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Reflectance anisotropy spectroscopy and reflection high-energy electron diffraction of submonolayer coverages of Si grown on GaAs(001) by molecular-beam epitaxy

D. A. Woolf
Department of Physics, University of Wales College of Cardiff, P.O. Box 913, Cardiff CF2 3YB, United Kingdom

K. C. Rose* and J. Rumberg
Institut für Festkörperphysik der Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany

D. I. Westwood
Department of Physics, University of Wales College of Cardiff, P.O. Box 913, Cardiff CF2 3YB, United Kingdom

F. Reinhardt
Institut für Festkörperphysik der Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany

S. J. Morris
Department of Physics, University of Wales College of Cardiff, P.O. Box 913, Cardiff CF2 3YB, United Kingdom

W. Richter
Institut für Festkörperphysik der Technische Universität Berlin, Hardenbergstrasse 36, D-10623 Berlin, Germany

R. H. Williams
Department of Physics, University of Wales College of Cardiff, P.O. Box 913, Cardiff CF2 3YB, United Kingdom

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The techniques of reflectance anisotropy spectroscopy (RAS) and reflection high-energy electron diffraction (RHEED) have been employed in concert to characterize the growth of submonolayer coverages of Si deposited onto GaAs(001) substrate crystals. The RHEED observations enabled the RAS spectra collected for a series of Si coverages in the range 0.005–1.000 ML to be interpreted in terms of changes in the sample surface structure. The following series of surface reconstructions evolved with increasing Si coverage from 0 to 1 ML: $c(4\times4)$, $c(4\times4)/(1\times2)$, (1×2), $(1\times2)/(3\times1)$, and (3×1). The fact that unique, but highly reproducible, RAS signatures were obtained for each of these surface phases demonstrates the applicability of a combined RHEED-RAS system for monitoring submonolayer heteroepitaxial growth with a surface sensitivity of the order of $\frac{1}{200}$ of a monolayer.

Considerable interest has been generated by the fabrication of semiconductor structures employing the technique of δ (or planar) doping.[1–3] For example, Si and Be δ layers incorporated within III-V semiconductor crystals have been used to fashion field-effect transistors;[4] nonalloyed Ohmic contacts;[5] light emitting diodes;[6] and, also to control metal/semiconductor interface barrier heights.[7] Furthermore, thin Si interlayers, of the order of 1–2 ML, have been used to alter and control the band offsets between III-V heterostructures,[8,9] to influence the Fermi-level position at the GaAs surface,[10,11] and also to induce a change in epilayer growth orientation, such that CdTe(001) may be grown onto GaAs(001) rather than the usual CdTe(111)B/GaAs(001) epitaxial combination.[12] A detailed understanding of the growth of Si/GaAs(001) is required in order that such δ-doped and interlayer structures may be utilized to their full potential. To this end, a number of recent publications have considered various aspects of the structural, electrical, and chemical nature of the Si/GaAs(001) interface.[13–17]

Reflectance anisotropy spectroscopy (RAS) has been shown to be a useful means of characterizing the clean GaAs(001) surface, since it is very sensitive to changes in the structure of the surface.[18] This method has also been demonstrated to be able to measure both n- and p-type bulk doping concentrations in GaAs (Ref. 19) due to the effect on its optical properties of the space-charge region near the sample surface.

In this paper data are presented from a comparative *in situ* reflection high-energy electron diffraction (RHEED) and RAS study of the growth of submonolayer coverages (0.005–1.000 ML) of Si/GaAs(001). The combination of the RAS and RHEED techniques has enabled the subtle changes in the surface structure, which occur within the submonolayer regime, to be monitored.

The Si/GaAs(001) structures were synthesized within a VG Semicon V80H molecular-beam-epitaxy (MBE) reactor. Substrate penetration, growth temperature, and MBE flux calibration details are presented elsewhere.[20] A VG LEG 110 RHEED system attached to the MBE reactor growth chamber was used to monitor the semiconductor surface structure. Positioned at a strain-free pyrometer viewport on the growth chamber was an in-house constructured RAS system. The optical layout of the combined MBE-RAS apparatus has been previously reported;[21] the design of the RAS equipment

TABLE I. RHEED observations of the Si/GaAs(001) surface structure as a function of Θ_{Si}.

Θ_{Si} (ML)	Reconstruction
0.00–0.06	$c(4\times4)$
0.07–0.10	$c(4\times4)/(1\times2)$
0.15	(1×2)
0.20–0.30	$\{(1\times2)\rightarrow(3\times1)\}$[a]
0.40	$(1\times2)/(3\times1)$
0.50–1.00	(3×1)

[a] (1×2) structure dominant, with onset of (3×1).

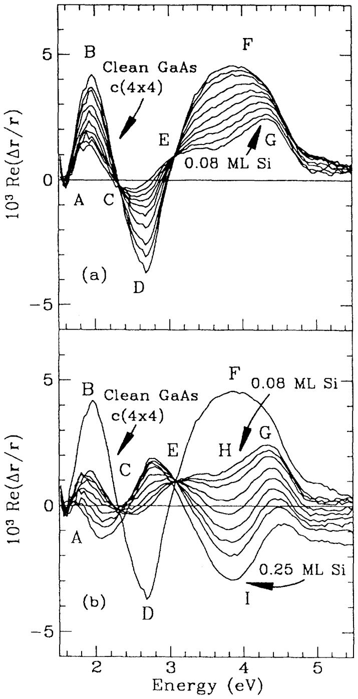

FIG. 1. RAS spectra for the growth of Si/GaAs(001). (a) $\Theta_{\mathrm{Si}}=0$; 0.005 ML; and 0.01–0.08 ML in increments of 0.01 ML. (b) $\Theta_{\mathrm{Si}}=0$ ML (for comparison); 0.08, 0.09, 0.10–0.20 ML (in increments of 0.02 ML), and 0.25 ML.

was based upon that due to Aspnes *et al.*[22] Spectra from 1.5 to 6.2 eV may be monitored by this particular optical setup; however, the light transmission of the strain-free window restricts the upper limit of the workable spectral range to 5.5 eV. The RAS system measures the difference (Δr) between the anisotropic complex reflectance (r) along the optical eigenaxes $[\bar{1}10]$ and $[110]$ within the (001) surface plane, normalized to the mean reflectance ($\bar{r}$):

$$\frac{\Delta r}{\bar{r}}=2\,\frac{r_{[\bar{1}10]}-r_{[110]}}{r_{[\bar{1}10]}+r_{[110]}}.$$

Only the real part of the RAS signal was investigated since even small residual strain effects associated with the pyrometer viewport affect the imaginary component of the RAS signature.[21]

Following the complete thermal desorption of the GaAs surface oxides at $\simeq600\,^{\circ}\mathrm{C}$ under an As_4 flux of $F_{\mathrm{As}_4}\simeq5\times10^{14}$ molecules $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, a sharp, clear GaAs(001)-(2×4) reconstruction was observed by RHEED. A 1-μm, undoped GaAs buffer layer was then grown at a rate of 1 $\mu\mathrm{m\,h}^{-1}$, with an $\mathrm{As_4/Ga}$ flux ratio of $\simeq0.8$, at a temperature of 580 °C. Following growth the sample was cooled to 400 °C for the deposition of the Si layers. During this cooling process the sample surface reconstruction altered from (2×4) to $c(4\times4)$. The Si was deposited from a standard 40-cm^{-3} VG effusion cell, ordinarily used for n-type doping of bulk III-V structures. The dopant source was rigorously calibrated from a large series of Hall effect and electrochemical C-V profiling measurements. The effusion cell temperature was set to $T_{\mathrm{Si}}=1120\,^{\circ}\mathrm{C}$ which yielded a Si flux of $F_{\mathrm{Si}}\simeq2.8\times10^{11}$ atoms $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ such that a single monolayer of Si would be deposited in $\simeq0.64$ h. To replicate the growth conditions usually encountered during δ doping, the As_4 flux was incident onto the sample surface at all stages throughout the experiment. Si coverages from 0 to 1 ML were investigated during this study; RAS and RHEED observations were taken after each Si evaporation so that the evolution of the Si/GaAs surface structure could be monitored throughout the experiment. Before depositing Si onto the GaAs(001)-$c(4\times4)$ surface, several RAS spectra were taken over a period of $\simeq40$ min; all of these spectra were identical, thus ensuring that possible background contamination effects could be neglected.

The development of the Si/GaAs surface structure, as determined by RHEED, is listed in Table I. Starting from a GaAs(001)-$c(4\times4)$ reconstruction the surface evolved via a mixed $c(4\times4)/(1\times2)$, (1×2), and mixed $(1\times2)/(3\times1)$ phases into a (3×1) structure as the Si overlayer thickness was increased to 1 ML. Between $\Theta_{\mathrm{Si}}=0.20$ and 0.30 ML it was noted that the strong (1×2) phase was accompanied by a weak (3×1) reconstruction, which increased in prominence with increasing Θ_{Si} such that at $\Theta_{\mathrm{Si}}=0.40$ ML the (1×2) and (3×1) phases appeared, by RHEED, to be coexistent.

The RAS signatures for the various stages of this experiment are displayed in Figs. 1 and 2. The original GaAs(001)-$c(4\times4)$ RAS spectra from the starting surface are shown, for comparison, in each case. The surface sensitivity of the RAS technique is dramatically demonstrated in Fig. 1(a), where Si coverages as low as $\frac{1}{200}$ ML were detected. Figures 1(a) and 1(b) illustrate the effect of the deposition of Si from 0 to 0.250 ML. Up to 0.200 ML three nodal points (A, C, and E) are observed at 1.6, 2.3, and 3.1 eV, respectively. With increasing amounts of Si within this 0–0.200 ML range it was noted that the line shape of the RAS spectra significantly developed around these nodal points, such that the maximum (B) at 1.95 eV and the minimum (D) at 2.7 eV, both decreased in amplitude. The second maximum RAS feature (F) not only decreased with increasing Si coverages up to 0.080 ML, but also shifted in energy from $\simeq3.8$ to 4.3 eV (G). This RAS energy shift was accompanied by the appearance of a structure within the spectrum (H) at $\simeq3.6$ eV which formed a minimum, or trough, (I) at $\simeq3.8$ eV as the Si overlayer thickness was increased to 0.200 ML. These spectra changes up to $\Theta_{\mathrm{Si}}=0.200$ ML were associated with an alteration of the surface structure from $c(4\times4)$ to (1×2). The way in which these spectra all pass through the

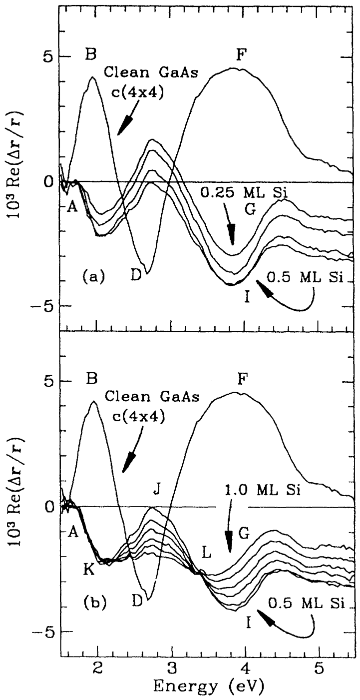

FIG. 2. The evolution of the RAS signatures during the completion of the monolayer growth of Si/GaAs(001). (a) $\Theta_{\rm Si}=0$ ML (for comparison), 0.25, 0.30, 0.40, and 0.50 ML. (b) $\Theta_{\rm Si}=0$ ML (for comparison); 0.50–1.00 ML (in increments of 0.10 ML).

three points strongly suggests that there may be, in fact, a superposition of two separate functions, where one is the clean GaAs(001)-$c(4\times4)$ spectrum and the other could be due to the evolving (1×2) structure. It is significant that the $c(4\times4)$ signal persists at Si coverages much greater than those at which the $c(4\times4)$ contribution vanishes in the RHEED observations. Kamiya *et al.*[23] state that whereas RHEED with a typical coherence length of $\simeq 2000$ Å is sensitive to long-range order, the RAS response is dependent upon the dimer orientation of the surface species, and hence is strongly influenced by short-range order, resulting in a coherence length of a few tens of Å. Thus this series of Si/GaAs observations suggests that even when the presence of the Si atoms upon the GaAs surface have eradicated the $c(4\times4)$ reconstruction a significant number of As-As bonds on the surface remain undisturbed and orientated along the [110] direction.

For $\Theta_{\rm Si}\geqslant 0.200$ ML, where a mixture of (1×2) and (3×1) surface phases were encountered, the RAS signals no longer passed through the nodal points A, C, and E [Fig. 2(a)]; such that each spectra replicated the same maxima and minima features, but were shifted to lower $\mathrm{Re}(\Delta r/\bar{r})$ values for each successive $\Theta_{\rm Si}$ increment in the range 0.20–0.50 ML. Between $\Theta_{\rm Si}=0.40$ and 0.50 ML the mixed $(1\times2)/(3\times1)$ surface phase was lost in favor of a dominant (3×1) structure. Figure 2(b) demonstrates the effect of increasing the Si coverage from 0.50 to 1.00 ML; within this coverage range only a sharp, clear (3×1) reconstruction was observed. The total dominance of the (3×1) phase was associated with another alteration in the development of the RAS signals: the features at points I and G increased in amplitude, whereas the peak at $\simeq 2.7$ eV (J) decreased in amplitude, tending towards the original minimum (D) in the GaAs(001)-$c(4\times4)$ spectra. These RAS changes were also noted to occur around two further, but not so well defined, nodal points (K and L) at $\simeq 1.7$–2.1 eV and $\simeq 3.4$ eV, respectively.

Thus the changes in the RAS spectra observed with increasing Si coverage can be categorized into three distinct phases. The first of these, where the spectra pass through the nodal points (A, C, and E), covers the range in which the $c(4\times4)$ and (1×2) RHEED patterns were noted to exist. The second RAS phase, in which the spectra shifted towards negative $\mathrm{Re}(\Delta r/\bar{r})$ values, coincided with the mixed (1×2) and (3×1) surface reconstructions. The final RAS phase, wherein nodal-like spectral behavior was again observed, corresponded with the existence of the (3×1) reconstruction.

The nature of the Si-(3×1)/GaAs(001) reconstruction requires comment within the context of this work. The Si-(3×1) structure has been observed on both the GaAs(001)-$c(4\times4)$ and (2×4) surfaces.[17,24] Fahy *et al.*[17] imply that the (3×1) reconstruction is an As-induced structure. Evidence for the effect of As on Si/GaAs(001) is also provided by Sorba *et al.*[16] who report the *same* Si/GaAs interface structure for epilayers grown with and without an As_4 overpressure, although the final surface reconstructions are *different*. Our own RHEED studies provide further support for the idea of an As-induced Si-(3×1)/GaAs(001) structure. After depositing 1 ML of Si on GaAs(001) and achieving the (3×1) structure, the As_4 flux was shuttered and the sample annealed at $\simeq 600\,^\circ$C. During the anneal a $(3\times1)\rightarrow(1\times2)$ transition was observed. The (3×1) was recovered if the annealing temperature was reduced and the As_4 flux allowed to impinge on the sample. Ashwin *et al.*[25] have discussed the manner in which submonolayer coverages of Si ($0.01\leqslant\Theta_{\rm Si}\leqslant 0.50$ ML) might be incorporated onto an As-rich GaAs(001) surface, under δ-doping conditions. For the Si atoms to be located, as potential donor species, on Ga sites within an As-terminated GaAs(001) surface plane it is suggested that any two neighboring Si atoms would be linked by either a Si-Si dimer, or by bonding to an intermediate As bridging atom (Si-As-Si) acquired from the incident As_4 flux.[17,25] Based upon these ideas, two mechanisms have been proposed to describe the aggregation of Si/GaAs: the first model prevents the Si-Si dimers from bonding to other Si atoms; while in the second case areas of expanding Si clusters form on the surface. Ashwin *et al.*[25] imply that both processes are expected to occur on the real Si/GaAs surface.

Previous GaAs(001) RAS experiments have shown that the signal at 2.7 eV (D) is related to the orientation of the As bonds on the surface.[18,23] Spectra from the As-rich GaAs(001)-$c(4\times4)$ and As-stabilized (2×4) reconstructions are completely different in that the 2.7-eV feature (D) has a negative $\mathrm{Re}(\Delta r/\bar{r})$ value for the $c(4\times4)$ phase, where the As bonds align along [110]; and, a positive $\mathrm{Re}(\Delta r/\bar{r})$ value for the (2×4) reconstruction where the As bonds are rotated by 90° and align along $[\bar{1}10]$.[18,23] For example, for Si/GaAs, as $\Theta_{\rm Si}$ increases, the fact that the 2.7-eV $\mathrm{Re}(\Delta r/\bar{r})$ value changes sign from negative to positive may be associated with a disruption of the original

$c(4\times4)$ [110] As-As bonds [Figs. 1 and 2(a)] and the formation of Si-Si bonds along $[\bar{1}10]$. This Si-induced reorganization process of the surface As bonding is perhaps followed by the incorporation of As onto the Si/GaAs(001) layer bonding along the original [110] direction, since the 2.7-eV feature in Figs. 2(a) and 2(b) consistently shifts to a lower $\mathrm{Re}(\Delta r/\bar{r})$ value. This bonding arrangement is consistent with the Si-(3×1) model proposed by Fahy *et al.*[17] Such an As adsorption process is not unreasonable since the Si was deposited with the As_4 flux incident onto the sample. The Si coverage at which the 2.7-eV $\mathrm{Re}(\Delta r/\bar{r})$ value starts to decrease in amplitude seems to be related to the change in surface reconstruction from (1×2) to (3×1). Furthermore, the evolution of the RAS spectra may be not only due to an increase in the Si coverage on the surface, but also as a result of the presence of As/Si/GaAs.

In summary, the heteroepitaxial growth of Si epilayers onto GaAs(001), within the overlayer thickness range 0–1 ML, has been simultaneously monitored *in situ* using RHEED and RAS. It has been demonstrated that the RAS technique is sensitive to the deposition of at least $\frac{1}{200}$ ML of Si on GaAs. Furthermore, these techniques have followed the evolution of the Si/GaAs surface structure, supporting the idea of the existence of an As-induced Si-(3×1)/GaAs(001) reconstruction for Si coverages of $\geqslant 0.5$ ML.

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[*] Present address: Abt. Oberflachenphysik, Fritz-Haber-Institut der Max-Planck-Gesselschaft, Faraday 4-6, D-14195 Berlin (Dahlem), Germany.

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