

X-ray photoelectron spectroscopy studies of initial growth mechanism of CdTe layers grown on (100)GaAs by organometallic vapor phase epitaxy

Syuji Sone, Mitsuru Ekawa, Kazuhito Yasuda, Yoshiyuki Sugiura, and Manabu Saji
*Department of Electrical and Computer Engineering, Nagoya Institute of Technology, Gokiso-cho,
Showa-ku, Nagoya 466, Japan*

Akikazu Tanaka
*Electronics Materials Laboratory, Sumitomo Metal Mining Co., Ltd., Suehiro-cho, Ohme-shi,
Tokyo 198, Japan*

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Variations of the GaAs surface conditions and the adsorption of the precursor elements of Cd and Te on the (100)GaAs substrate were studied by x-ray photoelectron spectroscopy at the initial stage of CdTe growth by organometallic vapor phase epitaxy. The stoichiometry of GaAs substrates was found to recover by annealing in the H₂ environment (500 °C, 5 min), while the surface was initially in an As-rich condition after etching with H₂SO₄:H₂O₂:H₂O (5:1:1). The preferential adsorption of Te on the GaAs surface was also observed. <100> oriented growth was obtained routinely when the GaAs surface was fully stabilized with Te after the H₂ anneal under the above conditions. <111> oriented growth resulted when dimethylcadmium was first introduced after the anneal.

Heteroepitaxial growth of Hg_{1-x}Cd_xTe (MCT) on GaAs substrates has been studied extensively for the possible use as high performance infrared detectors with large scale integration on a mechanically firm substrate. Despite all the above promising features, there remain several basic problems to be overcome for practical applications. The control of growth orientations is one of the tasks. It has been known in the epitaxial growth of MCT on GaAs that growth can proceed in two different orientations of <100> and <111> because of the large lattice mismatching between the grown layer and the substrate. Several mechanisms for this phenomenon have been proposed that were mainly based on the results in molecular beam epitaxy (MBE).¹⁻⁵ For organometallic vapor phase epitaxy (OMVPE), on the other hand, although a similar phenomenon has been observed, little has been studied, and some contradictions still remain in understanding the growth mechanisms.⁶ In OMVPE, the initial growth mechanism may be different from MBE, because the growth proceeds in a deoxidizing gas environment (H₂) and the growth is accompanied by a chemical reaction of the precursor. To understand this mechanism, we studied the variations of surface structures of GaAs substrates at the initial stage of CdTe growth by using x-ray photoelectron spectroscopy (XPS).

CdTe growths were carried out in a low-pressure OMVPE system operating at 60 Torr. The organometals used were diethyltelluride (DETe) and dimethylcadmium (DMCd), which were supplied from bubbler containers. Pd-diffused hydrogen was used as a carrier gas, and the total flow rate was controlled to be 1 ℓ/min during growth. The growths were conducted on <100> oriented GaAs substrates at a temperature of 420 °C.

The growth process was as follows: The (100)GaAs substrates were etched by H₂SO₄:H₂O₂:H₂O (5:1:1) for 5 min just before loading in the reactor. As a pretreatment for growth, the etched GaAs substrates were annealed in a hydrogen flow at 60 Torr at 500 °C for 5 min. At the end of this annealing, one of the organometals was introduced into the

reactor and this was kept flowing while the substrate was cooled from the annealing temperature of 500 °C to the growth temperature of 420 °C. As will be shown later, the first introduced reactant is a key to controlling the growth orientation. The CdTe growths were started by allowing the rest of the organometal to flow in. The feed mol ratio of DETe to DMCd was set to be 4, where the DMCd feed rate was fixed at 2 × 10⁻⁵ mol/min. The growth durations were 1-3 h.

The XPS measurements were carried out by using an SSX-100 system from Surface Science Instruments, which operated with a monochromatic Al K_α x-ray source at a base pressure of 1 × 10⁻¹⁰ Torr. Since the specimens were exposed inevitably to the laboratory atmosphere for a few tens of seconds to a few minutes during transportation from the growth cell to the analyzing chamber, careful sputter cleaning by Ar⁺ ions was needed to remove the adsorbed oxygen and carbon without changing the structure of the surface. The sputter cleaning procedure was optimized during a series of preliminary experiments, and was fixed through this experiment to be (30 s at 3 keV). Surface observations were carried out after each step of the above pretreatment and also after exposure to each organometal. To observe the effect of the H₂ anneal on the GaAs surface structure, the anneal was also carried out in a cleaned quartz cell where no CdTe deposit existed. The orientations of the grown layer were examined by x-ray Laue back reflection photography.

Prior to examination of the GaAs surface structures after processing in the reactor, the GaAs surfaces after etching and annealing in H₂ environment were studied. Figure 1 shows the results, where (a) is the XPS spectrum of a GaAs substrate after the chemical etch with the H₂SO₄ etchant and (b) is the spectrum after annealing in a hydrogen environment in the clean quartz cell. In the same figure, (c) is the spectrum from a sputter-cleaned surface which is considered to represent the stoichiometric GaAs surface. The integrated signal count ratios of As 3p to Ga 3s for these three cases are also shown in the figure. Although no obvious chemical

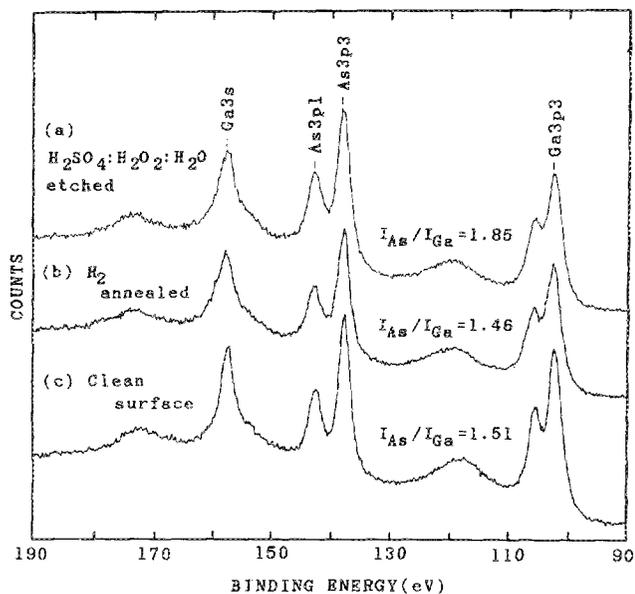


FIG. 1. XPS spectra from the Ga 3p to the Ga 3s region of GaAs surfaces, I_{As}/I_{Ga} shows the signal count ratio of the As 3p to the Ga 3s region: (a) etched by H₂SO₄:H₂O₂:H₂O, (b) H₂ annealed in a clean quartz cell after etching, and (c) sputtered after etching.

shift could be found among those spectra, variations were observed in the integrated signal count ratios of As to Ga. The chemically etched surface showed a higher As to Ga ratio than that of the sputtered surface. This indicates that the GaAs surface is in an As-rich condition after etching using a H₂SO₄ etchant, which agrees with a previous report.³ In contrast to this, when the H₂ anneal was carried out after etching in the H₂SO₄ etchant, the As to Ga ratio recovered to a value similar to that of the sputtered surface. This indicates that the deviation of the surface stoichiometry is recovered to the stoichiometric condition by annealing in a H₂ environment. A similar effect of H₂ annealing on the recovery of surface stoichiometry has been observed on the CdTe surface.⁸ The recovery of GaAs surface stoichiometry indicates that the growth starts on a stoichiometric GaAs surface in OMVPE when the anneal is carried out just before growth.

Once the organometal has been introduced in the reactor following annealing in the reactor, interesting features of adsorption were observed. Figure 2 shows the results, where (a) is the spectrum obtained after annealing in the reactor, and (b) and (c) are the results after exposing to the DETe and the DMCd during the cooling period, respectively. In the figure, the spectrum of GaAs surface annealed in the clean quartz cell is also shown as (d).

When the H₂ anneal has been carried out in the reactor, adsorbed Te was found on the GaAs surface. This Te was considered to come from decomposition of the residual CdTe deposit in the reactor. In contrast to this, no adsorption of Cd could be observed on the same surface. This indicates that Te rather than Cd is adsorbed preferentially on the GaAs surface.

When the annealed surface was exposed to DETe, an increase of the Te signal was observed. The thickness of adsorbed Te layers was estimated to be a few monolayers from the Auger signal intensities of Ga(LMM) and As(LMM)

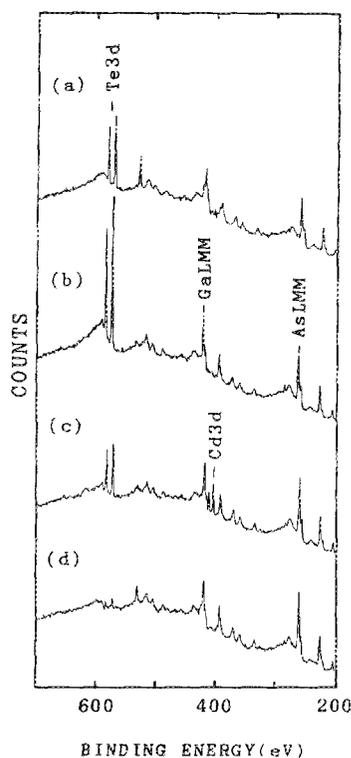


FIG. 2. XPS spectra of GaAs surfaces: (a) H₂ annealed in the reactor, (b) exposed to DETe after H₂ anneal, (c) exposed to DMCd after the anneal, and (d) H₂ annealed in a clean quartz cell after etching.

lines. Since the amount of DETe introduced during this period was enough for the growth of about 130 nm of CdTe layer if the DMCd was allowed to flow in, and the pyrolysis of DETe occurred efficiently during the cooling period,⁷ the GaAs surface was considered to be stabilized completely by the Te layer. It should be noted that although there was an excess of DETe, the accumulation of Te did not occur successively on the Te-stabilized surface.

In contrast to this, when DMCd was the first introduced reactant after the anneal, Cd could be observed on the surface. However, the intensity of Cd was less than that of adsorbed Te which came from residual CdTe as shown in Fig. 2(a). The amount of adsorbed Te in this case was smaller than that shown in (a); this was considered due to a decrease of the CdTe deposit in the reactor. These results indicate that Cd is hard to adsorb on the GaAs surface, and only a little can adsorb on the Te-adsorbed surface. Since the stoichiometric CdTe shows the intensity ratio of Cd 3d_{5/2} to Te 3d_{5/2} to be 83%,⁸ the amount of adsorbed Cd is apparently insufficient to form CdTe with adsorbed Te. When DMCd was introduced first, localized adsorption of Te occurred on the GaAs surface, and a small amount of Cd adsorbed on that surface.

CdTe growths were carried out by changing the introduced reactant just after the anneal. Interesting variations of growth orientation were observed there. When the DETe was introduced first, the x-ray Laue back reflection patterns showed that the grown layers were always <100> orientation. In contrast to this, when the DMCd was introduced first, the grown layers became either <111> oriented or <100> oriented layers with <111> regions. The surface mor-

phology of the $\langle 111 \rangle$ growth region was similar to that grown on a CdTe(111) *A* substrate, which showed three-dimensional growth characteristics with double positioning type twins.⁹ These results indicate that the orientation of the grown layers depends on the properties of the adsorbed element on the GaAs surface. $\langle 100 \rangle$ growth is obtained when the GaAs surfaces are fully stabilized by Te. This can be explained by formation of $\text{Te} \left\langle \begin{smallmatrix} \text{Ga} \\ \text{Ga} \end{smallmatrix} \right\rangle \text{Te} \text{---} \text{Te} \text{---} \text{Te} \left\langle \begin{smallmatrix} \text{Ga} \\ \text{Ga} \end{smallmatrix} \right\rangle$ bonding on the GaAs substrate proposed previously by Cohen-Solal *et al.*⁵ In the case of $\langle 111 \rangle$ growth observed in this experiment, however, growth is considered to start on the stoichiometric GaAs surface, and the surface is covered incompletely by Te. Thus, the previously proposed $\langle 111 \rangle$ growth mechanism of formation of $\text{Te} \left\langle \begin{smallmatrix} \text{Ga} \\ \text{Ga} \end{smallmatrix} \right\rangle \text{Te} \text{---} \text{As}$ is not applicable to this case.⁵ The locally adsorbed CdTe molecules are considered to cause the three-dimensional type $\langle 111 \rangle$ growth.

In summary, the variations of the surface structure of GaAs substrates at the initial stage of CdTe growth by OMVPE have been studied by XPS. The GaAs surface was in an As-rich condition after the $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ etching. The surface stoichiometry was recovered by annealing in a H_2 environment. Te adsorbed preferentially on the

$\langle 100 \rangle$ GaAs surface. When the GaAs surfaces were covered completely by Te, $\langle 100 \rangle$ oriented layers were obtained reproducibly; otherwise, $\langle 111 \rangle$ layers resulted.

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