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Auger Study of LPE Grown InGaAsP/InP Heterostructure

(Auger 전자현미경을 이용한 LPE에 의해서 성장된 InGaAsP/InP 이종접합계면에 대한 연구)

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要 約

Auger 전자현미경의 깊이 분포 분석기술을 이용하여 각기 다른 성장조건 즉, 각기 다른 확산 온도, 시간과 dopant 원소에 의해 LPE 성장된 InGaAsP/InP 이종접합면의 원소분포 상태를 깊이 방향에 대해 구하였다. 아울러 InGaAs 에피층 표면의 불순물도 Auger 전자현미경의 point analysis분석 기술을 이용하여 구하였다.

Zn 확산을 수행한 시편의 경우 Ga, P의 계면에의 응집이나 계면에서의 In이 줄어든 현상을 포함하여 커다란 grading 현상이 발견되었으며 표면으로의 In의 outdiffusion도 발견되었다. 계면에서의 Zn gettering 현상이 계면의 grading 현상이나 Ga, P의 응집, In양이 계면에서 줄어드는 현상을 야기시킨다고 생각되며 표면의 주된 불순물은 탄소와 산소로 밝혀졌다.

Abstract

Auger depth profiles of various InGaAsP/InP heterojunctions grown by liquid phase epitaxial techniques under different growth conditions such as diffusion temperature, diffusion time and dopants, have been obtained. The surface contaminations of InGaAs have been investigated.

We found that the samples with Zn diffusion exhibit significant interface grading phenomena including In depletion, Ga richness and P richness at the InGaAsP/InP interface, and In outdiffusion at the surface. The main surface contamination was found to be due to carbon and oxygen species. It can be suggested that Zn gettering takes a major role in such phenomena as interface grading, In depletion, and Ga and P richness at the interface.

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I. Introduction

Auger electron spectroscopy (AES) is rapidly emerging as a standard microanalytical technique in the modern laboratory.[1,2] AES has properties both as surface analysis tool, being sensitive only to the first few atomic layers of the sample

surface, and as the ultimate in spatial resolution (500Å) for the analysis of bulk solids. One of the primary interests in AES is the determination of the surface composition of the specimen. And the technique of depth profiling is accomplished by alternately eroding the specimen surface using the sputtering ion beam followed by Auger data collection, or by simultaneous sputtering during data collection. We applied the AES technique to analyze the interdiffusion phenomena at the InGaAsP/InP heterostructure interface grown by liquid phase epitaxy (LPE) and surface contaminations on the InGaAs surface.

The technique of LPE, in which an epitaxial layer is grown on a single-crystal substrate by deposition from a molten solution saturated at the growth interface, is used extensively to grow single crystal layers of semiconductor such as GaAs, GaAlAs, and GaP, as well as magnetic materials such as garnets, for numerous applications. A variety of optoelectronic, microwave, and magnetic bubble devices have been successfully fabricated from structures prepared by this method.

Most semiconductor LPE layers for practical applications are obtained by heteroepitaxial growth and many of them are ternary or quaternary alloys, which require growth solutions containing three or four components. The LPE growth of GaInAsP epilayers on InP substrates, and vice versa, is of particular interest because it permits the fabrication of heterostructure lasers and detectors for the 1.1-1.6μm wavelength region, which have potential applications in fiber optic communications. InGaAsP alloys lattice matched to InP can have any bandgap between 1.35 and 0.78 eV, corresponding to wavelengths between 0.92 and 1.6 μm.[10] For doubleheterostructure diode lasers, a simple InP/InGaAsP/InP structure gives carrier and optical confinement, since InP has a higher bandgap and lower refractive index than any of the lattice matched alloys.

Little is known, however, about the interfacial region between the different materials which form the heterostructure.[6,8] It is important to understand the interface problem since the performance of many heterojunction devices depend strongly on the chemical interface insofar as it influences the electrical junction, the conduction and valence bands, and the optical and electrical confinement propeıties.

In this work, AES techniques such as Auger depth profile and wide scan survey have been used to report the experimental results of interdiffusion phenomena at the InGaAsP/InP epitaxial interfaces and to determine the nature and the extent of the surface contamination resulting from the air exposure of InGaAs surface. Large amount of carbon and oxygen were observed on the wafer surface. We have also observed substantial interdiffusion effects at the interface of InGaAsP/InP and their dependence on the diffusion time and temperature, as well as dopants.

II. Auger Electron Spectroscopy

One of the primary interests in AES is the determination of the surface composition (within 5-20 Å) of the specimen. One can carry out the quantitative and qualititive Auger analysis, and also in some cases, the chemical state analysis of constituent atoms within this depth. By using an intert(Ar+) sputtering ion beam the analysis can be extended from near surface to a few micrometers into the specimen as the specimen surface is being eroded in a highly controlled fashion.

There is a series of physical processes we must consider to explain the Auger process fully. The first is the ionization of core electrons by ionizing radiation, which in the case of Auger electron spectroscopy is an incident electron beam impinging upon the surface. The electron beam must have sufficient energy to creat an electron core hole, which means the electron energy must be at least several times the energy of the Auger electron being studied. An electron can then be ejected leaving the atom singly ionized and at a higher energy level. To return to the ground state the atom will undergo either a radiative (photon) or non-radiative (Auger) de-excitation transition.

Auger de-excitation results when the energy released from the ionized atom is carried away by Auger electron, leaving the atom doubly ionized. The kinetic energies of the Auger electron are uniguely characteristic of the parent atom. The number of Auger transitions increase with increasing Z. Auger emission is non-isotropic in the case of crystalline samples. Fig.1 illustrates the process for a KLL transition where the incident electron causes a K shell electron to be emitted from the atom. An L-shell electron fills the vacancy created. The non-radiative de-excitation occurs when another L-shell (Auger)

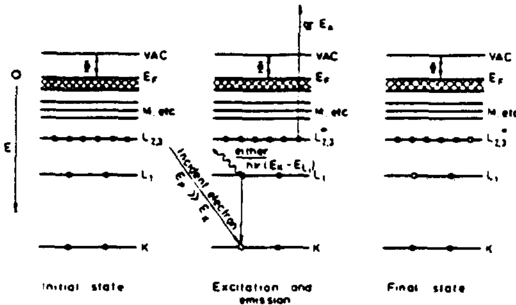

Fig.1. Auger excitation and emission process.

electron is emitted. The kinetic energy of this Auger electron is $E_{KE}=E_K-2E_{L^{2,3}}-\Phi$, where Φ is the work function of the specimen. The energy of the Auger transition can be highly affected by the chemical composition of the specimen and the binding energy of the valence electrons is very sensitive to chemical state.

Analysis of specimens in the 'as received' condition reveals their composition within the first-20 Å of the surface. This layer will usually consist of contamination in the form of hydrocarbons from the atmosphere, or in the case of 'clean' samples simply a native oxide formed on the specimen surface. The ability to remove this overlayer is important. This is most often accomplished in Auger systems by sputtering the specimen with inert beam of Ar ions. The technique of depth profiling is accomplished by alternatingly eroding the specimen surface using the sputtering ion beam followed by Auger data collection or simultaneously sputtering during data collection.

Auger electron spectroscopy has varied and wide ranging applications. Areas of major interest include thin film analysis for metallurgical, semiconductor and optical coatings, dopant determination, contamination, corrosion, elemental distributions and diffusion studies.

We applied the Auger electron spectroscopy to find out the outdiffusion and interdiffusion of InGaAsP/InP heterostructure interface resulting from annealing and dopant diffusion by depth profiling technique, and surface contamination from the air exposure by the Auger spectra analysis.

III. Experiments and Results

Auger measurements were carried out on a Perkin-Elmer PHI Model 610 Scanning Auger Microprobe (SAM). Samples were mounted on the standard carousel at 30° grazing incidence to the 5 KeV primary electron beam. The electron beam current was typically 300 nA in order to minimize the beam effects. Ion sputtering was performed by means of a Perkin-Elmer 04-303 differentially pumped ion gun using 3.5 KeV Ar+ ions. The ion beam was rastered over a region of 9 mm^2 in order to analyze only bombarded surfaces. Ion current density was 80 $\mu A/cm^2$ at a base pressure of $1.5*10^{-8}$ torr. Depth profiling was performed by sequentially monitoring the derivative peak to peak signals for the Auger transitions of In 390-415 eV; Ga 1055-1075 eV; As 1210-1235 eV; P 105-126 eV during alternative 3.5 KeV Ar ion bombardment for removal of successive atomic layers.

1. Surface Auger Spectra

The contamination is hard to see except after complete fabrication of the device. By using Auger spectra with conventional methods we determined the nature and extent of the surface contamination resulting from the air exposure of InGaAs surface. The Auger spectrum of InGaAs surface exhibits sulfur, boron, carbon, and oxygen contaminants, as shown in Fig. 2. Relatively a large amount of carbon, oxygen, and boron were found to be present on the wafer surface.[9,11] Fig.3 is the Auger spectrum of InGaAs surface

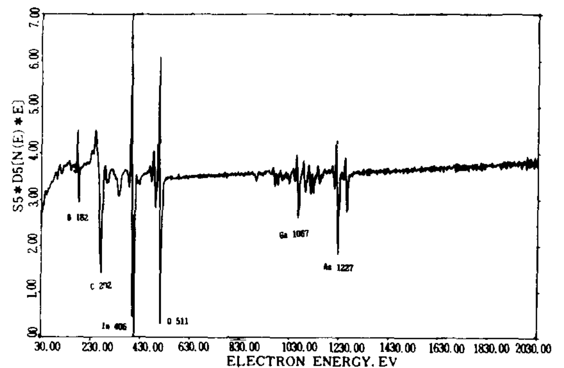

Fig.2. Auger spectrum of InGaAs epitaxial surface.

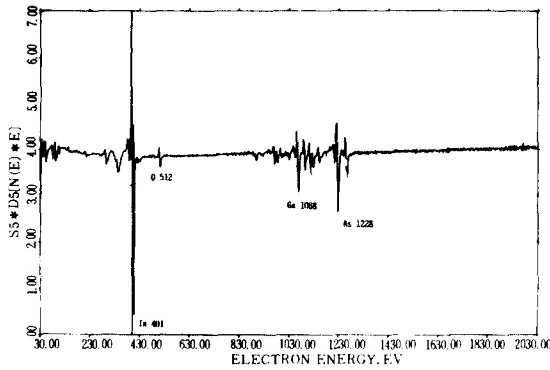

Fig.3. Auger spectrum of InGaAs epitaxial surface after Ar sputtering of 50 Å depth.

after sputter cleaning of the InGaAs surface by ~50Å, and it indicates that the carbon and boron peaks disappear, while the small oxygen signal remains in the spectrum. Thus it seems that the main surface contamination is due to carbon and oxygen species and that boron and sulfur are contaminated from the chemicals of other process.

2. *Auger Depth profiles*

The depth profiling was used to show that the outdiffusion and interdiffusion at InGaAsP/InP heterostructure interfaces depend on the diffusion time and temperature as well as different dopants. Obtaining profile data, the matrix effects and the sputter artificial effects such as preferential sputter effect and knock-on effect were ignored. Table 1. lists the various preparation conditions for different samples.

Table1. Samples prepared with different conditions for Auger depth profiling.

Sample Number	Dopant	Diffusion Temp.	Diffusion Time	Composition
1	–	as grown	–	$In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$/InP
2	–	600C	50hr	$In_{0.62}Ga_{0.38}As_{0.61}P_{0.39}$/InP
3	Zn	600C	15min	$In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$/InP
4	Zn	600C	1hr	$In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$/InP
5	Zn	600C	4hr	$In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$/InP
6	Zn	500C	4hr	$In_{0.62}Ga_{0.38}As_{0.61}P_{0.39}$/InP
7	Te	600C	50hr	$In_{0.62}Ga_{0.38}As_{0.61}P_{0.39}$/InP

The depth profiles of as-grown $In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$/InP heteroepitaxial layer and of $In_{0.62}Ga_{0.38}As_{0.61}P_{0.39}$/InP heteroepitaxial layer annealed at 600°C for 50 hours are shown in Fig. 4 and Fig. 5, respectively. We confirm that the annealing effect alone can not cause any significant interface grading while it induces In outdiffusion. As shown in Fig.6, the depth profile of $In_{0.72}Ga_{0.28}As_{0.61}P_{0.39}$/InP heterostructure interface with Zn diffusion of diffusion temperature 600°C and diffusion time 15 min, indicates that Zn diffusion causes significant grading at the interface. By comparison with Fig.5, we can conclude that the grading is due to Zn diffusion rather than the annealing effect. And we can also find a large amount of In outdiffusion being described later.

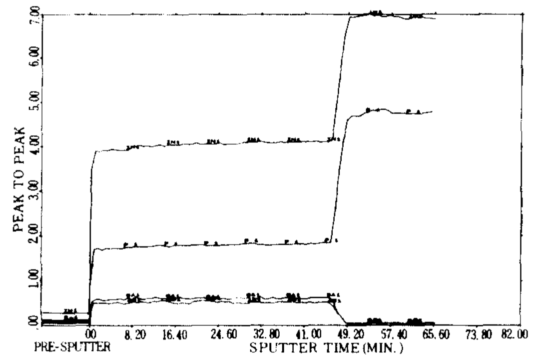

Fig.4. Auger depth profile of 'as grown' InGaAsP/InP interface.

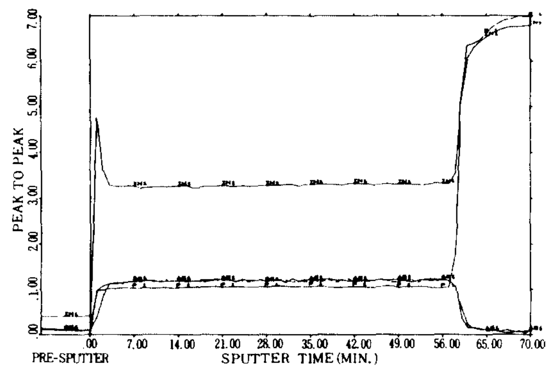

Fig.5. Auger depth profile of annealed InGaAsP/InP interface at 600°C for 50 hours.

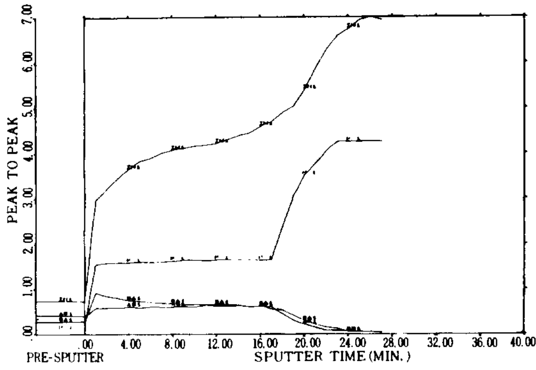

Fig.6. Auger depth profile of InGaAsP/InP epitaxial interface with Zn diffusion at diffusion temperature 600°C for 15 min.

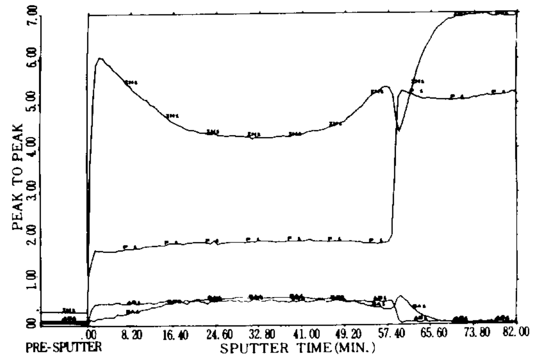

Fig.7. Auger depth profile of InGaAsP/InP epitaxial interface with Zn diffusion at diffusion temperature 600°C for 1 hour.

The profiles of the $In_{0.72}$ $Ga_{0.28}$ $As_{0.61}$ $P_{0.39}$ /InP heterostructure interface with Zn dopant at the diffusion temperature 600°C, depending on the diffusion time are shown in Fig. 7 and Fig. 8 for diffusion time 1 and 4 hours, respectively. As the diffusion time becomes longer, the interface grading becomes more conspicuous. We can conclude that Zn diffusion causes significant interface grading, outdiffusion and interdiffusion. Such phenomena increase with diffusion time.

Fig.9 is the depth profile of $In_{0.62}$ $Ga_{0.38}$ $As_{0.83}$ $P_{0.17}$/InP heterostructure interface with Zn diffusion at diffusion temperature 500 C and diffusion time 4 hours. It does not exhibit significant interface grading and In depletion at the interface. It appears that there is a threshold value of temperature between 500°C and 600°C at which significant interface grading and In depletion start to take place.

From the above experimental results, it can be stated that Zn diffusion causes significant interface grading, In outdiffusion, In depletion at the interface and Ga,P richness at the interface. Such effects are dependent upon diffusion time and temperature and increase as diffusion time. There may be critical point of temperature between 500°C and 600°C at which such effects start to take place. As in Fig.10, the depth profile of $In_{0.62}$ $Ga_{0.38}$ $AS_{0.83}$ $P_{0.17}$ /InP heterostructure interface with Te diffusion at diffusion temperature 600°C and diffusion time 50 hour. In depletion and Ga,P richness at the interface are not found. Thus it can be concluded that Zn must be responsible for such phenomena.

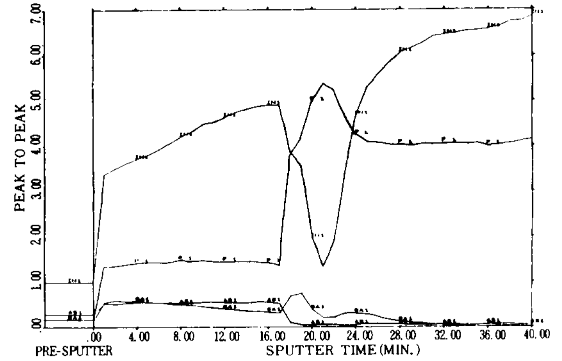

Fig.8. Auger depth profile of InGaAsP/InP epitaxial interface with Zn diffusion at diffusion temperature 600°C for 4 hours.

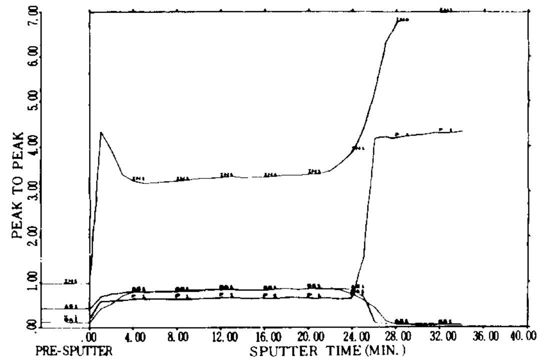

Fig.9. Auger depth profile of InGaAsP/InP epitaxial interface with Zn diffusion at diffusion temperature 500°C for 4 hours.

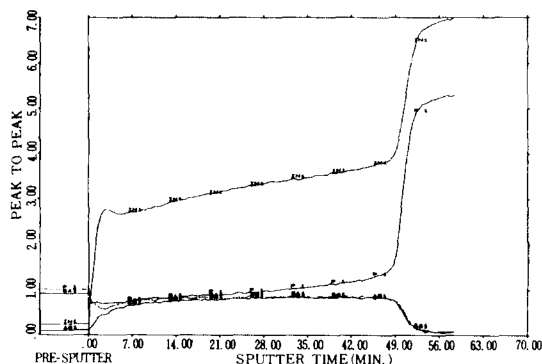

Fig.10. Auger depth profile of InGaAsP/InP epitaxial interface with Te dissusion at diffusion temperature 600°C for 50 hours.

It has been reported that there exists the gettering of Zn in InGaAsP/InP interfaces during heat treatment. The gettering is characterized by the migration of a dopant element during heat treatment, and its accumulation in specific regions. And it has been suggested that the Zn getters into a defect rich region at the interface.[4] This region could be present in the 'as grown' wafer or introduced during heat treatment due to effect such as the strain induced by a thermal expansion mismatch between the layers. Also, the gettering of Zn has been shown to increase monotonically with temperature and time, and seems to be consistent with a diffusion-limited process.[5,7,12]

Thus we can suggest that the Zn gettering phenomena cause the In depletion and Ga,P richness at the InGaAsP/InP interface, and that Zn gettering results from the defect on the 'as grown' wafer or the strain induced by a thermal expansion mismatch between the layers. Such In depletion and Ga,P richness at the interface increase monotonically with diffusion time. Any grading, depletion and richness of composition at the interface region can introduce additional strain, misfit dislocations, and other defects. These defects can have disastrous effects on device life, and reverse leakage current.

Secondary Ion Mass Spectroscopy (SIMS) has great sensitivity for trace level materials, such as dopants.[3] It uses ions to erode the sample surface while the sputtered ions are analyzed by either a quadropole or magnetic spectrometer. In order to analyze the relation between the phenomena at the interface and Zn diffusion completely, we need SIMS analysis of InGaAsP/InP interface.

IV. Conclusion

We have investigated the surface contamination of InGaAs surface using point analysis of Auger electron spectroscopy. The main surface contamination is due to carbon and oxygen species.

Boron and sulfur were also found to be present.

We have obtained Auger depth profile of InGaAsP/InP heteroepitaxial interface using depth profiling technique with Ar ion beam sputtering. The samples were prepared with different diffusion temperature and diffusion time, as well as different dopants. Zn diffusion causes significant interface grading, In depletion, Ga and P richness at the interface, and In outdiffusion at the surface. Such effects are found to be dependent upon diffusion time, diffusion temperature and dopants. As diffusion time increase, the effect is enhanced. It can be suggested that the Zn gettering at the interface region takes part iin such phenomena, and that the Zn gettering originates from the defects on the 'as grown' wafer or the strain induced by a thermal mismatch at the interface of InGaAs/InP.

Since AES can not detect extremely low concentration ($< 0.1\%$), we need to analyze the interface problem induced from dopant diffusion by SIMS analysis technique to find out accurate effects of Zn diffusion in the phenomena at the interface.

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