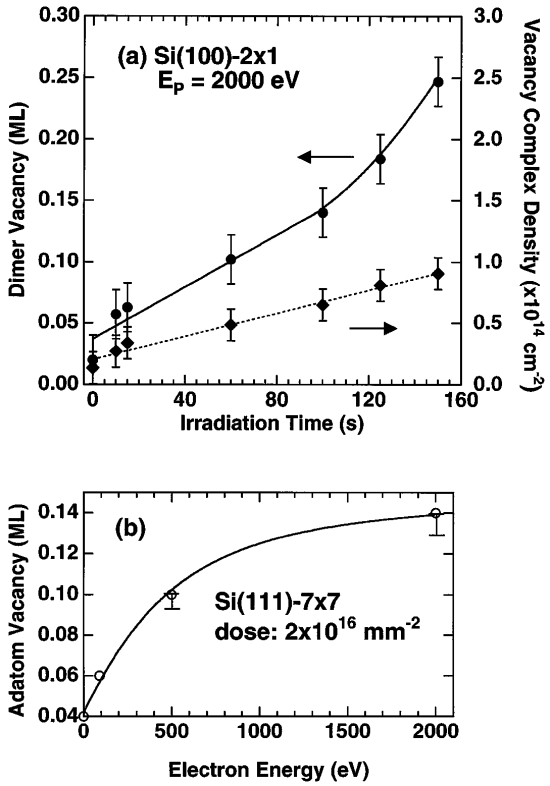

FIG. 2. (a) Dimer vacancy areas and vacancy complex densities as a function of dose for 2000 eV electrons for Si(100)-(2 × 1). The cross section for dimer vacancy creation is approximately linear below ~100 s. The flux of 6.4×10^{14} electron mm^{-2} s^{-1} corresponds to ~100 electrons s^{-1} per surface atom. (b) Adatom vacancy concentration for Si(111) as a function of primary electron energy. As discussed in the text, this represents the cross section for Si desorption.

to 0.65×10^{14} cm^{-2}. While the density of DV's more than quadrupled, the average size of a vacancy complex increased only ~50%. Thus, single DV creation was largely random, and the creation cross section in this linear regime was 1.2×10^{-20} cm^2 (the yield of 8×10^{-6} vacancies per electron divided by the atom density). After ~100 s irradiation, the vacancy concentration increased in a nonlinear fashion as existing pits influenced the probability of additional vacancy creation adjacent to them. The pit growth apparent in Fig. 1(b) reflects the tendency of defects to localize electronic excitations and to increase inelastic scattering events. It may also reflect the reduced energy barrier for atom displacement at a pit boundary. Similar fluence dependencies were obtained for adatom vacancy creation on Si(111)-(7 × 7) (not shown).

The changes evident in Fig. 1(c) were intrinsic to Si(100)-(2 × 1) because heating at 873 K for 2 min produced regrowth chains and islands, labeled RC and RI in Fig. 1(d) [15,16]. Small domains with $c(4 \times 4)$ symmetry appeared at steps and in regrowth layers, as for epitaxial growth of Si on Si(100) [17]. Individual DV's ordered into lines that were perpendicular to the dimer rows. Recovery of a surface that was this severely damaged was sluggish because defects reduced Si diffusion and influenced the (local) energetics associated with islands or steps. Equally sluggish recovery was observed when ion bombarded surfaces were annealed at 873–1123 K [18].

To demonstrate the generality of electron-induced Si surface modification and to determine its dependence on beam energy, we exposed Si(111)-(7 × 7) surfaces to beams having $E_p = 90$, 500, and 2000 eV to achieve a common fluence of 2×10^{16} electrons mm^{-2}. For the starting surface [inset of Fig. 3(a)], bright features within a 7 × 7 unit cell represent the corner adatoms adjacent to (dark) corner holes and center adatoms away from those holes. Irradiation with 90 eV electrons (0.5μA, 20 min) [8] 500 eV electrons (0.5μA, 20 min), and 2000 eV electrons (1.2μA, 500 s) increased the concentration of vacancies in the adatom layer from 4% to 6% [Fig. 3(a)], to 10% [Fig. 3(b)], and to 14% [Fig. 3(c)]. Images obtained at other bias voltages and polarities demonstrated that the changes were not related to adsorbates [7]. From Fig. 2(b), the vacancy concentration increased steadily with E_p. This indicates that processes related to Si $2s$ and $2p$ excitations followed by Auger decay were not

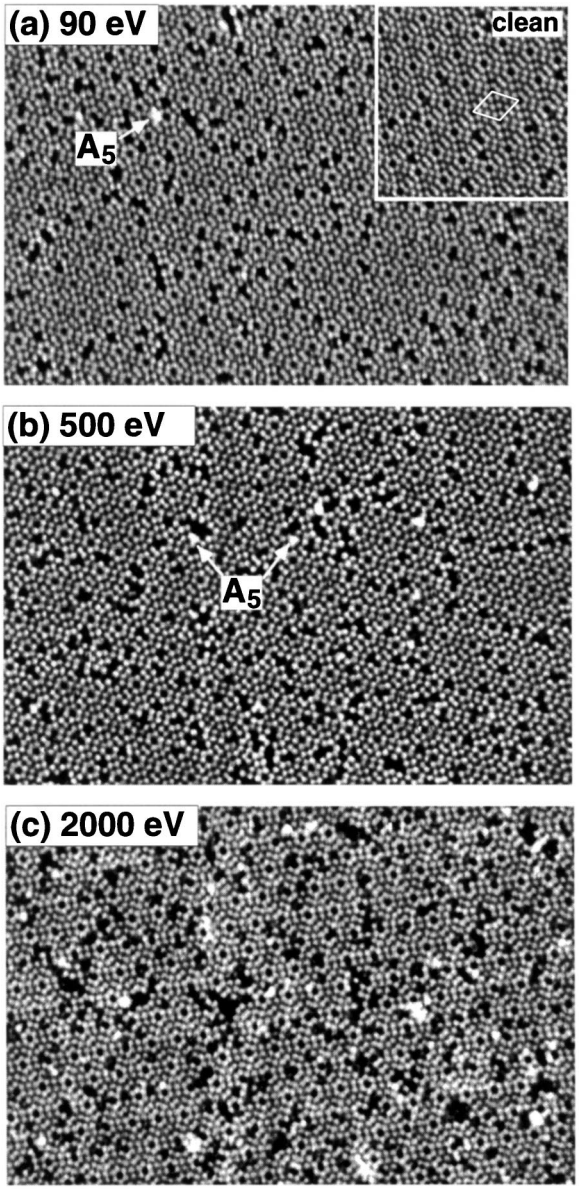

FIG. 3. Images after irradiation of Si(111)-(7 × 7) by electrons of primary energy (a) 90 eV, (b) 500 eV, and (c) 2000 eV. Vacancies in the adatom layer appear as dark features. The development of these vacancies is largely due to Si atom desorption though features like A_5 represent Si atoms trapped at a rest atom dangling bond. Desorption is random when the vacancy concentration is low. All images 330 × 500 Å^2; sample bias 1.7 V, tunneling current 0.4 nA.

important [19]. The ratio of vacancies at center sites relative to corner sites increased from 1 to 1.2 after irradiation for all energies, and single adatom vacancies appeared 1.3 times more frequently in the faulted half of the unit cell. The mean distance between vacancies decreased from ~28 Å for the clean surface to 20 Å after irradiation with 90 eV electrons. After 2000 eV irradiation, ~50% of the vacancies were present in the nearest-neighbor configurations, and complexes derived from up to 7 adatom vacancies were evident. The number of such complexes also increased with dose as existing vacancies influenced removal of nearby adatoms.

In Fig. 3, features like A_5 represent Si released from adatom sites and trapped at dangling bond sites of rest atoms. Though present, these extra terrace atoms were outnumbered by the vacancies by a factor of ~30 after irradiation with 90 and 500 eV electrons [20]. Neglecting them, the cross section for Si desorption from Si(111)-(7 × 7) follows directly from Fig. 2(b), ranging from 1×10^{-20} cm^2 for 90 eV electrons to 5×10^{-20} cm^2 for 2000 eV electrons. These values fall within the ESD range of adsorbates on surfaces [3,4].

While the cross section for desorption is a measure of long-term surface modification, it underestimates the effects of irradiation for Si(111)-(7 × 7) because vacancy-adatom pairs can be produced and a vacancy in the adatom layer can be annihilated by a single diffusing atom. Such vacancy annihilation was recently studied by Stipe *et al.* [21], using STM to displace an adatom at low temperature and to follow its return. They showed that adatom layer vacancies were short lived above 175 K. Our results suggest a follow-on experiment that examines surfaces irradiated at low temperature.

Si(100) differs from Si(111) in that the event that creates a single atom vacancy is followed by the escape onto the terrace of the now-unpaired atom of the original dimer. Damage accumulation is more profound because dimer vacancy annihilation requires the capture of two diffusing atoms. We cannot say how many of the features imaged as dimers or aggregates in Fig. 1(b) were produced by desorption and how many resulted when both atoms of a dimer were transferred to a surface. Nonetheless, the imaged terrace features account for only ~20% of the DV's (total cross section for vacancy creation 1.2×10^{-20} cm^2). We conclude that ESD is significant.

The results of Figs. 1–3 are important because they demonstrate that electrons produce structural damage that had not previously been considered. The question to ask is what is the physical origin of these electronic-induced changes? Hints can be gleaned from recent laser irradiation and STM-modification studies. For Si(111)-(7 × 7), Kanasaki *et al.* [22] studied Si atom desorption induced by 23–150 mJ-cm^{-2} laser irradiation. They reported enhanced desorption from the adatom layer when the photon energy was ~2 eV, an effect they related to dipole transitions involving occupied and empty surface states. H desorption from Si(100) has been attributed to $\sigma \rightarrow \sigma^*$ transitions activated by 6 eV electrons from an STM tip [23]. Stipe *et al.* [21] interpreted vacancy creation in terms of the occupation of localized antibonding σ^* levels that resulted in the displacement of center adatoms onto the terrace. Similar electron capture in antibonding resonances have been linked to ESD from Si(111) [24]. For Si(100), Kanasaki *et al.* did not observe Si desorption for 2.48 eV photons, showing that $\pi \rightarrow \pi^*$ transitions did

not contribute to bond breaking for surface dimers, but they were not able to gauge the effectiveness of transitions from dimer σ levels 3 eV below the valence band maximum to σ^* states near the conduction band minimum. They did not report desorption when there were electronic levels associated with defects.

Our studies differ from the above because surface atoms are exposed to hot carriers having a wide range in energy, as produced by the cascade of inelastic scattering events triggered by the 90–2000 eV primary electrons. Some of these electrons can induce localized direct transitions that allow a coupling to the nuclear motion. Others can be captured in localized surface resonance states. Localization involving excitations or resonant capture as the basis for Franck-Condon processes has been encountered in previous photon or local-probe techniques, but energetic electrons expand the range of accessible states. Experimentally, we observe that vacancy creation occurred randomly on ideal terraces for sufficiently wide-range excitations. With increased primary energy, the number of relevant hot carriers that can reach the surface increases [25]. Electron-hole recombination events that release energy in the surface region contribute to the overall dynamics.

To demonstrate that surface structural changes due to electron irradiation were not unique to Si, we irradiated cleaved GaAs(110). In this case, vacancies were produced randomly by desorption and transfer of atoms to the terrace. Subsequent photon irradiation using a low-power 2.3 eV laser resulted in atomic layer-by-layer removal [26]. This electron plus photon procedure has an advantage over chemically induced vacancy creation because it introduces no potential contamination.

With STM, we have differentiated modification involving desorption from modification involving vacancies that heal spontaneously. For metal surfaces, surface vacancies may be created by electron irradiation or by secondary electrons produced after high-energy photon absorption. Indeed, Ernst *et al.* [27] recently demonstrated vacancy creation for Cu(111) and (001) by tuning the photon energy of a laser to establish localized d-band holes. In all cases, surface defects introduced by the beam probe would alter the local reactivity. Indeed, one can speculate about the structural consequences of electron irradiation during growth or etching or other processing.

This research was supported by the U.S. Army Research Office. We thank B. Y. Han, S. J. Chey, and L. Huang for stimulating discussions.

[1] J. B. Pendry, *Low Energy Electron Diffraction* (Academic Press, London, 1974).
[2] C. J. Powell and M. P. Seah, J. Vac. Sci. Technol. A **8**, 735 (1990).
[3] R. D. Ramsier and J. T. Yates, Jr., Surf. Sci. Rep. **12**, 243 (1991).
[4] T. E. Madey and J. T. Yates, Jr., J. Vac. Sci. Technol. **8**, 525 (1971).
[5] R. J. Hamers *et al.*, Phys. Rev. B **34**, 5343 (1986).
[6] B. S. Swartzentruber *et al.*, J. Vac. Sci. Technol. A **7**, 2901 (1989).
[7] From C-*KLL* and Si-*LVV* intensities, the C concentration was below 1% on Si(100)-(2 × 1) after 300 s irradiation at 2000 eV (accumulation rate 3.2×10^{-5} ML s^{-1} for $\leq$2000 s). The O concentration was even smaller, and there was no metal contamination. When clean Si(100)-(2 × 1) was also placed in front of the LEED and AES guns with hot filaments but without applying a bias, the concentration of c-type defects increased by 4% after 150 s, possibly suggesting hydrogen adsorption, but the DV concentration did not change. There were no structural changes for Si(111)-(7 × 7) after 1200 s.
[8] The front panel of the Faraday cup was grounded. Electrons passed into the cup (~20 V) through a hole of 0.5 mm diameter. The leakage due to electrons emitted from the cup and captured by the ground plate was 9% at 2000 eV and 6% at 500 eV, as determined with a cup with 5 : 1 aspect ratio.
[9] Z. Zhang *et al.*, Surf. Sci. **369**, L131 (1996).
[10] T. Uda and K. Terakura, Phys. Rev. B **53**, 6999 (1996).
[11] Z. Zhang *et al.*, Phys. Rev. Lett. **74**, 3644 (1995).
[12] J. van Wingerden *et al.*, Phys. Rev. B **55**, 4723 (1997).
[13] B. Borovsky *et al.*, Phys. Rev. Lett. **78**, 4229 (1997).
[14] T. Yamasaki *et al.*, Phys. Rev. Lett. **76**, 2949 (1996).
[15] R. J. Hamers *et al.*, J. Vac. Sci. Technol. A **8**, 195 (1990).
[16] Y. M. Mo *et al.*, Phys. Rev. Lett. **66**, 1998 (1991).
[17] Z. Zhang *et al.*, Surf. Sci. **369**, 69 (1996).
[18] H. Feil *et al.*, Phys. Rev. Lett. **69**, 3076 (1992); H. J. W. Zandvliet, Surf. Sci. **377–379**, 1 (1997).
[19] The cross sections for core excitation would increase above the Si $2p$ and $2s$ binding energies but would then decrease as $1/E_p$. See L. C. Feldman and J. W. Mayer, *Fundamentals of Surface and Thin Film Analysis* (Elsevier, New York, 1986), p. 131.
[20] Accommodation of the missing atoms at steps was negligible because the terraces were ~1500 Å wide.
[21] B. C. Stipe *et al.*, Phys. Rev. Lett. **79**, 4397 (1997).
[22] J. Kanasaki *et al.*, Phys. Rev. Lett. **80**, 4080 (1998); K. Ishikawa *et al.*, Surf. Sci. Lett. **349**, L153 (1996).
[23] T.-C. Shen *et al.*, Science **268**, 150 (1995). See also R. S. Becker *et al.*, Phys. Rev. Lett. **65**, 1917 (1990); M. Schwartzkopff *et al.*, J. Vac. Sci. Technol. B **14**, 1336 (1996).
[24] M. Martel *et al.*, Science **272**, 385 (1996).
[25] The typical ESD yield of adsorbates on surfaces tracks the secondary electron yield (Ref. [4]), and this would show a turn-down by 2000 eV. Here, the excitations that lead to vacancy creation are at lower energy and the electron concentration in the surface region would not scale with the yield.
[26] B. Y. Han, C. Y. Cha, and J. H. Weaver, J. Vac. Sci. Technol. A **16**, 490 (1998); B. Y. Han, K. Nakayama, and J. H. Weaver (unpublished).
[27] H.-J. Ernst *et al.*, Science **279**, 679 (1998).