Composition Change and Surface Morphology Induced by Ion Sputtering for III-V Semiconductors Using AES

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In general, it is well known that ion sputtering induces surface roughening for III - V semiconductors containing phosphorus. It is of interest whether the surface roughening is related to the composition change. We examined InP and GaP surfaces for the composition change and surface roughening induced by ion sputtering. The initial surfaces were prepared by cleaving in UHV and they were not covered with any contaminated and oxidized layers. It was shown that for In and P the composition changes were about +10% and -10%, and for Ga and P +20% and -20%. For GaP the composition change was larger than that of InP. Sputtering cones on the InP surfaces could be clearly seen. But ion sputtering did not induce the surface roughening of the GaP surfaces. Consequently, we have obtained the interesting result that although the surface roughening of the GaP surface was not induced, the composition change of the GaP surface was large.

1. Introduction

In daily and practical analytical work using electron spectroscpies, ion sputtering is commonly used for making clean surfaces [1]. Depth profiling methods with ion sputtering are also done to analyze multilayered systems and atomic interdiffusion at interfaces [2]. During ion sputtering, true information becomes obscure because of atomic mixing and surface roughening and an information depth affects interfacial resolution. The estimation method using these three parameters (atomic mixing, surface roughening, and information depth) has been proposed [3].

Analysists are generally required to obtain compositional depth profilings and also the elemental concentration of each layer. For multi-elemental systems in particular, atomic mixing and selective sputtering result in concentration errors. This problem can be solved when the sputtering conditions are well-adjusted using the intra-laboratory standard samples whose composition and thickness are determined by other reliable techniques or when very similar material systems are systematically investigated. When the material system is rarely analyzed, however, it is very difficult to estimate the error of the concentration from the intrinsic value. Thus, we studied the composition change in III-V binary chemical compound semiconductors.

It is generally well-known that surface roughening is easily generated for the P-related III-V compound semiconductors [4]. It is of great interest whether a correlation exists between the surface roughening and the composition change. In this report, we will describe composition changes due to the ion sputtering of InP and GaP cleaved surfaces that have no contaminated layers and oxidized layers.

2. Experimental

The specimens used were cut from InP and GaP wafers. To prepare their (110) surfaces, we cleaved the rectangular specimens in a vacuum of less than 2×10^{-10} Torr. The specimens were measured by using a scanning Auger microscope (PHI, Model-670*xi*). Ion sputtering was done using Ar^+ ions with energy of 1 keV or 2 keV and the incident angle of the ion beam was 37 degrees from the surface.

Table 1. The sputtering rates and current density of the ion beam

Energy		2 keV	1 keV	2 keV
Rastered Area		7 x 7 mm^2	2 x 2 mm^2	1 x 1 mm^2
InP	Sputtering rate (for SiO_2)	0.4 nm/min	2.9 nm/min	18.0 nm/min
	Ion current density	0.45 $\mu A/cm^2$	6.99 $\mu A/cm^2$	28.78 $\mu A/cm^2$
GaP	Sputtering rate (for SiO_2)	0.4 nm/min	4.8 nm/min	14.7 nm/min
	Ion current density	0.61 $\mu A/cm^2$	9.80 $\mu A/cm^2$	47.90 $\mu A/cm^2$

The sputtering rates were varied by changing the rastered area of the ion beam. The sputtering rates and current density of the ion beam are summarized in Table 1.

AES spectra were obtained for the kinetic energy of 30 to 1930 eV in steps of 1.0 eV and each step lasted 20 msec. AES spectra were accumulated twenty times. AES direct mode spectra were smoothed by using the PHI's software and then differentiated by using the Savitsky-Golay algorithm. Thus, the peak-to-peak distances of these spectra were used as peak intensities.

We measured the AES spectra of the as-cleaved surfaces and the sputtered surfaces. The sputtered depths were 0.5, 1, 2, 5, 10, 50, and 500 nm. These were calculated by using the sputtering rate for the thermal SiO_2 specimen. The primary electron beam energy and current were 5 keV and 10 nA. AES spectra were measured at three points on atomically flat terraces without steps, and each analyzed area was 10x10 μm^2. The electron beam did not hit the specimen surfaces during ion sputtering.

3. Results and Discussion

Figures 1 and 2 show the AES differential spectra from InP and GaP as-cleaved surfaces. The O KLL Auger peak was not detected in these spectra because the surfaces of InP and GaP were cleaved just before the measurements in the vacuum. The carbon signal in Fig.1 is probably contamination that occurred during the accumulation of the AES spectra. This is because it was not detected at the beginning of the spectra accumulation.

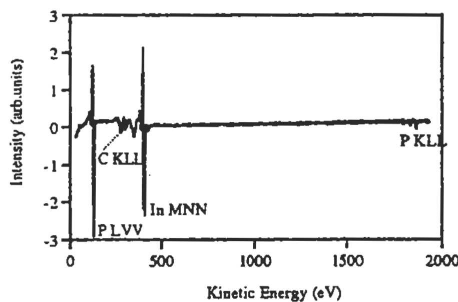

Fig. 1. AES differential spectrum from InP as-cleaved surface.

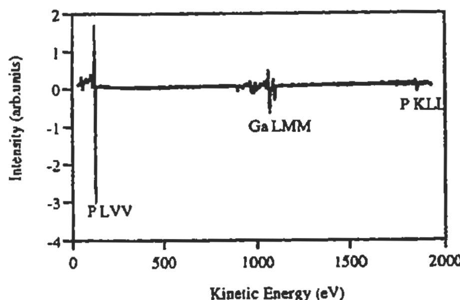

Fig. 2. AES differential spectrum from GaP as-cleaved surface.

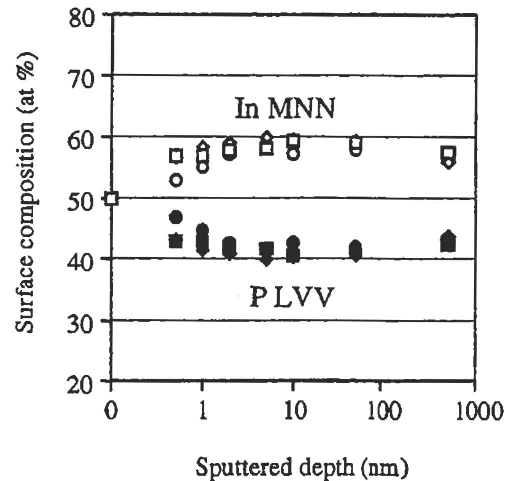

Fig. 3. Composition calculated using the surface composition of the InP as-cleaved surface against the sputtered depth. Symbols are; □ In (Ip=2 keV, R=7), ■ P (Ip=2 keV, R=7), ◇ In (Ip=1 keV, R=2), ◆ P (Ip=1 keV, R=2), ○ In (Ip=2 keV, R=1), and ● P (Ip=2 keV, R=1). Here Ip and R are respectively the ion beam energy and the rastered area.

Figures 3 and 4 show the surface composition changes for InP and GaP at the sputtered depths. The relative sensitivity factors were obtained from the InP and GaP as-cleaved surfaces under the assumption that In or Ga, and P compositions were 50 at%, and they were applied to the AES spectra obtained from sputtered surfaces. It is shown that the composition changes were about +10% and -10% for In and P, +10 to +20% and -10 to -20% for Ga and P. As the sputtered depth increases, it is clear that the composition change in GaP is larger than that in InP. It is found that as the ion sputtering rate increases for a depth less than about 5 nm, the surface composition changes slowly.

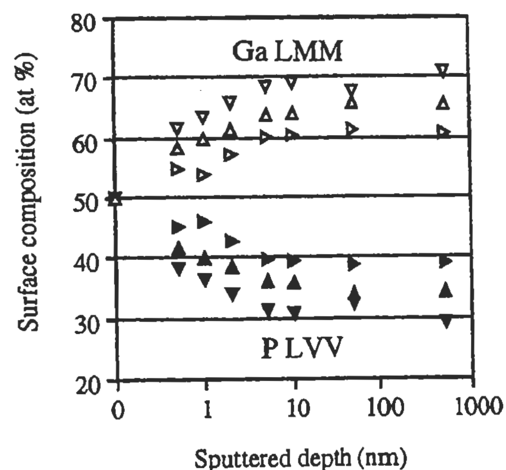

Fig. 4. Composition calculated using the surface composition of the GaP as-cleaved surface against the sputtered depth. Symbols are; △ Ga (Ip=2 keV, R=7), ▲ P (Ip=2 keV, R=7), ▽ Ga (Ip=1 keV, R=2), ▼ P (Ip=1 keV, R=2), ▷ Ga (Ip=2 keV, R=1), and ▶ P (Ip=2 keV, R=1). Here Ip and R are respectively the ion beam energy and the rastered area.

At about above 50 Å, the sputtered surface compositions for InP are almost constants, regardless of the ion sputtering conditions. The sputtered surface composition for GaP also seems to be constant at about above 50 Å and it depends on the ion sputtering conditions. One of the reasons for these results is considered to be the rate of the ion induced diffusion. In InP it is much faster than the ion sputtering rate and in GaP it is as fast as the ion sputtering rate. It is necessary to examine these points in detail.

Figures 5(a), 5(b), and 5(c) show the SEM (secondary electron microscope) images of the 5000 Å sputtered InP surfaces for the three ion sputtering conditions. The surface (Fig. 5(a)) with the lowest rate of ion sputtering has sputtering cones and spherical structures at the apex of the sputtering cones. The surface (Fig. 5(c)) with the highest rate of ion sputtering seems to be an undulating structure. It is considered that the surface (Fig. 5(b)) with the medium rate of ion sputtering is a mixed structure of Figs. 5(a) and 5(b). Figures 6(a), 6(b), and 6(c) show the SEM images of the 5000 Å sputtered GaP surfaces for the three ion sputtering conditions. Sputtering cones are induced on the InP surface, but there is no surface roughening induced on the GaP surface.

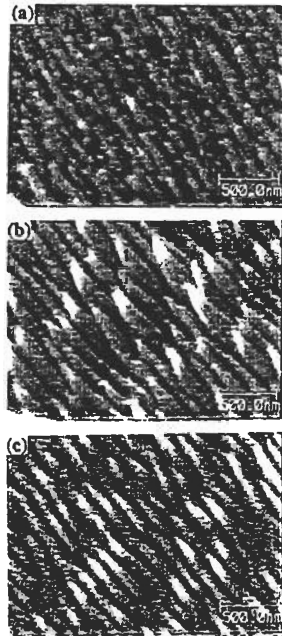

Fig. 5 (a). SEM image of the InP surface sputtered by using the ion beam of 2 keV and R = 7x7 mm^2. The sputtered depth is 500 nm estimated by using the sputtering rate (0.4 nm/min) for SiO_2. (b). SEM image of the InP surface sputtered by using the ion beam of 1 keV and R = 2x2 mm^2. The sputtered depth is 500 nm estimated by using the sputtering rate (2.9 nm/min) for SiO_2. (c). SEM image of the InP surface sputtered by using the ion beam of 2 keV and R = 1x1 mm^2. The sputtered depth is 499.8 nm estimated by using the sputtering rate (18.0 nm/min) for SiO_2.

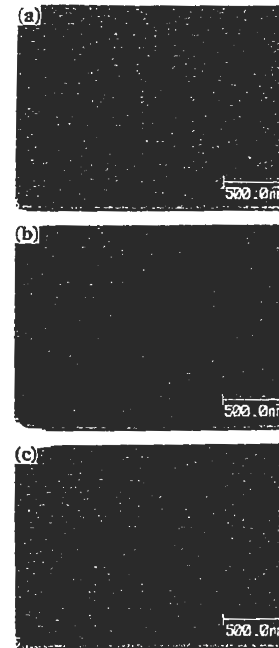

Fig. 6 (a). SEM image of the GaP surface sputtered by using the ion beam of 2 keV and R = 7x7 mm^2. The sputtered depth is 500 nm estimated by using the sputtering rate (0.4 nm/min) for SiO_2. (b). SEM image of the GaP surface sputtered by using the ion beam of 1 keV and R = 2x2 mm^2. The sputtered depth is 500 nm estimated by using the sputtering rate (4.8 nm/min) for SiO_2. (c). SEM image of the GaP surface sputtered by using the ion beam of 2 keV and R = 1x1 mm^2. The sputtered depth is 499.8 nm estimated by using the sputtering rate (14.7 nm/min) for SiO_2.

Further investigation is needed to estimate fine surface morphology in high magnitude observation using AFM (atomic force microscopy).

It has been suggested that the small particles composed from In atoms form a shadow on the surface where P atoms are selectively removed by ion sputtering [5,6] and this results in cone-shape formation. The TEM (transmission electron microscope) observation showed that the spherical structure consists of In atoms [7].

4. Summary

We examined the composition change and surface roughening of InP and GaP as-cleaved surfaces induced by ion sputtering. It is shown that for In and P, the composition changes in the surfaces after sputtering are 60% and 40%, and for Ga and P, 60 to 70% and 30 to 40%. For a depth less than about 50 Å, it was found that the surface composition changes is slowly as the rate of ion sputtering increases. It was observed that the composition changes of GaP are larger than those of InP. Sputtering cones were clearly seen on the InP surfaces. But the ion sputtering did not induce surface roughening of the GaP surfaces.

Consequently, we obtained the interesting result that although the surface roughening of the GaP surface was not induced, the composition change of the GaP surface was large.

References

[1] for example, J. C. Riviere, section 2.3.3.1 " Preparation of a clean surface" in Practical Surface Analysis Vol. 1, Edt. By D. Briggs and M. P. Seah, Wiley, 1990.

[2] for example, S. Hofmann, chapter 4 " Depth Profiling in AES and XPS" in Practical Surface Analysis Vol. 1, Edt. By D. Briggs and M. P. Seah, Wiley, 1990.

[3] S. Hofmann, J. Surface Analysis, **3**, 389 (1997).

[4] T. Ogiwara, T. Harada, and S. Tanuma, J. Surface Science Soc. Jap., **14**, 472 (1992); **14**, 595 (1992) (in Japanese).

[5] C. M. Demanet, J. B.Malherbe, N. G. van der Berg and Vijaya Sankar, Surf. Interface Analysis, **23**, 433 (1995).

[6] Y. Homma, J. Surface Analysis, **3**, 641 (1997).

[7] M. Nozu, M. Tanemura and F. Okuyama, Surf. Sci. Lett. **304**, L468 (1994).