

In Situ Observation of MBE-Grown GaAs(001) Surfaces Using Surface Photo-Absorption and Reflectance Difference

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Surface photo-absorption (SPA) spectra for $c(4\times 4)$ and Ga-stabilized (4×2) surfaces with respect to a $(2\times 4)\beta$ surface are observed and compared with reflectance difference spectra. SPA spectral features around 470 nm and between 500 and 800 nm are assigned to As and Ga dimers, respectively. The temporary appearance of the $(2\times 4)\beta$ phase during the surface conversion from $c(4\times 4)$ to (4×2) by a Ga supply is shown by using the time-resolution capability of SPA spectrum measurement.

Reflection high energy electron diffraction (RHEED) has been used routinely to characterize GaAs surfaces during molecular beam epitaxy (MBE) growth. This technique detects the existence of long-range structural order on the growing surface and is insensitive to the chemical identity of the surface species. Optical probes such as reflectance difference (RD)¹⁾ and surface photo-absorption (SPA)²⁾, on the other hand, provide information complementary to that provided by electron diffraction because optical reflectance in the visible and near-uv regions responds to local atomic structures rather than to long-range order. These methods enable us to determine the chemical identity of the surface species on the basis of the peak energies of reflection spectra with the help of theoretical calculations that attribute each spectral feature to a certain chemical bond.³⁾

RD measures the real part of the difference between the near-normal-incidence reflectances of light linearly polarized along the two principal axes, $[110]$ and $[T10]$, in the (001) surface.¹⁾ It is known that RD responds to surface reconstructions¹⁾ and can measure static spectra without changing surface structures.⁴⁾ In SPA measurements,²⁾ p-polarized light impinges on the (001) surface at an angle of incidence close to the Brewster angle for GaAs in order to minimize the intensity of reflected light and to increase the contribution of the surface relative to that of the bulk. Since SPA observes a reflection intensity change when surface structures are modified, it is necessary to obtain a well-defined *reference* surface whose SPA spectrum cannot be determined. However, SPA has some advantages over RD. First, SPA does not rely on polarization change. Thus it is immune to the effects of birefringence of optical windows. Second, it provides the possibility of measuring time-resolved spectra using a multi-channel analyzer. Furthermore, SPA responds not only to dielectric polarization parallel to the growing surface as does RD but also to that perpendicular to the surface, which is

isotropic in the surface plane and therefore undetectable by RD.⁵⁾

We show these capabilities of SPA by observing Ga-stabilized surface formation. It is shown through time-resolved SPA spectra that a stable $(2\times 4)\beta$ -like structure appears temporarily during the conversion from the $c(4\times 4)$ surface to the Ga-stabilized (4×2) surface.

Experiments were performed with a MBE system equipped with a RD and SPA measurement system previously described.²⁾ Briefly, p-polarized light from a Xe lamp enters the chamber at an angle of incidence of 70° and reflected light is dispersed with a spectrograph and detected with a photo-diode array. For RD measurement, light polarized along $[010]$ or $[100]$ from a Xe lamp is incident on the substrate nearly vertically and reflected light is dispersed by a monochromator and detected with a photomultiplier after passing through a photoelastic modulator and an analyzer. The effect of birefringence of the window is removed by taking a reference spectrum with the incidence polarization along $[T10]$ or $[110]$.

The SPA spectra were observed with an exposure time of 0.2 s successively and stored in a computer. The stored data can be displayed either as a spectrum at a specified time during the Ga supply or as an evolution of reflectance change during the Ga supply at a fixed wavelength. It should be noted that observing similar temporal evolutions of RD spectra requires the repetition of the same surface treatment that causes the RD transient of interest because RD measurements are usually performed using phase sensitive detection for a fixed wavelength.⁶⁾ It is assumed that exactly the same phenomenon is reproduced in every measurement, which might not be the case. In SPA, transient spectra are obtained with a *single* run which is advantageous when the repetition of the phenomenon of interest is difficult or time consuming to achieve.

We produced a (2x4) β reference surface by adjusting the As beam equivalent pressure (BEP) and/or substrate temperatures. The surfaces were characterized using well-known RHEED patterns such as (2x4) α , β , γ ⁷ and c(4x4). The Ga supply rate was fixed at about 0.25 monolayers (ML) per second as determined using RHEED oscillation observed with the [110] azimuth.

1) Conversion from c(4x4) to (2x4) β

In order to establish the SPA spectrum of the c(4x4) surface with respect to the (2x4) β surface, we observed SPA spectra when a GaAs(001) surface is converted from c(4x4) to (2x4) by reducing As BEP from 4.1×10^{-3} Pa by two orders of magnitude. Figure 1 shows four typical curves for different incidence azimuths. The curve for an azimuth of [T10] has a peak at 470 nm and the curve for an azimuth of [110] has an inverted peak

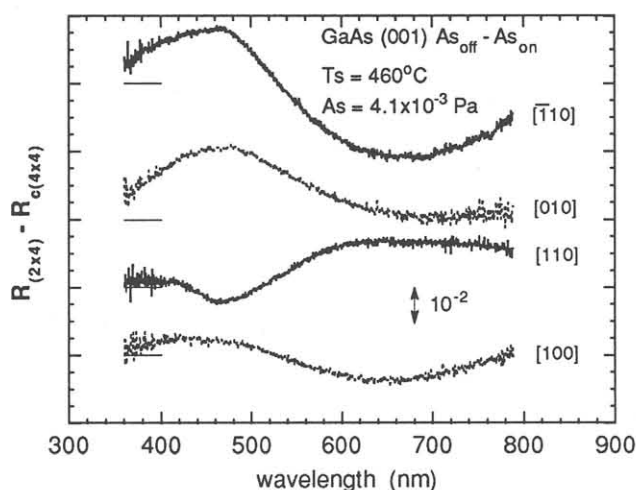


Figure 1
SPA spectra showing the surface change from c(4x4) to (2x4) by terminating As flux. The SPA signal was observed for 4 incidence azimuths of [T10], [010], [110], and [100].

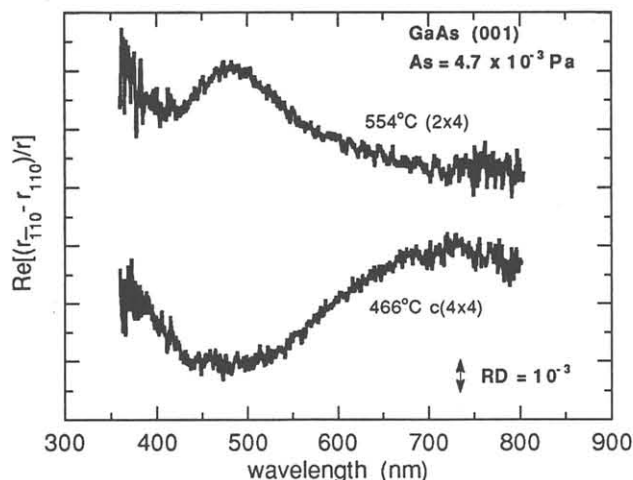


Figure 2
RD spectra for the (2x4) surface and for the c(4x4) surface obtained by changing substrate temperature with As BEP kept at 4.7×10^{-3} Pa.

at the same wavelength. The peak is caused by As dimers according to the RD spectra discussed below. Figure 2 shows RD spectra for two As-stabilized GaAs(001) surfaces. The upper curve was obtained for the (2x4) β surface prepared at 554°C under an As BEP of 4.7×10^{-3} Pa. According to Chang and Aspnes,³⁾ the peak at 470 nm is caused by electronic transitions from lone pair orbitals of As atoms to anti-bonding orbitals of As dimers which are parallel to [T10]. Lowering the substrate temperature to 466°C converted the surface to c(4x4), which showed the lower RD spectrum in Fig. 2. The lower curve shows an inverted peak at the same wavelength as the upper one, indicating that the As dimer direction on the c(4x4) surface is perpendicular to that on the (2x4) surface.

Combined with the RD observation shown in Fig. 2, the SPA spectra in Fig. 1 indicate that the peak at 470 nm is also related to the As dimer bonds on the (001) surface. In fact, we can qualitatively understand these features if we apply the selection rule for a diatomic molecule to As dimers, in which the interaction between light and electrons occurs only for electric fields polarized along the bond axes. In this model, we expect the reflectance for the (2x4) surface to be larger than that for the c(4x4) surface when the incidence azimuth is [T10] and smaller when the incidence azimuth is [110] since As dimers on the (2x4) surface are parallel to [T10] while those on the c(4x4) surface are parallel to [110], as shown schematically in Fig. 3.

The SPA spectrum with the incidence azimuth of [010] is similar to that for the incidence azimuth of [100]. With these azimuths, incident light interacts with As dimers on the (2x4) surface as well as those on the c(4x4) surface, which requires a quantitative approach in order to understand the spectra.

2) Dynamical behaviors of a GaAs(001) surface during a Ga supply on (2x4) β and c(4x4) surfaces

We observed evolutions of the SPA spectra during a Ga supply on As-stabilized surfaces to investigate changes in surface structures caused by a Ga influx. Figure 4 shows the SPA spectra observed during a Ga

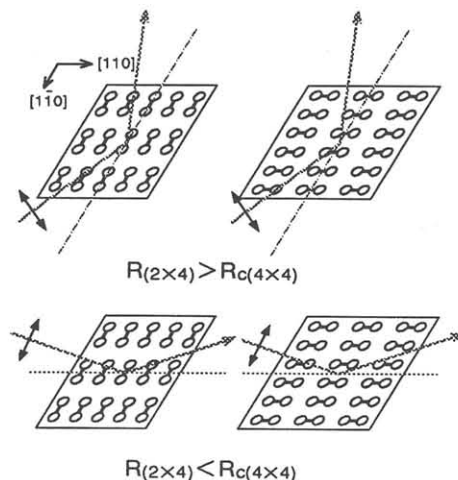


Figure 3
Schematic illustration of interaction between light with different incidence azimuths and As dimer bonds on the (2x4) and c(4x4) surfaces.

supply on a $(2 \times 4)\beta$ surface. SPA spectra measured with the Ga supply for 1 s (0.25 ML of Ga deposited) are represented by the thick solid line for the $[T10]$ azimuth and by the thick dotted line for the $[110]$ azimuth. Those measured with the Ga supply of 4 s (1 ML of Ga deposited) are represented by the thin solid line for the $[T10]$ azimuth and by the thin dotted line for the $[110]$ azimuth. With the initiation of the Ga supply on $(2 \times 4)\beta$, SPA signal increases monotonically at every wavelength for the $[110]$ azimuth as represented by the thick and thin dotted lines. For the $[T10]$ azimuth it also increases at almost every wavelength except around 450 nm where the reflection intensity remains unchanged as represented by the thick and thin solid lines.

The signals for both the $[110]$ and $[T10]$ azimuths are saturated when about 1 ML of Ga is supplied at $t = 4$ s. In the initial stage before the saturation, SPA spectra

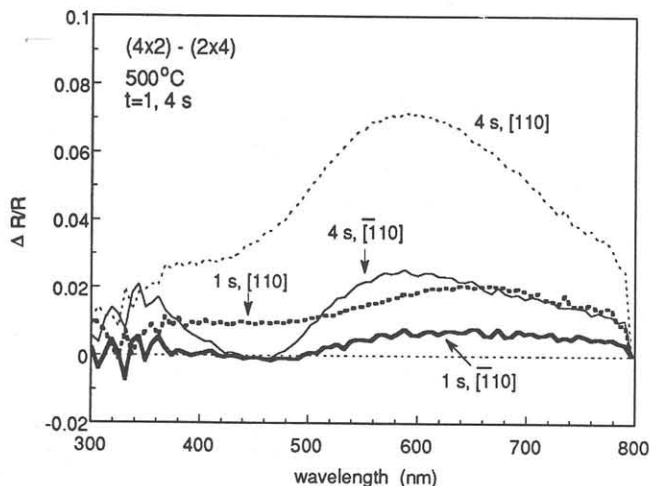


Figure 4

SPA spectra during a Ga supply on a $(2 \times 4)\beta$ surface. The thick dotted ($[110]$ azimuth) and the thick solid ($[T10]$ azimuth) lines represent the spectra 1 s after the Ga supply began. The thin dotted ($[110]$ azimuth) and the thin solid ($[T10]$ azimuth) lines represent the spectra 4 s after the Ga supply began when about 1 ML of Ga was deposited.

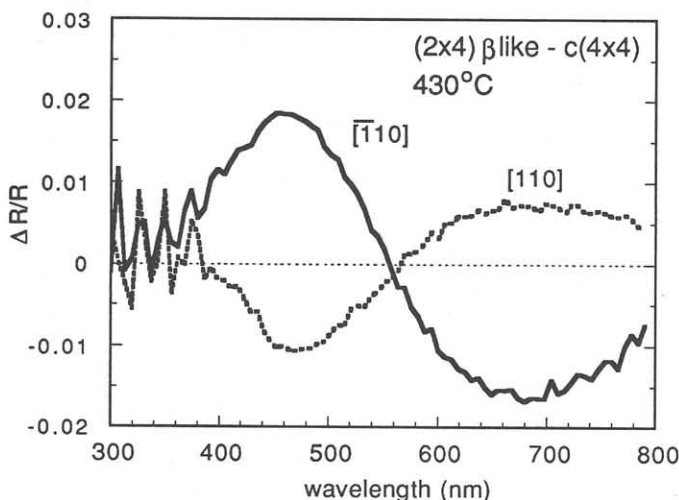


Figure 5

SPA spectra during a Ga supply on a $c(4 \times 4)$ surface. The dotted ($[110]$ azimuth) and the solid ($[T10]$ azimuth) lines show the spectra when 0.5 ML of Ga was deposited.

exhibit a broad peak around 650 nm for $[110]$ (thick dotted line) and $[T10]$ (thick solid line). The peak gradually shifted to shorter wavelengths until the reflection intensity change was saturated. The thin dotted (the $[110]$ azimuth) and the thin solid ($[T10]$ azimuth) lines show SPA spectra when the reflection intensity change was saturated with 1 ML of Ga deposited on the surface.

Comparison between the curves for the $[110]$ and $[T10]$ azimuths at $t = 4$ s shown by the thin dotted line and by the thin solid line, respectively, indicate anisotropic contribution in the range between 500 and 800 nm; SPA signal is larger for $[110]$ than for $[T10]$. This anisotropic SPA signal is believed to be caused by Ga dimers as discussed by Aspnes et al.¹⁾

Around 350 nm, the SPA signal is nearly equal for both azimuths at $t = 4$ s indicating SPA is isotropic in this wavelength region. This structure has not been detected by RD because RD responds only to the surface anisotropy. In contrast to the anisotropic signal between 500 and 800 nm, this peak may be related to Ga back bonds.⁵⁾

The absence of SPA response around 450 nm with the incidence azimuth of $[T10]$ is not yet understood. Since this wavelength region coincides with the As dimer spectrum shown in Fig. 1, one possibility is that a decrease in reflection intensity due to a loss of As dimers caused by deposited Ga atoms is compensated by an increase in reflection intensity around 450 nm due to Ga adsorption.

Next we investigated evolution of SPA spectra when Ga is supplied on a $c(4 \times 4)$ surface. The spectra shown in Fig. 5, which were obtained with a Ga supply of 0.5 ML, are similar to the ones shown in Fig. 1, which were obtained when the surface was converted from $c(4 \times 4)$ to (2×4) by As desorption. Therefore, we deduce that a $(2 \times 4)\beta$ surface emerges from $c(4 \times 4)$ during the Ga supply before a Ga-stabilized surface is formed.

In conclusion, we observed the SPA spectra for $c(4 \times 4)$ and Ga-stabilized (4×2) surfaces with respect to $(2 \times 4)\beta$ surface. Using the time-resolution capability of SPA spectrum measurement, we showed the temporary appearance of the $(2 \times 4)\beta$ phase during the surface conversion from $c(4 \times 4)$ to (4×2) by a Ga supply.

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