

Structures and phases of cleaved Ge and Si surfaces

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The consequences of recent new data concerning (2×1) and (1×1) cleaved structures of Ge and Si are examined. It is concluded that a two-phase structure for cleaved surfaces is a possibility. Attention is drawn to the role of surface inhomogeneities in pinning higher-energy structures. These factors need further elucidation before current efforts at determining structures can be assessed.

Recent renewed interest in cleaved surfaces of Ge and Si has been aroused by (a) new angle-resolved photoemission measurements,¹⁻³ (b) improved energy calculations including spin-polarization effects,⁴⁻⁶ and (c) the new finding^{7,8} that cleaved Ge surfaces, if produced at near 4 K, show a (1×1) low-energy electron diffraction (LEED) pattern instead of the normal (2×1) pattern.

Recently, new models have been proposed^{4,6} for the structures in an effort to obtain better matches to some of the photoemission data than from the buckled surface model.⁹ However, the " π -bonded" models, although showing a better fit to some of the photoemission data, have provided a worse fit to LEED data than the buckled model,¹⁰ and unlike the latter do not appear to account for the ready conversion of the (2×1) to a (1×1) structure on slight adsorption, nor the phenomenon of surface mating.¹¹

An important aspect is the energy of a structure which is usually expected to show a minimum. The π -bonded Si models have been shown to have lower energy than a (1×1) relaxed surface, and the latest calculations^{5,6} show that buckling tends to increase the energy of Si relative to a relaxed (1×1) surface. This feature was argued to militate against buckled surfaces in the cases of Ge and Si.^{4,6}

In this article we draw attention to two important factors that should be taken into account in considering cleaved surfaces. Firstly, the new Ge data may well indicate that (2×1) surfaces, in fact, consist of (2×1) and (1×1) patches so that previous efforts to match both photoemission and LEED data on the basis of theories of single-phase surfaces may have been misleading. Secondly, real surfaces differ from theoretical surfaces in possessing large numbers of defects and strains which can cause structures and phases to be pinned despite possessing a theoretically higher energy.

We first consider the new liquid-He cleaved-Ge

data. As first shown by Aristov and co-workers,⁷ and confirmed in a somewhat different experimental arrangement by the present authors⁸ (Fig. 1), the usual half-order LEED spots are missing when Ge is cleaved in ultrahigh vacuum at near 4 K. They were, however, present in Si cleaved under the same liquid-He cooled arrangement as Ge, and on Ge as well as Si at higher-temperature (≥ 40 -K) cleavages.

These results can be explained on the basis of the stability of the two phases as illustrated schematically in Fig. 2. We consider two possibilities, that the (2×1) phase energy is lower than that of the (1×1) as in Fig. 2(a), or that it is higher as in Fig. 2(b). In either case it is necessary to assume an activation energy hump between the structures. Such a hump is a feature of cleaved Ge and Si surfaces. For example, the (2×1) Ge surface makes an irreversible transi-

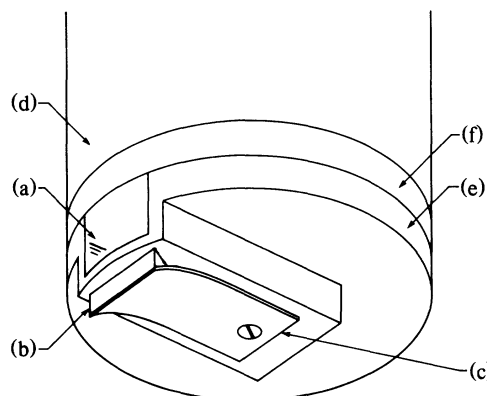


FIG. 1. Diagram of crystal holder used for low-temperature cleavage. (a) Cloven face of crystal; (b) cleaver wedge; (c) spring plate holding wedge; (d) tube holding cryogenic liquid; (e) copper crystal holder; (f) copper termination of liquid container.

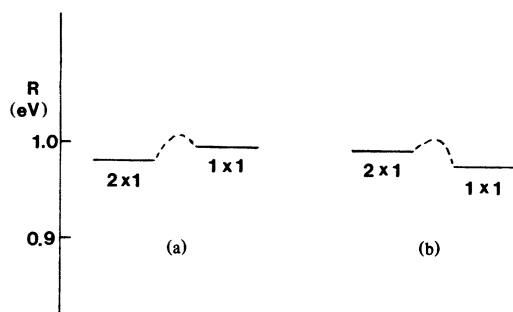


FIG. 2. Schematic diagram of energy per surface atom R vs structure. The relative heights of activation energies are schematic only. The energies of the annealed structures [Ge (2×8); Si (7×7)] are not known but are presumably lower than for the other structures since they are the equilibrium phases.

tion to a (2×8) structure on heating (~ 15 min) to about 130°C , and the (2×1) Si converts to (7×7) on heating in the region $210\text{--}425^\circ\text{C}$. These transition temperatures are known to be affected by the presence of obvious defects such as steps, and even the degree of vacuum.¹²

The metastable, activation energy pinned, nature of cleaved surfaces arises from the manner of their formation, namely, by an advancing crack around whose tip tensile forces cause rupture of bonds. The preferred direction of the (2×1) surface on the three-fold symmetric substrate has been shown to be determined by the direction of progression of the crack.¹³

The observation that only a (1×1) phase was detected on Ge if cleaved at a sufficiently low temperature is explicable only by Fig. 2(b). The energy associated with the cleavage is presumably insufficient to surmount the barrier to the (2×1) structure. Once formed, the structure does not convert to (2×1) due to the activation barrier. If results of Si energy calculations apply to Ge, the buckled model for (2×1), which has a higher energy than (1×1), is consistent with Fig. 2(b). In the case of Si, a (2×1) structure was observed even at liquid-He cleavage. Therefore either Fig. 2(a) applies, namely, the (2×1) structure has a lower energy than the (1×1), or Fig. 2(b) applies but the cleavage energy is sufficient to surmount the phase barrier. The surface then consists of both (1×1) and (2×1) phases.

If one assumes that the general nature of results for Si regarding the order of surface structure energies also to Ge, the above results suggest some inferences. The π -bonded model, which has a lower energy than a (1×1) surface,⁶ is consistent with the Si observations but not with the Ge data. To make it applicable one needs to hypothesize some way to prevent the (2×1) structure forming below about 40 K in the case of Ge but not Si. On the oth-

er hand, the buckled model explains the Ge data, and also the Si data if the latter cleaved surface has both (2×1) and (1×1) phases.

The possibility of the existence of metastable surface structures that are not of minimum energy, such as the (2×1) buckled surface H model, requires specification of surface features that could pin them. Obvious features are cleavage steps which have been mentioned previously, and which could be associated with strained regions. However, there are numerous other known defects which cause various degrees of energy change, but whose role in affecting surface phases has not been highlighted. We draw attention to several of these.

Even in highly pure samples there are substantial concentrations of interstitial H, C, and O atoms. Assuming a uniform distribution of as low as 10^{16} cm^{-3} , each impurity atom is spaced about 200 bond lengths from another with concomitant lattice distortions of several bond lengths around each. A calculation for the Si vacancy shows that atoms in the fifth shell surrounding the vacancy still have displacement amplitudes of up to 20% of those in the first surrounding shell (taken as 0.3 \AA).¹⁴ This involves about 30 atoms in a surface plane around each vacancy. In addition, there are various minor strains with other point and area defect origins. For example, on cleaved GaAs showing sharp LEED intensities with very little background, careful analysis of the LEED beams suggested a mosaic spread of out-of-plane misorientation of up to 0.24° and domain sizes down to 400 \AA .¹⁵ Other aspects of surface domains with respect to Fresnel zone and LEED beam coherence¹⁶ have been discussed in detail, and it is concluded that surface coherence is disturbed by various inhomogeneities, not specifically identified, every few hundred angstroms. These disturbances have not been considered in calculations of ideal surface energies, but clearly of sufficient density to affect surface structures. It now appears that such considerations need to be incorporated in drawing conclusions about real surfaces.

The precise fashion in which a surface structure may be pinned by the presence of irregularities such as the above is a difficult theoretical problem. Microscopic model Hamiltonians for systems which may undergo a structural phase transition are nonlinear. Calculations for specific defect assemblies are difficult. However, we believe such theoretical approaches need to be developed for surfaces.

The possibility that (2×1) surfaces actually consist of (2×1) plus (1×1) patches also needs to be tested experimentally. The mere presence of half-order LEED beams is insufficient *per se* to provide evidence. Although a LEED analysis was carried out for a single-phase H model surface,¹⁷ the fit obtained, although fair, was not sufficiently good to verify that structure as a single phase. From the considerations

in this paper, it appears that cleavage at very low and at room temperatures might give different relative (1×1) and (2×1) phase proportions, resulting in different ratios of fractional to integral order beams. This would cause surface inhomogeneities in LEED measurements, and indeed such have been noted in

the past,¹⁸ which were not correlated with steps. A full experimental test of the hypothesis is not easy because of the sensitivity of LEED beams to cleavage perfection. However, it seems desirable to attempt this in order to clarify the structures on which proper analysis of data can be based.

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