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Effect of reconstruction of a semiconductor surface on the crystal growth

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It is well established that most low-index semiconductor surfaces reconstruct in contact with vacuum or vapor. Covalent bonding considerations imply that they also reconstruct in contact with the liquid. Conventional precipitation theory shows that these first-order transitions should have important consequences on the growth of the crystal. The kinetics of the Si (111) 2×1 to 7×7 reconstruction are explained and the consequent effect upon the growth is found in the observation by de Kock *et al.* of a 6-orders-of-magnitude drop in vacancy cluster concentration at a pull rate of 0.5 cm/min.

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Low energy electron diffraction (LEED) experiments have shown[1] that a great many of the low-index surfaces of the Si and GaAs type semiconductors reconstruct, i.e., undergo a phase transformation that displaces the surface atoms from the positions they would occupy if the bulk crystal were simply truncated. Such reconstructions have been observed for Si surfaces growing by chemical vapor deposition (CVD) as well as for cleaned and cleaved surfaces in contact with vacuum.[2] Most of these transitions are first order and appear to liberate a significant heat.[3] [It is very difficult to measure this heat experimentally, but a value of 300 erg/cm^2 or 0.2 eV/atom has been estimated for the Si (111) 2×1 surface.[4]]

Unfortunately, LEED experiments cannot detect a surface reconstruction unless a well-ordered $n\times m$ surface superlattice ($n>1$) is formed from which electrons may be diffracted. Thus, any reconstruction having the periodicity of the bulk lattice goes undetected as do partially amorphized and contaminated surface structures. A surface in contact with a liquid cannot be observed by LEED, or similar techniques, at all.

However, for cases such as the (100) surfaces of these crystals, it is obvious that the unreconstructed surface could not be stable whatever second phase it might contact. [For the unreconstructed (100), every surface atom would have two of four bonds dangling.] When one considers that it is the covalent nature of these crystals which determines the nature of their reconstruction,[5] it is evident that the reconstruction of the surface in contact with its own metallic liquid should be essentially the same as it is in contact with vacuum or vapor.

In the development of the theory of crystal growth, it has long been recognized that the low-index surfaces of most crystals are singular, i.e., correspond to an orientation at which the surface energy per unit area function has a discontinuous derivative with orientation, and that this fact has profound effects on the manner of growth on these surfaces.[6–10] However, this theory has generally been developed with reference to metallic or molecular crystals and has neglected the semiconductors and their reconstructed surfaces. (As a matter of fact, several metal surfaces also reconstruct.)

Because the reconstruction transition may be first order with a significant release of energy and may require a superlattice with several atomic spacings, it lowers the surface energy of the low-index planes relative to the vicinal planes. Thus, the reconstructed planes are much more singular than the unreconstructed planes, and surface energy becomes a discontinuous function of orientation. This effect is doubtless the source of the discontinuity at (100) on GaAs observed in both CVD[11] and liquid phase epitaxial (LPE) growth.[12]

From a consideration of the conventional theories of crystal growth,[6–10] it is evident that the increase in singularity and the appearance of energy discontinuities concomitant with reconstruction must have important consequences on the manner and quality of crystal growth. For example, as noted by Abbink *et al.*,[2] the possibility of reconstructing the riser of a growth step provided that it be several atomic layers high may explain the observation that such risers are almost never one layer high.[2,11,12] Moreover, Rode has pointed out the relation between reconstruction and terrace formation in LPE growth.[12] Here we shall propose a relation between reconstruction and the entrapment of excess vacancies.

Let us now consider the particular case of the (111) surface of Si. When freshly cleaved from the bulk, this surface exhibits a 2×1 LEED pattern which transforms irreversibly to a 7×7 pattern at temperatures ranging from 350 to 390 °C, depending on the density of surface steps, in 10-min isochronal annealing experiments.[13] The metastable 2×1 reconstruction is widely believed to result from simple displacements of the surface atoms to positions of local equilibrium.[14] However, the stable 7×7 reconstruction is generally believed to involve a major rearrangement of the surface with the creation of surface vacancies at 26.5% of the surface lattice sites.[5,15,16]

Let us assume that the usual activation barrier-limited kinetics (Fig. 1) determines the time τ required to observe the appearance of the 7×7 LEED pattern:

$$\tau(T)=\tau_0\exp[\Delta H(2\times1)/kT], \tag{1}$$

where k is Boltzmann's constant, T is temperature, and $\Delta H(2\times1)$ is the activation barrier for the metastable 2×1 to the 7×7 reconstruction. Also,

$$\tau_0=(1/\nu_0)\exp[\Delta S(2\times1)/k], \tag{2}$$

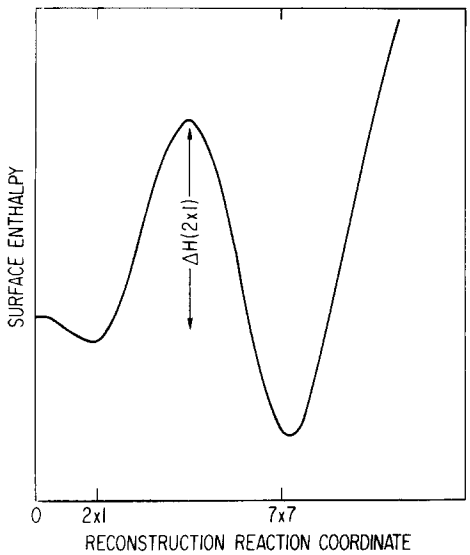

FIG. 1. Schematic representation of the activation barrier between the 2×1 and 7×7 reconstructions of a Si (111) surface.

where $\Delta S(2\times1)$ is the entropy of the barrier and ν_0 is the attempt frequency for the transition, which will be taken to be a typical phonon frequency. Here we shall take

$$1/\nu_0 = 1.0\times10^{-13} \text{ sec}. \tag{3}$$

As the prevailing opinion[5,14] is that the 7×7 reconstruction requires a large concentration of surface vacancies while the 2×1 contains none, one may make the reasonable approximation that

$$\begin{aligned} \Delta H(2\times1) &= \Delta H_f(V_S), \\ \Delta S(2\times1) &= \Delta S_f(V_S), \end{aligned} \tag{4}$$

where $\Delta H_f(V_S)$ and $\Delta S_f(V_S)$ denote the enthalpy and entropy of formation of a surface vacancy, V_S, in the 2×1 surface.

Whereas $\Delta H_f(V_S)$ has not been measured, the enthalpy of formation of the bulk vacancy, $\Delta H_f(V_B)$, is known to be[17] about 2.4 eV. It has been shown that one may account for this value, and other properties of the vacancy, simply and accurately in terms of the macroscopic cavity model.[4,17,18] In this model, $\Delta H_f(V_B)$ is calculated as simply the surface enthalpy of a cavity of one atomic volume having the equilibrium shape of a macroscopic cavity in the crystal. For Si this shape is a regular octahedron having only (111) surfaces. This same model predicts

$$\Delta H_f(V_S) = \tfrac{3}{4}\Delta H_f(V_B) \tag{5}$$

for the unreconstructed (111) surface simply because a surface vacancy would have $\frac{3}{4}$ the area of a vacancy in the bulk, i.e., only six (111) cavity surfaces would be created as contrasted with eight in the bulk. Thus, for Si we estimate

$$\Delta H_f(V_S) = 1.8 \text{ eV} = \Delta H(2\times1). \tag{6}$$

$\Delta S_f(V_S)$ has not been measured either. The entropy of formation of bulk vacancies[19] is about $1.1k$ for the neutral state and about $6.7k$ for the ionized states V_B^+ and V_B^-. It would seem reasonable that the relevant states of the surface vacancy should be ionized due to band bending and surface state effects directly related to the reconstruction pattern and thus to the surface vacancies involved.[20] Let us assume this and further that the entropies are also simply proportional to the surface area:

$$\Delta S_f(V_S) = \tfrac{3}{4}\Delta S_f(V_B). \tag{7}$$

Thus, we estimate

$$\Delta S(2\times1) = 5.0k. \tag{8}$$

Using Eq. (1) with (3), (6), and (8) one calculates τ for temperatures of interest as

$$\begin{aligned} &\tau(350\,^\circ\text{C}) = 5500 \text{ sec}, \quad &&\tau(390\,^\circ\text{C}) = 720 \text{ sec}, \\ &\tau(425\,^\circ\text{C}) = 150 \text{ sec}, \quad &&\tau(1412\,^\circ\text{C}) = 3.6\times10^{-6} \text{ sec}. \end{aligned} \tag{9}$$

As mentioned above, 600-sec isochronal annealing experiments[13] showed the 7×7 pattern to appear after annealing between 350 and 390 °C, depending on the density of surface steps or the angle α of misorientation off the true (111). (See Fig. 2.) Lower temperatures sufficed for surfaces with fewer steps or smaller α. It was shown[13] that the data could be fitted with the empirical formula for the annealing temperature

$$T(\alpha) \simeq T^* - \text{const}/\tan\alpha, \tag{10}$$

with $T^* = 425\,^\circ$C a limiting value for very high step density that was never attained. A variation with $\tan\alpha$ would imply that the reduction from T^* is proportional to the mean tread width. In terms of the present discussion, one could explain this variation of $T(\alpha)$ qualitatively by noting that once some small region of the surface transforms, the transformation would tend to propagate because of the heat liberated. The surface migration of the atoms expelled to form the vacancies in the 2×1 might also help to propagate the transition. In either case, the propagation would be stopped at the riser of a step. Therefore, at least one transition event is required for each tread, but just one might suffice for an entire tread. The 7×7 pattern will be seen as soon as most of the treads have transformed.

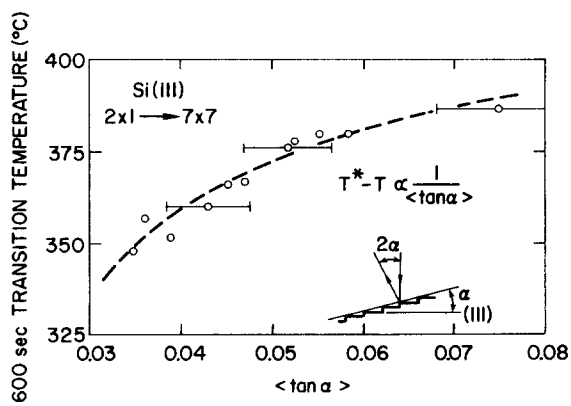

FIG. 2. Data from isochronal annealing experiments in Ref. 13.

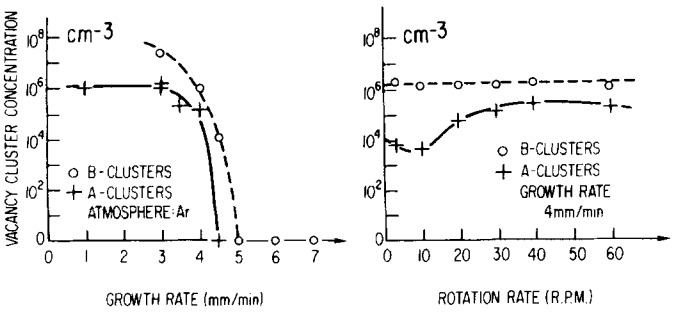

FIG. 3. Data from melt-grown Si experiments in Ref. 21.

It seems that the data are not yet adequate to justify the fitting of a detailed statistical model, but because the calculated temperature for $\tau = 600$ sec lies between 390 °C, the highest temperature observed, and 425 °C, the rough extrapolation, the present estimates cannot be far off. Indeed, the maximum possible error in τ at 425 °C would seem to be a factor of 4.

Now consider the growth of Si from its own melt at 1412 °C the normal (111) surfaces, i.e., in its equilibrium shape. If the rate of growth is sufficiently rapid that surface planes do not have time to reconstruct to the 7×7, or some other low-energy configuration containing many vacancies, before they are buried by new growth, we should expect the mode and quality of growth to be quite different from that obtaining for slower growth on the reconstructed surface. In particular, slow growth from either vapor[2] or melt[10,12] proceeds by the lateral motion of steps. As the risers of these steps are typically 400 Å high,[2,12] it is easy to imagine that large regions of the reconstructed surface may be buried, trapping the vacancies involved in the pattern. If all the vacancies in the 7×7 pattern were to be buried by 400-Å layers and did not subsequently escape, the concentration of such vacancies would be $2\times10^{19}/\text{cm}^3$, which is 3 orders of magnitude greater than the equilibrium concentration. Even if the supersaturation of vacancies were a small fraction of this, it would produce a large concentration of vacancy clusters which would be expected to appear in striations. Just such striations of large vacancy clusters are, in fact, seen[21,22] in slow-grown Si.

When the crystal is grown fast enough that low-energy reconstruction does not occur, we should expect that the mode of growth would be more vertical, as on nonsingular surfaces,[9] and that no significant supersaturation of vacancies should be trapped. In Fig. 3, we see that the concentration of both types of vacancy cluster that are observed drop abruptly more than 6 orders of magnitude at a pull rate of 0.5 cm/min.[21] This pull rate corresponds to 3.8×10^{-6} sec per layer as compared with the calculated value, 3.6×10^{-6} sec in (9) above. While this level of agreement must certainly be fortuitous, it lends strong support to the assumptions upon which the calculation was made.

One may consider the alternate hypothesis that the variation in vacancy cluster density is related to an instantaneous remelt effect.[21-24] Instantaneous remelt may occur either due to the rotation of the crystal seed in an asymmetric thermal environment[23] or due to convective turbulence.[24] In the former case, the critical pull rate would be a linear function of the rotation rate.[21,23] Experimentally, variation of the rotation rate has no effect on concentration of the smaller B clusters and only secondary effect on the larger A clusters.[21] (See Fig. 3.) In either case, one would have to hypothesize that the remelting surface layer contained at least 10^3 times as many vacancies as the growing surface layer and does not revert to the growing surface when the crystal begins to grow again.[22,24] This does not seem to be a plausible alternative to the reconstruction mechanism.

The cutoff of the cluster concentration is so abrupt that one would conclude that some cooperative phenomenon is involved. A possible mechanism is a roughening of the unreconstructed growing surface[9,10] which would prevent the formation of a reconstruction pattern until surface migration had smoothed it again. A detailed exploration of this problem is beyond the scope of the present paper.

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A Schottky-diode acoustic memory and correlator*

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Experiments demonstrate that images of acoustic signals can be stored for tens of msec in a matrix of Schottky diodes on a silicon surface adjacent to a lithium niobate surface-wave delay line. The experiments show charging times of the order of 10 nsec.

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The storage of acoustic signals by differential charging of traps in a silicon surface adjacent to a lithium niobate surface-wave delay line has been demonstrated by Bers, Cafarella, and Stern[1-3] and Hayakawa and Kino.[4] They observed storage times of the order of 0.1–1 msec and charging times of 0.1–1 μsec. A similar effect with much longer storage time has been observed by Coldren[5] and Davis[6] in monolithic structures of zinc oxide on silicon. In this letter we report storage of acoustic signals on a matrix of Schottky diodes on the silicon surface in a sandwiched silicon–lithium niobate structure. The measurements show storage times of 10 msec and charging times of the order of 10 nsec.

When the Schottky diodes are forward biased by a short voltage pulse, applied across the silicon–lithium niobate structure, the electric field from the surface wave will induce a proportional charge on each diode, which adds to the uniform charge due to the voltage pulse. The charge accumulated on each diode will reverse bias them after the voltage pulse is turned off and remain there for a period of time determined by the current through the reverse-biased diodes. The underlying silicon surface will be depleted to a depth proportional to the charge. The stored pattern can then be read out by scanning with an acoustic read pulse and monitoring the voltage generated across the structure. Since this voltage is inversely proportional to the depletion depth when the silicon is uniformly doped, the output is a time scan of the stored charge on the Schottky-diode matrix. It should be noted that the output signal is the correlation between the stored signal and the reading signal.

Recording of phase and amplitude of the acoustic signal requires either that the plate pulse is short compared to the period of the acoustic signal or that it is a burst of pulses coherent with the carrier frequency of the acoustic signal.[1] In the latter case the burst must be short compared to the inverse bandwidth of the signal. A plate pulse which is long compared to the period of the acoustic signal will record the power envelope of the signal.[4] The mechanism is then the generation of a dc acoustoelectric voltage which adds to the applied plate pulse. Readout can, in this case, be obtained as a correlation between the stored envelope and the convolution signal generated from two oppositely propagating acoustic signals. This principle has been applied by Grudkowski and Quate to read out the charge induced on Schottky barriers by an optical image projected onto the surface of a gallium arsenide delay line.[7,8] When

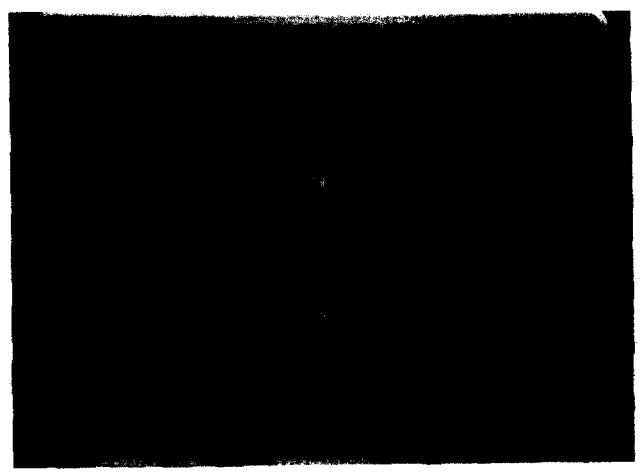

FIG. 1. Convolution between a long pulse (16 dBm) and a double pulse (18 dBm) 5 msec after the storage of a similar double pulse (25 dBm). The double pulse consists of two pulses, each of 150-nsec duration with the second delayed by 400 nsec. The convolution output is envelope modulated with the autocorrelation of the envelope of the double pulse. Time scale, 200 nsec/div.