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In situ Observation of Superstructures on Epitaxially Grown Semiconductor Surfaces under Hydrogen Atmosphere

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To analyze surface structures and growth mechanisms in gas-phase epitaxy, we developed an in situ x-ray diffractometer for the metalorganic chemical vapor deposition (MOCVD) that combines a goniometer and reactor chamber. Consequent measurements of P-rich InP(001) surface grown by MOCVD shows the surface has a (2×1) structure. Calculation based on a P-dimer model suggest that this structure is composed of P-dimers whose bonding is parallel to the $[\bar{1}10]$ direction and indicates indium displacement in the second layer.

Key words: gas-phase growth, metalorganic gas, MOCVD, surface, X-ray diffraction

1. INTRODUCTION

Owing to the high throughput and uniformity of the epitaxial films, metal organic chemical vapor deposition (MOCVD) is used to fabricate III-V based semiconductor devices for the high speed telecommunications and optical device applications. To obtain devices of good quality, a fundamental understanding of crystal growth is still important. However, owing to the large absorption of the electron beams in a gas environment, it is difficult to use ordinary electron-based techniques, such as reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED) to evaluate surface structures. To investigate growth procedures, traditionally, optical techniques, for example, reflectance anisotropy measurement (RAS/RDS) and surface photoabsorption (SPA), have been used[1, 2]. These techniques use the anisotropic absorption of the bonding of atoms and molecules on the surface [3–5]. However, the wavelength is longer than atomic bondings, it is still difficult to investigate surface structures in the angstrom region.

Recently, x-ray diffraction technology has been applied for surface structure analysis in the gas-phase environment [6]. This technique provides information related to the long-range periodicity on the surface, similarly to RHEED/LEED. It complements optical techniques, such as RDS and SPA, which allow us to observe the localized chemical state on the surface. Additionally, as in the traditional crystal structure analysis, surface x-ray diffractions can be treated with kinematical scattering theory, which makes it possible to determine atomic structures without any assumptions. In this work, we investigated a P-rich InP(001) surface prepared by MOCVD in an atmospheric hydrogen environment.

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2. BASES

The surface structure analysis by x-ray diffraction was firstly applied to a GaAs-Al interface in 1979 by Marra and Eisenberger [7], and that two years later applied to investigate Ge(001) surfaces [8]. Since the number of atoms for x-ray scattering on surfaces is smaller than in bulk crystal, highly bright x-ray sources are necessary in order to obtain sufficient signals, and synchrotron radiation sources have been mainly used for this purpose [9–13].

Figure 1 shows a typical arrangement of surface x-ray diffraction, where α and β are the incident angle and reflected angle from the surface, and θ and 2θ are the rotational angles of the samples and detector. For surface x-ray diffraction, small α and β are used ($\sim 0.2°$) and the scattering vector Q should be parallel to the surface, which makes it possible to investigate laterally ordered structures, similarly to RHEED. Additionally, at grazing incident angles, penetration lenghths of x-rays are very small in a total reflection region. This feature reduces x-ray scattering from bulk crystal and results in a relatively low background noise to the signals.

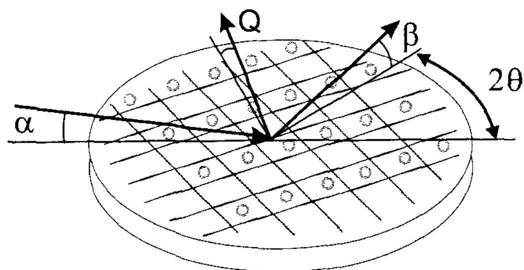

Figure 1. Layout for surface x-ray diffraction

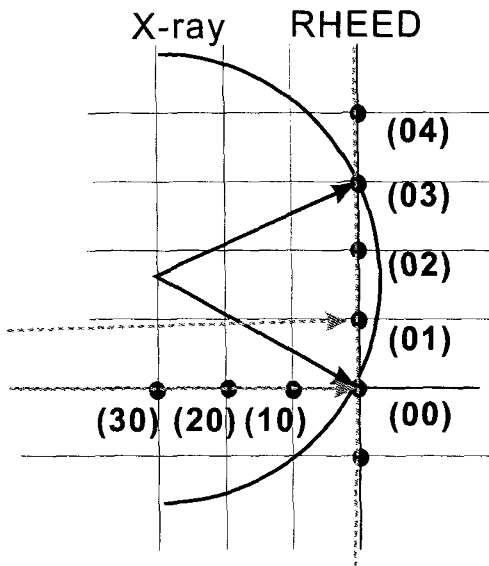

Figure 2 Ewald spheres for x-rays and electrons in reciprocal space.

Figure 2 shows Ewald spheres for surface x-ray diffraction and RHEED. Since the Ewald sphere of electrons can be treated as a flat plane, electron diffractions occurred at several lattice points, and the multiple scattering effect should be considered when interpreting the intensity of the diffractions. In contrast to electron diffractions, x-ray diffractions can only occur at one lattice point at the same time, and this enables a highly quantitative intensity measurement for accurate determination of surface structures. Additionally, x-ray diffraction can be treated as a framework of single scattering theory, and this makes it easier to determin surface structures.

3. EXPERIMENTAL

To satisfy the requirements for both x-ray diffraction measurement and MOCVD epitaxial growth, we developed a goniometer system combined with a reactor chamber. Figure 3 is a schematic drawing of the z-axis goniometer and material gas delivery system. Precise details are described elsewhere [14]. Since atomically flat surfaces are necessary for x-ray measurement, the MOCVD system was carefully designed to achieve an industrial quality epitaxial growth, which is sufficient for x-ray measurement. All instruments were set up at the BL24XU experimental station of the SPring-8 synchrotron facility to obtain an x-ray source with high brilliance.

The InP epitaxial growth was performed in the reactor chamber set on the goniometer using trimethylindium (TMI) and tertiarybutyl phosphine (TBP) for group III and V elements, respectively. Just-oriented InP (001) Fe-doped semi-insulating, epi-ready wafers were used as substrates. A 0.12-μm InP layer was formed in 15 minutes under the following conditions: 550°C, 76 Torr of hydrogen, 3.2×10^{-6} of TMI, and 2.9×10^{-4} mol/min of TBP (V/III ratio of 90.6). After the supply of TMI was stopped, the substrate was cooled with the TBP flow maintained until the substrate reached 300°C. The substrate was then annealed at 350°C for 1 hour in a hydrogen environment to desorb excess phosphine atoms and alkyl species.

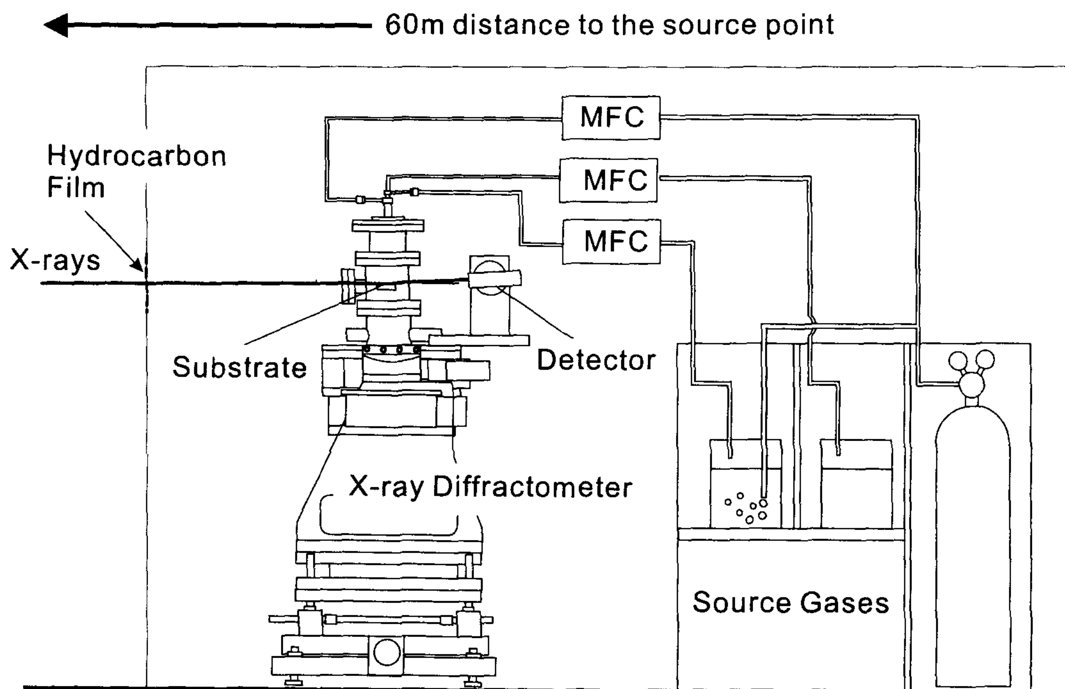

Fig. 3. Schematic view of the z-axis x-ray goniometer and gas source delivery system. All equipment is set in a

cabinet whose internal pressure is kept lower than the atmospheric pressure.

Film quality was checked by atomic force microscopy (AFM) after growth. Figures 2(a) and (b) show AFM images of the center and edge of the substrate. Large terrace structures with no islands are observed in both images. Additionally, weakly parallel ridges along [110] are also observed. Note that these ridges also appear on the circumference of the substrate, suggesting long-range uniformity over the whole wafer. The step height of each terrace is about 0.29 nm, which corresponds to a mono-layer height of InP (001) crystal, indicating an atomically flat surface, which is required for the surface x-ray diffraction measurement.

After annealing, the surface structure was evaluated using grazing incidence x-ray diffraction under a 31 Torr H_2 flow [2]. X-ray diffractions of $\frac{1}{2}(\bar{2}20)$ and $\frac{1}{2}(220)$ in reciprocal space were used as unit vectors (10) and (01) for the surface structure, respectively. To reduce the background noise from bulk crystals, incident angles of x-rays were set to the critical angle of InP crystal, around 0.2 degrees. Because of the small divergence of the synchrotron source, the irradiated area on the wafer was about 6 mm along the x-rays and 1 mm perpendicular to the x-rays. During measurement, we used 0.06-nm x-rays, which correspond to the second peak of the undulator source at the BL24XU beamline. Upstream of the goniometer, the x-rays were monochromatized by (220) reflection of a set of diamond crystals and collimated as 0.1 mm (V) and 1.0 mm (H) with x-y slits. To eliminate the first-order x-rays and scattering from the paths, a 0.5 mm aluminum sheet was set at the entrance port of the experimental hutch. A NaI detector and a solar slit with 0.2 degree divergence was used to detect Bragg diffractions from the surface structures. Typical measurement time was 15 min for each diffraction point, and the measured area in reciprocal space ranged from (0 0) to (2 2), owing to the limited beamtime.

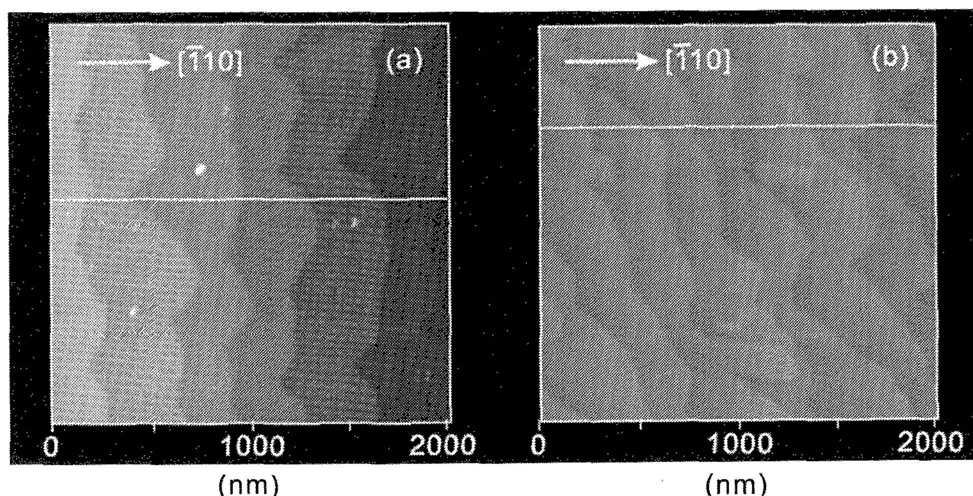

Fig. 4. (a) AFM image of the center of InP (001) grown by MOCVD. The thickness of the epitaxial layer is 0.12 μm. (b) AFM image of the edge of an InP substrate. Weakly parallel ridges along [110] are observed in both images. The step height along the white lines in the images is about 0.29-nm, which corresponds to a mono-layer height of InP (001) crystal, indicating that the grown surface is of high quality.

4. RESULTS AND DISCUSSION

Figure 5 shows relative x-ray intensity for each reciprocal lattice point. Bragg diffractions with 1/2-th order along the (1 0) direction were observed with no fractional order diffraction along the (0 1) direction, suggesting that the InP(001) surface was mainly composed of a (2×1) structure. Additionally, no 1/4-th order diffraction along the (1 0) and (0 1) directions was observed, indicating no extra domains of (2×4)/c(2×4), which are detectable by x-ray diffractions. The x-ray intensity from the structure did not change during the one-day measurement time, which means this (2×1) structure is very stable. The domain size along the (1 0) direction was estimated to be more than 40 nm from the FWHM value of the (3/2 0) diffraction. This value is smaller than the terrace width and length, suggesting independent (2×1) domains on these terraces.

[2]Note that providing a highly purified H_2 flow is required to avoid unexpected changes of the surface structure in UHV environment and contaminations form the environment.

Considering the atomic structures of V-element terminated surfaces, such as As-rich GaAs(001), one possible model is the buckled P-dimer structure shown in Fig. 6. The lack of intensity on some lattice points, for example, (3/2 1), can be explained by the internal atomic re-arrangement in the (2×1) unit cell. This assumption is supported by the calculated structure factors of the (2×1) structure. From a comparison with the calculated and measured structure factors [15], the displacement of P atoms and In atoms was estimated to be about 20% and 2%, respectively.

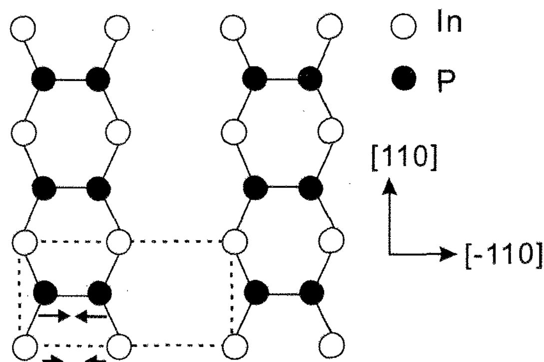

Fig. 6. Schematic model of the (2x1) structure. P and In atoms shifted about 20% and 2% along the arrows.

5. CONCLUSION

In conclusion, the properties of a P-rich InP (001) surface prepared by MOCVD and annealed at 350°C in H_2 were investigated using an in situ x-ray diffractometer that combines a goniometer and reactor for MOCVD growth. The results revealed (2×1) domains on the reconstructed InP(001) surface in the hydrogen atmospheric environment. The domain size obtained from the FWHM values of surface Bragg diffractions is smaller than the terrace width and length, suggesting multiple domains on the terrace structure. A comparison of the observed and calculated structure factors indicates the existence of P-dimers and indium atom displacement.

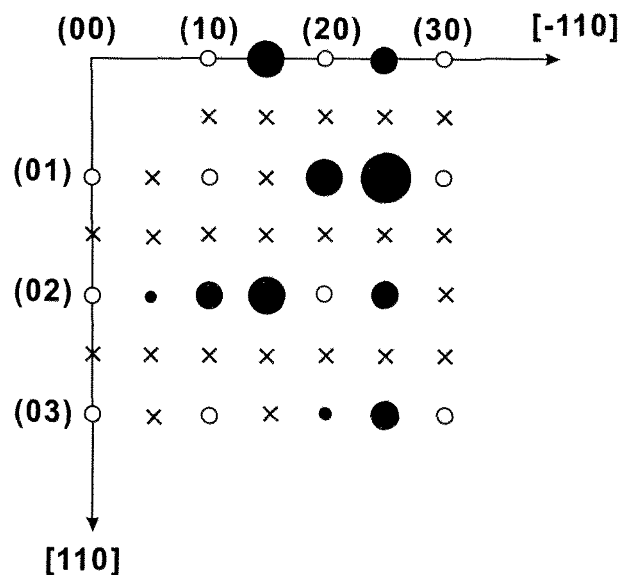

Fig. 5. Intensity of fractional Bragg reflection for each reciprocal lattice point. Open and filled circles indicate reflections from bulk crystal and the surface structure, respectively. At the cross points, no clear reflections were observed.

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