EFFECT OF V/III RATIO ON THE OPTICAL PROPERTIES OF LPMOVPE GROWN UNDOPED GaAs EPI-FILMS

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Abstract - Low temperature photoluminescence spectroscopy is used extensively to study the distribution of defects, concerning the type and impurity in a semiconductor film. Typical photoluminescence spectra are observed in a near band edge region. The undoped GaAs epitaxial layers grown by low pressure metal organic vapor phase epitaxy under different V/III ratios, an optimum ratio corresponding to a minimum number of shallow impurities was clearly identified. The V/III ratio has strong effect on the optical properties of undoped GaAs epitaxial layers. When the V/III ratio was varied from 45 to 87, the electron concentration, n, of undoped GaAs increased with increasing V/III ratio. Below the V/III ratio of 45 in our case, the sample exhibited a p-type behavior, which has been identified by photoluminescence as well as depth profiling by Electro-chemical Capacitance Voltage (ECV) profiler.

A. Introduction

Metal Organic Vapor Phase Epitaxy (MOVPE) is well known for the growth of epitaxial GaAs, related III-V compounds and their heterostructures. MOVPE has been successfully employed to grow high performance devices such as, lasers, solar cells, MESFETs, and QWs heterostructures, superlattices, HEMTs and other electronic and optoelectronic devices. Little understanding is evident in the literature to the effect of systematic variation of V/III ratio on the optical behavior in epi-GaAs film. Hence, present paper reports the results from the effect of V/III ratio on the optical properties of undoped GaAs epitaxial layers by photoluminescence spectroscopy and determine a optimum V/III ratio for device quality epitaxial layers by MOVPE approach.

B. Experimental

The undoped GaAs epitaxial layers were grown in low pressure horizontal MOCVD reactor. The source materials were trimethylgallium (TMGa), arsine(AsH_3, 100%) and palladium purified H_2 as a carrier gas. Both Cr-doped semi-insulating GaAs and Si-doped n^+GaAs (100) substrates (epi-ready) supplied by American Xtal Technology, offset by 2° towards [110] direction were used for epitaxial growth process. During the growth, the substrate temperature and pressure inside the reactor were kept at 700°C and 100 Torr, respectively. The TMGa flow rate was 10 SCCM and the AsH_3 flow rate were varied from 25 to 50 SCCM in order to obtain the different stoichiometric epilayers, to reach a total flow rate of 2 SLPM. The V/III ratios of the samples were varied from 21 to 87. The details of the growth procedure can be found elsewhere [1].

Photoluminescence (PL) measurements were carried out at 4.2K using a MIDAC Fourier Transform PL (FTPL) system. An Argon ion laser operating at a

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wavelength of 5145A^0 were used as a source of excitation. The exposed area was about 3 mm^2. PL signal was detected by a LN$_2$ cooled Ge-Photodetector whose operating range is about 0.75-1.9ev, while resolution was kept at 0.5mev.

C. Results and discussion

Fig.1 shows the Fourier Transform Photoluminescence (FTPL) spectrum of one of the undoped GaAs epilayer recorded at 4.2K at a laser excitation power of 100mW. Two characteristic photoluminescence bands were obtained from all the samples, such as exciton complexes and acceptor related transitions. In the exciton related region, the peaks were identified as the radiative recombination of a free exciton (FE)(1.5152eV), exciton bound to neutral donor (D^{0}X)(1.5141eV), an ionized donor (D$^+$X)(1.5133eV), and exciton bound to neutral acceptor (A^{0}X)(1.5125eV). The emission due to the free exciton was observed in our samples and confirms their high purity [2] and the peak intensity due to FE is higher compared to peak intensity due to D-A pair.

The other PL bands were also observed around 1.49eV (GaAs acceptor related region). The FWHM of this band was about 3.0meV. Three of the more common impurities incorporated during the MOCVD growth of undoped GaAs epilayer which may include C, Zn, Mg [3]. The PL peaks at 1.490eV and 1.4933eV (weak shoulder compared to peak intensity at 1.490eV at 4.2K) are due to donor-to-acceptor transition (DA) and the conduction band-to-acceptor or donor-to-valence band (DV)(also called free-to-bound, FB) transition, respectively. At low temperatures (eg. 4.2K), the donor originated transition (DA) dominate over the conduction band originated transition (FB) and when the temperature is increased from 4.2K, DA pair intensity decreases rapidly because of donor ionization energy and it is confirmed by Fig.2.

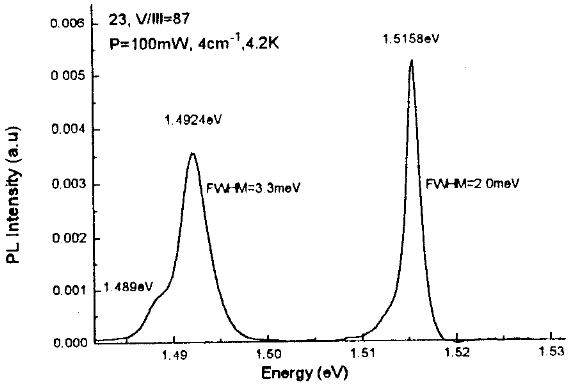

Fig.1: PL spectrum of undoped GaAs at 4.2K

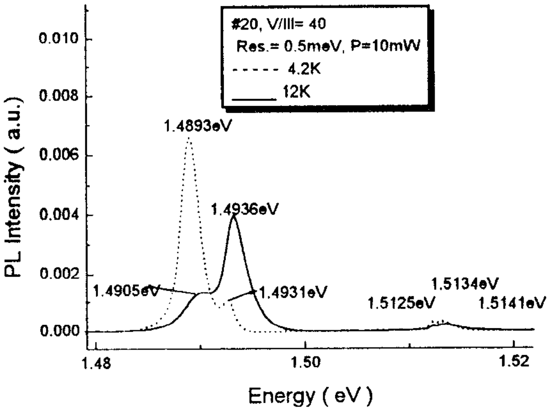

Fig.2: Temperature variation of PL spectra of GaAs

C.1. Effect of V/III ratio: Undoped GaAs

To observe the effect of V/III ratios on the impurity incorporation in GaAs epilayers, we have shown in Fig.3 that the PL spectra of undoped GaAs with different V/III ratios at 4.2k at 100mW laser power. Usually the information on the dopant density is difficult to obtain through PL. However, some attempts have been made to relate the strength of different recombinations involving impurities to their actual densities or to the compensation ratios[4]. Fig.3 depicts the peak intensity of the

(D^oA^o) transition due to carbon and the peak intensities of the D^oX and A^oX as a function of V/III ratios. From the figure it is seen that the intensities of the luminescence lines due to the (D^oX), (A^oX), and (D^oA^o)(C) are strongly dependent on the V/III ratios. The relative intensity ratios of D^oX and A^oX is the qualitative information of the dopant species incorporated during growth in GaAs epilayers. The intensity of the D^oA^o(C) transition decreases with increasing V/III ratio.

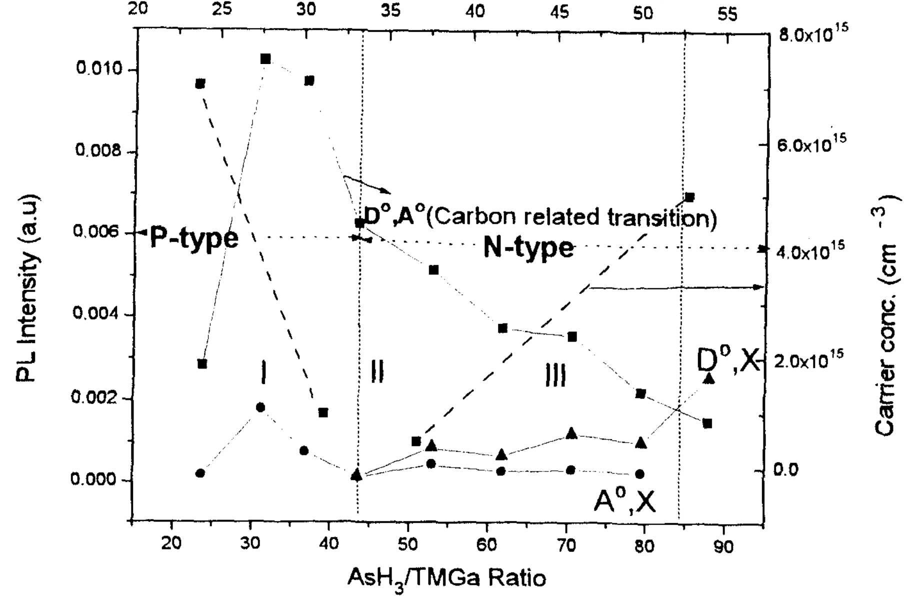

Fig.3: PL intensities of (D^oA^o),(A^oX),(D^oX) and carrier concentrations (p/n) (dotted lines) from ECV profiler vs. V/III ratios of undoped GaAs epi-films.

RegionI: The carrier concentration in undoped GaAs is sensitive to the V/III ratios. From the figure, it is seen that the carrier type changes from p-to n-type as V/III (>45) ratio increases. This behavior results from a decrease in the electrically active carbon concentration in the epitaxial layer as the V/III ratio is increased. The electrical behavior with changing V/III ratio can now be understood through the mechanism of carbon removal by the AsH_3 [5]. At low V/III ratios, there is relatively little AsH_3 present , so the efficiency of H combining with the CH_X radicals is low. These radicals can further decompose or react with other growth constituents on the surface, leading to carbon incorporation and hence exhibits p-type conduction. Carbon is the main impurity that is intrinsic to the growth process and has its soure in the organic ligands attached to the metals.

Region II: In this region the net carrier concentration $|N_A\text{-}N_D|$ is very low, when the carbon and the unintentional donor concentrations are approximately equal. This can be clearly seen from the figure.

Region III: As the V/III ratio is increased, more AsH_3 present and thus H is present, and tends to reduce carbon incorporation. In this region the D^oX /A^oX exciton *ratios increases with increasing V/III ratios indicating more donor* incorporation and hence more n-type behavior. At the V/III ratio of 82, D^oA^o intensity is very low compared to D^oX intensity. Also in this region the exciton intensity is very large compared to the D^oA^o intensity. The flow rate of AsH_3 and TMGa beyond this V/III ratio crossing point are 48 and 10 SCCM, respectively. Therefore, the density of C atoms incorporated in epilayers is low under these growth conditions. This data obtained from PL spectra was found consistent the type determination obtained by Electro-chemical Capacitace Voltage (ECV) profiler.

The most common donors used in the MOCVD of III-V semiconductors are Si, S, Se and Te; common acceptors include C, Zn and Mg. The material can become highly resistive when the carbon and the unintentional donor concentrations are approximately equal. A further increase in the V/III ratio results in donor-dominated conduction, and the material becomes n-type. Germanium originating as a contaminant in AsH_3 has been suggested as the dominant donor[6]. The n-type carrier concentration increases because of Ge concentration increases with the AsH_3 concentration. The V/III ratio at which the conductivity changes type is dependent on the purity of the precursors as well as the AsH_3 decomposition efficiency. The variation of conductivity type with V/III ratio in undoped GaAs provides an example of how strongly the growth process can affect the electrical characteristics of the material and the growth process.

The concentration of substitutional impurities incorporated in As or Ga sites during the growth depends on the nature of impurities present in the gases as well as on the thermodynamics of the growing crystal which determines the concentration of sites available for impurities [5,6]. At a fixed growth temperature the ratio of As to Ga available sites is a function of the two gas (AsH_3 and TMGa) partial pressures and our experimental conditions varies with the AsH_3 partial pressure. At low AsH_3 partial pressures a purely thermodynamics controlled growth favors the incorporation of carbon in arsenic sites to produce acceptors. However, the analysis of low temperature PL spectrum (Fig.1) shows that some Mg and Zn are also present in the layers. As the AsH_3 partial pressure increases, the concentration of C acceptor decreases while that of Mg and eventually Zn increases[3]. When the V/III ratio crossed 45, the sample shows n-type conduction and N_D increases with increasing V/III ratio. We believed that the probable presence of Ge gives the contribution of increasing N_D, as it is very efficient n-type dopant of GaAs.

D. Conclusions

Undoped GaAs epilayers which were grown under the growth conditions of different V/III ratios were characterized using photoluminescence. The purpose of this work was the optimization of epitaxial growth parameters. We applied this method to determine the optimum V/III ratio of our MOVPE growth process. The same analysis can be done with other growth parameters, such as, the substrate temperature, total gas flow, reactor total pressure and the reactants partial pressures. Studies of photoluminescence at 4.2K indicate the emission of free exciton and confirmed the high quality of the film. This method is useful for the understanding of the impurity incorporation during the MOVPE growth.

E. References

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