lower temperatures (e.g., by using a synchrotron radiation source). It would be particularly interesting if the data were to indicate a maximum in $\xi(T)$, consistent with the recently observed maxima in the adiabatic compressibility [see, e.g., Ref. 15, and E. Trinh and R. E. Apfel, J. Chem. Phys. 72, 6731 (1980)], as such behavior could rule out the spinodal possibility.

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Buckling Reconstruction on Laser-Annealed Si(111) Surfaces

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Angle-integrated photoemission and low-energy electron-diffraction studies of laser-annealed Si(111) surfaces show that a buckled reconstruction takes place upon laser quenching. No long-range order exists but a short-range 2×1 reconstruction is present.

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There is much interest in laser-annealed Si(111) surfaces,[1-3] because of the apparently perfect regrowth of the surface layer (no reconstruction)[1] and of the cleanness of the surface after laser annealing.[4] If the top layer is a simple termination of the bulk, then theoretical models[5] for a perfect, unreconstructed Si(111) surface ought to predict the surface electronic structure. However, if the top layer is disordered,[6] then evidence of this disorder should be reflected in the surface density of states as measured by photoemission spectroscopy. In this Letter, we report a photoemission study of laser-annealed Si(111) surfaces. Our results clearly show that the peak in the surface state density is not located in the band gap as expected for a relaxed unreconstructed surface layer,[7] but instead, the surface states peak ~0.5 eV below the top of the valence band. The opening of a gap[8] in the dangling-bond density of surface states upon laser annealing is attributed to a buckling of the surface atoms. Low-energy electron-diffraction (LEED) studies of flat and stepped Si(111) surfaces show the presence of very weak half-order spots, after laser annealing, consistent with a buckled (2×1)-like reconstruction. The weakness and diffusivity of the half-order spots for the flat Si(111) surface suggests a lack of long-range order in the top silicon layer.

The photoemission LEED chamber used a double-pass cylindrical-mirror analyzer (CMA)[9] with 0.25 eV energy resolution and a resonance lamp radiation at 11.7 eV (Ar), 16.8 eV (Ne), or 21.2 eV (He), incident at an angle 70° measured from the sample normal. The n-type Si(111) samples ($\rho \sim 1\ \Omega$ cm) were cleaned by argon sputtering (1 kV, 10 μA/cm^2 for 3 h) followed by thermal annealing at 1000 °C by resistive heating. The LEED pattern obtained after such a treatment was a very sharp 7×7. In all cases, Auger analysis revealed that less than 1% of an impurity monolayer was present at the surface. The laser was a Q-switched Nd-doped yttrium aluminum garnet laser (1.064 μm) equipped with a frequency doubler. A typical Q-switched pulse gave ~0.4±0.2 J/cm^2 at 5320 Å in a 10-nsec pulse as estimated from the threshold for order-disorder transition of the 7×7 LEED pattern at 0.2 J/cm^2 and 1130 K.[10,11] Refracting prisms eliminated the 1.06-μm radiation from the optical path. To uniformly laser anneal the sample over the complete 2×0.6 cm^2 area, ~600 shots were fired at a rate of 10 shots/sec while the sample was slowly translated in front of the beam. After laser annealing, the LEED pattern was recorded on polaroid film and angular intensity profiles recorded with a Vidicon camera interfaced to a minicomputer.[9]

The photoemission results are summarized in Fig. 1. In order to match the bulk feature[12] at −4.8 eV the photoemission spectra for the laser-annealed surfaces had to be shifted by −0.15 eV, thus shifting their Fermi energy by the same amount. This shift is due to a change in band bending,[13] similar in sign and magnitude to that occurring for the Si(111)-(2×1) surface.[14,15] The main feature characterizing the laser-annealed spectra is a strong dangling-bond surface peak located at −0.85 eV below E_F. Note that the strength of the mostly p_z-like surface states in the 0–1-eV region is greatly reduced because of the acceptance angle of the CMA (42°± 6° with respect to the normal).[16] The back-bond states located at −2 and −8 eV are suppressed and enhanced, respectively, for laser-annealed surfaces as shown in Fig. 1.

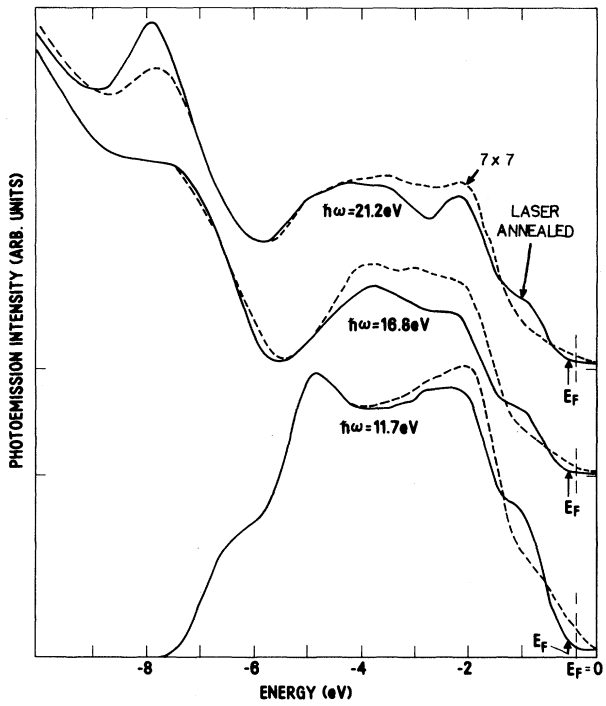

FIG. 1. Photoemission spectra of a thermally annealed 7×7 surface (dashed lines) and of the same surface laser annealed with 400 mJ/cm^2 energy density at 5320 Å (solid line) for three different photon energies (21.2, 16.8, and 11.7 eV). The vertical scale is linear and the energy scale is referenced to the Fermi energy associated with the 7×7 surface. The arrows indicate the position of the Fermi energy associated with the laser-annealed surfaces, thus indicating the change in band bending.

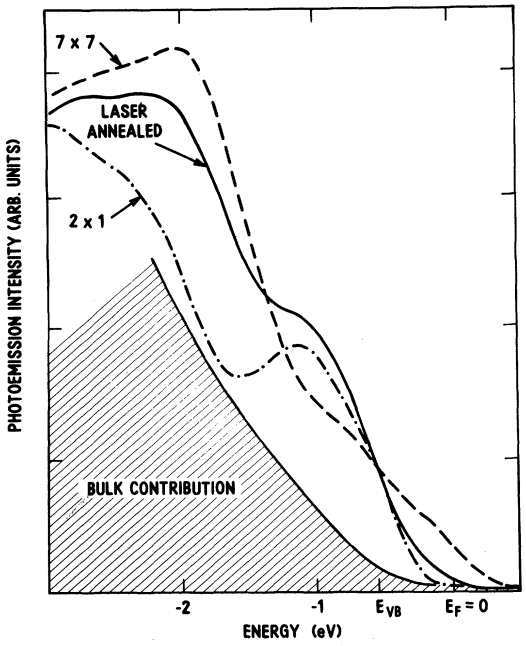

FIG. 2. Details of the photoemission spectra around the top of the valence-band region for three different types of surface. The photon energy is 11.7 eV and the horizontal energy scale is referenced to the Fermi energy of the clean 7×7 surface. The bulk contribution to the ultraviolet-photoelectron spectra is indicated by the hatched area.

The shift in the dangling-bond state and the intensity changes of the two back-bond surface states are features characteristic of the differences between Si(111)-(2×1) and -(7×7) surfaces.[9,12] These differences are shown in more detail in Fig. 2 for the top of the valence-band region for the 7×7, 2×1, and laser-annealed surfaces. The dangling-bond surface states are split into two weak peaks in the case of the 7×7 surface but lose the weak metallic character both for the 2×1 and laser-annealed surfaces. If our laser-annealed surfaces were simply disordered 7×7 surfaces, the dangling-bond intensity at −0.85 eV would remain constant or decrease slightly.[17] However, Fig. 1 shows that this surface state increases in intensity by nearly a factor of 2 from the 7×7 to the laser-annealed surface. Thus an increase in number of dangling-bond states has occurred which we attribute to an increase in the number of surface atoms in a (2×1)-like reconstruction. However, the strength of the back bond at −1.8 eV for the laser-annealed surfaces is halfway between those for the 7×7 and 2×1 surfaces (Fig. 2) indicating a possible mixture of some (7×7)-like and some (2×1)-like regions. The local structure of the laser-annealed surfaces apparently is mainly a (2×1)-like geometry since the dangling bond shows such a large increase. This is confirmed by more detailed LEED analysis which we now present.

Upon laser annealing, the LEED pattern changes from the stable 7×7 to an apparent 1×1 one when the pulse energy is large enough (0.20–0.4 J/cm^2 at 530 nm). For this 1×1 surface, broad, weak streaks are present at the half-order position for primary energies larger than 55 eV as shown in Fig. 3, curve *a*. The LEED intensity profile is recorded along the $\langle 0\bar{1}\rangle$ direction, passing through the $(\bar{1}1)$ and the $(\bar{1}0)$ spots. At this primary electron energy (75 eV), the $(\bar{1}1)$ spot is much more intense than the $(\bar{1}0)$ spot. A broad and weak peak is present at the half-order position characteristic of a 2×1 reconstruction with intensity ~0.02 times the $(\bar{1}1)$ intensity. Next, the

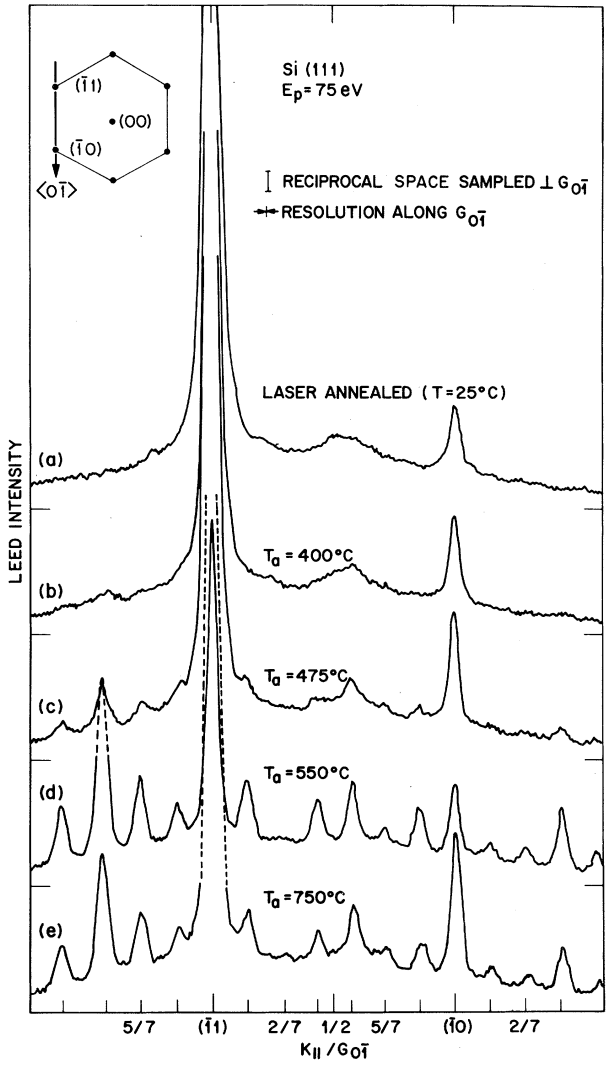

FIG. 3. LEED intensity profile of the $(\bar{1}1)$ and $(\bar{1}0)$ spots taken along the $\langle 0\bar{1}\rangle$ direction for $E_p = 75$ eV. All the curves are taken with the same gain with the sample at room temperature. The temperature T_a corresponds to the thermal annealing temperature to which the sample was subjected for 5 sec subsequent to the laser anneal.

laser-annealed sample was thermally annealed by resistive heating to a temperature T_a for 5 sec and cooling to room temperature where the LEED pattern was recorded. In Fig. 3, curves *b*–*e* show the evolution of the LEED pattern after various intermediate thermal annealing treatments. The 7×7 pattern starts to appear for $T_a = 475$ °C with the broad half-order streak into $\frac{3}{7}$ and $\frac{4}{7}$ spots, characteristic of the 7×7 reconstruction. This change is due to a rearrangement of disordered, small domains with 2×1 symmetry into larger domains with 7×7 symmetry. The intermediate curves *b* and *c* show contributions from both types of domains. We also note that in curve *d*, in contrast to the strong 7th-order spots, the intensity of the integral-order spots is low. Annealing to higher temperature ($T = 750$ °C) restores the strength of the integral-order spots as shown by curve *e*. Our LEED observations confirm that our laser-annealed Si(111) surface is not an unreconstructed termination of the bulk. The data are consistent with the presence of disordered domains with 2×1 periodicity. For vicinal surfaces greater than 1° from (111) we find that the half-order intensity in LEED is suppressed but appears after moderate annealing to $T_a \approx 350$ °C. We have also verified experimentally that, as in the case of the cleaved 2×1 surface, the 2×1 domains are aligned by steps, i.e., much sharper half-order spots oriented perpendicular to the step direction are obtained on the laser-annealed vicinal surfaces.[18,19]

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Determination of the Permeation Coefficient in a Lyotropic Smectic Liquid Crystal by Annealing Elementary Edge Dislocations

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Elementary edge dislocations in a lyotropic smectic liquid crystal have been observed with use of a new technique. Their annealing dynamics are related to the permeation coefficient λ_p, which appears in the viscoelastic equations for a smectic, yielding $\lambda_p = 1 \times 10^{-30}$ cm^2/poise in hydrated dimyristoyl phosphatidylcholine. The associated self-diffusion coefficient anisotropy $D_\perp/D_\parallel = 2\times 10^{12}$ is many orders of magnitude larger than that found in earlier attempts where the effect of structural defects may have prevailed.

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Helfrich first suggested that the anomalously large flow viscosities of smectic liquid crystals were due to the effects of slow interlayer permeation.[1] Although permeation has since been found to limit other dynamical properties of the smectics,[2,3] valid measurements of the permeation coefficient λ_p have been impeded by structural defects that short circuit this slow process. We have avoided these difficulties by using the annealing rate of elementary edge dislocations to determine λ_p. Elementary edge dislocations in a smectic liquid crystal, which are important to its mechanical properties[4] and which have possible biophysical application,[5] are the abrupt terminations of single layers. They have been observed only in thermotropic liquid crystals near a smectic-*A* to -*C* phase transition.[6] In this Letter, we outline a more general technique that we have developed to observe individual dislocations and their annealing; details will be presented elsewhere.

Our samples were formed from hydrated dimyristoyl phosphatidylcholine (DMPC), a phospholipid of biophysical interest.[7] Above 23 °C, fully hydrated DMPC forms a smectic-*A* phase, the L_α phase, with the lipid molecules in bilayers intercalated with water layers.[7] Thin samples of DMPC lightly doped with a fluorescent analog were aligned between two closely spaced fused quartz plates with the bilayers parallel to the interface. The plates were spread at a slight wedge angle φ. To accommodate the wedge angle in the liquid crystal, there must be an array of edge dislocations spaced a/φ, where a is the smectic-layer repeat distance; this structure resembles a low-angle tilt boundary in a crystal. By measuring the fluorescence intensity excited in a small laser-illuminated spot, we obtain a measure of the number of bilayers at that spot. For the photon statistics to be good enough to resolve in a reasonable time, the intensity change due to one bilayer, the sample had to be less than 50 bilayers thick. Ideally, the fluorescence intensity scanned along a line parallel to the sample thickness gradient should yield a regular staircase waveform where each step corresponds to the edge of a single bilayer.

Scans of fresh samples in the L_α phase showed many irregularly spaced up and down steps, giving the appearance of peaks (Fig. 1). In contrast, scans of samples annealed for 2–4 weeks at 35 °C reproducibly showed the regular steps of the

