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LETTER TO THE EDITOR

Electron-stimulated athermal surface recrystallization of Si(100)

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Abstract

Low energy (<40 eV) electrons may be used to athermally release the compressive stress in a Si(100) surface layer induced by Ar^+ ions (<100 eV) (Narushima *et al* 2001 *Appl. Phys. Lett.* **79** 605). In particular, we have strong evidence that the stress relaxation depends only on the number of irradiated electrons. This indicates that complete relaxation is not promoted by a thermal activation mechanism, but by a non-thermal mechanism. In this letter, we show using scanning tunneling microscopy (STM) that the underlying cause of the athermal surface stress relaxation is recrystallization of the surface atoms. Our STM observations show characteristic features to support our hypothesis. The electron-irradiated surface does not have the thermally generated 2×1 surface reconstruction, but instead a 1×1 reconstruction, which is slightly closer to the positions of a 'bulk-terminated' surface.

A low energy electron beam, typically under 5000 eV, is routinely used to investigate the structural and chemical properties of surfaces [1, 2]. We assume that these electrons do not cause structural changes. But this conventional wisdom is not valid. The first apparent report by Nakayama *et al* [3] was that energetic electrons (90–2000 eV) induce defects on clean Si(111) and (100) surfaces, indicating that atomic scale surface modification towards disorder occurs under electron beam irradiation. We have found the opposite phenomenon, that complete restoration of the disorder-induced surface stress of Si(100) occurs for electrons of low energies between 3.75–40 eV [4]. Upon irradiating the disordered Si surface, disorder-induced compressive stress completely relaxed. We have found the key point to explain

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this difference. The stress relaxation was found to depend only on the number of irradiated electrons and was independent of the total energy deposition [4]. This indicates that the physical mechanism promoting this complete relaxation is not thermal but athermal. We suggest that there is a threshold around 40–90 eV (in the case of Si) between athermal and thermal electron–surface atom interaction processes in the surface layer. At energies below the threshold, the electrons can heal the damage, for example, caused by low energy Ar^+ ions. In this letter, we shall show using scanning tunneling microscopy (STM) that the origin of the athermal surface stress relaxation is recrystallization of the surface atoms so that, from a microscopic viewpoint, the surface dimerization is restored or, from a macroscopic viewpoint, surface periodicity is restored.

The samples of Si(100) for STM observations were exposed to Ar plasmas generated by DC glow discharges to perform ion and electron irradiation. Before electron irradiation, we performed ion irradiation and prepared a damaged layer on a Si(100) surface to test the healing effect that was previously demonstrated by surface stress measurements [4]. Ar ion irradiation of the sample to introduce disorder in the surface was performed at room temperature (300 K) using a plasma. The DC plasma of Ar gas was discharged at a pressure of 10 Pa, with a current between the grids of 20 mA and an applied voltage of 400 V. From Langmuir probe measurements [5], the electron temperature, electron density and space potential (V_p) were 3 eV, 6.5×10^5 cm^{-3} and +5 V at the sample position, respectively. For Ar ion irradiation, a negative DC bias (V_b) of -60 V was applied to the Si sample to attract the ions. The average damage depth in the sample was obtained by TRIM calculation [6] to be 1 nm. No peak of the Auger electron signal of Ar was observed on the surface after ion irradiation even though its sensitivity is very high in this case, as the primary energy is 3 keV. Electron irradiation was performed after ion irradiation at room temperature, using the Ar plasma at a positive V_b of +30 V. The electron penetration depth in this energy range is comparable to the damage depth [7]. The plasma had a space potential V_p and the incident energy of the irradiated species was given by $E_i = e|V_p - V_b|$. Since our experimental set-up was complex, we checked that the sample surface was being successfully irradiated by monitoring the current through the sample directly, using it as a current probe. To generate a non-contaminated plasma, we prebaked grids of the DC plasma at a high temperature of 1200 °C for longer than 12 h. In addition, we baked the gas piping by using highly purified Ar gas (99.9995%) and a combination of particle filters. We also conducted the crucial test of placing the Si(100)-(2×1) surface in the vicinity of, but not actually in, the plasma for periods of time (5 min and 0.5 h) to see whether the surface was being contaminated or not by the plasma; in all cases, the surface remained clean, which was checked by STM. If metal contamination existed on the surface, ordered structures induced by the metal contamination would be observed with STM before and after the flashing [8, 9]. However, we have observed no ordered structure on surfaces exposed to the plasma. In addition, these surfaces always recovered to the original clean Si(100)-(2×1) surfaces, without any other ordered structures being present, by high temperature flashing. Then, we performed ion and electron irradiation with the non-contaminated plasma and also obtained surfaces irradiated with the ions and electrons without any contamination.

STM can directly observe the change of surface morphologies and structures as the change in surface stress occurs. To achieve surface modification without contaminating the surface, however, we must be very careful. Three possible sources of contamination must be considered: impurities from the gas line, residual water inducing C-type defects [10] and sputtered materials from the grids or chamber walls. The first two factors were prevented by careful baking. For the third source of impurities, the sample surface was set so as not to face towards the DC grids to avoid any contamination, checked with STM. A clean surface was obtained by flashing the sample around 1050 °C [14] with the direct current heating method in an ultrahigh vacuum

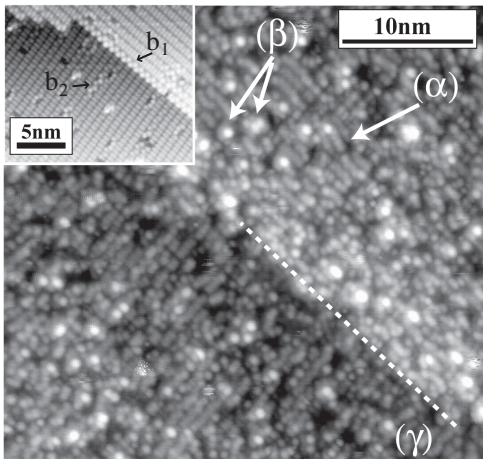

Figure 1. Initial ion bombarded Si(100) surface at 65 eV: $V_s = -1.5$ V, $I_s = 0.10$ nA. (α), (β) and (γ) show the positions of observed features. The inset shows the typical clean Si(100) surface before the ion bombardment. (b_1) at the S_A steps and (b_2) in the terrace indicate the zigzag structure of buckled dimer.

(UHV) with a base pressure of lower than 1×10^{-8} Pa. Cleanliness of the surface was initially confirmed to minimize the C-type defects to under 0.1% at least.

Surface stress changes which developed during ion bombardment and electron irradiation were monitored through sample bending using the optical microcantilever method. We used Si(100) microcantilevers as samples with dimensions of 450 μm $\times$ 50 μm $\times$ 2.0 μm whose long side is parallel to the $\langle 011 \rangle$ axis. One end of the microcantilever sample was fixed on a mount near a quartz window in a UHV chamber, while the other was free. A laser light beam incident on the back side of the sample at the free end was reflected through the UHV window and detected by a position-sensitive detector (PSD). A deflection of the free end of the lever was determined by monitoring the position of the reflected laser light on the PSD. This method allows *in situ*, real-time detection of the deflection. We calibrated our detection system with a piezoelectric element and confirmed a resolution of better than 0.1 nm in the deflection. The surface stress change was obtained from the deflection using Stoney's formula [11]. Details of the experimental method are described elsewhere [4, 12, 13].

We performed ion bombardment of the clean surfaces in order to introduce surface disorder. Figure 1 shows the initial stage ($\lesssim$1 s) of a disordered surface. It seems that the degree of disorder is small since the original morphology of the surface is maintained. The disordered surface, however, has some notable features:

(α) 2 $\times$ 1 dimer rows are partially destroyed and they are cut and bent,
(β) bright points are observed at intervals,
(γ) the structure of monatomic steps is generally maintained.

Feature (α) could result from energetic irradiated Ar ions. Ions able to transfer more kinetic energy on impact than the displacement energy of Si ($E_d = 14$ eV [18]) will thus create a lattice defect pair in the damaged layer of a depth around 1 nm. On the surface, a Si–Si bond may be broken by the ions and rebonded with another Si atom, inducing bending of the dimer row. Also, atoms in the underlying bulk material could be moved to other sites by the Ar ions and dimer rows on the top surface are seen as bent. Feature (β) could be due to

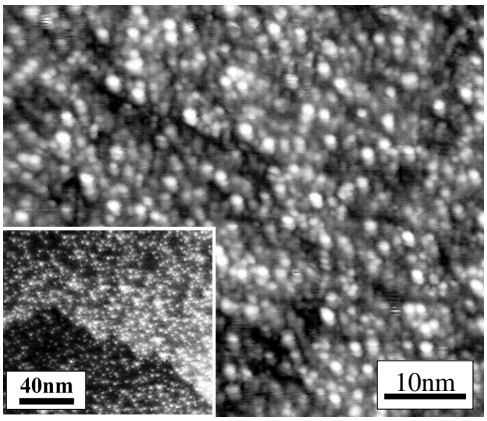

Figure 2. Ion-bombarded Si(100) surface at 65 eV for 10 s: $V_s = -1.5$ V, $I_s = 0.10$ nA. The integrated ion current is 46.1×10^{-4} A s cm^{-2}. The inset shows a wider area image of the same ion-bombarded surface.

surface dangling bonds from undimerized atoms, or displaced Si atoms in adatom sites, with low coordination, and high-energy dangling bonds. The feature (β) is thought not to be caused by residual oxygen for the location of bright spots, which are randomly located due to random attack of the ion irradiation, while in previous STM observations on the initial oxidation of Si(100) surfaces by Cahill and Avouris [15], the centre of the bright spots typically lies in the middle of a dimer row and only rarely lies between dimer rows. In recent years, we have also performed STM observations of the initial stages of thermal oxidation on Si(100) as another research theme, a detailed report of which will appear elsewhere. We have observed numerous bright spots identical to those that Cahill and Avouris observed, which form under various temperatures (including room temperature) and oxygen partial pressures, but we have never observed bright spots appearing the same as the feature (β). Due to this evidence, we suppose that this feature (β) is not attributable to the residual oxygen. Therefore, the feature could be due to real ion bombardment. The feature (γ) indicates that surface morphology and substrate structure are roughly maintained. If the structure of the substrate crystal of Si were completely destroyed by ion bombardment, monatomic height steps would not be preserved. Therefore, ion bombardment is able to affect only short range movement of Si atoms from the original lattice sites to neighbouring sites.

After prolonged Ar ion irradiation (10 s at 65 eV), as shown in figure 2, the feature (α) was not seen at all, while the features (β) and (γ) may still be seen. In addition, we found some dim clusters in the figure. It seems that displaced Si atoms conglomerate into new structures. On the other hand, monatomic height steps were still observed. This also indicates that the ion bombardment is able to affect only short range transfers of Si atoms even under these conditions.

Previously, we reported the evolution of compressive stress up to -0.37 N m^{-1} during ion irradiation of 65 eV by using a similar Ar plasma by rf discharge [4, 12]. We expect two main sources of defective compressive stress. The first is the decay of the intrinsic stress due to the surface reconstruction. It is known that the anisotropy in the local dimer structure directly influences the surface stress, as the stress parallel to the dimer bonds is tensile while that perpendicular is compressive. The difference in surface stress between these anisotropic directions was theoretically expected to be between 1.1 and 3.2 N m^{-1} and tensile [16, 17]. Since the theoretical value is much bigger than the observed value, it is likely that the dimer

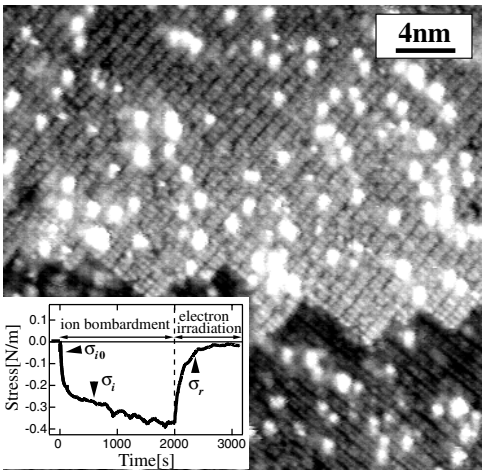

Figure 3. Si(100) surface irradiated by electrons at 25 eV for 11 s, after ion bombardment at 65 eV for 7 s: $V_s = -1.5$ V and $I_s = 0.10$ nA. The integrated ion and electron currents are 22.6×10^{-4} and -32.2×10^{-2} A s cm^{-2}, respectively. The inset shows the time dependence of the surface stress evolution during ion bombardment at 65 eV and the subsequent electron irradiation at 10 eV [4]. The stress values of σ_{i0}, σ_i and σ_r, which are estimated by ion and electron currents, correspond to the surfaces of figures 1–3, respectively.

row structure of the reconstructed surface would be *partially* destroyed. Indeed our STM data of the ion-bombarded surface shows that the local reconstruction has been disrupted.

The second source is expansion of the defective layer. Since the peak of the surface disorder exists at a depth around 1 nm [4, 12], we cannot explain the compressive stress based only on the destruction of the surface reconstruction. The result of STM observation shows corroborating evidence that subsurface atoms could be moved, in features (α) and (β). Thus, the two expected sources of disorder-induced compressive surface stress are consistent with the detailed structures identified by STM imaging of the disordered surfaces.

The inset of figure 3 shows the surface stress evolution during ion bombardment at 65 eV and the subsequent electron irradiation at 10 eV [4]. The surface layer expanded relative to the Si substrate lattice due to ion irradiation. The following electron irradiation acted on this layer, and complete relaxation of the disorder-induced stress occurred. Complete relaxation was independent of the degree of surface disorder. In addition, the macroscopic restoration was dominated by an athermal mechanism. In previous work [4], we showed that very low energy electron irradiation of 3.75–40.0 eV has the capacity to recover the original surface stress condition.

In this letter, by means of STM observations, we shall show the restoration from disorder to order at an atomic scale to reveal its origin. Figure 3 shows an occupied-state image of the Si(100) surface irradiated with electrons at 25 eV for 11 s after ion bombardment at 65 eV for 7 s. Surprisingly, the entire disordered surface has been restored to a highly *ordered structure*. Furthermore, our observations of a well-ordered surface strongly suggest that the subsurface damage has also been healed. This surprising result of surface re-ordering is consistent with the complete surface stress relaxation by electron irradiation, i.e. our expected (athermal) mechanism of recrystallization under electron irradiation must be correct.

The electron-irradiated surface structure greatly resembles the dimerized Si(100)-2 $\times$ 1 surface generated at high temperatures. However, if this restoration process results from an athermal process, some traces of the athermal nature must be observable in the resultant surface

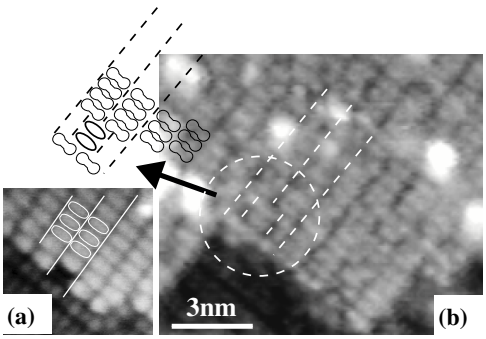

Figure 4. Detailed comparison between (a) a typical thermally annealed surface and (b) an electron-irradiated surface after ion bombardment (expanded image of figure 3). Out-of-phase dimers are seen in the broken circle.

structure. Under our experimental conditions, recrystallization by electron heating does not occur, because the temperature rise during electron irradiation was no more than about 3 K. The temperature change was measured by using the bimetal effect of the Si/Al cantilever [4]. We can also explain the extremely low temperature rise, using a quantitative estimation. We consider the energy balance in steady state of thermal diffusion and blackbody radiation following Stefan–Boltzmann's law as thermal emission terms and also electron influx as a heat source term. While thermal recrystallization needs a temperature of more than 600 K, this process proceeded at almost room temperature. In addition, from the surface stress measurement, the process was found to depend only on the number of irradiated electrons and was independent of the total energy deposition. Considering these two results, the restoration process must be athermal.

Figure 4 shows that there are some minor differences between a thermally annealed surface and a surface restored by low energy electron irradiation. It is believed that dimerization involves recombining the four dangling sp^3 electrons of two surface atoms into occupied σ bonds and a weak π bond [21, 22] accompanied by contraction of the interatom spacing. In general, Si dimers of the thermally annealed surfaces appear as elliptically shaped protrusions in occupied states such as those shown above, and the individual atoms are not usually resolved. In contrast, in figure 4, while most of the atoms on the restored surface appear to be paired, our measurements show some *slightly resolved* dimer atoms. This may be due to dimer atoms which have not completely dimerized, or substrate differences leading to a lack of flipping.

A similar image of the slightly pairing 2×1 surface has been reported by Xu *et al* [23]. They performed STM observations of laser-irradiated Si(100) surfaces, showing that the dimerized top layer can be selectively removed by a pulsed Nd:YAG laser with a fluence below the melt threshold. The atoms in the laser-uncovered second layer are close to positions of a 'bulk-terminated' 1×1 structure, but with a slight pairing. Based on the fact that the 2×1 dimerized structure is recovered by thermal annealing or by the high fluence of laser irradiation, there is an *energy barrier* for the transition from the laser-induced to the dimerized 2×1 structures. According to their interpretation, our restored Si(100) surface by low energy electron irradiation could also be a similar metastable state.

The other traces of athermal restoration were identified at steps and around C-type defects. It is known that on thermally annealed Si(100) surfaces buckled dimer features (seen as zigzag structures) are observed both at the S_A steps (b_1) and in the terrace (b_2), as shown in an inset of figure 1, while the restored surface has no buckled dimer features. The $c(4 \times 2)$ buckling structure is the most stable on the Si(100) surface. Although STM cannot detect the

buckling in a terrace because of rapid flipping between two states in mirror symmetry, it can recognize buckled dimers because of the pinning at steps and around C-type defects. Ordering of the buckling would need harmonic interactions over several neighbouring dimers, at least. Thus, the lack of buckled features suggests that short range ordering even over several dimers may have been lost on the recrystallized surface. This disappearance of buckling is induced by disorder of the surface, a deduction which is supported by detailed STM images. The dimers on the recrystallized surface differ from those on the annealed surface and their shapes show many kinds of unusual structures, as seen in figure 4(b). Their disorder kills the short range order.

In figure 4, 'out-of-phase dimerization' has occurred in the broken circle. In the thermally clean surface, all the dimer structure is perfectly ordered 2×1 and there are no out-of-phase dimers as seen in the figure. These phase shifts, antiphase boundaries, occur during Si on Si(100) homoepitaxy, when two islands, which have nucleated independently, meet [19, 20]. We might conclude that the existence of these shifted dimers means that all the movement of Si atoms is only over a very short range. However, most of the dimer positions have recovered to form rows, which suggests that the initial change in position by ion irradiation could have occurred around the original lattice position. Therefore they are able to return to the original position. These three features support the hypothesis that the Si(100) surface reconstruction may be athermally produced by low energy electron irradiation.

In conclusion, we revealed using STM that the underlying cause of surface stress relaxation is athermal recrystallization of the surface atoms. Electrons sometimes behave against our expectations. In general, we believe that higher energetic particles can penetrate deeper inside materials. The electron, having extremely low kinetic energy ($\ll$70 eV), can, however, penetrate to unusual depths because it cannot lose its own energy via any energy loss process [7]. The higher energy electron irradiation ($>$90 eV) induces surface defects in the Si surface by electron excitation due to the cascade of inelastic scattering events. Nakayama *et al* [3] reported structural modifications by 'mild' electron irradiation of 90–2000 eV with STM studies. But their 'mild' condition was stronger than our condition; a higher incident energy and a higher electron dose (about 20 times the value when the surface stress completely relaxed). The extremely low energy electron irradiation in this letter achieves restoration of a destroyed structure. This indicates that the use of the electrons changes from disorder to order. A plausible mechanism of the athermal restoration observed here is ionization-enhanced diffusion (IED) via the charge state transition of defects where no energy loss occurs [24]. In defective Si, electron irradiation promotes athermal diffusion of defects [25]. Such a charge state transition mechanism may occur on the Si surface [26]. Some traces of the athermal restoration on the surface structure could be observed, such as a slightly pairing (1×1) structure and an absence of buckled dimers and out-of-phase dimerization features derived from the athermal process of electron irradiation. In demonstrating that surfaces can have the capacity of self-healing, these results suggest new opportunities for atomic-scale surface engineering.

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