GaSb-Growth Study by Realtime Crystal-Growth Analysis System
Using Synchrotron Radiation Photoelectron Spectroscopy

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A system has been developed for realtime crystal-growth analysis by photoelectron spectroscopy, using vacuum ultraviolet (VUV) light from synchrotron radiation. This system consists of a VUV synchrotron radiation beamline and growth/analysis apparatus in which photoelectron spectroscopy is performed. A "non-scanning" photoelectron spectroscopy measurement method that uses only electron energy dispersion on a multi-channel detector achieves sub-second resolution. This system was used to monitor the GaSb-growth process by alternately supplying Ga and Sb molecular beams; the changes in the chemical state were analyzed with sub-second resolution. The Ga supply resulted in a Ga-full surface; Ga droplets formed on this surface, in which the Sb atoms remained lying on the Ga layer. The Sb supply did not change the ratio of Ga and Sb atoms at the surface from the initial value. These results show that, exposure to an Sb flux causes a crystal surface to once again become an Sb-rich surface although Ga droplets were previously formed during exposure to a Ga flux a GaSb surface was thus successfully grown.

KEYWORDS: realtime analysis, sub second, GaSb, molecular beam epitaxy, core-level, photoelectron spectroscopy, synchrotron radiation, growth mechanism

1. Introduction

Several techniques have been developed to clarify the dynamics of crystal growth, for example, reflection high energy electron diffraction (RHEED), grazing incidence X-ray diffraction (GIXD), surface photo-absorption (SPA), and reflectance difference (RD). These conventional techniques provide information about surface structure or electric potential. However, from the viewpoint of surface reactions, it is important to obtain information about changes in chemical bonding. Furthermore, in crystal growth, such as molecular beam epitaxy (MBE), it usually takes several seconds to complete the growth of one atomic monolayer (ML). To analyze this crystal growth process, sub-second time resolution is needed. Therefore, we have developed a new realtime surface analysis system that uses photoelectron spectroscopy, which is one of the most powerful methods for obtaining information about chemical bonding.

When used for realtime analysis, conventional X-ray photoelectron spectroscopy has two problems: (1) insufficient surface sensitivity and (2) a long data-acquisition time due to low photoelectron intensity. To overcome the first problem, we use vacuum ultraviolet (VUV) light from synchrotron radiation (SR) for the excitation light source. Our system consists of a VUV synchrotron radiation beamline, a growth chamber, and a photoelectron measurement system. To achieve sub-second acquisition for the core-level photoelectron spectrum, we use a "non-scanning" electron measurement method, in which a multi-channel detector (MCD) obtains the photoelectron spectrum by utilizing only energy dispersion on this MCD. The second problem is solved by using this non-scanning measurement method together with the increased photoelectron intensity achieved by using VUV light from SR.

In this paper, we first describes our realtime analysis system and measurement method. We then report on the feasibility of crystal-growth analysis using subsecond photoelectron spectroscopy. We selected GaSb growth for realtime analysis because it is important to control the ratio of the Sb flux to the Ga flux when growing high-quality GaSb crystals, in contrast with GaAs growth, in which it is not necessary to control the ratio so precisely. With RHEED, which is a typical realtime observation method, the patterns show a similar 1 x 3 superstructure regardless of the V/III ratio. Therefore, photoelectron spectroscopy, which can directly monitor the surface ratio of V/III, is the most suitable method for realtime observation. Furthermore, the Sb vapor pressure is relatively low even during crystal growth. This is advantageous for photoelectron spectroscopy.

2. Description of Realtime Analysis System

2.1 High-photon-intensity VUV beamline

Figure 1 shows a side view of the beamline and growth/analysis apparatus. This beamline, ABL-3B, is connected to the Normal-conducting Accelerating Ring at the NTT SOR.

The beamline was designed to be as compact as possible; the distance from the SR source to the analysis chamber is less than 10m. The main components are a front-end section with a bending-magnet source, a front focusing mirror, a "grasshopper" monochromator, a rear focusing mirror, and a chamber for differential pumping. The front focusing mirror ensures high photon intensity. To accept a SR beam with a wide horizontal divergence angle of 20 mrad at an incident angle of 87° and to horizontally focus the SR beam onto the exit slit position of the monochromator, the length of the front focusing mirror should be 1.38 m and the curvature radius should be 63.9 m. To form such a long cylindrical mirror, we used a novel bending device that uses a beam with a C-shaped cross section. A conven-

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tional beam with an H-shaped cross section would cause plastic deformation. (The details are described in ref. 5.)

2.2 Growth/analysis apparatus

Figure 2 is a schematic view of the growth/analysis apparatus as seen from the beamline. It consists of a sample introduction chamber (I), a sample preparation chamber (II), a realtime growth analysis chamber (III), a chamber for changing the sample transfer direction (IV), and a conventional MBE growth chamber (V).

These chambers are separated by manual valves. Chambers I and II are each evacuated by a 50-l/s turbo molecular pump. Chambers IV and V are each evacuated by a combination of an ion pump and a titanium sublimation pump. The MBE chamber (V), which has a liquid nitrogen shroud, allows buffer layers to be grown to provide a clean flat surface for realtime analysis. Therefore, it incorporates an electron gun and screen for RHEED, and a sample manipulator with a sample heater, a beam monitor with an ion gauge, and up to six effusion cells.

In the realtime growth/analysis chamber (III), crystal growth and photoelectron spectroscopy are performed at the same time. It thus contains a photoelectron analyzer (shown as 1) and up to three effusion cells (2). This photoelectron analyzer is based on a hemispherical electron analyzer with a 279.4 mm diameter and a seven-pole electrostatic field lens. It was modified by installing a fast multi-channel detector for high-speed data acquisition.
of photoelectron spectra. The photoelectron analyzer is fixed to the chamber at the take-off angle of photoelectrons, which is 25° from the sample surface, to increase surface sensitivity. A conflat flange (3) is used as a port for the SR beamline. The incidence angle of the SR beam is 4° from horizontal.

Since the effusion cells are at the bottom of the chamber the sample surface should face downward to enable solid sources to be used. If the sample surface is parallel to the horizontal plane, the SR cannot irradiate it. Therefore, we gave the sample surface a 20° tilt, resulting in an incident angle of the SR beam of 16° to the sample surface. This geometry enabled us to install a sample manipulator (4) from the top of the chamber at an angle of 20° to the vertical as shown in Fig. 1. This manipulator can move a sample along three axes, x, y, and z (z axis tilted 20°), and rotate it about the z axis. In addition to these main parts for realtime growth analysis by photoelectron spectroscopy, there is a monochromatized X-ray source (5) and RHEED apparatus (6) (the electron gun cannot be seen and only the screen is shown in Fig. 2). A 1500-l/s turbo molecular pump was used to evacuate the chamber to a high vacuum pressure (10⁻⁹ Torr) even while the effusion cells were operating.

### 2.3 Photoelectron measurement with sub-second time resolution

To obtain a core-level photoelectron spectrum with sub-second acquisition time, we used a "non-scanning" measurement technique, which we describe below in detail. We used an angle-integrated-type hemispherical electron analyzer consisting of an electrostatic lens, an entrance slit, a pair of hemispheres, and a multi-channel detector (MCD). Photoelectrons collected by the electrostatic lens are focused onto the entrance slit. The path of these electrons is then bent by the electrostatic field between the inner and outer hemispheres. The path is determined by the kinetic energy of the electrons. As a result, electrons reach different points along the radial direction of the MCD, depending on their energy. This type of analyzer can thereby simultaneously detect electrons in a certain kinetic energy range and their kinetic energy corresponds to their position on the MCD. A photoelectron spectrum can thus be obtained by using only the energy dispersion on this MCD. Since the electrostatic field of the electron lens is fixed and the retarding electric field is fixed (not scanned), this method is called "non-scanning".

Non-scanning measurement is not usually used because electrons cannot be detected uniformly by the different channels of an MCD, with the result that the measured spectrum is strongly influenced by the sensitivity of each channel in the MCD. Therefore, in the conventional "scanning" photoelectron measurement method, the electron energy is analyzed by scanning the electrostatic field of the lens, and all channels of the MCD are used for detecting the photoelectrons of a particular kinetic energy. However, the non-scanning method greatly decreases spectrum acquisition time because the electrostatic field does not have to be reset and all detected electrons are used for the spectrum. Therefore, to enable non-scanning measurement, we used an MCD whose electron detection efficiency has very low positional dependence.

### 3. Analysis of Alternating Supply Growth on GaSb(001)

Using this realtime analysis system, we grew crystals by alternately supplying Ga and Sb beams and monitored the photoelectron spectra with sub-second resolution. The samples were n-type GaSb(001) doped with Te to a carrier density of 3.9 x 10¹⁴ cm⁻³. They were annealed at 530°C, then 20-µm-thick buffer layers were grown at 500°C in the MBE growth chamber (V). The c(2 x 6) RHEED pattern was then observed on these samples. Next, the samples were transferred to the growth/analysis chamber (III). Details of the initial sample preparation are described in ref. 8.

In the realtime analysis experiment, the substrate temperature was elevated to 580°C during exposure to an Sb flux at 3 x 10⁻² Torr. The Ga deposition rate was estimated to be 1.5 ML/min from the period of the RHEED intensity oscillation for the GaSb MBE growth. To ensure high surface sensitivity to Ga 3d and Sb 4d core-level photoelectrons in the photoelectron measurements, the photon energy was set at 90 eV, calibrated using Au Fermi-level measurement. The total energy resolution was determined to be 0.3 eV for non-scanning measurements of Ga 3d (the pass energy of the electron analyzer was 33 eV) and 0.4 eV for those of Sb 4d (the pass energy was 66 eV).

Figure 3 shows the time dependence of the Ga 3d photoelectron intensity every 0.5 s and the shutter state of the Sb and Ga cells. Figure 4 shows the Ga 3d spectra measured in the non-scanning mode at points (a), (b), and (c) in Fig. 3. The Ga 3d spectrum consists of intensity counts corresponding to the binding energy. Each point in Fig. 3 is the sum of all these intensity counts of

![Fig. 3. Change in Ga 3d photoelectron intensity with time. The shutter states of the Ga and Sb cells are shown at the top.](image-url)
the Ga 3d spectrum.

The limit on the time resolution of this system was experimentally obtained by measuring the time for taking this Ga 3d spectrum. When we set the data recording time to 50 ms, which is the net time for detecting photoelectrons in the MCD, it took 65 s to obtain 600 spectra (not shown here). This means we measured one spectrum every 109 ms. Therefore, this realtime analysis system takes at least about 60 ms per spectrum when the spectra are measured continuously, with most of the time being spent in transferring data from the MCD to the controlling computer, displaying the data on the display, and storing the data on disk. Therefore, 60 ms is the limit of this system at present. However, this result shows that this system could measure one photoelectron spectrum every 0.1 s.

Figure 5 shows the difference spectra of (b) minus (a) and (c) minus (b) from Fig. 4. The (c)–(b) spectrum exhibits two features at 18.8 and 19.6 eV of binding energy (BE). The peak at 18.8 eV is probably due to two peaks of $d_{3/2}$ and $d_{5/2}$ spin-orbit splitting at about 18.6 and 19.0 eV; these two peaks are observed as a single peak because of the low signal-to-noise ratio. The BE values of 18.6 and 19.6 eV are almost the same as the surface components of Ga 3d for GaSb. The difference spectrum of (b)–(a) is broader and smoother. The center is located at around 19.2 eV, which corresponds to bulk GaSb. This broad shape indicates an increase in the intensity of this bulk and the above-mentioned surface component contributions. Thus, in the very early stage of Ga deposition, the bulk component and the surface component increase, and thereafter, only the surface component continuously increases. These results show that the difference in the chemical-state intensity ratio between the initial and post reaction processes can be detected sufficiently well, demonstrating the feasibility of chemical-state analysis with sub-second time resolution using this realtime growth/analysis system.

In this experiment, we also found that the ratio of the maximum to the minimum photoelectron intensity of Ga 3d between the Sb supply state and the Ga supply state was different from that of Sb 4d. This ratio was 1.23 for Ga 3d and 1.03 for Sb 4d. If the top layer of atoms simply changed from an Sb layer to a Ga layer, the ratios should be equal. So, we investigated the origin of the intensity change to clarify why this difference occurs by changing the shutter sequence, and then analyzing the time dependence of the Ga 3d and Sb 4d intensities. The shutter sequence (top of Fig. 6) had a purging period of 10 s inserted between the Sb and Ga supplies, unlike that shown in Fig. 3.

As shown in Fig. 6, the intensities of the Sb 4d and Ga 3d were almost saturated at 10 s after the Sb cell was closed, and the intensities changed only a little when a Ga flux was supplied. These results indicate that the changes in the photoelectron intensities are mainly induced by Sb desorption. Furthermore, if Ga is grown layer-by-layer, the Ga 3d intensity should increase linearly. However, the intensity changes when Ga was supplied were far smaller than those expected from layer-by-layer growth of 0.25-ML Ga. Therefore, the supplied Ga atoms grew in a three-dimensional (3D) manner. Under the same experimental conditions, RHEED showed only a 1 x 3 pattern and did not show any spots due to 3D structures. These results suggest that the Ga atoms did not form crystals, but rather formed droplets.

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Fig. 5. Difference between Ga 3d photoelectron spectra in Fig. 4. The smoothed data are shown by solid lines.
on the surface at this substrate temperature. Furthermore, the number of Ga atoms at the surface reached a maximum only due to Sb desorption since the formation of Ga droplets means that more Ga atoms cannot stay at the surface layers. Therefore, we call this a “Ga-full surface”.

During the purging period after Ga supply, the intensity immediately recovered to the same level as during the purging period before Ga supply for both Ga 3d and Sb 4d. Because the surface area of these droplets is fairly small compared with the area of the substrate surface, the contribution of the droplets to the photoelectron intensity should be negligible. Therefore, the formation of Ga droplets is consistent with our finding that the photoelectron intensity during the purging period after Ga supply was at the same level as that during the purging period before Ga supply. However, the Ga 3d intensity increased and the Sb 4d intensity decreased during Ga supply, although the increase and decrease were very small. Considering the finite time in takes to form a Ga droplet, the two changes during and after Ga supply can be explained as follows. The supplied Ga atoms spread two dimensionally during the initial stage. These Ga atoms then gather and form droplets. When this gathering and formation time is of the order of seconds, the photoelectron intensity from the spreading Ga atoms can be detected. However, because the Ga atoms immediately form droplets, the contribution of the Ga atoms to the photoelectron intensity disappears within several seconds after Ga supply. Since this sequence occurs during Ga supply, only small changes are observed in the photoelectron intensities even during Ga supply. Furthermore, during the purging period after Ga supply, the photoelectron intensity immediately recovers to the same level as during the purging period before Ga supply.

From the difference spectrum between the Sb supply and non-supply states, we can assign the chemical state of Sb atoms adsorbed under Sb-flux exposure before desorption. Figure 7 shows the difference spectrum for Sb 4d obtained by subtracting the spectrum corresponding to 40 s from the spectrum corresponding to 29 s in Fig. 6. The chemical component assignments for $d_{5/2}$ are also shown in this figure. Since these spectra are obtained by subtracting a later time spectrum from an earlier time spectrum, the peaks show where species disappeared and the troughs show where they appeared. In Fig. 7, the peak and trough of $d_{5/2}$ are located at “S1” and “S2”, respectively. They are consistent for $d_{3/2}$ and are located at around a BE of 33 eV. Because “S1” corresponds to Sb–Sb bonding, the peak shows that the Sb atoms, which were adsorbed with Sb–Sb bonding under Sb-flux exposure, disappeared from the GaSb surface, that is, desorbed. This shows that, under Sb exposure, an Sb-rich surface contains Sb atoms bonding only to Sb atoms lying on the GaSb surface.

By using the Ga 3d intensity change, the desorbed Sb thickness can be estimated. From the viewpoint of simple photoelectron attenuation, the desorbed Sb thickness is given by

$$d = \lambda \sin \theta \ln \frac{I_0}{I_{10}},$$

where $\lambda$ is the mean free path and $\theta$ is the take-off angle of photoelectrons. In the Ga 3d intensity change in Fig. 6, the intensity ratio of the Sb supply state to the 10-s state after the Sb supply stopped is 0.86. Here, when $\lambda = 5$ Å and $\theta = 25^\circ$ are used, $d$ equals 0.31 Å. Because the distance between the Sb layer and the Ga layer along the [001] direction is 1.5 Å, this estimated thickness indicates that the coverage of desorbed Sb atoms is less than 1 ML from the viewpoint of the layer attenuation model. Although, to estimate the coverage correctly, the surface conditions such as the atomic arrangement should be known, we can roughly estimate the coverage.
by dividing the thickness by the distance between the Sb and Ga layers along the [001] direction. We calculated the coverage of desorbed Sb atoms to be roughly 0.2 ML. From this estimate we found that only 0.2 ML of Sb desorption causes an Sb stabilized surface to change to a Ga-full surface. This shows that the Ga-full surface is not stabilized by the Ga atomic layer and that Sb atoms remain on the surface, although Ga droplets are also formed on this surface.

In Fig. 6, when Sb-flux exposure was started, both the Ga 3d and Sb 4d intensities recovered within about 1 second to the same levels as during the Sb supply period before the purging period. This shows that the ratio of Sb to Ga atoms at the surface does not change during Sb-flux exposure before or after Ga deposition. Therefore, the surface recovers to the Sb-rich condition when Sb-flux exposure is started, even after formation of Ga droplets. This situation is the same as the case with no purging in Fig. 3, although the number of repetitions is more than in the case in Fig. 6. In both cases, after these alternative growths, the GaSb surfaces became as Sb-rich as the initial surface before growth. This shows that the crystal surface after growth is as good as the initial surface and that epitaxial growth was achieved. However, because the contribution of Ga-droplets to the photoelectron intensity is fairly small, as mentioned above, we cannot say whether the Ga-droplets do or do not disappear.

We also performed GaSb growth under the same conditions in another experiment; only a 1 x 3 RHEED pattern was observed, although the background intensity changed. This shows that, by using realtime analysis with synchrotron radiation photoelectron spectroscopy, we can obtain elemental and chemical information that cannot be observed by RHEED.

4. Conclusion

We have developed a novel realtime crystal-growth analysis system that uses photoelectron spectroscopy. The light source is vacuum ultraviolet (VUV) from synchrotron radiation. The system consists of a VUV synchrotron radiation beamline and growth/analysis apparatus for "non-scanning" photoelectron spectroscopy measurement. It achieves sub-second time resolution of photoelectron spectrum measurements.

To demonstrate the feasibility of this system, we monitored the GaSb growth process by alternately evaporating Ga and Sb and analyzed the changes in chemical states with sub-second resolution. From this experiment we found that the ratio of maximum to minimum photoelectron intensity of Ga 3d between the Sb supply state and the Ga supply state is different from that of Sb 4d. We therefore analyzed the photoelectron intensity change with a shutter sequence in which purging periods were inserted before and after supplying Ga and Sb. We found that Ga droplets formed on the Ga-full GaSb(001), in which the Sb atoms remained lying on the Ga layer. During Sb-flux exposure, the component ratio did not change compared with that of the initial surface. This shows that the crystal surface quality does not change and that successful growth was obtained. These results show the effectiveness of this realtime analysis system. By using this method, we can obtain supplementary information in addition to the structural information obtained from other realtime analysis methods, such as RHEED.

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