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A LEED INVESTIGATION OF (111) ORIENTED Si, Ge AND GaAs SURFACES FOLLOWING PULSED LASER IRRADIATION

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ABSTRACT

The low energy electron diffraction (LEED) patterns obtained from clean (111) oriented Si, Ge and GaAs single crystals subsequent to their irradiation with the output of a pulsed ruby laser in an ultra-high vacuum (UHV) environment suggest that metastable (1x1) surface structures are produced in the regrowth process. Conventional LEED analyses of the Si and Ge surfaces suggest that they terminate in registry with the bulk but that the two outermost interlayer spacings differ from those of the bulk. For the case of Si these changes are a contraction of 25.5 ± 2.5% and an expansion of 3.2 ± 1.5% between the first and second and second and third layers respectively.

INTRODUCTION

The results of recent experiments in which single crystal semiconductors are irradiated with the output of a laser in an ultra-high vacuum (UHV) environment demonstrate that the epitaxial regrowth process extends to the outermost surface layers and that clean, well-defined surface structures are produced [1-4]. In particular, the low energy electron diffraction (LEED) spot patterns obtained from surfaces of Si [4-6] and Ge [5](111) oriented single crystals indicate that metastable (1x1) structures can be produced with this process. These observations are to be contrasted with the reconstructed surface arrangements present after a standard in situ preparation technique (cleavage or sputtering followed by thermal annealing). Although extensively investigated [7], the successes achieved in the structural determinations of the reconstructed surfaces have been quite limited. Thus a previous investigation aimed at determining the geometric structure in the outermost layers of Si(111) attempted to avoid the difficulties arising from the reconstruction by using impurities (~5% of a monolayer of Te) to stabilize a (1x1) structure and a conventional LEED analysis was performed [8]. However, it is difficult to assess the effects due to the presence of impurities and thus compare results of this investigation with predictions of various model calculations.

Since the (1x1) surface structures obtained by laser irradiation are also observed to be atomically clean [1], we have initiated detailed LEED analyses of these surfaces. Results for the Si(111) surface suggest a bulklike layer termination exhibiting no ordered lateral reconstruction with first to second and second to third interlayer spacings contracted by 25.5 ± 2.5% and expanded by 3.2 ± 1.5% with respect to bulk values. Initial results for the Ge(111) surface show similar types of relaxations. While (1x1) spot patterns are obtained from both the (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces of GaAs, the loss of As from the selvedge region and the presence of nonstoichiometric Ga results in a high degree of disorder as shown by the intensity of diffuse background scattering.

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EXPERIMENTAL DETAILS

A conventionally equipped UHV surface analysis facility was used in these investigations and after bakeout at ~525 K the background pressure was typically < 2.5×10^{-8} Pa. For laser annealing, the light from a Q-switched pulsed ruby laser was coupled into the UHV system through a glass window and irradiated the samples in the vacuum environment. After insertion, the (111) oriented samples (Si, Ge and GaAs) were sputtered with Ar^+ ions and then irradiated using the single mode (TEM_{oo}) output of the ruby laser. The beam diameter was ~3.5 mm. Using a constant pulse duration time of 15×10^{-9} sec, appropriate energy densities for producing good quality LEED patterns were determined to be ~2.0 J/cm^2 for Si, ~1.7 J/cm^2 for Ge and ~0.3 J/cm^2 for GaAs. The technique of Auger electron spectroscopy (AES) was used to monitor the levels of impurities present in the surface regions of the samples [1]. The intensities of the diffracted electron beams were measured with a Faraday cup operated as a retarding field analyzer [9]. By equalizing the intensities and diffraction angles of intense diffraction peaks in symmetrically related beams, the surface normal was aligned to within ±0.1° of the incident beam direction. Symmetrically equivalent beams were averaged to produce a data base which contained the mean profiles.

CALCULATIONAL DETAILS

The experimental I-V profiles for the laser produced (111)-(1x1) surfaces of both Si and Ge have been compared with profiles obtained from fully dynamical LEED calculations. To date, the calculations for both surfaces have been based on assumed structural models which have allowed only for relaxations in the interlayer spacings of the bulk terminations. Since alternate interlayer spacings of the (111) truncation of the diamond lattice are quite small (e.g., 0.78 Å for Si), the effects of both intra- and interlayer multiple scattering were treated using the angular momentum (or L) representation. Tests were performed to assure that adequate numerical convergence was obtained in the calculations, and seven phase shifts and ten atomic layers were found to be sufficient.

In order to determine reasonable values for the nonstructural parameters (the scattering phase shifts, the surface region Debye temperature Θ_D, and the imaginary component V_{oi} of the optical potential) used in LEED calculations, extensive tests were performed to study the influences of these parameters on the calculated I-V profiles. The explicit calculations described below, for both Si and Ge, were performed using phase shifts obtained from truncated-free-atom (TFA) potentials which were constructed in a manner to contain full-Slater-exchange contributions. Values of Θ_D equal to 550 K and 400 K were used for Si and Ge, respectively. For Si, V_{oi} = 4.5 eV was employed, while a V_{oi} corresponding to a constant amplitude attentuation coefficient, λ_{ee}, of 6.5 Å was used for Ge. Also, the real component of the optical potential was varied individually for Si and Ge in order to obtain the best overall agreement with the respective data base.

RESULTS

A sharp (1x1) LEED spot pattern was obtained from the Si(111) surface after sputtering and irradiation with 5 laser pulses (~2.0 J/cm^2). Detailed measurements, using the Faraday cup, of the angular distribution of electrons scattered from this surface showed no evidence of superlattice reflections. Intensity vs. voltage (I-V) profiles were obtained for all of the {10}, {01}, {20}, and {02} beams and three of each of the {11} and {21} beams. The indexing (also for Ge and GaAs) is such that the (10) and (01) beams lie in the $[10\bar{1}]$ and $[\bar{1}2\bar{1}]$ azimuths respectively.

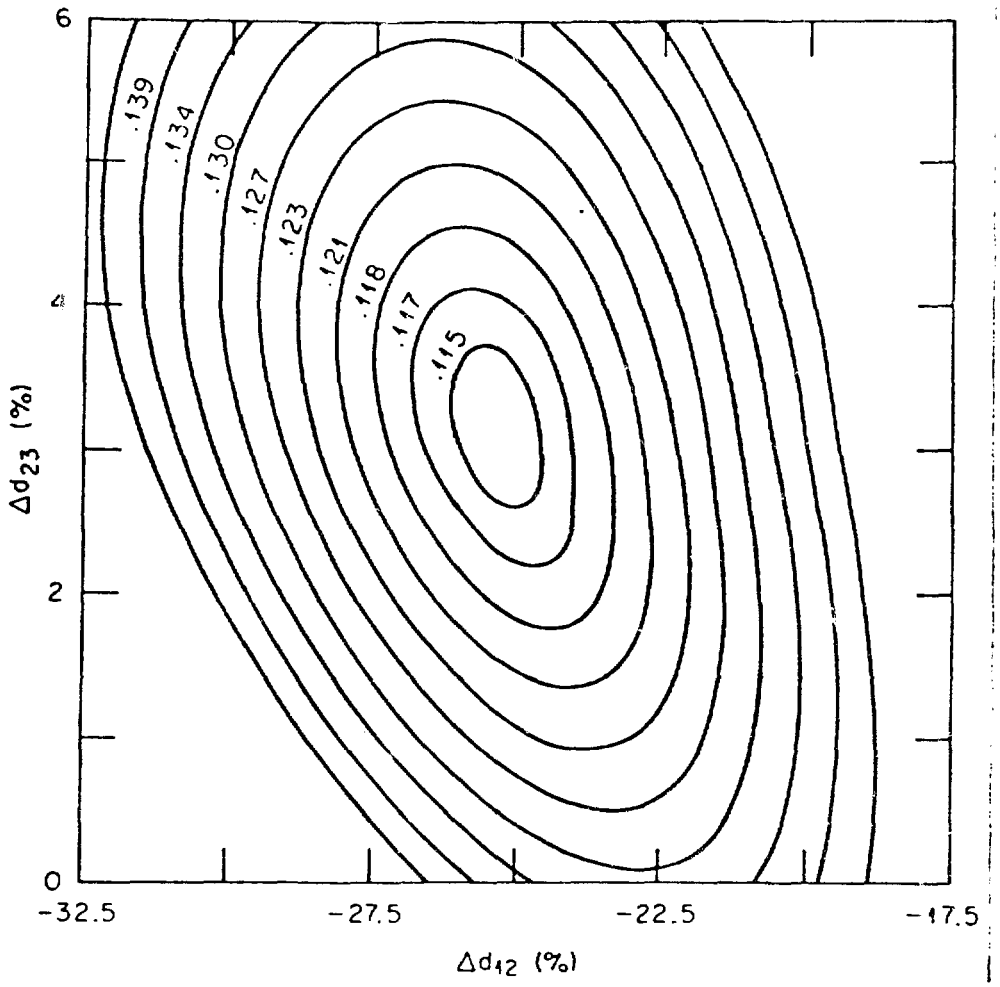

Fig. 1. Six beam optimal R-factor contour map to illustrate the effects of variation of the second interlayer spacing, d_{23}, with variation of the first interlayer spacing, d_{12}.

Calculations were performed in which both the first and second interlayer spacings, d_{12} (bulk value = 0.78 Å) and d_{23} (bulk value = 2.35 Å), were varied over reasonable ranges. Results of the calculations can be conveniently presented using the optimal R factor (as defined by Zanazzi and Jona [10]), for fixed d_{12} and d_{23}, which is the minimum value of R obtained for variation of the real component of the optical potential. The changes in the six beam optimal R factor with these variations are illustrated by the contour map shown in Fig. 1. Results shown in this figure suggest that d_{12} is contracted by 25.5 ± 2.5% and d_{23} is expanded by 3.2 ± 1.5%. Profiles calculated using these values are shown in Fig. 2 which also contains the corresponding experimental profiles and single beam R factors determined for each comparison. The six beam R factor corresponding to Fig. 2 and determined as the minimum of Fig. 1 is 0.115 [11]. This value indicates a very good agreement between calculated and experimental profiles in a conventional LEED analysis, and suggests that the proposed structural model is highly probable. The relaxed interlayer spacings along with the resulting bond lengths are summarized in Table I.

Although a sharp (1x1) LEED pattern was obtained from the Ge(111) surface after sputtering and irradiation with 5 laser pulses (~1.7 J/cm^2), weak half order reflections could be detected at several electron energies. However, the maximum intensity in these reflections was never more than a few percent of the

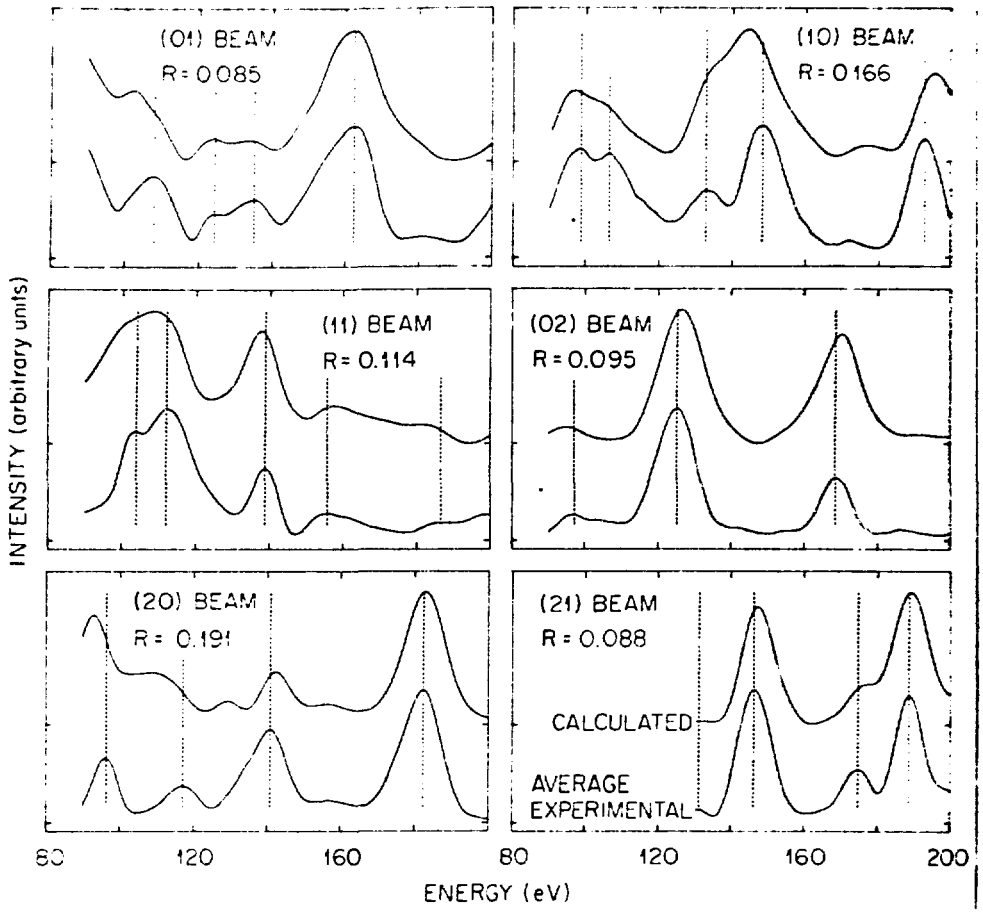

Fig. 2. A comparison of the averaged experimental I-V profiles with calculational results for $d_{12} = -25.5\% \pm 2.5\%$ and $d_{23} = 3.2\% \pm 1.5\%$.

intensity of the integral order beams. Thus, in view of the results obtained from the Si(111) surface, a similar LEED anlaysis was performed using only integral order beam intensity distributions. While not yet completed, the initial results of this analysis show similar types of relaxations with the best values being $d_{12} = -14.5\%$ and $d_{23} = 2.7\%$. The resulting changes in the interlayer spacings and bond lengths are listed in Table II.

Both the (111) and $(\bar{1}\bar{1}\bar{1})$ faces of GaAs have been examined with LEED subsequent to sputtering and irradiation with 5 laser pulses (~0.3 J/cm^2). Although it is well known that laser irradiation results in the loss of As from the selvedge region, (1x1) diffraction patterns were obtained from both polar faces subsequent to irradiation. However, the quality of the LEED spot pattern (integral order beam intensity vs. diffuse background intensity) obtained from

TABLE I
Lattice parameters for Si(111) in Angstroms

	Interlayer Spacings		Bond Length Between Layers	
	D_{12}	D_{23}	Si_1-Si_2	Si_2-Si_3
Si(111)-bulk truncation	0.784	2.352	2.352	2.352
Si(111)-present work	0.585	2.427	2.294	2.427

TABLE II
Lattice parameters for Ge(111) in Angstroms

	Interlayer Spacings		Bond Length Between Layers	
	D_{12}	D_{23}	Ge_1-Ge_2	Ge_2-Ge_3
Ge(111)-bulk truncation	0.817	2.450	2.450	2.450
Ge(111)-present work	0.699	2.516	2.413	2.516

the As terminated side was far superior to that obtained from the Ga terminated side. Results of AES not only indicate a loss of As from the selvedge region of both faces, but also the change in the Ga CCV transition lineshape suggests that Ga is present in nonstoichiometric sites on both faces [12].

DISCUSSION

From the information contained in a LEED spot pattern, it is possible to determine not only the symmetry and size of the surface unit cell but also the presence of ordered reconstruction. Since well ordered, reconstructed surfaces are produced on the (100) and (110) orientations of Si subsequent to laser irradiation [2,4], the absence of any superlattice reflections in the spot patterns obtained from the (111) surface is unique. While this observation indicates that long range ordered reconstruction does not exist in the (111) surface, additional information about the geometric arrangement, interlayer spacing and order within the surface region must be obtained by other types of measurements. The results obtained from the detailed LEED analysis presented here provide part of this information. Although only ordered structural models were tested in this analysis, the quality of agreement as determined by the value of the R factor, when compared with similar analyses for other surfaces, suggests a highly probable structural determination. Also, the R value obtained in this Si(111) analysis is the smallest ever obtained in a LEED analysis of a semiconductor surface. Furthermore, the size of contraction in the first interlayer spacing determined in this analysis is almost the same in magnitude as that predicted by total energy calculations [13]. While the first to second interlayer spacing determined for the Te stabilized (1x1 structure [8] is similar to that obtained in this investigation, it is not obvious that identical surface structures are present following the two different surface preparations.

The observation that heating to ~700 K subsequent to laser annealing converts the (1x1) to a (7x7) structure suggests that under the combined time and temperature conditions present during the laser annealing process the atoms in the outermost layers are not able to diffuse, after the regrowth of the molten region (~5000 Å), into the ordered geometric arrangements corresponding to a reconstructed surface [5]. However, it is conceivable that some type of defect remains in the surface layer after laser irradiation and thus effectively quenchs the reconstruction. Although impurities (Te) have been used as the stabilizing component [8], the laser irradiated surface is "atomically" clean [1] and thus this type of defect can be ruled out. The question of order and the extensive defects can be examined by comparing the intensity of diffuse scattering for both the (1x1) and (7x7) surface structures, and such work is in progress.

While the results of the LEED analysis of the Ge(111) surface are still preliminary, they suggest that the interlayer relaxations are similar to those determined for the Si(111). It should be noted that an expansion in d_{23}, determined for both surfaces, is consistent with an expected charge redistribution

resulting from the contraction in d_{12}. However, calculations of the magnitude of this relaxation have not been performed to date. Although the presence of weak intensity at the half order positions suggests that some form of rippling may be present in the surface region, the weakness of these beams has prevented the acquisition of intensity vs energy profiles. Nevertheless, LEED calculations using structural models which include rippling in the top layer are being performed to assess the possibility of such a geometric arrangement.

In view of the previous Rutherford backscattering results [14] showing a loss in As and a change in stoichiometry in the surface region, it is somewhat surprising that a LEED spot pattern was obtained from the GaAs surfaces. More surprising is the observation that a better quality LEED pattern was obtained from the As terminated side as compared with the Ga terminated side. However, for both surfaces the intensity of the diffuse background scattering was much larger than that observed for either the Si or Ge (111) surfaces. The intensity of diffuse scattering suggests the presence of some form of disorder for both terminations. Additional characterization of the surface region, using several spectroscopic techniques, is required before attempting to determine the geometric arrangement.

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