Technical Report

Reference Materials Used in My Laboratory

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Abstract

Semiconductor superlattices are expected as an useful standard material for the evaluation of depth profile analysis. I produce a reference materials made of GaAs/AlAs multi layered thin film with individual layer thickness of 10 nm programmed in advance. Six periods structure of GaAs/AlAs are prepared on GaAs (100) surface by using MOCVD and MBE method. Determination of the thickness for individual layer and the confirmation of flatness at the interfaces are carried out by the observation of TEM lattice images. Quality of these semiconductor superlattices are good enough to evaluate sputter assisted depth profile analysis. I adapt them as a reference material for the evaluation of depth resolution in my laboratory.

1. Introduction

I have AES (PHI SAM-670xi), XPS (PHI ESCA-5500) and a lot of standard materials in my laboratory. Pellets of Gold, Silver and Copper are used as the reference standard materials for the kinetic energy of the respective electron in AES and XPS. Electron beam diameter measurement tool made of gold mesh supplied from PHI is used to measure the primary electron beam diameter in FE-AES. Reference sample of 48 kind of elements, collected them on one sample holder which is a product of GELLER Co. Ltd., are used to measure the sensitivity factor of the elements.

Among all those important reference materials, the most frequently used is the sample to measure the sputtering rate and to evaluate the depth resolution. Depth profile analysis is the most popular application in the surface characterization. Depth resolution in ion sputter assisted depth profile analysis is an important value, especially in analyze the structure of laminated multi layered thin films such as magnetic metal multi layered thin films and semiconductor superlattices. Therefore, the standard material in order to evaluate the depth profile analysis is important, even though in daily work of AES and XPS. I possess several authorized standard materials, e.g. tantalum pent oxide thin film supplied from NPL, Cr/CrO and Ni/Cr multi layered thin film from NIST. These are supplied in a small pellet form for the depth profile analysis. I adapt the sample of using to suit the purpose and the occasion of the analysis. However, I rarely adapt these authorized standard samples, because it is a wasteful to use in daily work. These authorized standard samples are very expensive. Then, I usually adopt silicon wafer with the thermal oxide thin film of the thickness 100 nm as a reference material in daily work. Silicon oxide film is used not only in my laboratory but also widely used in many surface analytical laboratory in Japan, which is supplied from JEOL in a wafer form of the size 3 inch diameter. We can obtain at least 34 pellets of the size 10x10 mm square from this wafer. In order to be used a reference material widely, this point is important. Then, I attempt to produce a wafer of semiconductor superlattices made of GaAs/AlAs, and have been investigated as a reference material for the evaluation of ion sputter assisted depth profile analysis.

2. Experimental

From a standpoint of view mentioned above, I produced a reference material made of GaAs/AlAs multi layered thin film on the GaAs wafer of the size 3 inch in diameter. In this study, superlattices of GaAs/AlAs with equivalent structure were grown by epitaxial methods of MBE and MOCVD, and were evaluated as a reference material for the depth profile analysis. In general consideration, there might be some differences in quality of GaAs/AlAs laminated multi layered structure between epitaxial growth methods of MBE and MOCVD, especially those might be shown in the controls of the growth rate and flatness in the interface of alternating multi layers. MBE method might have the advantage in the control of layer thickness, because the reason of reflection high energy electron diffraction (RHEED) can be used as a monitor for the thickness of thin film during epitaxial growth. On the other hand, MOCVD method might have the advantage in the interface flatness, because the reason of MOCVD is a deposition method based on the mono-layer adsorption of metalorganic molecules and thermal reaction at the surface of the substrate.

Hetero epitaxial growth of GaAs/AlAs were carried out in HITACHI Cable Advanced Research Center during November 1994 through March 1995. Six periods of GaAs/AlAs thin films were grown on GaAs (100) single crystal substrate of the size 3 inch in diameter. Epitaxial methods of molecular beam epitaxy (MBE) [1] and metalorganic chemical vapor deposition (MOCVD) [2] were used for the growth of multi layered thin film structure. Thickness control of the individual layers were made by growth rate. Growth rate for the single phase layer of GaAs and AlAs on GaAs substrate were measured by the preliminary experiment in advance. Multi layered thin film with the individual layer thickness of 10 nm programmed in advance were grown in order to evaluate the depth resolution in AES. Six periods of GaAs/AlAs multi alternating layered thin films were prepared on silicon doped GaAs single crystal (100) just surface. General conditions of the epitaxial growth for GaAs/AlAs in MOCVD and MBE were as follows. In MOCVD method, used raw materials of metalorganic compounds were tri-methyl gallium, tri-methyl aluminum, arsine diluted in H_2 and H_2 as a carrier gas. Growth rate of GaAs layer on GaAs (100) surface was 0.5 nm/sec and that of AlAs 0.2 nm/sec at the temperature of 650 C. On the other hand, in MBE method, solid metals of gallium, aluminum and arsenic were used on the epitaxial growth of GaAs/AlAs thin films. Epitaxial growth rate of GaAs layer was 0.3 nm/sec and of AlAs 0.15 nm/sec at the temperature of 530 C.

Determination of the thickness for individual layer and evaluation of the flatness at interfaces for GaAs/AlAs alternating multi layered thin films were carried out by transmission electron microscopy (TEM). Cross sectional slice sample with a (110) cleaved surface was prepared for taking a high resolution photograph of TEM lattice image. TEM lattice images of GaAs/AlAs superlattices by using JEOL JEM-2000EX/TOP-STAGE under the condition of 200 kV accelerating voltage were carried out at JEOL Datum Co., Ltd.

Depth profile analysis by using AES was carried out to examine the interface abruptness on the composition of GaAs/AlAs. Multi layered thin films with individual thickness of 10 nm programmed in advance were used in this experiment. Depth profile analysis was performed by using AES (PHI-SAM-670xi) equipped with field emission electron gun, coaxial type cylindrical mirror analyzer and differential pumping type ion gun. Conditions of ion gun were Ar^+ ion energy 1 keV, incident angle 7 degrees with respect to the sample surface and sputtering rate 0.29 nm/min for SiO_2. Accelerating voltage of primary electron beam was 5 kV, total probe current was 10 nA and incident angle was 90 degrees with respect to the sample surface. Base pressure in the analytical chamber was $1x10^{-10}$ Torr. Measured Auger peaks were Al-LVV (68eV) and Al-KLL (1396eV). Depth resolution were defined by 16-84% transition width of the interface for the depth profile.

3. Results and discussions

3-1 Lattice image observation by TEM

Figure 1 shows the cross sectional TEM lattice image for alternating laminated multi structures of GaAs/AlAs superlattices grown by (a) MOCVD and (b) MBE method respectively. These multi beam interference lattice images were obtained by (000), (111) and (002) equivalent diffracted electron beams. Since the lattice constant of GaAs is almost equal to that of AlAs, lattice distance of (002) corresponds to one atomic layer of GaAs or AlAs (d=0.283 nm). Then the thickness of individual layer were precisely determined by counting the number of interference spots along [001] direction [3,4]. Dark area in the cross sectional TEM lattice image correspond to GaAs layer and bright area AlAs. Clear contrast in the GaAs/AlAs interfaces indicates one monolayer level abruptness in both superlattices for MOCVD and MBE. Individual and total thickness of the epitaxial layers programmed in advance were 10 nm and 120 nm respectively. Calculated thickness of individual layers by counting a number of interference spots were shown in table 1. Obtained total thickness of GaAs/AlAs alternating laminated structures grown by MOCVD method was 112.4 nm and by MBE 116.4 nm. GaAs/AlAs grown by MOCVD has a relatively large error in individual and total thickness, which might be caused by the error of estimated epitaxial growth rate of the individual layer. It might be more difficult to control

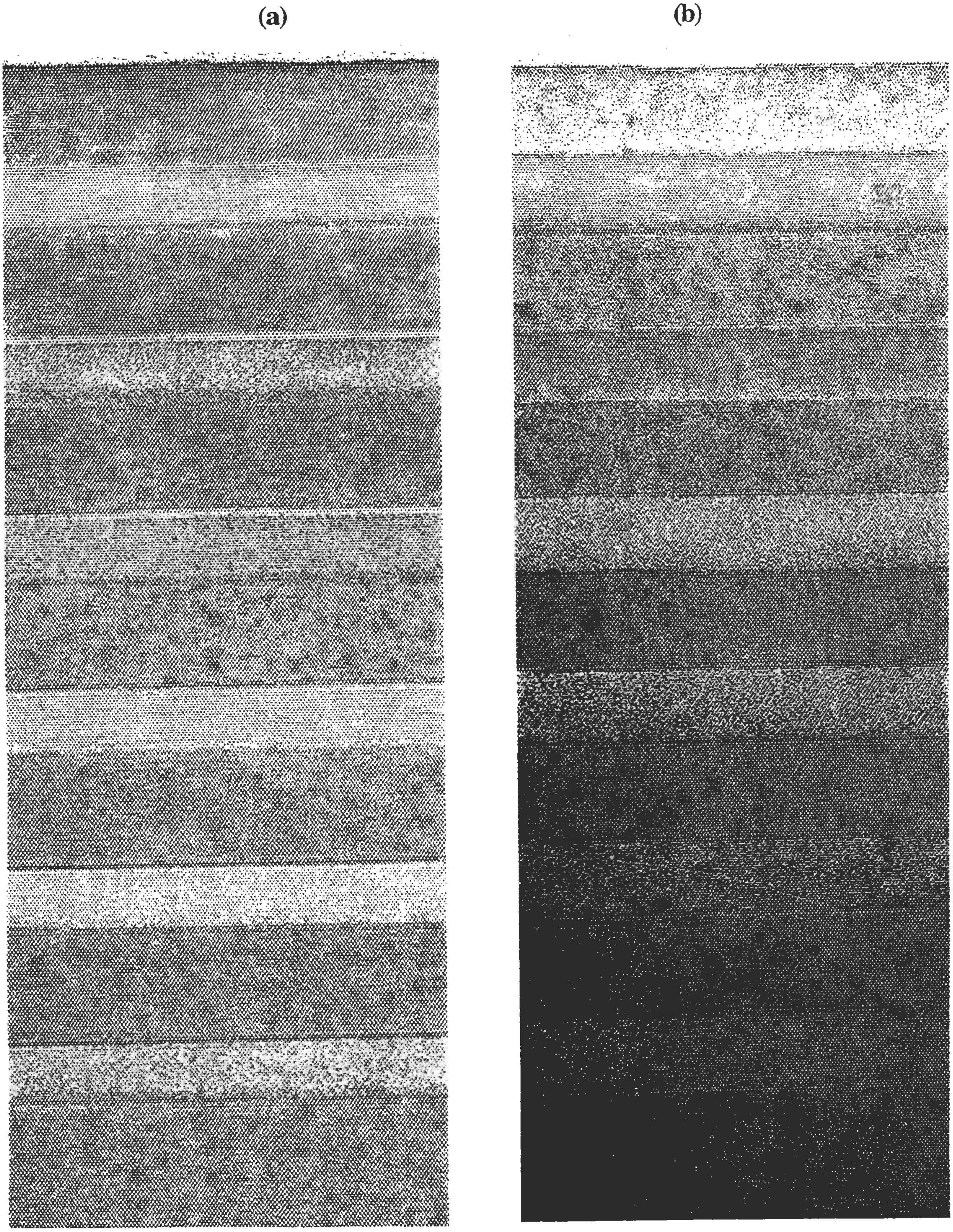

Fig. 1 TEM lattice images for 6 periods of GaAs/AlAs superlattices with individual layer thickness of 10 nm programmed in advance grown by (a) MOCVD method and (b) MBE.

Table 1 Calculated thickness for individual layers of GaAs/AlAs by counting a number of interference spots on cross sectional TEM lattice images.

	MOCVD		MBE	
	Number of Spots	Thickness (nm)	Number of Spots	Thickness (nm)
GaAs	41	11.58	35	9.89
AlAs	24	6.78	32	9.04
GaAs	42	11.87	36	10.217
AlAs	24	6.78	31	8.76
GaAs	44	12.43	37	10.45
AlAs	23	6.50	32	9.04
GaAs	43	12.15	38	10.74
AlAs	24	6.78	32	9.04
GaAs	45	12.71	37	10.45
AlAs	21	5.93	33	9.32
GaAs	45	12.71	37	10.45
AlAs	22	6.22	32	9.04
Total	398	112.44	412	116.39

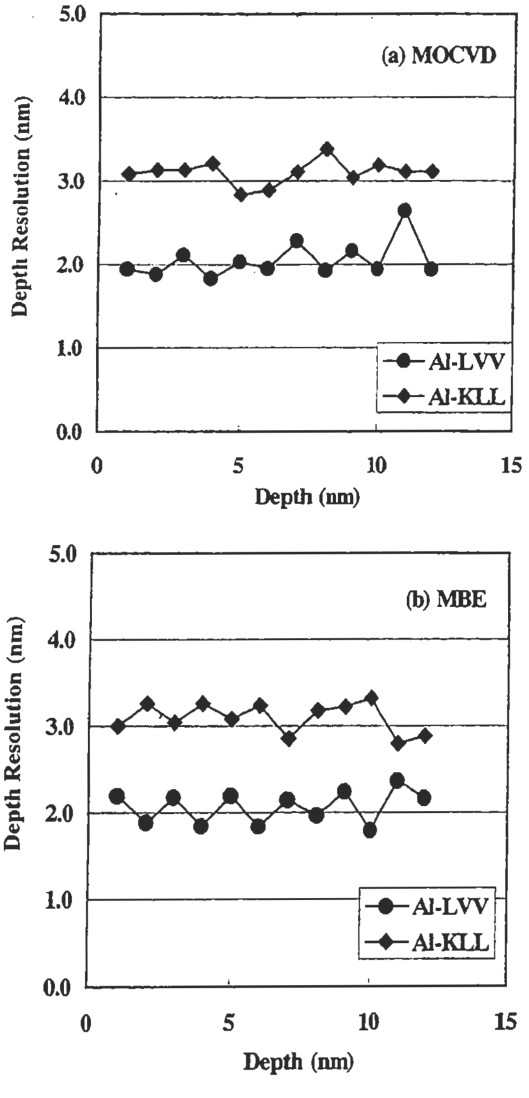

Fig. 2 Depth resolution obtained by sputter assisted AES using Al-LVV and Al-KLL for GaAs/AlAs superlattices grown by (a) MOCVD and (b) MBE

the thickness of the epitaxial layer in MOCVD compared with MBE method in the case of this experiment.

3-2 Evaluation for depth resolution with AES

Principal factors limiting depth resolution in ion sputter assisted depth profile analysis are surface roughness of the sample, inelastic mean free path (IMFP) of Auger electron and atomic mixing [5,6]. In the case of this sample, depth resolution deterioration caused by surface roughness can be neglected because the substrate is ideally mirror polished. Depth resolution value can be improved close to IMFP value, when the atomic mixing effect reduced. In order to compare the depth resolution at the interfaces between MOCVD and MBE sample by using ion sputter assisted AES, analytical conditions of AES should be sufficiently optimized. In sufficiently optimized analytical conditions, the shift between two of the depth profiles for Al-LVV and Al-KLL along the sputtering time axis were observed. Depth profile of Al-KLL appears earlier than Al-LVV in every layers of GaAs/AlAs interfaces [7]. This shift on the sputtering time axis between Al-LVV and Al-KLL corresponds to 2.5 nm, which is equivalent to the difference of IMFP between Al-KLL and Al-LVV. IMFP values for Al-KLL (1396 eV) and for Al-LVV (65 eV) are calculated to be 3.0 nm and 0.5 nm respectively [8]. Appearance of this phenomenon shows the sufficient improvement of the depth resolution.

Figure 2 shows the change of depth resolution values as a function of depth from topmost surface. Depth resolution values were obtained by the draw a diagram method using an enlargement for respective interface range of the depth profile. Those depth resolution values are kept constant with increase of the depth from topmost surface of the sample. Deterioration of the depth resolution with increase of the depth was not observed in sufficiently optimized analytical conditions of sputter assisted AES. Mean value of the depth resolution of Al-LVV for the sample grown by MOCVD is equivalent to that of MBE. But a little difference was observed between leading edge of aluminum (GaAs/AlAs) and trailing edge (AlAs/GaAs). Mean values of the depth resolution obtained at leading edge and trailing edge were 2.2 nm and 1.91 nm respectively. Mean value of the depth resolution for leading edge was greater than that of trailing edge. This mean value of 1.91

nm for Al-LVV at trailing edge is the highest value in this experiment using AES equipment in my laboratory. On the other hand, depth resolution values obtained by Al-KLL were also equivalent in MOCVD and MBE as shown in Figure 2. But mean values of the depth resolution for leading edge and trailing edge were 3.0 nm and 3.2 nm respectively. Mean value of the depth resolution of Al-KLL for leading edge was smaller than that of trailing edge, on the contrary in the case of Al-LVV.

Recently, Analytical Laboratory of ULVAC-PHI Co. Ltd., utilized this GaAs/AlAs superlattices grown by MOCVD as a reference sample on the depth profile analysis by using new type floating ion gun under the condition of accelerating voltage 0.1 kV. Depth resolution value of 1.3 nm was achieved in this experiment. Though, Estimated IMFP of Al-LVV is 0.5 nm, this value of the depth resolution 1.3 nm might be an unprecedented value which had never been attained by other experiment in sputter assisted depth profile analysis.

4. Conclusion

Superlattices of six periods of GaAs/AlAs in alternating multi layered structures were grown on the single crystal substrate of GaAs (100) just surface by MBE and MOCVD method. Individual layer with the thickness of 10 nm programmed in advance were grown under the control of growth rate. Determination of the thickness for individual layer of GaAs/AlAs thin films were carried out by the observation of TEM lattice images. Depth resolution value of 1.91 nm at trailing edge for Al-LVV was attained by using AES equipment in my laboratory. In addition, depth resolution value of 1.3 nm was achieved in Analytical Laboratory of ULVAC-PHI using new type floating ion gun under the condition of accelerating voltage of 0.1 kV.

This reference material for the depth profile analysis is not the certified standard sample. Lateral distribution on the thickness of individual layer throughout the wafer of the size 3 inch in diameter is one of the important subject, which must be conformed by taking a high resolution photographs of TEM lattice image or by any other method. Standard sample must be certified by a number of authorized institutes. However, quality of these GaAs/AlAs superlattices reported in this paper are useful enough to evaluate the depth profile analysis in electron spectroscopy. I adapt them as a reference material for the evaluation of depth profile analysis in my laboratory. It is very convenient to use these reference materials to characterize the depth profile analysis as for daily work in surface analysis.

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