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Surface Second-Harmonic Generation (SHG) Study of Epitaxial Growth of GaAs

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Second-harmonic generation (SHG) observed in reflection from the growing surface of GaAs is reported. In a specific configuration of the polarization and crystal azimuth, only the surface specific component was observed. Combined with the RHEED observation, we found that SHG is only sensitive to the chemical constituent on the surface, while the RHEED is sensitive to long-range ordering of the surface reconstruction. By observing the intensity variations of SHG in various polarization and azimuths, we infer the relevant components of surface second-order nonlinear susceptibility tensor.

1. Introduction

During this decade, surface reflection SHG is being recognized as a unique tool for studying semiconductor surfaces: its symmetry; structure, including surface step structure; chemical constituents, etc. are important potential subjects [1]. As an optical method, SHG or SFG (sum-frequency generation) is capable of remote sensing, is a non-destructive method, and can be applied in any dense environment, such as in liquids, high pressure gases, or even at interfaces of different materials, provided that the light can pass through them. Further, by employing a non-linear effect, it can be made to be sensitive to only the surfaces or interfaces.

However, the studies have been rather limited to centrosymmetric crystals such as silicon and germanium. This is because one can only enjoy the surface-specific nature of reflection SHG for crystals having a center of symmetry. On the other hand, the situation is quite different for compound semiconductors, because, not having a center of symmetry, SHG is a strongly allowed process in bulk crystals, thus hampering the observation of surface SHG. However, Stehlin et al. have shown that for "low-index" surfaces there exist special optical arrangements in which the bulk SHG has zero contribution [2]. The present authors have shown that by observing the rotational anisotropy of the SH intensity one can deduce the contribution from the surface, which, due to interference with the strong bulk contribution, is observed to be "magnified" [3].

In this article we present our observations of the epitaxial growth of GaAs by SHG, employing the growth-interruption method. We make use of Stehlin et al.'s surface-specific configuration, together with RHEED (reflection high-energy electron diffraction) observations.

2. Experimental

Figure 1 shows the experimental arrangement. An ultrahigh vacuum chamber; whose base pressure was

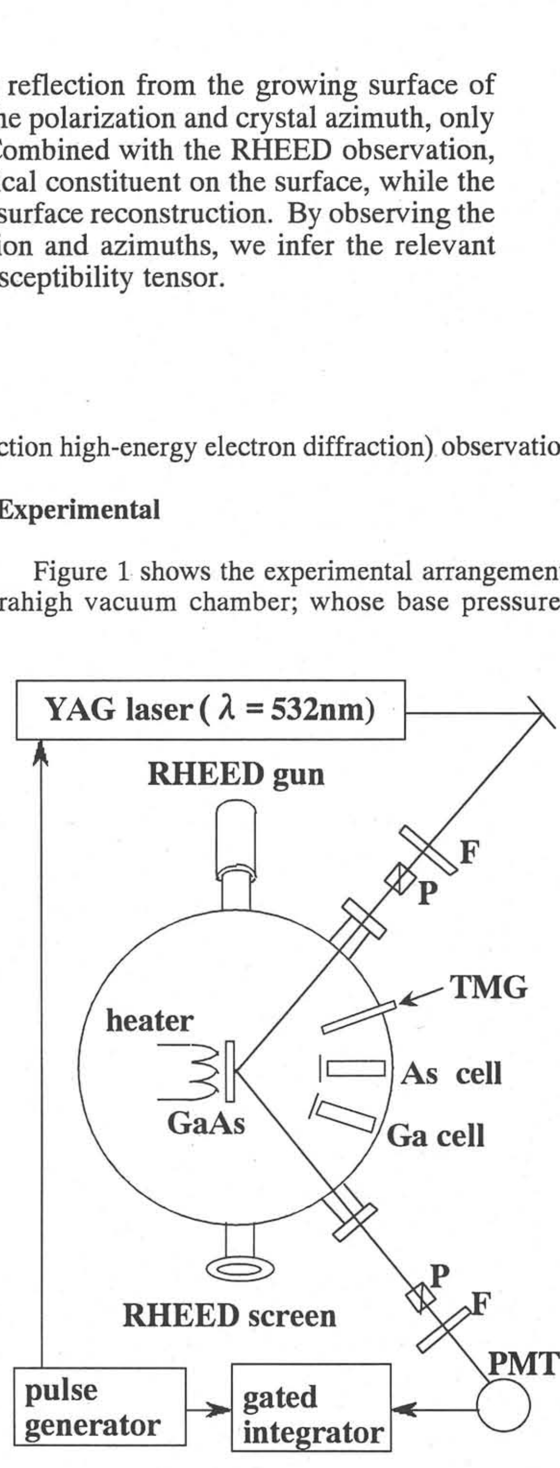

Figure 1. Experimental Setup

2×10^{-10} Torr when cryoshrouded with liquid nitrogen, and having source ports for metal Ga, As, and trimethylgallium (TMG), was used. Two fused-quartz windows allowed the inlet and outlet of a laser beam and SHG radiation lying in a horizontal plane. The RHEED gun was located so that the electron beam intersected with the optical plane at an angle of 45°; a fluorescent screen was located in the opposite direction. We used green (532 nm) light from a frequency-doubled YAG (yttrium aluminum garnet) laser (Quanta-Ray GCR150) as a light source, the output of which was set to about 10 mJ with a repetition rate of 10 Hz. After cutting off the fundamental and parasitic higher harmonic components with glass filters (Y45 and CM500), and passing through a polarizer, the laser light was introduced into the chamber so as to hit the surface of GaAs. The reflected second-harmonic light of wavelength 266 nm was detected using a solar-blind photomultiplier (R166) after passing it through a polarizer and a glass filter (U330). The output of the photomultiplier was fed to a gated integrator which was synchronously triggered with the YAG laser. The averaged output of the gated integrator (averaging number 30) was recorded with a pen chart recorder. The RHEED pattern was monitored with a CCD camera; the intensity of some fractional streak was recorded with the same pen recorder.

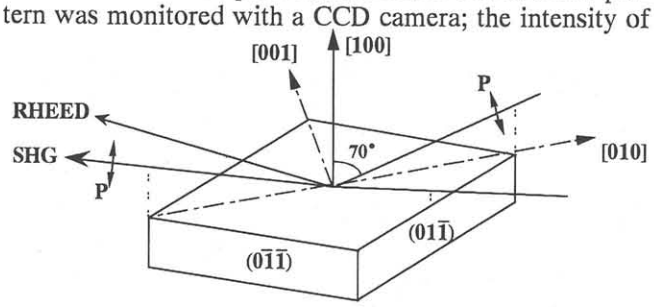

Figure 2. Optical Arrangement

Figure 2 shows the optical and RHEED arrangements. The GaAs sample studied was a silicon-doped, n-type, nominal (001) cut (±0.05°) single crystal with a carrier density of 1.5×10^{18} cm^{-3}. P-polarized light was directed in the <100> azimuth so as to hit on the (001) face with an angle of incidence of 70°. The SHG was also detected in the p-polarization. The electron beam of the RHEED gun was in the azimuths of either [110] or [1-10]. On the sample a fresh layer of GaAs was deposited homoepitaxially using TMG and solid-source As before the experiment.

3. Result and discussion

Figure 3 shows the time variation of the SHG signal and the RHEED intensity of a sample maintained at 510°C in an As atmosphere without Ga (TMG) supply. A period of about 2 minutes was inserted during which the As supply was turned off, inducing the surface to become a Ga-stabilized (3x1) structure. After again opening the As shutter, this Ga-rich surface returned again to the As-stabilized (2x4) reconstruction, mimicking the layer-by-layer growth in the alternate supply mode, or migration-enhanced epitaxy. The As flux was estimated to be

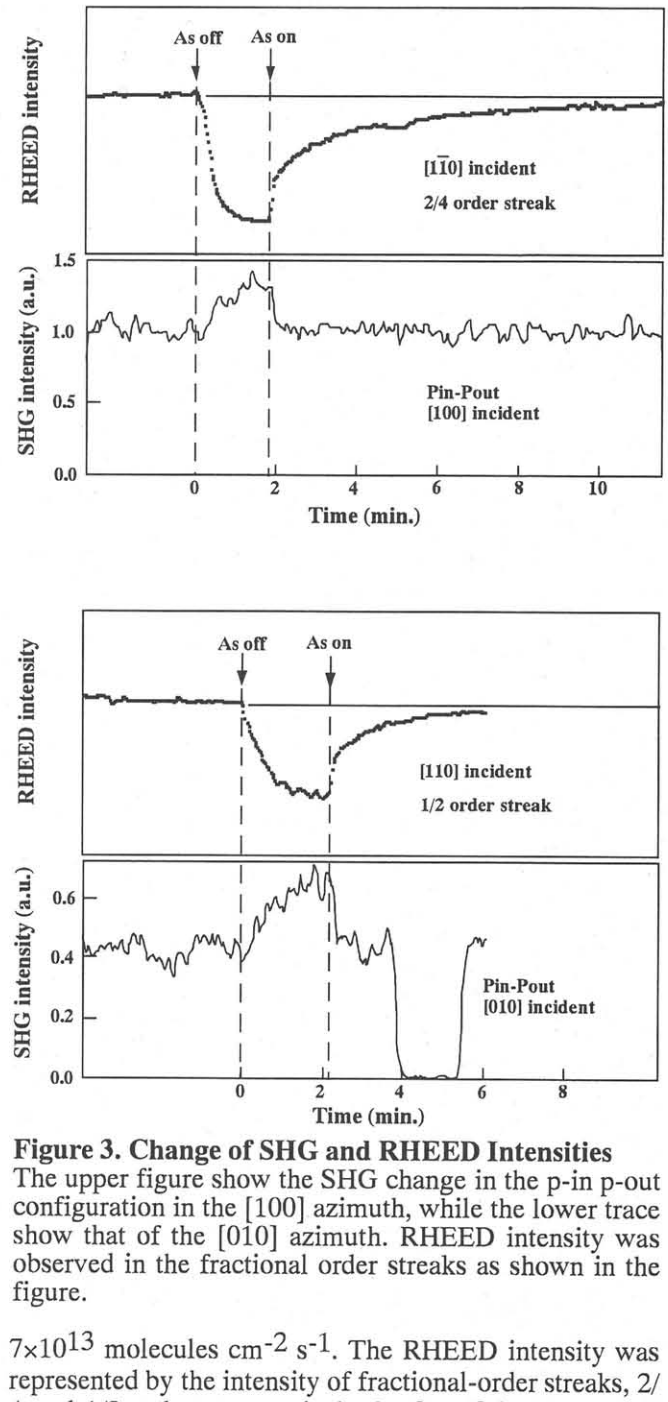

Figure 3. Change of SHG and RHEED Intensities
The upper figure show the SHG change in the p-in p-out configuration in the [100] azimuth, while the lower trace show that of the [010] azimuth. RHEED intensity was observed in the fractional order streaks as shown in the figure.

7×10^{13} molecules cm^{-2} s^{-1}. The RHEED intensity was represented by the intensity of fractional-order streaks, 2/4 and 1/2 orders, respectively for [1-10] incidence and [110] incidence.

In Fig. 3, it must be noted that the intensities of SHG in the [100] incidence and [010] incidence are different, showing an anisotropy in the steady states before time = 0 and after t > 2 min. As is seen in Fig. 3, in the off-period of As, the SH intensity increases, while the RHEED intensity decreases seemingly exponentially, corresponding to the As desorption. The RHEED pattern undergoes a change from 2x4 to 3x1. Although the signal-to-noise ratio (S/N) was poor regarding the SH intensity, the changes in the SH intensity and that of RHEED seem to be similar during this period. However, after a re-supply of As, distinguishing features are observed for the SHG and RHEED: the SHG returns to its steady state value immediately and the RHEED intensity recovers in two steps, fast recovery to about 1/3 of its original value and then a slow exponential recovery. Finally, the RHEED pattern goes back to 2×4. A similar slow recovery process corresponding to the migration period of GaAs molecules, or small islands on the As plane, has been extensively studied by Horikosi et al. [4] in migration-enhanced epitaxy, although they observed it in the specular reflection of RHEED. However, a restoration of the flatness of the surface, corresponding to the specular spot intensity, and the recovery of a long-range order, corresponding to the fractional streak intensity, can be considered to be correlated with each other. It is therefore concluded that SHG monitors the amount of excess gallium, while RHEED is a representative of the long-range ordering, provided that at the instance of As resupply the excess gallium rapidly makes bonds with As to form either GaAs molecules or islands. These molecules or islands would "migrate" on the surface to find a step or a kink in order to stabilize; eventually a long-range order is established and a flat surface is restored.

Finally, we describe the SH intensity changes which take place in other configurations. Table I summarizes the results. In this table the entry "Bulk Allowed" does not necessarily mean that SHG is only due to the bulk component. The interference effect described in ref. 2 makes these components to contain surface contributions. It is readily seen that the overall symmetry remains C_{2v}, because we did not observe any change in P-in S-out configuration in x [100] or y [010] azimuths. This also means that the surface tenstor element ξξz = ηηz does not change, due to the on-off of the As. In τηε ξ [110] and η [1-10] azimuths, the SH intensity change is opposite in sign, i.e. the P-in P-out intensity decreases in τηε ξ azimuth and decreases in τηε η azimuth, and S-in P-out decreases in τηε ξ azimuth and increases in τηε η azimuth. This leads to a suggestion that the relevant surface tensor element would be zξξ - zηη. (Here we followed the convention of listing only the suffix for the surface susceptibility tensor elements . [5])

Table I. SHG Changes during As-off Period

Azimuth	Polarization	Selection Rule	Change
x [100]	P-in P-out	Surf. Specific	Increased
"	P-in S-out	Bulk Allowed	No change
ξ[110]	P-in P-out	Bulk Allowed	Increased
"	S-in P-out	Bulk Allowed	Decreased
y [010]	P-in P-out	Surf. Specific	Increased
"	P-in S-out	Bulk Allowed	No change
η [1-10]	P-in P-out	Bulk Allowed	Decreased
"	S-in P-out	Bulk Allowed	Increased

4. Summary

We observed surface reflection SHG from the GaAs crystal to which the supply of As was interrupted. The surface-specific, as well as bulk-surface interference components of SHG changed during the off period of As, and returned to their original value immediately after the resupply of As.. The results were interpreted in terms of the structural change of the surface, in relation to "migration-enhanced" epitaxy.

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