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Grazing Incidence X-ray Reflectometry: A Tool For Monitoring Growth Procedure In Nano-meter Scale

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Grazing incidence x-ray reflectometry was applied for monitoring the initial stage of indium phosphide epitaxial growth in gaseous environment. A change of reflectivity with various flows of phosphorous source suggests that reflectivity intensity has dependence on the thickness of adsorbing phosphorous layers. Changes of reflectivity were also monitored before and during the growth process under various growth conditions, such as substrate temperature and quantity of material sources. From the changes of reflectivity at beginning of growth, adsorbing phosphorous layers still exist at the initial stage at low temperature, which was not observed at high temperature growth.

Key words: grazing incidence x-ray reflectivity, vapor-phase growth, MOCVD, InP

1. INTRODUCTION

Grazing incidence x-ray reflectometry is known as a tool for evaluating thin film structures, such as semiconductor, magnetic materials, and organic thin-films. This technique provides several information about layer thickness, density in each layers, and imperfections at surfaces and interfaces. It has also been applied to analyze organic structures on substrates [1], and extended to self-organized single molecules on water [2]. Owing to the recent development of highly bright x-ray sources, it has become possible to also evaluate clean surfaces of metal and semiconductor materials in an ultra high vacuum [3], and changes of morphology, step-terrace structures and several surface structure characteristics have been revealed.

However, this technique has rarely been used for surfaces in gaseous environment due to the difficulty of combining an x-ray diffractometer and growth system. For vapor-phase epitaxy growth, using ordinary electron-based techniques, such as reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED), is very difficult due to the large absorption of the electron beams. Optical techniques such as reflectance anisotropy measurement (RAS/RDS) and surface photoabsorption (SPA), have also been used [4, 5] for evaluating the growth procedure. These techniques use the anisotropic absorption of the bonding of atoms and molecules on the surface [6, 7, 8], and can reveal local chemical conditions on surfaces. However, since the wavelength is longer than atomic bondings, it is difficult to investigate surface structures in the angstrom region.

To overcome these problems, we developed a grazing incident x-ray reflectometry system that combines an x-ray goniometer and metalorganic vapor phase epitaxy apparatus. Figure 1 illustrates the idea schematically. Most of the x-rays are impinged upon the substrate at the grazing incidence condition, and reflected, scattered and diffracted x-rays are collected at both grazing angle and higher exit angles. These measurement can be performed before, during, and after the growth procedure, and much information related to the crystal growth can be obtained, including surface structures of InP(001) [9] and several growth modes using reflectivity [10, 11]. In this paper, we report our study of the initial stage of InP epitaxial growth.

2. INSTRUMENTS

To satisfy the requirements for both the growth system and x-ray measurements, a z-axis goniometer [12] was selected for gas-phase growth. With this arrangement, the surface normal does not changed during the measurement and gas-flow patterns to the surface are maintained, which is very important for good growth. Additional movement of scattering vectors in the reciprocal space is carried out by moving the detector stage along the vertical and horizontal direction

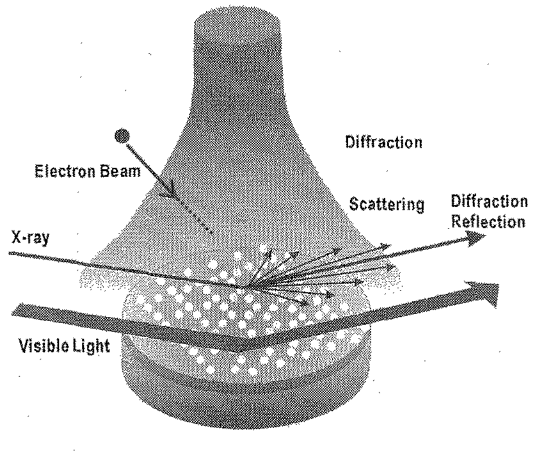

Fig. 1. Schematic layout of x-ray reflectivity measurement in gaseous environment.

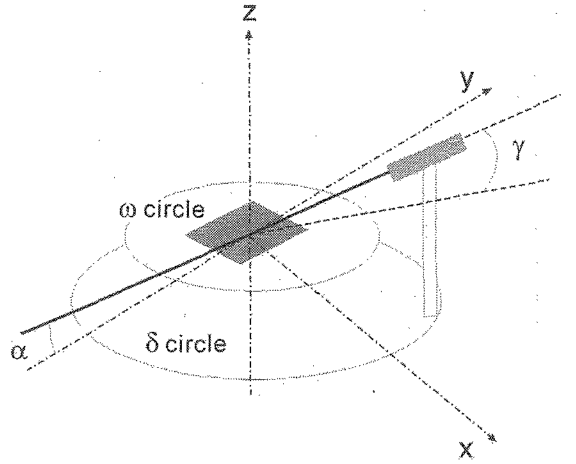

Fig. 2. Schematic geometry of a z-axis goniometer.

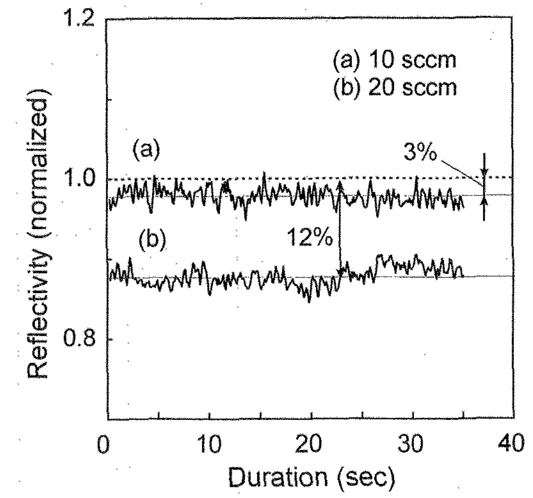

Fig. 3. Change of reflectivity with TBP = 10 sccm and 20 sccm.

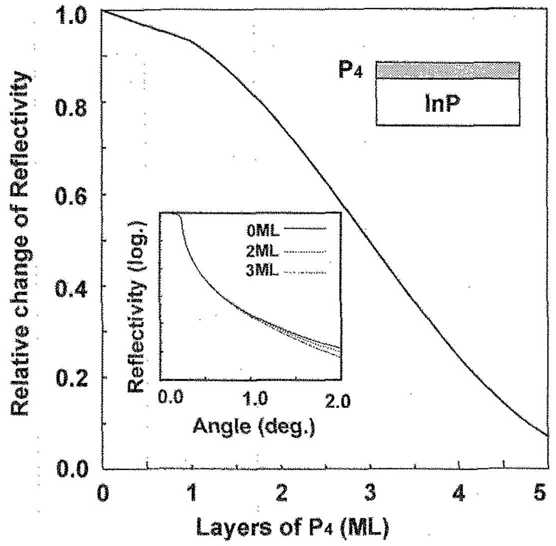

Fig. 4. Calculated reflectivity with various conditions.

independently.

The z-axis goniometer has four axes movement similar to a conventional four-axes diffractometer but movement of some axes are different. Figure 2 shows a schematic drawing of the z-axis goniometer. In this geometry, two axes, ϕ and χ, are omitted and additional axes, α and β, are introduced. Although there are some limitations on the movement, most of the range in reciprocal space is covered. The detailed geometry and movement for the z-axis arrangement are described in ref. [13].

The reactor chamber was designed to satisfy the condition for both epitaxial growth and x-ray measurement. The chamber was set on the ω stage and connected with the δ stage by fixing plates. The rotation of the sample stage, which was also set on the ω stage, is isolated from the reactor chamber by inserting a double-sealed rotary flange between the reactor chamber and ω stage. Beryllium foils of 0.5-mm thickness were used as the window material for the incoming and outgoing x-rays. All parts of the chamber, including the window flanges, are water-cooled to prevent the windows breaking during sample heating.

3. EXPERIMENTAL

All experiments were performed in the x-ray goniometer installed at the BL24XU beamline of the SPring-8 synchrotron facility. Details of the instrument are described elsewhere [14]. Before the x-ray measurement, an InP homo-epitaxial layer was grown on (001) substrates using tertiarybutylphosphine (TBP) at room temperature and trimethylindium (TMI) at 25 °C as precursors. Details of the experimental procedure for MOVPE growth are also described in Ref. [14].

After forming buffer layers, x-rays were introduced into the reactor chamber and the intensity of reflected x-rays was measured while varying the growth conditions. X-ray beams of 0.124 nm wavelength were introduced on the surface at 1.2° and 1.9° from the surface. An ion chamber was used for monitoring incident x-ray intensity, and a scintillation (NaI) detector with vertical 150 and 300 micrometer slits was used. The direction of x-ray beams was [110], which suppresses the effect of atomic steps on the surface. The change of reflectivity was measured during various growths while varying substrate temperature and the TBP and TMI flow. After each x-ray measurement, the substrate was annealed in a TBP flow until the reflectivity recovered to its initial value.

4. RESULTS AND DISCUSSION

Figure 3 shows the x-ray reflectivity at $\alpha = 1.9°$ with TBP flows of 10 and 20 sccm and substrate temperature (Ts) of 400°C. All data were normalized by the reflectivity just after the formation of the buffer layer. A decrease of reflectivity was observed when TBP flow was increased at 20 sccm. Since the increase of TBP is believed to flatten the surface of substrates, increased surface roughness should not be the reason for this intensity decrease. The reason is therefore thought to be the reflectivity change due to the change of the thickness of adsorbing phosphorous layer.

To check this possibility, theoretical reflectivity of P_4/InP was calculated for several P_4-layer thicknesses. Figure 4 shows the change of reflectivity at 1.9°. The inset shows the calculation model and incident angle

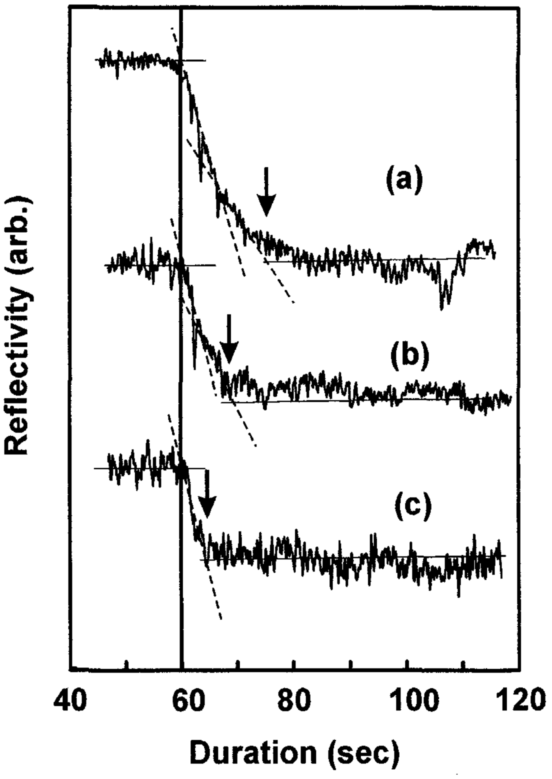

Fig. 5. Changes of reflectivity with various growth conditions.

dependence of reflectivity with varying P_4-layer thicknesses from 0 to 3 ML. At the incident angle of 1.9°, reflectivity was very sensitive to the thickness of P_4 layers, although changes of reflectivity were very small at smaller incident angles. When 2 ML P_4 is adsorbed, reflectivity decreases about 20%, which is consistent with the observation. It should be noted that the absolute thickness and density of the phosphorous layer was not confirmed since structures of phosphorous layer were unknown. These results suggest that phosphorous overlayers of some MLs are formed at lower temperature, and the thickness of these layers depends on the TBP flows.

Figure 5 shows changes of reflectivity with (a) Ts = 400 °C, TBP = 5 sccm, TMI = 20 sccm, incident angle α = 1.2°, (b) Ts = 400 °C, TBP = 25 sccm, TMI = 20 sccm, α = 1.2° and (c) Ts = 500 °C, TBP = 25 sccm, TMI = 100 sccm, α = 1.9°. The vertical line at 60 sec indicates the start of growth.

Since reflectivity is very sensitive to surface morphology, the change of reflectivity corresponds to roughening and flattening of the surface, which are caused by the formation and disappearance of small islands on the substrate. At Ts = 400 °C and Ts = 500 °C, rapid decreases of reflectivity were observed at the beginning of the growth, suggesting degradation of surface morphology due to the formation of small islands. Additionally, a different tendency in reflectivity changes was observed between Ts = 400 °C and 500 °C. At Ts = 400 °C, two contributions, indicated as broken lines in (a) and (b), were observed at the initial stage. This was more clearly observed at the small TBP flow of 5 sccm in the figure (b). In contrast with these results, only one composition was observed in the transition region at Ts = 500 °C.

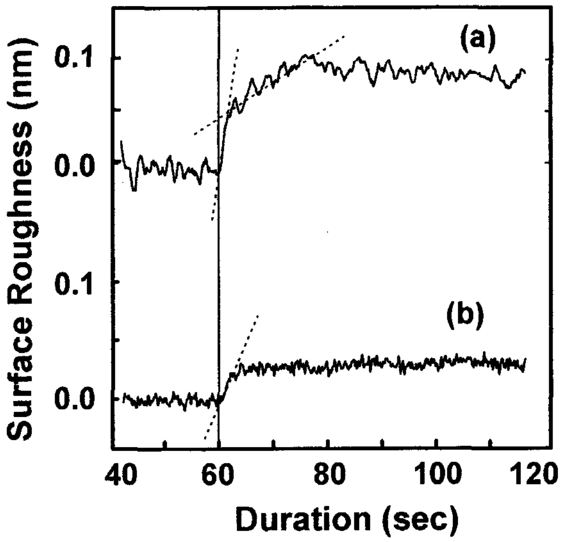

Fig. 6. Changes of surface roughness during growths.

This is more clearly shown in the change of surface roughness which was calculated from the reflectivity using the Debye-Waller factor. Figure 6 shows the change of roughness during the growth at (a) Ts = 400 °C, TBP = 5 sccm, TMI = 20 sccm, incident angle α = 1.2° and (b) Ts = 500 °C, TBP = 25 sccm, TMI = 100 sccm, α = 1.9°. Surface roughness at Ts = 400 °C was estimated to be about 0.1 nm, and that at Ts = 500 °C was less than 0.05 nm. Considering that 1 ML of InP is about 0.29 nm, this change of roughness can be explained by the formation of small islands with a height of less than 1 ML. At Ts = 500 °C, surface roughness monotonically increased within about 5 seconds after the start of growth, and remained constant thereafter. However, roughness at Ts = 400 °C rapidly increased after the start of growth, and gradually increased over a period of several ten seconds, and then leveled off.

Considering the formation of phosphorous overlayers, this can be explained qualitatively by different growth modes at the initial stage. Figure 7 shows the growth models for the initial stage at low and high temperature. At high temperature, the thickness of phosphorous overlayer should be small due to the high desorption rate of phosphorous molecules. In this case, extraneous phosphorous on the substrate is immediately consumed by the formation of small islands after the start of growth, which explains the rapid decrease of reflectivity. After all adsorbed phosphorous molecules are extinguished, an equilibrium state between provision and consumption of indium atoms is reached, and surface morphology does not change. At low temperature, the quantity of additional phosphorous is larger than that at high temperature. At the beginning of the growth, both the formation of small islands and thinning of phosphorous layer occur, resulting in the rapid decrease of reflectivity. In this case, the probability that large islands are formed is higher due to the excess phosphorous overlayers, which would explain the large surface roughness at lower temperature. After the phosphorous overlayer is consumed, the equilibrium state is again reached.

5. CONCLUSION

In conclusion, we performed real-time x-ray reflectivity measurements during MOVPE indium-phosphide growth. At 400 °C, a change of reflectivity was observed with varying TBP flow, suggesting a change of phosphorous overlayer. Changes of reflectivity during growth were also observed at 400 and 500 °C. At Ts = 400 °C, two-stage decreases of reflectivity were observed, suggesting the formation of small islands and degradation of surface morphology. At 500 °C, a monotonic decrease of reflectivity was observed, which was different from the case at low temperature.

Considering the existence of phosphorous overlayers, this is qualitatively explained by a different growth mode at the initial stage. At high temperature, the effect of phosphorous overlayers was small, and ordinary growth occurred after rapid consumption of extraneous phosphorous layers. When the substrate temperature was low, phosphorous overlayer thickness was large, and initial growth has two stages. After the start of growth, large islands were formed using thicker phosphorous overlayers, resulting in the rapid decrease of reflectivity. When the thicker phosphorous layer was consumed, decrease of reflectivity became slower, and reached in the equilibrium state.

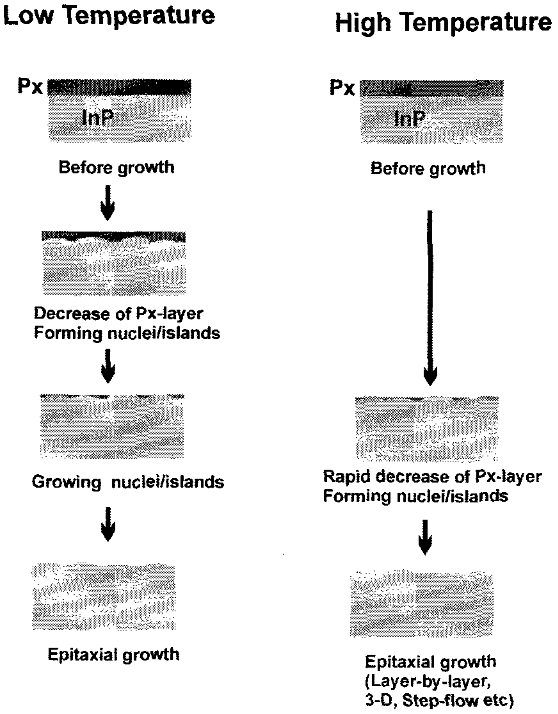

Fig. 7. Growth model at the initial stage for low and high temperature.

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