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Observations of "Clean" Surfaces of Si, Ge, and GaAs by Low-Energy Electron Diffraction*

Abstract: The {100}, {110} and {111} surfaces of silicon, germanium and gallium arsenide, cleaned in ultra-high vacuum by heat-treatments alone or by ion-bombardments followed by anneals, were studied with the display-type low-energy electron diffraction technique. Most surface structures reported in the literature by others could be reproduced, namely, Si(111)7, Ge(111)8, GaAs(111)2, and GaAs(100)1. Some, however, could not, namely, Si(111)5 and Ge(111)12. Two unreported structures were found to exist, even simultaneously, on the GaAs{100} surface and six different structures were detected on Si{110} surfaces after annealing treatments at different temperatures. The significance of a "clean" state of semiconductor surfaces, as identified by the observation of low-energy electron diffraction patterns, is discussed.

1. Introduction

Low-energy electron diffraction (LEED) gives direct information about the structure of a surface of a solid and is thus a most powerful means for revealing the effect on surface structure of a variety of parameters, including temperature, heat treatment, and the nature and density of surrounding gases. Owing to the very slight penetrating power of the low-energy electrons employed, the information concerns only a very few of the uppermost atomic layers of the solid. If they are non-crystalline, such as glassy oxides, the information is rather scarce, as the scattered radiation is diffused over a large area with no immediately recognizable pattern. If the surface layer is crystalline, then a characteristic pattern is observable, and the better the order within the surface layer, the better will be the sharpness of the pattern. Hence, surfaces which are partially or completely covered with an amorphous layer of adsorbed material will yield only a poor LEED pattern or no pattern at all.

A perfectly clean crystalline surface, on the other hand, will always yield a very well-defined LEED pattern, yet the converse is not necessarily true, and observation of a sharply defined pattern is not necessarily a proof that the surface producing it is perfectly clean, i.e., free of all impurities. As has been stated before,[1a] achievement of the atomically clean state is a three-dimensional problem, and it is in fact quite unlikely that the presence of a few percent of impurities on the surface can be avoided with techniques employed at present. These impurities may originate in the bulk and diffuse onto the surface during heat treatments used in the cleaning process, or may originate in the experimental surroundings (walls of the vacuum system, residual gases, etc.), reacting with the surface at high temperatures.

The first extensive studies of clean surfaces of semiconductors were carried out by Farnsworth and co-workers[1b] using a Faraday-cage electron-collector LEED system. More recently, a display-type LEED apparatus was developed by Germer and co-workers[2,3] at the Bell Telephone Laboratories. This stimulated a considerable amount of work, done mainly by Lander and Morrison[4-7] and by MacRae[8,9], aimed at achieving and demonstrating LEED patterns of clean surfaces of semiconductors. It was decided that whenever one and the same pattern was observed after a variety of treatments of the surface (heating, ion bombardments and anneals, chemical reactions with gases, etc.), such a pattern would be called that of an atomically "clean" surface. The essential meaning of this

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statement is that, during the treatments, the nature and the concentration of the surface impurities remain unchanged or, alternatively, that any change in either does not affect substantially the LEED pattern. Nonetheless there are cases, in which different treatments of a surface (mostly temperature anneals) give rise to different patterns. Examples are given in the literature for the {111} surfaces of silicon and germanium.[4,5] If a given diffraction pattern can be linked reproducibly to a given temperature range, then obviously the phenomenon could be interpreted as being due to the existence of different crystalline surface phases which are stable in different temperature ranges, just as in many solids there are different bulk phases that are stable at different temperatures. If confirmed, this would be interesting indeed and still more so if phase changes were to be found on the surface of solids that do not exhibit bulk phase transitions or exhibit them in different temperature ranges. We may anticipate later discussion herein by remarking that the present work has yielded no conclusive evidence that such a situation exists for any of the three materials studied. As will be discussed later, one result of the present study was that in some cases several different structures of the same surface were indeed observed after different heat treatments. There was, however, no unique and reproducible relationship between a given pattern and the heat treatment producing it. These surface "phase transitions" are thus different from those commonly encountered in the bulk of pure solids; it appears probable that they are caused by substitutional impurities within the surface layer.

The present paper is concerned with a study of clean semiconductor surfaces using a Varian LEED system. The surfaces observed were the {111}, {100} and {110} surfaces of Si, Ge and GaAs. Although many of these surfaces have been studied with display-type LEED systems before,[4–9] that part of the paper that deals with them should be useful for two reasons. One is that in a few cases discrepancies were found to exist between the published data and the author's observations. The other is that, where agreement was found, the results were achieved with cleaning treatments different from those reported in the literature. The remainder of the paper is concerned with surfaces that have not been studied with display-type LEED systems before and whose structure appears interesting.

2. Nomenclature

In our descriptions of surface structures we will adhere to the conventions of nomenclature described by Wood,[10] calling $\mathbf{a}_s$ and $\mathbf{b}_s$ the unit-mesh vectors of the surface structure, and $\mathbf{a}$ and $\mathbf{b}$ the corresponding unit-mesh vectors of the underlying substrate structure. If, on the {hkl} surface of material M, the relations are: $\mathbf{a}_s = m \times \mathbf{a}$ and $\mathbf{b}_s = n \times \mathbf{b}$, ($m$ and n being rational numbers), the surface is said to be reconstructed* and then the shorthand notation for this surface will be: M(hkl) $m \times n$ or, if $m = n$, M(hkl) m.

3. Materials and procedures

The samples used in the present study were cut out of larger crystals with the following electrical characteristics: Si, $3–5 \times 10^3$ ohm cm, p-type; Ge, 30–40 ohm cm, n-type; GaAs, 2.3×10^{-3} ohm cm, n-type. The Si samples were vapor-polished with the HBr technique[11] and, occasionally, chemically polished in a rotating Teflon beaker with a mixture consisting of 1 part by volume of 48–49% conc. HF, 2 parts glacial acetic acid, and 3 parts of 70% conc. HNO_3. The Ge samples were solution polished with the NaOCl process[12] and, occasionally, vapor-polished with the HI technique.[13] The GaAs samples were solution-polished with the NaOCl process.[12] Samples that had been stored for more than one day after the polishing operation were always rejuvenated[14] immediately before introduction into the LEED system: Si and Ge with HF, and then quenching in ethyl alcohol; GaAs with concentrated NaOH, then HCl and, finally, quenching in ethyl alcohol.

The procedures followed for achievement of the clean state were heat treatments[14] and argon-ion bombardments followed by anneals. The procedure followed for a given surface is reported below in detail when this is deemed necessary. The heat treatments were started after achievement of the base pressure in the LEED system (5×10^{-10} Torr); after the initial outburst of gas from the heated sample the pressure in the system never rose above 1×10^{-8} Torr and was mostly in the range between 5×10^{-10} and 5×10^{-9} Torr with the sample at about 1000°C or above.

4. The {111} surfaces

• *Silicon* {111}

Schlier and Farnsworth[15] were the first to report that the clean {111} surface of silicon is reconstructed with a multiplicity of 7 and that a different phase, with much larger multiplicity, could be obtained after a particular treatment. Lander and Morrison later confirmed the existence of a Si (111) 7 structure and reported also having observed a Si (111) 5 structure by cooling slowly through the range between 750° and 600°C.[4] We have been able to observe the Si (111) 7 structure with all samples investigated. This is in fact one of the easiest LEED patterns to

* Here the term *reconstructed* applies to a clean surface with reference to a plane parallel to it within the bulk. We note that elsewhere it has been used, actually more extensively, to apply to rearrangements of atoms of metal surfaces under the influence of a large number of foreign atoms with which the metal atoms make a composite surface mesh. In the latter case *reconstruction* means that foreign atoms, when adsorbed upon the surface, cause surface atom rearrangement to incorporate the new atoms in a complex mesh.

obtain in excellent quality with relatively short heat treatments,[14] Fig. 1a.* We have been unable, however, to observe the Si (111) 5 structure, either after several long high- and low-temperature anneals or after cooling cycles with rates as slow as 65 degrees/hour. We conclude either that the surfaces observed by Lander and Morrison contained impurities favoring the formation of the Si (111) 5 structure in the cited temperature range, or that our samples contained impurities that inhibited it. The evidence so far is therefore very strong that the Si (111) 7 structure is that of the clean surface. It should be recalled that clean {111} surfaces of silicon, obtained by cleaving in ultra-high vacuum, have actually a different structure.[6] The latter, however, is only metastable and converts irreversibly to the Si (111) 7 structure upon heating.

• *Germanium* {111}

While Farnsworth and coworkers[15,16] have reported observation of half-integral order beams and a few weaker unidentified beams, Lander and Morrison[5,6] have reported observation of Ge (111) 8 structure, which, with heat treatment, exhibited a first-order transition to a more complicated structure, possibly Ge (111) 12. We have found no evidence of the latter structure or transition and, in fact, no evidence for any structure other than Ge (111) 8, which can be obtained without use of ion bombardment,[14] Fig. 1b. Our observations confirm, then, that Ge (111) 8 is the structure of the "clean" surface. Cleaved surfaces, just as in the case of silicon, have a different, metastable structure.[6] Since few satisfactory photographs of the Ge (111) 8 diffraction patterns are available in the literature, we reproduce in Fig. 2 four patterns obtained at four different electron voltages.

• *Gallium arsenide* {111}

Both the Ga and the As faces of the {111} surface of GaAs have been studied by MacRae,[9] who used ion bombardment and anneals to observe doubling of the surface unit mesh on the Ga face and disorder on the As face. We have looked at the Ga face only and were able to confirm MacRae's result. It may be of interest to point out that this surface can be cleaned without use of ion bombardment: we have observed excellent patterns of the GaAs (111) 2 structure, Fig. 1c, simply after prolonged heating (up to 7 hours) in vacuo at about 600°C of samples that had been subjected to the preliminary treatments described in Section 2. This result is in accordance with Thurmond's recent statement[17] that GaAs vaporizes congruently at temperatures lower than about 660 ± 100°C. Other patterns of the GaAs (111) 2 structure obtained with heat treatment alone are presented in Fig. 3.

* This figure and subsequent ones appear in the grouping on pages 381-386.

5. The {100} surfaces

• *Silicon* {100}

Schlier and Farnsworth[15] have reported observation of two different structures on the Si {100} surface: one is characterized by half-integral-order beams in the (110) azimuth, thus indicating a doubly-spaced surface net (Si (100) 2); the other consists of an 8% expansion of the Si (100) 2 structure. Lander and Morrison,[4,5] on the other hand, have observed a four-fold superlattice, i.e., a Si (100) 4 structure only. We have observed the existence of $\frac{1}{2}$-order spots, justifying the Si (100) 2 structure, but have not been able to observe $\frac{1}{4}$-order spots. The patterns appear identical to those of the Ge (100) surface depicted in Fig. 4. Hence, the present evidence speaks in favor of a Si (100) 2, rather than a Si (100) 4, structure of the clean surface. It must be noted, however, that our crystals were cleaned by heat treatments only, whereas Lander and Morrison used ion bombardment and anneals, which, on the (100) surface, result in somewhat clearer diffraction pictures.

• *Germanium* {100}

The {100} surface of germanium appears to have a structure, as in Fig. 4, which is identical to that of the corresponding silicon surface[5]; hence, the comments and reservations expressed in the section above apply as well to the Ge (100) 2 (or Ge (100) 4).

One reason why heat treatments alone are not as efficient in cleaning this surface as in cleaning others is that prolonged heating at high temperatures leads to pitting and consequent exposure of new surfaces. The new surfaces exposed are (111) facets, as can be demonstrated directly with LEED, Fig. 5. The diffraction pattern exhibits spots that originate from the original {100} surface directly beside spots that originate from the newly developed {111} facets. The former can be distinguished from the latter by observing the way in which they move on the screen when the electron energy is varied. Very similar effects have been reported by other authors: by MacRae[18] for the growth of epitaxial nickel oxide pyramids on nickel surfaces; by Lander and Morrison[19] for the pitting of silicon surfaces caused by treatment with aluminum; by Taylor[20] for the pitting of tungsten {111} surfaces and by Anderson and Danforth[21] for the pitting of tungsten {100} surfaces heated in oxygen. The sequence of photographs (*b*), (*c*) and (*d*) in Fig. 5 shows how, with increasing electron energy, four spots originating from the {111} facets first converge toward the 20 spots of the {100} structure (Fig. 5b), then coincide with them (Fig. 5c), and finally diverge (Fig. 5d), always moving along antiparallel ⟨110⟩ directions. The phenomenon is explained best on the basis of the reciprocal lattice and Ewald sphere, as was done pictorially by Anderson and Danforth[21] for

tungsten surfaces. Figure 6 depicts a schematic cross section through the reciprocal nets of two surfaces inclined at an angle α to one another. Two positions of the Ewald sphere show how beams originating from different surfaces can coincide, and then move in different directions with varying electron energy. Direct experimental proof that the extra facets are {111} surfaces is provided by rotating the sample about 55° so as to have almost normal incidence on the {111} faces. Figure 7 shows that one observes, in this case, the hexagonal pattern with three-fold symmetry that is characteristic of {111} planes.

• *Gallium arsenide* {100}

Information about the {100} surface of compound semiconductors was provided by Haneman's study of InSb {100} surfaces, on which a doubly-spaced lattice was reported.[22] No observations of {100} surfaces of any other compound semiconductor by the display-type LEED technique have been available. We have looked at GaAs {100} surfaces cleaned by argon-ion bombardment followed by anneals and have found two different structures. One is characterized by the patterns depicted in Fig. 8 and drawn schematically in Fig. 9a.† It is obvious that the pattern has no four-fold symmetry. The rows of diffraction spots are parallel to a ⟨110⟩ direction, which we may call a'^*, rotated, of course, 45° away from the cube edge a^*; see Fig. 9a. Also parallel to a'^* are lines of diffused intensity which are indicative of a tendency toward six-fold multiplicity in the b'^* direction and disorder along the a'^* direction. If we follow the convention of referring the surface structure to that of the substrate then the relations are: $\mathbf{a}_s = 6\mathbf{a}$, $\mathbf{b}_s = 6\mathbf{b}$, and the shorthand notation is GaAs (100) 6 with disorder. But it may be more illustrative to describe the structure in terms of the rotated system a', b', namely, neglecting the disorder: $\mathbf{a}_s = 6\mathbf{a}' = 6(\mathbf{a} - \mathbf{b})$; $\mathbf{b}_s = \mathbf{b}' = \mathbf{a} + \mathbf{b}$, the shorthand notation becoming GaAs (100) $6 \times 1 - 45°$.

The second stable structure observed is illustrated by the patterns in Fig. 10. It displays well-resolved $\frac{1}{4}$-order spots along the b'^* direction with some diffuse scattering elongated in the b'^* direction and located midway between two successive rows of spots, as in Fig. 10a. With patient annealing, these diffused lines become better resolved and reveal the existence of 1/8-order features, Fig. 10b. The reciprocal net is represented schematically in Fig. 9b and is defined thus: $\mathbf{a}_s = 8\mathbf{a}$; $\mathbf{b}_s = 8\mathbf{b}$, the shorthand notation being GaAs (100) 8 with some disorder or, alternatively: $\mathbf{a}_s = 2\mathbf{a}' = 2(\mathbf{a} - \mathbf{b})$; $\mathbf{b}_s = 8\mathbf{b}' = 8(\mathbf{a} + \mathbf{b})$, the shorthand notation being GaAs (100) $2 \times 8 - 45°$ with some disorder.

This structure was obtained after repeated ion-bombardment and annealing treatments (at about 500°C). Thereafter, heat treatments at about 550°C changed the structure into the GaAs (100) 6, but further ion-bombardments followed by anneals at 500°C had no effect on the latter structure.‡ The GaAs (100) 8 structure, however, could be recovered by heating at yet higher temperatures (~600°C), although some features of the GaAs (100) 6 structure often remained, Figs. 10c and 10d. In fact, coexistence of the two structures was easily found on part of the surface, as shown by the photographs in Fig. 11, the rest of the surface exhibiting one or the other of the two basic structures.

A similar lack of systematic reproducibility was encountered on the Si {110} surface, as is discussed in Section 5, below. At this stage, the only valid remark open to us is that both structures were observed on one occasion or another, the samples being simply heat-treated in good vacuum and never intentionally exposed to contaminating atmospheres. More information is needed before it can be stated that one, or both, or neither of the observed structures is that of the clean GaAs {100} surface.

It should be pointed out, however, as an alternate to the above, that the existence of two different clean structures on GaAs {100} is not unreasonable on crystallographic grounds. A look at the X-ray structure of GaAs will reveal that the {100} planes, like the {111} planes, consist also of alternate layers of Ga and As. There is then a "Ga" {100} surface and an "As" {100} surface. These are not equivalent, not only for the obvious reason that the top layer is populated by different atoms in the two cases, but also for the reason that the second layer is bonded to the first in such a way as to make the two ⟨110⟩ directions that lie on the surface not equivalent. For example, on a "Ga" {100} surface the As atoms in the second layer are bonded to the surface Ga atoms along the ⟨110⟩ direction which we may call a'. On an "As" {100} surface, the second-layer Ga atoms are arranged along the other ⟨110⟩ direction, which we may call b'. Neither surface has four-fold symmetry, but only two-fold. These qualitative arguments do not explain, of course, the surface reconstruction, but they do make it appear reasonable that two different structures may exist on GaAs {100} surfaces, one with emphasis on the a', the other with emphasis on the b' direction. Whatever structure one obtains after the cleaning process would then be a matter of chance. In practice, owing to the inevitable presence of steps, one would rather expect to observe coexistence of the two structures (as in Fig. 11) more often than either of the two structures alone. This would explain, incidentally, why LEED patterns of Si and

† Labels with asterisks refer, as is customary, to crystallographic axes in reciprocal space.

‡ To avoid confusion it should be stated that *all* patterns reported in the present paper were observed after the samples were quenched to room temperature from whatever treatment is described.

Ge {100} surfaces seem to possess four-fold, rather than two-fold, symmetry. These elemental semiconductors have, in fact, two types of {100} surfaces as well, but since the atoms in the first and in the second layer are the same, the resulting structures should be related to one another by a simple rotation through 90° about the [001] direction. Each of these structures has only two-fold symmetry, but coexistence of the two in equal amounts would yield a pattern with four-fold symmetry.

6. The {110} surfaces

• *Silicon* {110}

No prior LEED studies of this surface have been reported to date but it provides another example of a surface exhibiting different structures after different heat treatments. It is an interesting surface *a priori* because if it were not reconstructed it would be expected to consist of flat-top corrugations along the ⟨110⟩ directions and would therefore have very many natural steps, which may favor the occurrence of multiple reflections. It is in fact possible that such a stepped surface might be responsible for the LEED pattern that we have invariably obtained initially, i.e., after the first cleaning heat-treatment in vacuo ($T \sim$ 900–1000°C). Figure 12 depicts four patterns of this structure, which appears to be too complicated for unambiguous indexing and which we will tentatively call the "initial" structure. It exhibits a few 1/5-order features and a number of spots whose motion on the screen, as a function of electron energy, is not quite normal but yet is not typical of extraneous facets.

Annealing at high temperatures (>1200°C) of the "initial" structure often produces a pattern characterized by 1/5-order spots along the cube edge and normal spacing along the face diagonal. Figure 13 gives photographs and Fig. 14a a schematic drawing of the observed pattern. It is obvious in this case that $\mathbf{a}_s = 5\mathbf{a}$ (where $\mathbf{a}$ is the cube edge: $|\mathbf{a}| = 5.43$ Å) and $\mathbf{b}_s = \mathbf{b}$ (where $\mathbf{b}$ is the face diagonal: $|\mathbf{b}| = 3.84$ Å) and, hence, the shorthand notation is Si (110) 5 × 1. More prolonged annealings at high temperature sometimes produce a pattern in which the fractional-order spots near the ½-order position appear to be noticeably closer to one another than allowed by a five-fold multiplicity, Fig. 15. Experimental precision is not sufficient to determine whether the super-net is seven- or nine-fold and the structure may be tentatively referred to as Si (110) 7 (9?) × 1.† On other occasions, the same fractional-order spots coalesce into a single one at the ½-order positions, giving rise to the patterns depicted in Fig. 16 and Fig. 14b, which clearly must be identified with a Si (110) 2 × 1 structure.

† It is possible, of course, for the super-net to be even twice as large, namely, with a multiplicity of 14 or 18 or, possibly, 16.

It is not impossible that, despite their repeatedly-tested stability in wide temperature ranges, the two latter structures could be merely steps toward the formation of another structure, depicted in Fig. 17, for which $\mathbf{a}_s = 4\mathbf{a}$ and $\mathbf{b}_s = 5\mathbf{b}$, or in shorthand notation: Si (110) 4 × 5. This structure appears almost always after repeated anneals of the 2 × 1 structure, although it was also observed directly after heat treatment of the 5 × 1 structure. In either case some disorder is apparent through the diffuse-scattering lines elongated in the a^* direction.

Finally, if the 5 × 1 structure is annealed at lower temperatures (700–800°C) one often observes a complicated pattern for which indexing was not attempted, Fig. 18. It may be a consequence of twinning of the 4 × 5 or the 5 × 1 modifications, or it may have the status of a very complicated, untwinned structure in its own right. We will refer to it as the Si (110) *X* structure.

It was impossible to establish a recipe for obtaining, reproducibly, any of the surface structures described above. Six samples were used and most of them exhibited all structures. Only some trends were detectable which provide a relation between the annealing temperatures after which a structure is observed and the prehistory of the surface. For example, the 5 × 1 structure is likely to appear at high temperatures ($T >$ 1200°C) after the "initial" or the *X* structure, and at intermediate temperatures (between 1000° and 1200°C) after the 4 × 5 structure. The latter structure, and the 2 × 1 structure, always appeared at high temperatures irrespective of the starting condition. The *X* structure, on the other hand, had the tendency to appear at low temperatures (between 700° and 800°C) following the 5 × 1 structure. No forthright statement can be made, at the present stage, as to which, if any, of the observed structures is that of the clean Si (110) surface.

• *Germanium* {110}

With the {110} surface of germanium cleaned by ion bombardment, Schlier and Farnsworth[15] observed half-integral order beams and also weaker beams, neither integral nor half-integral order. We found that, in contrast to the {111} and {100} surfaces, the {110} surfaces could not be cleaned satisfactorily by heat treatments alone, inasmuch as we consistently observed heavy background and poorly defined spots of the substrate lattice only. Argon-ion bombardment improved the background and contrast and a number of new spots appeared. Figure 19 depicts the patterns observed at four different electron energies. There is little doubt that this pattern is almost identical to the one that we have called Si (110) *X*, particularly when we compare Fig. 19b and Fig. 18a. No structure other than this Ge (110) *X* was detected on any sample.

• *Gallium arsenide* {110}

The {110} surface of GaAs, together with those of other III-V semiconductors, has been studied with LEED by MacRae and Gobeli.[8] There is little doubt that the surfaces investigated by these authors were as clean as is possible in the present state of the art, for they were obtained by cleavage in ultra-high vacuum. It was found that the unit mesh at this surface has the same dimensions as the substrate unit mesh, i.e., the surface structure may be referred to as GaAs (110) 1. We have obtained the same structure on surfaces that were prepared as described in Section 3 and then simply subjected to heat treatments, *in vacuo*, of 8–10 hours at about 600°C. Figure 20 shows that, although the quality of the pattern is not as good as that obtained by MacRae and Gobeli with freshly cleaved surfaces, it is nevertheless surprisingly well defined. This obviously means that "clean" {110} surfaces of GaAs can be attained, in good vacuum, by heating alone, which again accords with Thurmond's statement[17] that GaAs vaporizes congruently at temperatures lower than about 660 ± 100°C.

7. Discussion

Agreement or disagreement between the present results and those obtained by other workers has been pointed out above in appropriate subsections. Some of the discrepancies between the earlier results obtained by Farnsworth and coworkers with a Faraday-cage electron-collector system and more recent results obtained with display-type LEED instruments may be explained as follows.

First, there is a contradiction in the fact that early statements in the literature denied the possibility of obtaining clean surfaces of germanium by heating only[23] (although these statements were later modified[16]), whereas more recent results obtained with the more modern equipment show that this can indeed be done.[14]

This contradiction, however, may be only apparent. Although the pressures attained were about the same (10^{-9}–10^{-10} Torr), there is little doubt that the residual gases present in the earlier instruments were different from those present in modern, ion-pumped instruments. The residual atmosphere in the latter is known to consist mostly of H_2, which is favorable for reduction of surface oxides and, to a lesser extent, of Ar, N_2, CO, CH_4 and little He. Of these, only CO and CH_4 are likely to contaminate the surface with carbon atoms, while still helping to eliminate oxides. In the older instruments, the residual-gas spectrum was likely to comprise much higher relative concentrations of H_2O, CO_2, and CO. It is possible that such an atmosphere prevented cleaning by heat treatments alone. Furthermore, even with modern equipment, we have indeed found that the {110} surface of germanium does not produce a well-defined pattern when subjected to heat treatments only.

Using the residual-gas argument, one could also assert that parameters such as the nature and the concentration of the impurities left over on "clean" surfaces were different for the two types of instruments, and that therefore agreement should be expected only for those surface structures that are particularly insensitive to these parameters. These structures would be the Si (111) 7, and possibly the Si (100) 2 and the Ge (100) 2, with a further possibility being the Ga face of GaAs (111).

Another observation as to the significance of residual gases is that the "lifetime" of LEED patterns within the system was found to be very long. The quality of any pattern, as visually estimated, never changed when the samples were left idle in the system at base pressure for a few days. It was found on one occasion that a Ge (111) 8 pattern observed with a sample kept idle in the system for eighteen days was just as sharp and well-defined as that observed immediately after the cleaning treatments. Some possible conclusions are that the residual gases in the LEED system have negligible sticking coefficients for the surfaces investigated, or that these gases do not affect the observed surface structures at room temperature.

The agreement among observations made with different LEED systems of the display type may be considered moderate, inasmuch as four structures could be reproduced perfectly [(Si (111) 7, Ge (111) 8, GaAs (111) 2, GaAs (110) 1)] two could be reproduced with but minor doubts [(Si (100) 4 (or 2?) and Ge (100) 4 (or 2?))], and two structures could not be reproduced at all [(Si (111) 5 and Ge (111) 12)]. Surface structures agreeing with those of the existing literature are those with which observation of LEED patterns is easiest (with the exception of the Ge (111) 8 pattern). It is of interest, in this connection, to point out that excellent, well-resolved patterns of the Si (111) 7 and GaAs (110) 1 structures could be observed from the *edge* faces of the plate-like samples used for the study of the Si {110} and GaAs {100} surfaces, respectively, as shown in Fig. 21. These results are interesting for two reasons. The first is that, in spite of the fact that these edge faces (approximately 6 mm × 0.5 mm) were not intentionally subjected to any lapping, polishing or other preliminary treatments prior to the heat-cleaning treatments in vacuo (except for the Si samples that were vapor-polished), still they exhibit excellent patterns. The remaining reason is that the patterns depicted in Fig. 21 were observed at the same time that the front surfaces of the corresponding samples exhibited very different structures (discussed in Section 6 in connection with Si {110} and Section 5 in connection with GaAs {100}). This proves quite directly that if the multiplicity of structures observed on the Si {110} and the GaAs {100} surfaces is related to the presence of impurities, which is possible, then these same impurities have no effect on the Si (111) 7 and GaAs (110) 1 structures, as far as could be determined with LEED.

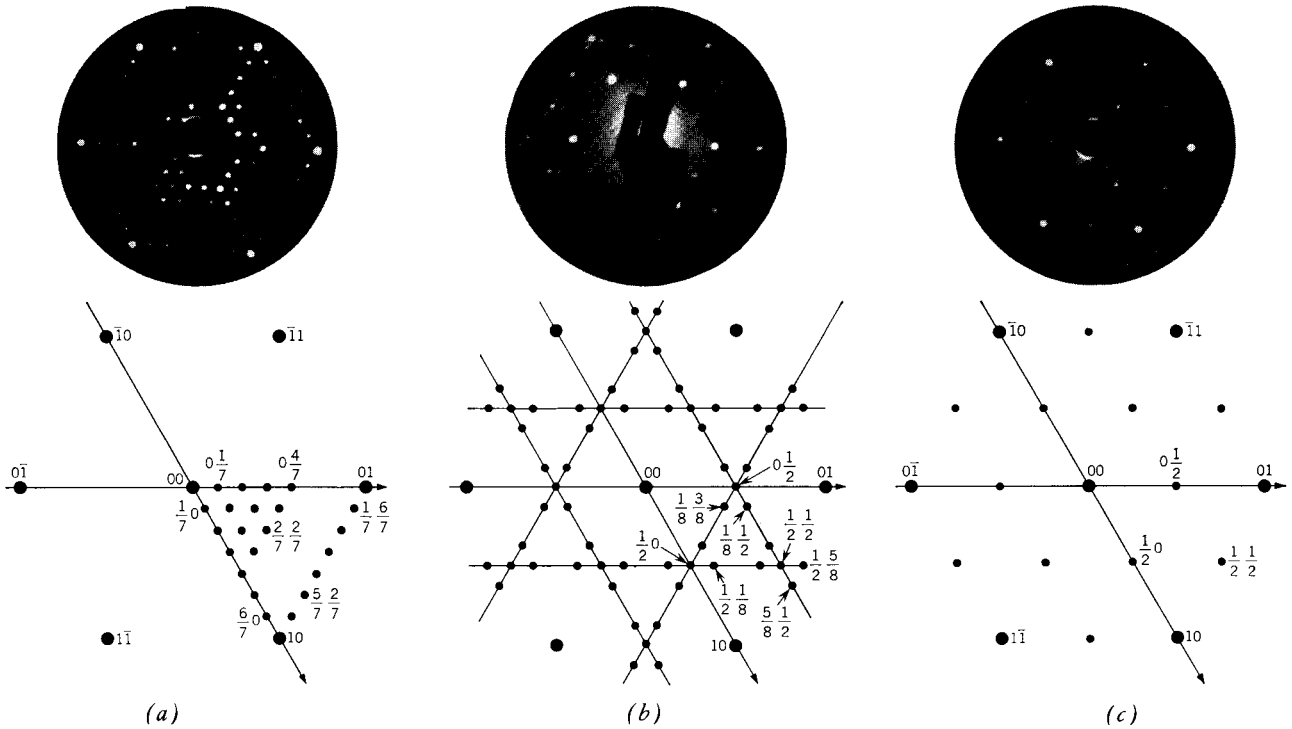


Figure 1 Representative LEED patterns of "clean" {111} surfaces of: **(a) silicon.** Above—pattern of Si(111)7 observed at 38 V; below—schematic drawing of the pattern. The large circles represent the "normal" spots, i.e., the spots due to the underlying substrate mesh; the small circles, drawn only in one sextant, represent the "fractional-order" spots due to the surface supermesh. A few of these spots have been labelled with corresponding fractional-order indices. **(b) germanium.** Above—pattern of Ge(111)8 observed at 56 V; below—schematic drawing of the pattern. The large circles represent the "normal," the small circles the "fractional-order" spots. **(c) gallium arsenide.** Above—pattern of GaAs(111)2(Ga side) observed at 48 V; below—schematic drawing of the pattern. Large circles represent the "normal," the small circles the "fractional-order" spots. All surfaces were cleaned by heat treatment only.

Figure 2 LEED patterns of the Ge(111)8 structure: (a) at 20 V, (b) at 33 V, (c) at 68 V, (d) at 95 V.

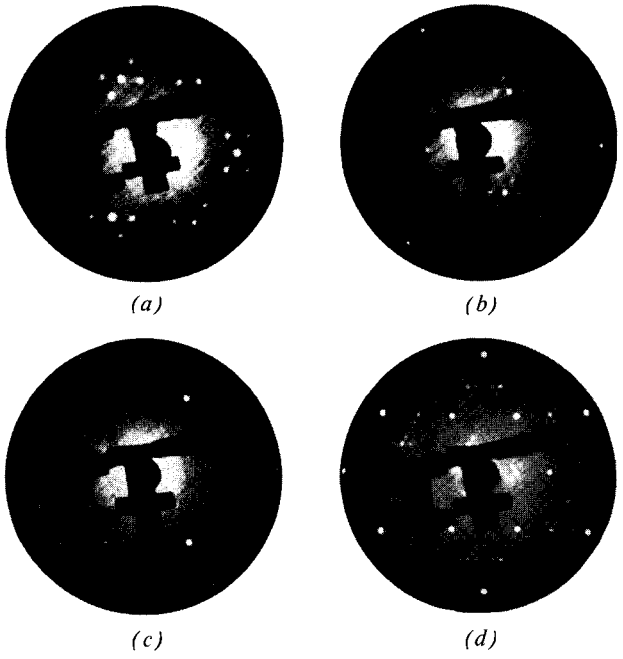
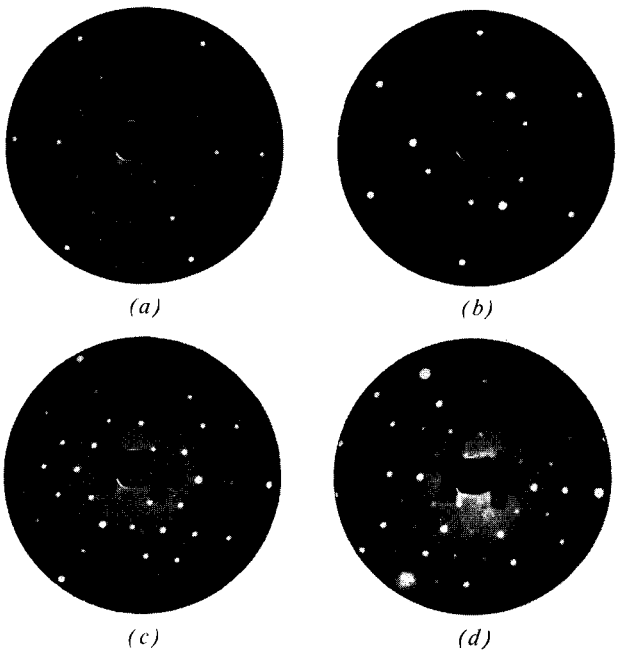


Figure 3 LEED patterns of the GaAs(111)2 (Ga side) structure (surface cleaned by heat treatment only): (a) at 66 V, (b) at 97 V, (c) at 106 V, (d) at 118 V.



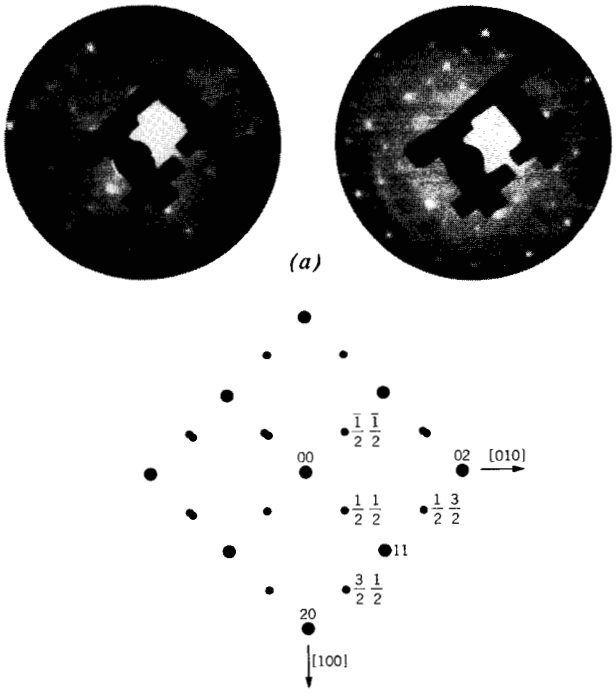


Figure 4 LEED patterns of the Ge(100)4(or 2?) structure (surface cleaned by heat treatment only): (a) at 154 V and 200 V, (b) schematic drawing with representative indexing.

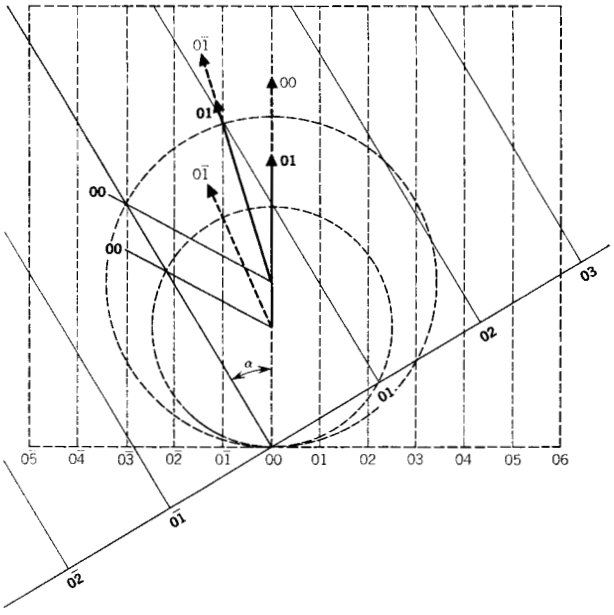


Figure 6 Schematic cross section through the reciprocal nets of two surfaces inclined at an angle α to one another. Normal incidence is assumed onto the horizontal surface and the two circles represent equatorial cross sections of two positions of the Ewald sphere. At the lower electron energy (smaller circle) the 01 beam from the inclined surface coincides with the 00 beam of the horizontal surface. With increasing electron energy, the 01 beam of the inclined surface moves of course toward the 00 beam (of the inclined surface) and on its way (larger circle) coincides with the $0\bar{1}$ beam of the horizontal surface.

Figure 5 Pattern of Ge(100)2 with features belonging to {111} facets. (a) The four spots below the center surround the 00 spot of the {100} surface and converge on it with increasing electron energy but belong to four types of {111} facets (120 V). In (b) (174 V), (c) (176 V) and (d) (181 V), the conversion of groups of four spots due to {111} facets toward each one of the ⟨20⟩ spots of the {100} surface is shown.

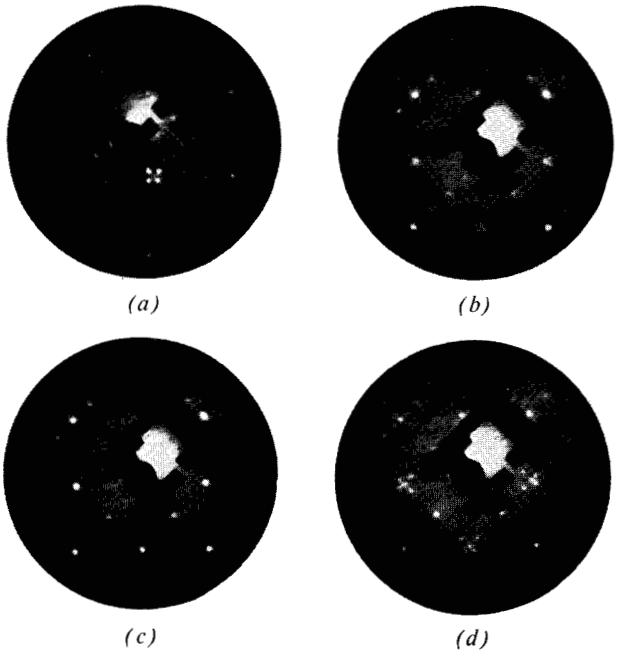
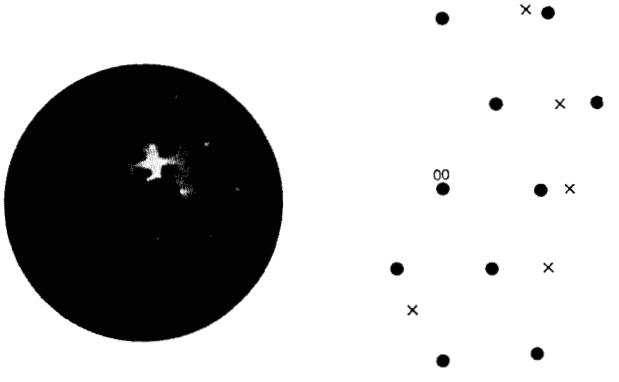


Figure 7 Oblique incidence (about 48°) of the electrons on a Ge {100} surface containing {111} pits. (a) Photograph of pattern exhibiting both {111} and {100} features. (b) Sketch of pattern: the circles identify the spots belonging to {111} facets and move toward the (here visible) 00 spot with increasing voltage. The crosses identify spots belonging to the (100) surface and move out of the field of view to the right, toward "their" 00 spot, with increasing electron voltage.



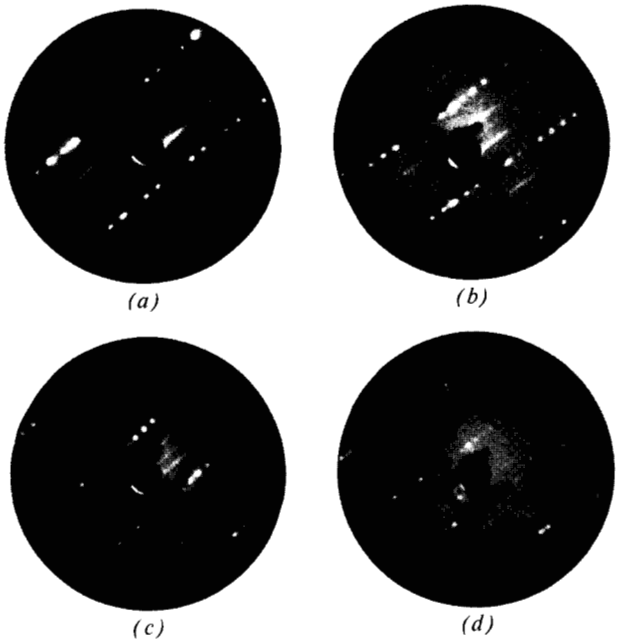


Figure 8 Representative patterns of the GaAs(100)6 structure with some disorder. (a) At 38 V, (b) at 49 V, (c) at 62 V, (d) at 92 V. The 00 spot is visible just slightly to the right of center.

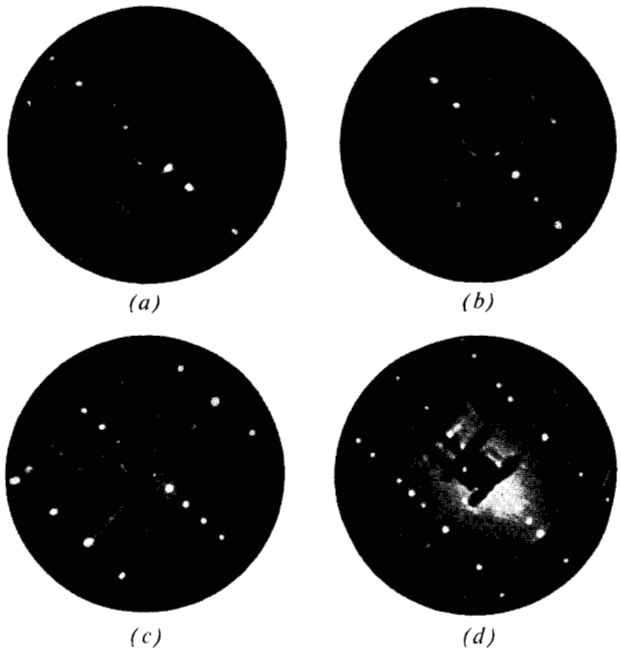
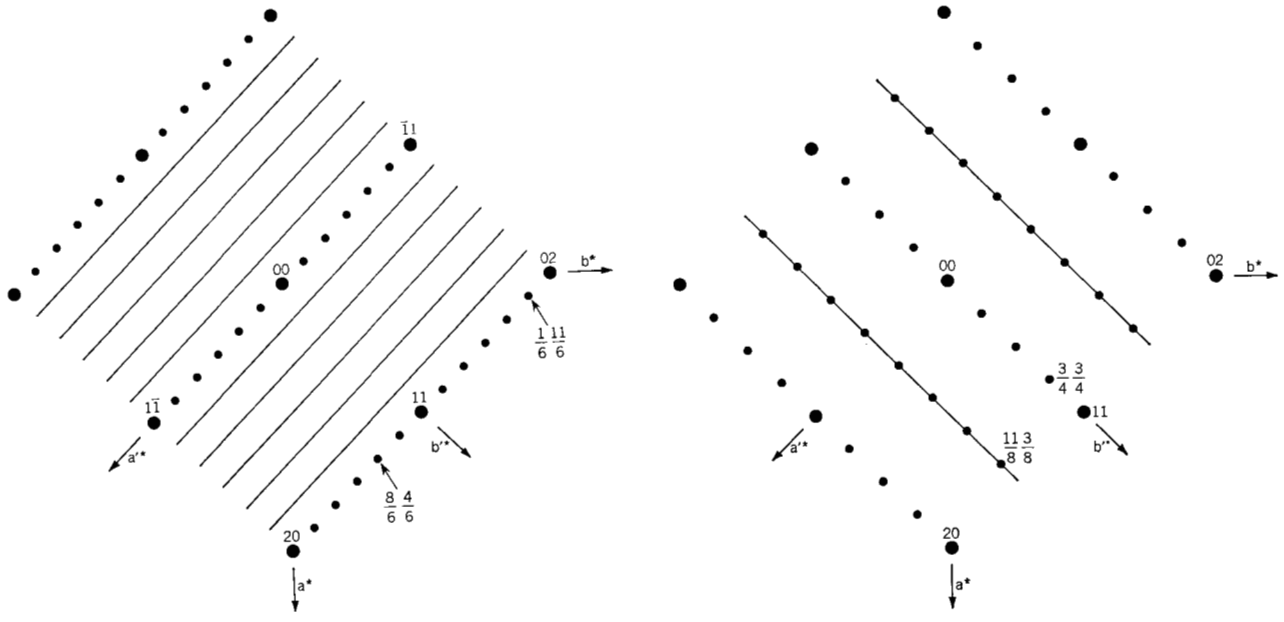


Figure 10 Patterns of the GaAs(100)8 structure. (a) 26 V, streaks of diffuse scattering visible. (b) 23 V, streaks partially resolved into ⅛-order spots. (c) 39 V, (d) 67 V. In (c) and (d) some features of the GaAs(100)6 structure are visible.

Figure 9 Schematic drawings with partial indexing of LEED patterns observed with {100} surfaces of GaAs. The large circles represent the "normal," the small circles the "fractional-order" spots, the solid lines represent streaks of diffuse scattering. Reciprocal-net axes are shown dotted. (a) GaAs(100)6, (b) GaAs(100)8.



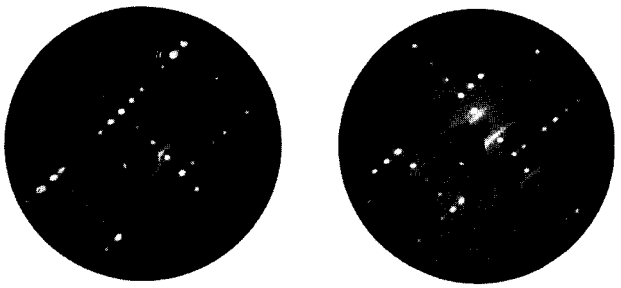


Figure 11 Patterns showing the coexistence (including the streaks) of the GaAs(100)6 and GaAs(100)8 structures.

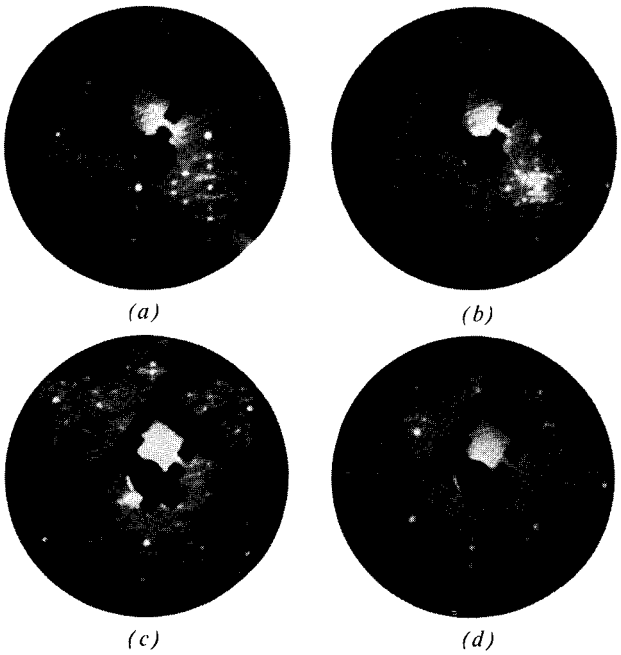


Figure 12 Patterns of the Si(110) "initial" structure. (a), 66 V, and (b), 76 V, show the surroundings of the 00 spot. (c), 40 V, and (d), 93 V, show the ⟨10⟩ and ⟨11⟩ spots and their surroundings.

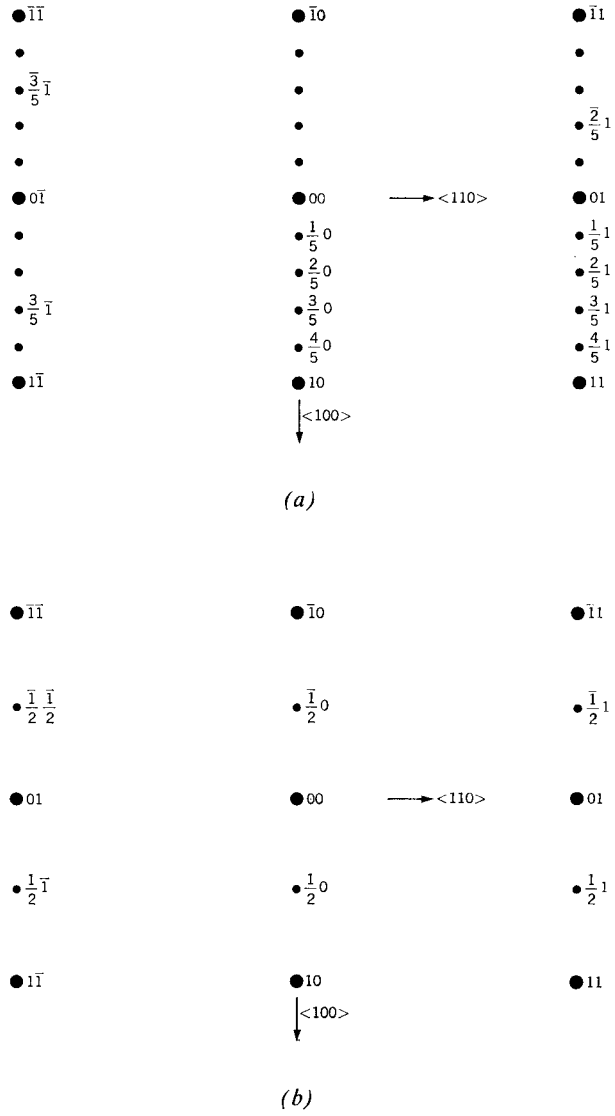
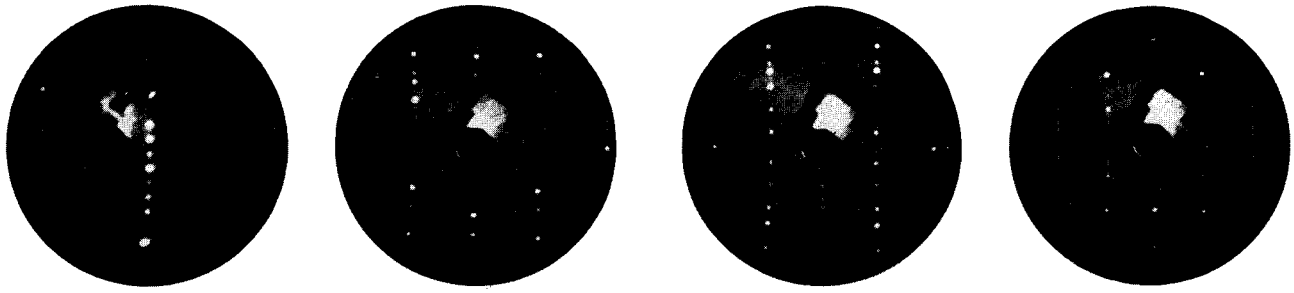


Figure 14 Schematic drawings of (a) the Si(110)5 × 1 and (b) the Si(110)2 × 1 structures. The large circles represent the "normal" spots (but intensity of 01 spot is mostly zero), the small circles identify "fractional-order" spots. The arrows indicate the directions of the (labelled) cube edge and the face diagonal *on* the {110} surface.

Figure 13 Patterns of the Si(110) 5 × 1 structure. (a) Surroundings of the 00 spot (slightly right of center), at 35 V, (b) 92 V, (c) 122 V, (d) 126 V.



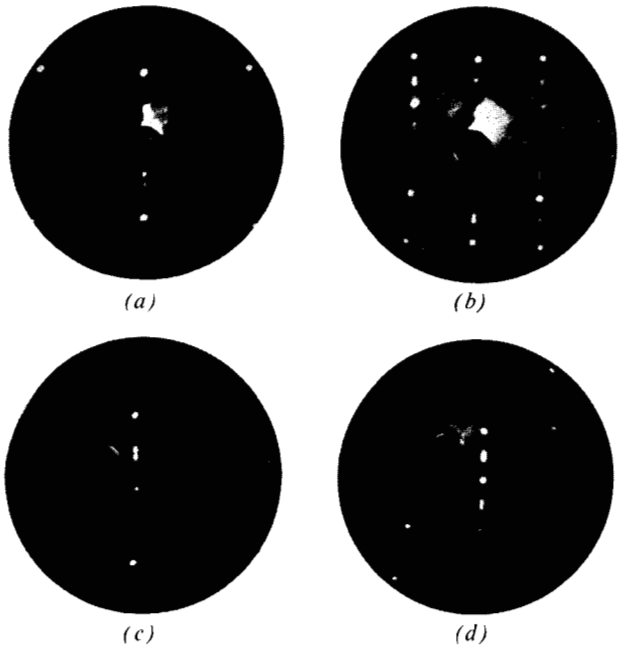


Figure 15 Patterns of the Si(110)7(9?)×1 structure, (a) 36 V, (b) 87 V. In (c), 34 V, and (d), 70 V, are shown surroundings of the 00 spot (slightly right of center).

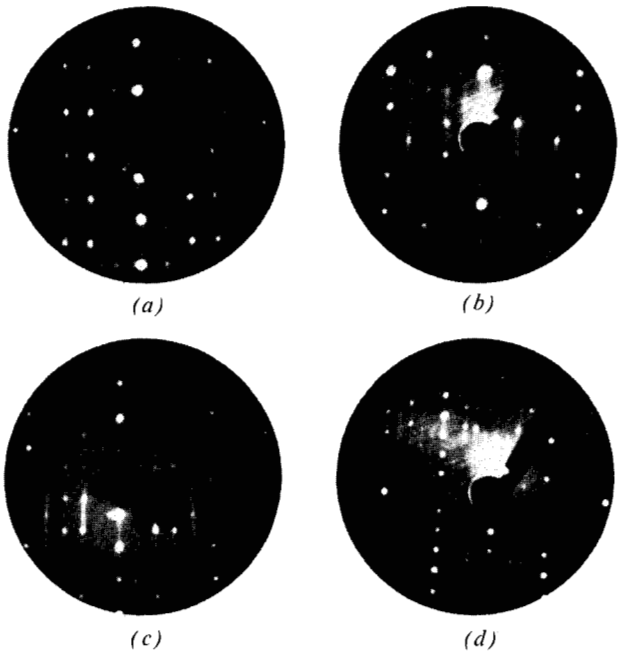


Figure 17 Patterns of the Si(110)4×5 structure with streaks. (a) 34 V, (b) 41 V, (c) 56 V, (d) 120 V.

Figure 16 Patterns of the Si(110)2×1 structure. (a) 36 V, (b) 36 V, 00 spot visible slightly right of center, (c) 90 V, (d) 137 V.

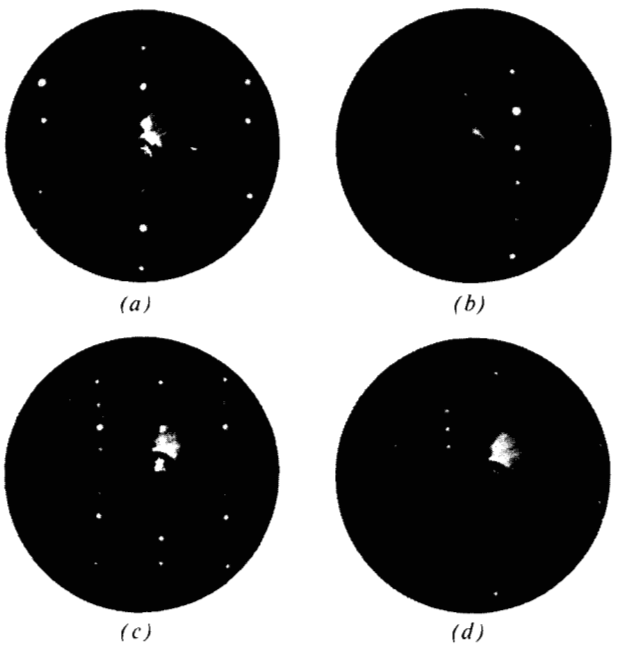
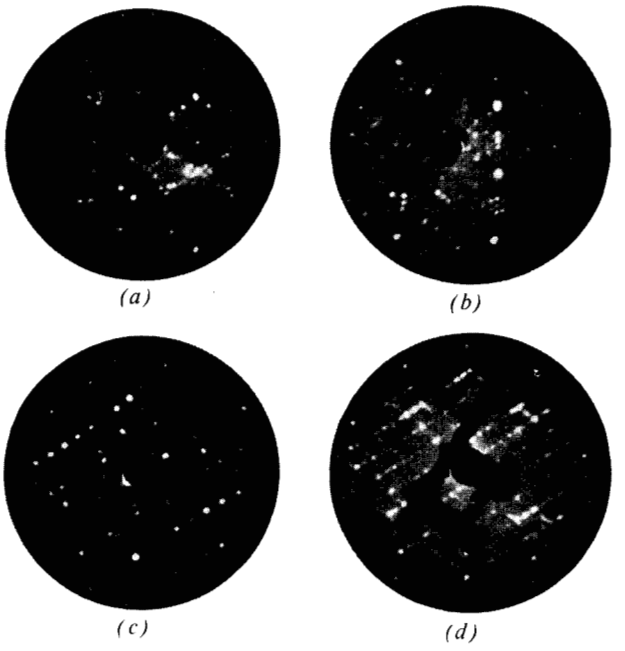


Figure 18 Patterns of the Si(110)X structure. (a), 30 V, and (b), 44 V, show surroundings of the 00 spot. In (c), 30 V, and (d), 89 V, the 00 spot is obstructed by the sample.



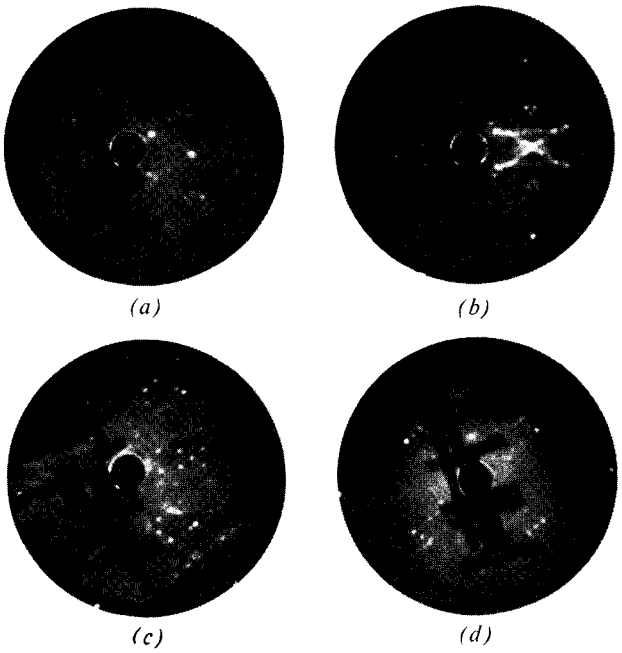


Figure 19 Patterns of the Ge(110)X structure. (a), 20 V, (b), 26 V, and (c), 42 V, show surroundings of the 00 spot. (c) 86 V. Compare with the Si(110)X patterns in Fig. 18.

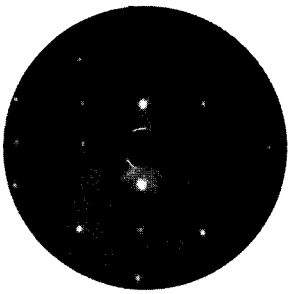
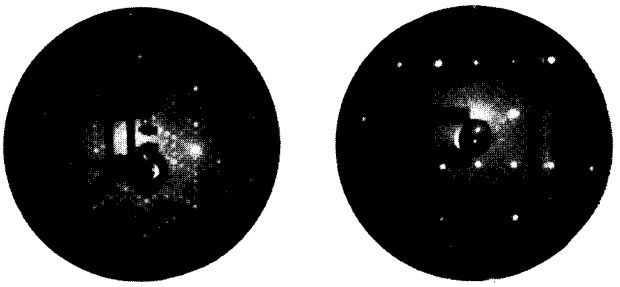


Figure 20 LEED pattern of the GaAs(110)1 structure at 97 V. Surface cleaned with heat treatments only.

Figure 21 (a) Pattern of the Si(111)7 structure from the *edge* face of a {110} sample, 84 V; (b) pattern of the GaAs(110)1 structure from the *edge* face of a {100} sample, 120 V. A few extraneous features due to unidentified facets are also visible.



In summary, then, the present study has revealed the following: 1) Some surfaces exhibit one and only one structure irrespective of the heat treatments to which they were subjected (specifically, Si (111) 7, Ge (111) 8, GaAs (111) 2, and GaAs (100) 1). 2) Other surfaces exhibit different LEED patterns after different heat treatments, but the relationship between any given pattern and the treatment producing it is not unique and is not well reproducible. Thus, pattern A may be observed on a given surface after long anneals at intermediate temperatures; pattern B may suddenly appear after an anneal of the same surface at higher temperatures. Subsequently, pattern A may or may not be recovered by an anneal duplicating the previous intermediate temperatures; if it is not recovered it may reappear after further annealing at high temperatures. Furthermore, whatever sequence is observed for one sample is not always reproducible with another of the same origin, even though both patterns A and B will be observed after different heat treatments. The most striking examples of this behavior are provided by the Si {110} and possibly by the GaAs {100} surfaces, as discussed earlier. It is obvious that in such cases one cannot decide, with the evidence at hand, which, if any, of the observed patterns is that of the clean surface. Instead, it appears reasonable to temporarily consider all such observed patterns as being intrinsic patterns (i.e. belonging to the clean surface), with the understanding that the intrinsic structures may still persist when the surface contains a few percent of substitutional impurities. It is hoped that further work will allow us to sort out the different structures and to relate them to known amounts of known impurities.

A concise review of the surface structures that were discussed in the present paper is given in Table 1 on the page following.

Table 1 Structures observed by LEED on Si, Ge, and GaAs surfaces. Those denoted by asterisks are believed to be intrinsic. The nomenclature is as described in Section 2.

{hkl}	Silicon	Germanium	Gallium Arsenide
{111}	Si (111) 7(*)	Ge (111) 8(*)	GaAs (111) 2(*) (Ga face)
{100}	Si (100) 4 (2?)(*)	Ge (100) 4 (2?)(*)	GaAs (100) 6 GaAs (100) 8
{110}	Si (110) "Initial" Si (110) 5 × 1 Si (110) 7 (9?) × 1 Si (110) 2 × 1 Si (110) 4 × 5 Si (110) *X* [a]	Ge (110) *X*	GaAs (110) 1(*)

[a] For Si {110} the first number refers to the multiplicity in the *a* direction (|a| = 5.43 Å, cube edge), the second to the multiplicity in the *b* direction (|b| = 3.84 Å, cube diagonal).

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