In situ spectroscopic ellipsometry of GaAs(001) surface reconstructions

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GaAs(001) surface reconstructions prepared by molecular-beam epitaxy were studied *in situ* by spectroscopic ellipsometry (SE) and reflectance difference spectroscopy (or reflectance anisotropy spectroscopy) as a function of temperature. Simultaneous measurements of the dielectric function by SE and the reflectance difference $\Delta r/r$ allow us to identify surface and bulk-related contributions to the optical anisotropy $\Delta\varepsilon=\varepsilon_{\bar{1}10}-\varepsilon_{110}$. For the (2×4), the $c(4\times4)$, and the (4×2) reconstructions we find resonances in $\mathrm{Im}(\Delta\varepsilon)$ at 2.9, 2.6, and 2.25 eV at $T=80$ °C. Although the resonance at 2.9 eV coincides with the E_1 bulk transition and also shows the same temperature dependence, they can be distinguished, because the surface contribution changes the sign when switching from the (2×4) to the $c(4\times4)$ reconstruction and the bulk contribution remains the same. [S0163-1829(96)06320-5]

The most useful technique to measure the optical anisotropy induced by the reconstruction of semiconductor surfaces has so far been reflectance difference spectroscopy [(RDS), also termed reflectance anisotropy spectroscopy].[1] On (001)GaAs it has been used to identify the surface reconstruction,[2] to monitor the growth kinetics,[3] and to measure the surface stoichiometry.[4] Spectroscopic ellipsometry (SE), on the other hand, has been employed to measure the critical point energies of GaAs, their type and dimension, line-shape broadening, and the possible influence of many-particle effects.[5–7] *In situ*, SE has been proposed to control the growth by organometallic molecular-beam epitaxy[8] and the temperature during molecular-beam epitaxy (MBE).[9] Despite the widely acclaimed surface sensitivity of SE, it has not yet been employed to determine the optical anisotropy induced by the surface reconstruction. In this paper we show that this can indeed be done by simply taking the difference of the SE response in two perpendicular directions (in our case the [110] and the $[\bar{1}10]$ direction on the GaAs(001) surface). We call this technique spectroscopic difference ellipsometry (SDE). Similar to RDS, the surface-induced optical anisotropy $\Delta\varepsilon=\varepsilon_{\bar{1}10}-\varepsilon_{110}$ of the surface layer can be gained if the bulk dielectric function of the substrate ε_0 is known. In the case of SDE, however, ε_0 is part of the measurement itself and does not have to be measured separately as is the case for RDS.

The well-documented RDS response of the As-terminated (2×4) reconstruction[1,2,4,10] shows a resonance around 2.6 eV at growth temperatures (600 °C), which is attributed to electronic transitions involving the As dimers present on the surface.[11] The energy value for this resonance is close to that of the E_1 transition of the bulk. To gain insight into the nature of this electronic transition, it is of interest to study its temperature dependence. Thus, in addition to demonstrating the technique of SDE and comparing it to RDS, we present in this paper the surface-induced optical anisotropy $\Delta\varepsilon$ of different GaAs(001) surface reconstructions obtained from the RDS and the SDE measurements at different temperatures.

The experiment was performed in a MBE chamber that was equipped with an ellipsometer for *in situ* SE.[12] Strain-free windows[13] were used for optical access to the samples at an incident angle of 72.5°. Undoped, nominally (001) oriented, epiready GaAs substrates were used for the investigation. Two (10×40)-mm^2 large samples were cleaved out of the same wafer in such a way that the long side of one sample is oriented along the [110] direction and that of the other piece along the $[\bar{1}10]$ direction. Both samples were mounted side by side with In on a 2-in. Mo sample holder. After loading to the MBE chamber the oxide was thermally desorbed in an As_4 flux corresponding to a beam equivalent pressure (BEP) of 4×10^{-6} Torr. A 1-μm-thick undoped GaAs buffer layer was grown with a growth rate of 0.5 μm/h at a substrate temperature of 580 °C. After growth the (2×4) surface reconstruction was observed by reflection high-energy electron diffraction (RHEED). This surface reconstruction was then quenched to room temperature by lowering the substrate temperature and the As beam flux. Since the RHEED pattern remains unchanged during this procedure, we assume that the reconstruction does not change. To prepare the $c(4\times4)$ reconstruction, the As_4 beam flux was decreased at a lower substrate temperature (500 °C) after the RHEED pattern has changed to the (2×2) symmetry characterizing this surface structure. The Ga-rich (4×2) reconstruction was prepared either by depositing Ga with a low growth rate at a substrate temperature of 580 °C and a low As_4 beam flux corresponding to a pressure of 2×10^{-7} Torr or by carefully annealing the substrate in vacuum above 650 °C. While monitoring the RHEED, the Ga deposition or the annealing was stopped at that moment when the twofold periodicity of the (2×4) changed to the fourfold periodicity of the (4×2). This sample was transferred at high temperatures and a pressure below 2×10^{-10} Torr into the adjacent buffer chamber that was free of arsenic. After the preparation of the different surface reconstructions, the MBE chamber was pumped to a pressure below 2×10^{-11} Torr to avoid the

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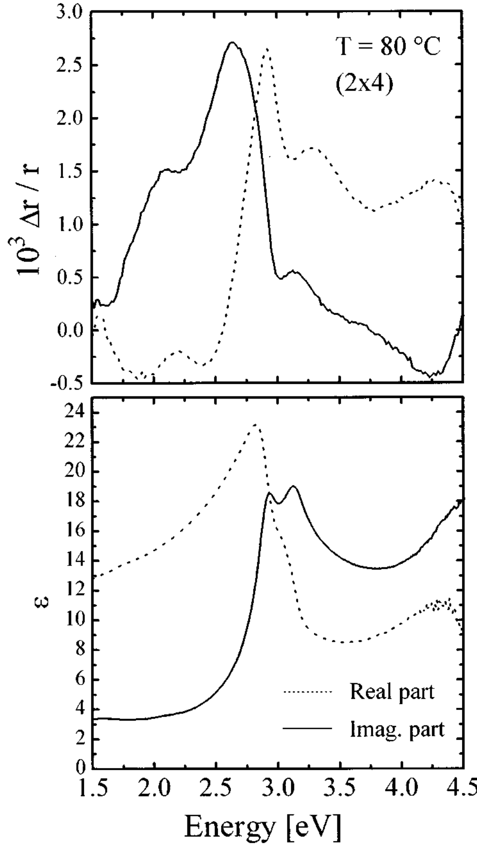

FIG. 1. Real (dotted line) and imaginary (solid line) parts of the reflectance difference $\Delta r/r$ and the spectroscopic ellipsometric response ε_0 of the GaAs(001)-(2×4) surface reconstruction at 80 °C.

contamination of the surface or the change of the surface reconstruction due to residual As_4 during the measurements.

SDE was performed with a commercially available spectroscopic ellipsometer[12] equipped with a prism monochromator and a 1024 silicon diode detector array. The fixed angle of incident is 72.5°. The optical alignment of the ellipsometer was arranged such that the oval (15×35)-mm^2 light spot covered both samples to the same amount. A small aperture behind the analyzer allows for the measurement of only one sample at a time. SE of the optical anisotropy induced by the surface reconstructions along the two principal axes can now be performed by only moving the aperture from one sample to the other. A sample rotation or a movement of any optical element would introduce slight but unknown geometric changes and would spoil this very sensitive measurement and can be avoided this way.

For comparison with SDE, we have performed RDS with a homemade spectrometer utilizing the standard setup according to Aspnes.[1] By measuring both samples subsequently, which again corresponds to a rotation of the sample by 90°, a residual strain in the window can be taken into account and subtracted from the data. The full spectrum acquisition time is 1 min for the SDE data and 3 min for the RDS data.

Figure 1 shows the real and the imaginary part of the measured RDS response $\Delta r/r$ (upper part) of the (2×4) surface reconstruction and the bulk dielectric function ε_0

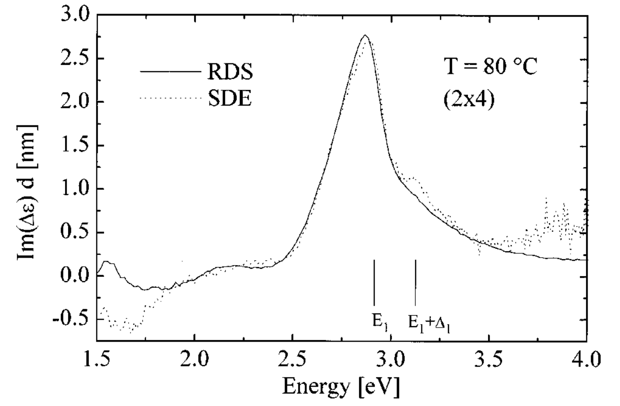

FIG. 2. Imaginary part of the surface-induced optical anisotropy $\Delta\varepsilon = \varepsilon_{\bar{1}10} - \varepsilon_{110}$ of the GaAs(001)-(2×4) surface reconstruction at 80 °C.

(lower part) of GaAs at 80 °C. The dominant feature of the RDS response at 2.9 eV is to be compared to that typically measured at 2.6 eV at growth temperatures of 600 °C.[1,2,10] The observed shift to higher energy is due to the lower temperature. It exactly corresponds to the shift of the E_1 bulk transition in the same temperature range as will be discussed below.

In order to extract the surface-induced optical anisotropy of the dielectric function $\Delta\varepsilon$, we employ a three media model consisting of bulk GaAs as substrate, a thin ($d \ll \lambda$) surface layer representing the reconstructed surface, and the vacuum as ambient. The analytic formalism summarized by Hingerl, Aspnes, and Kamiya[14] was used to calculate $\Delta\varepsilon$ from the SDE response:

$$id\Delta\varepsilon = \frac{\rho_{110} - \rho_{\bar{1}10}}{\rho_{110} + \rho_{\bar{1}10}} \frac{\lambda}{2\pi} \frac{(\varepsilon_0 - 1)(\varepsilon_0 \cos^2\phi - \sin^2\phi)}{\cos\phi(\varepsilon_0 + \varepsilon_0\cos^2\phi - 2\sin^2\phi)}.$$

$\rho_{110}(\rho_{\bar{1}10})$ equals the measured $\tan\psi\,\exp(i\Delta)$ values with the s-polarized component of the light oriented along the [110] direction ([$\bar{1}$10] direction). For ε_0, the bulk dielectric function, we take the arithmetic average of the two measurements; ϕ is the angle of incident for the SE measurement (72.5°).

For the case of the RDS measurement ($\phi = 0°$) $\Delta\varepsilon$ reduces to the well-known expression[1]

$$id\Delta\varepsilon = \frac{\Delta r}{r} \frac{\lambda}{4\pi}(\varepsilon_0 - 1) \quad \text{with} \quad \frac{\Delta r}{r} = 2\frac{r_{110} - r_{\bar{1}10}}{r_{110} + r_{\bar{1}10}}.$$

The result of this calculation for the measurements of the (2×4) surface reconstruction at 80 °C is shown in Fig. 2. The imaginary part of $\Delta\varepsilon$ extracted from the RDS response and the SDE both show a resonance at 2.9 eV with a shoulder 240 meV above this value. The line shape and the absolute value of $\Delta\varepsilon$ obtained with both measurement techniques show excellent agreement. The better signal-to-noise ratio of the RDS with respect to the SDE measurement is expected, since the former employs a modulation technique in combination with a lock-in amplifier, whereas the latter originates from taking the difference of two spectra only. The spectral resolution of the SDE, however, is better than that of the RDS.

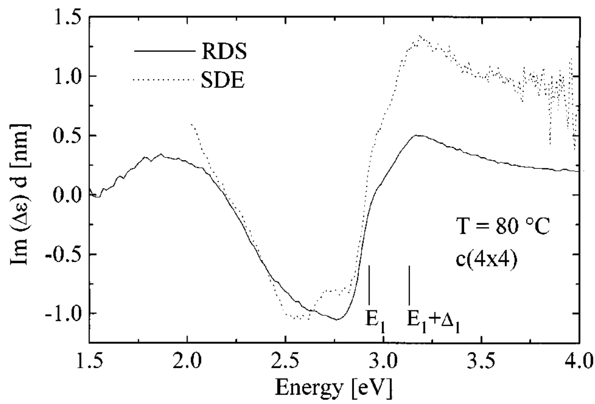

FIG. 3. Imaginary part of the surface-induced optical anisotropy $\Delta\varepsilon=\varepsilon_{\bar{1}10}-\varepsilon_{110}$ of the GaAs(001)-$c(4\times4)$ surface reconstruction at 80 °C.

The imaginary part of $\Delta\varepsilon$ of the GaAs(001)-$c(4\times4)$ surface reconstruction measured by RDS and SDE at 80 °C is shown in Fig. 3. The rotation of the surface dimers of this reconstruction with respect to the (2×4) reconstruction results in a change of sign of $\Delta\varepsilon$.[10] In addition, the 2.9-eV resonance is shifted to lower energy (2.8 eV) and a second resonance at 2.6 eV is observed. The positive signal above 2.85 eV shows the signature of the E_1 and $E_1+\Delta_1$ transitions of the bulk. Again, the RDS and the SDE measurements give comparable results, except for the difference in the ratio of the absolute values of the two resonances involved in the spectra. This might be due to the different penetration depths because of the different angles of incidence used in both measurements.

The imaginary part of $\Delta\varepsilon$ of the Ga-terminated (4×2) reconstruction at 80 °C is shown in Fig. 4. Similar to the response of the $c(4\times4)$ reconstruction, the signal is negative, i.e., $\varepsilon_{\bar{1}10}<\varepsilon_{110}$, in agreement with the 90° rotation of the Ga dimers with respect to the As dimers of the (2×4) reconstruction. At low temperatures two distinct resonances at 2.25 and 2.6 eV can be observed. To higher temperatures, the amplitude of the latter feature decreases and the spectrum shifts to lower energies. At growth temperatures it corresponds to the 1.8-eV feature observed in RDS in earlier work.[10]

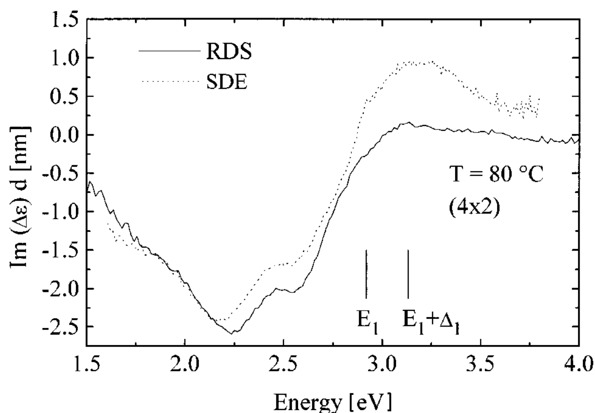

FIG. 4. Imaginary part of the surface-induced optical anisotropy $\Delta\varepsilon=\varepsilon_{\bar{1}10}-\varepsilon_{110}$ of the GaAs(001)-(4×2) surface reconstruction at 80 °C.

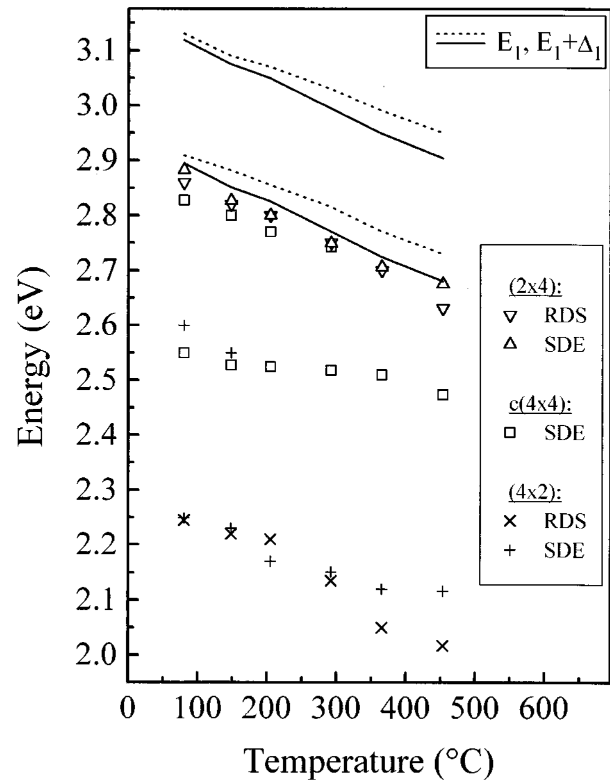

FIG. 5. Temperature dependence of the dominant contributions in Im($\Delta\varepsilon$) (symbols) and the E_1 and $E_1+\Delta_1$ transition of the bulk (lines). Dashed lines, oscillator fit to Im(ε_0); solid lines, fits of the second derivative spectrum $d^2\varepsilon_0(\omega)/d\omega^2$ to analytic critical-point line shapes; triangles, (2×4) reconstruction; squares, $c(4\times4)$ reconstruction; and crosses, (4×2) reconstruction.

SDE and RDS measurements were performed at substrate temperatures ranging from 80 °C up to 500 °C [above which the $c(4\times4)$ changes to a (2×4) reconstruction]. The temperature was measured with a W/Re thermocouple on the backside of the sample holder. Special care was taken for the specification of the actual surface temperature. The thermocouple reading was calibrated not only to the oxide desorption temperature at 580 °C but also to data in the literature by directly comparing the own ellipsometric spectra with those measured by Maracas *et al.*[9] The respective surface reconstruction was simultaneously monitored by RHEED in order to be sensitive to any changes in the reconstruction at higher temperatures.

The temperature dependence of the spectral features contained in Im($\Delta\varepsilon$) is shown in Fig. 5 together with that of the E_1 and $E_1+\Delta_1$ bulk transitions extracted from the dielectric function. The energy positions were determined in the case of the surface anisotropy spectra by fitting Lorentz oscillators to the Im($\Delta\varepsilon$)d spectra. In the case of the E_1 and $E_1+\Delta_1$ bulk transitions two different approaches are currently employed for the analysis of the dielectric function by different groups: Maracas *et al.*[9] use a seven-oscillator model, whereas Lautenschlager *et al.*[5] employ a fitting of the second derivative spectrum $d^2\varepsilon_0(\omega)/d\omega^2$ to analytic critical-point line shapes. In the former procedure, the obtained E_1 and $E_1+\Delta_1$ critical-point energies are influenced by the parameters of the five additional oscillators. The latter

procedure subtracts the background and especially takes into account the line-shape dimensionality of the critical points involved in the optical response. We have employed both techniques in order to estimate the error that can be made in the analysis of the dielectric function. The dotted line in Fig. 5 shows the result of a three-oscillator fit and the solid line that of the 2D critical-point line-shape analysis. In the oscillator fit the oscillator around 4.5 eV does not influence the two oscillators for E_1 and $E_1+\Delta_1$. This is expected to result in higher critical-point energies and a weaker temperature dispersion E_1 and $E_1+\Delta_1$. The dotted line thus represents an upper limit for the analysis of the critical-point energies.

Two Lorentz oscillators have been used to fit $\mathrm{Im}(\Delta\varepsilon)d$ of the (2×4) reconstruction. Within the sensitivity of the measurement and the fitting procedure their energy positions coincide with that of the E_1 and the $E_1+\Delta_1$ bulk transitions obtained from the line-shape analysis and also show the same temperature dependence. For the sake of clarity Fig. 5 shows only the energy positions of the dominant low-energy feature.

For the $c(4\times4)$ reconstruction, only the SDE measurements have been analyzed. Because of the better spectral resolution compared to the RDS measurement, the fitting procedure is more reliable for the former and results in larger error bars for the latter. Three Lorentz oscillators have been used to fit the data: two for the surface response with $\varepsilon_{\bar{1}10}<\varepsilon_{110}$ $[\mathrm{Im}(\Delta\varepsilon)d<0]$ and one for the $E_1+\Delta_1$ bulk transition with $\varepsilon_{\bar{1}10}>\varepsilon_{110}$. The best fit can be obtained by adding a fourth Lorentz oscillator for the E_1 bulk transition at 2.93 eV without a change of the resonance position of the other peaks. The high-energy branch around 2.8 eV shows the same temperature dependence as the dominant feature of the (2×4) reconstruction; however, the low-energy branch, which is well separated from the bulk E_1 signature, displays a different temperature dispersion.

The optical response $\mathrm{Im}(\Delta\varepsilon)d$ of the (4×2) reconstruction has been fitted with three Lorentz oscillators. Similar to the As-terminated $c(4\times4)$ reconstruction, one oscillator coincides with the $E_1+\Delta_1$ bulk transitions (one for the E_1 bulk transition may be hidden within the broad structure around 3 eV). One resonance around 2.5 eV is observed only at low temperatures and the dominant feature lies at energies below 2.3 eV.

The measured optical anisotropy of all three surface reconstructions involves resonances around the E_1 and the $E_1+\Delta_1$ bulk transitions with $\varepsilon_{\bar{1}10}>\varepsilon_{110}$. Of special interest is the optical response of the (2×4) reconstruction. The 2.9-eV features (at high temperatures around 2.6 eV) has so far been attributed to electronic transitions involving the As dimers and thus directly linked to the existence of the (2×4) reconstruction.[1–4,10,11] Skepticism about this interpretation is justified due to the coincidence of this feature with the E_1 bulk transition. Anisotropic bond polarizabilities or strain may give rise to a RDS and a SDE signal at the bulk critical-point energies, which would mean that the 2.9-eV feature is not related to the surface reconstruction. In this respect the low-temperature optical response of the $c(4\times4)$ reconstruction is very interesting and may solve this uncertainty. For this reconstruction we do find both the E_1 and the $E_1+\Delta_1$ bulk signature with $\varepsilon_{\bar{1}10}>\varepsilon_{110}$ at 2.9 and 3.13 eV, respectively, and the surface response at 2.83 eV with $\varepsilon_{\bar{1}10}<\varepsilon_{110}$. Only because of the different polarity of both contributions we are able to distinguish them. For the (2×4) reconstruction both the bulk and the surface contribute with the same polarity $\varepsilon_{\bar{1}10}>\varepsilon_{110}$ to the signal and are thus difficult to distinguish. In this respect our measurements are in favor with the previous interpretation of the 2.9-eV feature to be linked to the reconstruction (in agreement with a recent work by Esser *et al.*[15]). However, the agreement of the energy values and the temperature dispersion point to a strong coupling of the electronic surface states to the bulk states. Surface strain induced by the surface reconstruction, most likely due to the As dimerization, may also still contribute to the optical anisotropy.

In conclusion, we have investigated the three main surface reconstructions of the GaAs(001) surface with *in situ* spectroscopic ellipsometry as a function of temperature. Employing a simple difference technique we were able to measure an optical signature in ellipsometry that is induced by the surface reconstruction. Within the theoretical framework of a three media model we have calculated the surface-induced optical anisotropy $\Delta\varepsilon=\varepsilon_{\bar{1}10}-\varepsilon_{110}$ of the different reconstructions. The optical anisotropy spectra obtained from RDS measurements performed on the same samples for comparison show excellent agreement with the ellipsometric measurements. The dominant contributions in the imaginary part of $\Delta\varepsilon$ at 80 °C are resonances for the (2×4), the $c(4\times4)$, and the (4×2) reconstructions at 2.9, 2.6, and 2.25 eV, respectively. In all cases, however, oscillators at the energy values of the E_1 and the $E_1+\Delta_1$ bulk transitions have to be included to fit the experimental results satisfactorily.

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