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Electrochemical Capacitance-Voltage (EC-V) of AlGaAs: C Growth by Metalorganic Chemical Vapor Deposition (MOCVD) for Atomic Interdiffusion

P. L. Gareso[1]

[1]Department of Physics, Faculty of Mathematics and Natural Sciences Hasanuddin University, JL. Perintis Kemerdekaan Km 10, makassar 90245 Indonesia
*E-mail: pgareso@gmail.com

ABSTRACT

Electrochemical capacitance-voltage (EC-V) method has been used to investigate the effect of carbon tetrachloride to AlGaAs layer. The AlGaAs layers doped with carbon were grown using metalorganic chemical vapor deposition (MOCVD) at temperature growth of 650°C. Electrochemical capacitance-voltage (EC-V) has been used to measure the etchback (the growth rate) AlGaAs layer. Scanning electron microscopy (SEM) was also used to confirm the EC-V results to measure the thickness of the AlGaAs:C layers. The samples were grown at various temperatures and CCl_4 flow rate on (001) oriented *p*-GaAs. Based on the EC-V measurement, it was found that the etchback was strongly dependent on growth temperature and CCl_4 flow rates. In comparison to the previous results of GaAs:C superlattices, the hole concentration in AlGaAs:C was much higher than in GaAs:C at the same growth condition (growth temperature = 700°C, CCl_4 flow = 0.89 μmol/min) with the etchback rate in AlGaAs:C slower than in GaAs:C.

Keywords: *Carbon tetrachloride, electrochemical capacitance voltage, etchback rate*

1. INTRODUCTION

Interdiffusion of heterostructures has been explored since the early 1980s as a promising technique for both the tuning of the quantum well (QW) emission/detection wavelength as well as monolithic integration of optoelectronic devices on a single chip [1-3]. Interdiffusion or intermixing, as it is sometimes known, is achieved typically through an annealing step. The exchange of elements between the quantum well and barrier is driven by the concentration gradient of each element which occurs at the quantum well/barrier interface. In this way, the composition of the materials near the interface is altered, typically changing the initially square well potential to approximately a double error function potential. As the shape of the potential is changed, the energy eigen states of electrons and holes within the quantum well are altered. Typically, the effective bandgap of the quantum well is increased after intermixing, resulting in blueshift of the emission wavelength. Hence, by using planar masking technology, devices with differing functionalities such as a laser, modulator and a waveguide could be integrated onto a single chip.

Carbon atom is recently used as dopant atom in the semiconductor devices such as integrated optoelectronic devices since

carbon doping is well suited for optoelectronical devices where high temperature annealing is required to initiate the interdiffusion. Carbon is used in this present study because it has low diffusion coefficient compare to conventional dopant such as Mg, Zn and Be [4,5]. Moreover, carbon doping shows high doping concentration [6,7], and high solid solubility [8]. These features make carbon suitable for electronic and optoelectronic devices such as heterojunction bipolar transition (HBTs) [9] and laser diodes [10,11]. Since chlorine radical created by CCl_4 affects the growth rate of AlGaAs layers, therefore, we first find the optimum growth of AlGaAs doped with carbon.

In this work, We investigate the optimun growth condition of carbon doped structure by performing the electrochemical capacitance-voltage measurement in order to achieve high quality material for atomic intermixing.

2. EKSPERIMENTAL

The samples used in this work were grown by metalorganic chemical vapour deposition (MOCVD) using a horizontal flow AIXTRON AIX 200/4 reactor with a rotating susceptor. MOCVD is an epitaxial deposition process using vapour phase reaction between metalorganic compounds of the group-III elements and hydrides of the group-V elements. The precursors of AlGaAs layers are metal alkyls (group-III elements), namely trimethylgallium (TMGa), and trimethylaluminium (TMAl), while for the group-V element is arsine (AsH_3). These species are introduced in the chamber using ultrahigh-purity hydrogen (obtained by diffusing hydrogen through a palladium silver alloy membrane).

The source used for C doping in the MOCVD reactor is CCl_4. Due to the etch-back effect of the Cl radicals, a serie of AlGaAs samples were grown to study this effect. AlGaAs layer was grown at various temperature and CCl_4 flow rate on (001) oriented *p*-GaAs. The growth temperature of AlGaAs from 700ºC to 750ºC. The V/III ratio was kept constant at 37. Trimethylgallium (TMGa), trimethylaluminium (TMAl), and AsH_3 were used as precursors with flow rates of 20, 30, and 39 µmol/min, respectively. CCl_4 was used as the C-dopant source with flow rates varying from 0.89 µmol/min to 30 µmol/min. The AlGaAs structures consisted of a 0.2 µm undoped GaAs buffer layers, a 0.5 µm $Al_{0.6}Ga_{0.4}As$ layers doped with carbon and followed by a 20 nm GaAs capping layers. The schematic diagram of the AlGaAs structures are shown in Figure 1.

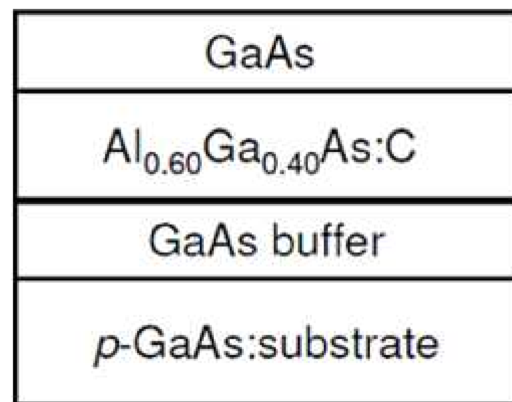

Fig. 1 Schematic of the structures of AlGaAs:C layers used for studying the etchback of CCl_4.

The electrochemical capacitance-voltage (EC-V) profiling measurements were carried out with a BIO-RAD PN4300PC profiler using NaOH:EDTA as an electrochemical etching solution for GaAs. Scanning electron microscopy (SEM) was used to measure the thickness of the layers.

3. RESULTS AND DISCUSSION

Depth profiling of carrier concentration by conventional C-V measurements is limited by the breakdown voltage of the Schottky diode, especially in the case where the epilayer has a very high doping concentration. To overcome this limitation, EC-V was used to measure the carrier concentration of highly doped epilayers. A Schottky diode is formed at the surface of the semiconductor material which is in contact with an electrolyte. A very small voltage needs to be applied during EC-V measurements to avoid breakdown of the Schottky diode. A very large depth can be profiled by using a step-by-step etching process and measuring. In this work, the electrochemical capacitance voltage measurements were carried out with a BIO-RAD PN4300PC profiler using NaOH: EDTA as an electrochemical etching solution for GaAs. The dissolution or the etching process of semiconductors depends mainly on the presence of holes. In the case of *n*-type material where electrons are the majority carriers, holes have to be generated for dissolution to take place. This can be done by illuminating the electrolyte/semiconductor junction with light which is strongly absorbed near the surface region of the semiconductor. In case of *p*-type materials where holes are sufficient, dissolution is achieved under forward bias.

Previous results investigated the etchback of CCl_4 to the superlattices of GaAs doped with carbon atom using electrochemical capacitance measurement [12]. This results showed the effect of CCl_4 to the GaAs with varrying three different temperatures and flow rate of CCl_4. Based on these studies, they found that the hole concentration strongly depends on the growth temperature. The hole concentration of samples grown at 700ºC is significantly lower than the samples grown at 650ºC and 600ºC. The reasons for reduction of the growth rate by CCl_4 is as the temperature growth increased the formation of $GaCl_4$ or $GaCl_3$ is also increased. These molecules are formed as a result of the reaction CCl_4 with TMGa. Since GaCl and $GaCl_3$ are volatile, these molecules are subsequently desorbed into the outward stream of carrier gas.

As a comparison with GaAs doped with carbon atom, the AlGaAs layers doped with carbon were also grown. The EC-V profiles of carrier concentration of $Al_{0.6}Ga_{0.4}As$: C samples with varying growth temperature and CCl_4 flow rate are shown in Figure 2. (a) and (b) respectively. Dependence of growth temperature in $Al_{0.6}Ga_{0.4}As$:C to the hole concentration is not observed in this temperature range, although a small difference in the etch-back is observed. A

signifcant increase in hole concentration at the high CCl_4 flow rate was observed with a very little change in etchback at high CCl_4 flow rate. In addition to this, the hole concentration in the $Al_{0.6}Ga_{0.4}As$: C is much higher than in GaAs: C at similar growth condition (growth temperature=700ºC,CCl_4 flow =0.89 μmol/min) with the etch-back rate in $Al_{0.6}Ga_{0.4}As$:C is smaller than in GaAs:C [13].

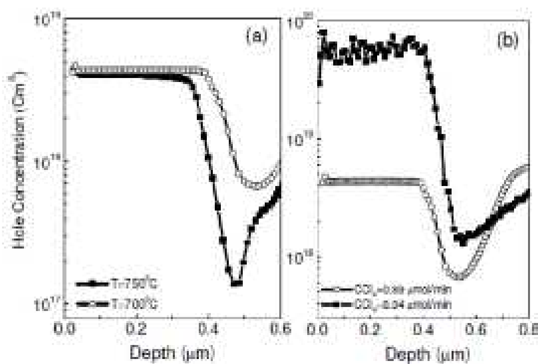

Fig. 2 (a) EC-V depth profile of carrier concentration of $Al_{0.6}Ga_{0.4}As$: C samples with two different growth temperatures. (b) EC-V depth profile of carrier concentration of $Al_{0.6}Ga_{0.4}As$:C samples grown at 700±C with two different CCl_4 flow rates.

This is probably due to the $AlCl_3$ in the reaction of CCl_4 and AlGaAs which is less volatile than $GaCl_3$ (reaction of CCl_4 and GaAs). Therefore, the etchback rate will be slower for AlAs than for GaAs and as a result C is incorporated more efficiently in the AlGaAs layer than GaAs layers. Al-C bond strength is higher than Ga-C bond strength [14] leading to enhanced incorporation of carbon in AlGaAs when compared to GaAs. Figure 3 Shows the cross-sectional SEM images of the AlGaAs:C layers to determine their thickness. A summary of the results AlGaAs is listed in Table 1, also the results of GaAs is listed in comparison to the AlGaAs layers.

Table 1. Comparion the actual thickness of AlGaAs layer doped with carbon at various temperature

Samples	Growth temperature (ºC)	CCl_4 flow rate (μmol/min)	V/III ratio	Actual thickness (μm)	Target thickness (μm)
$Al_{0.6}Ga_{0.4}As$:C	700	30	37	0.43	0.5
$Al_{0.6}Ga_{0.4}As$:C	750	30	37	0.47	0.5
GaAs:C [12]	700	30	37	0.28	0.5

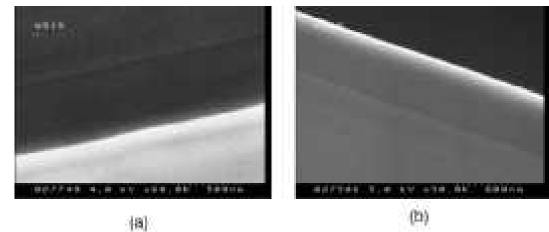

Fig. 3 SEM cross section images from two different $Al_{0.6}Ga_{0.4}As$: C samples. (a) Gowth temperature = 750ºC, and CCl_4 = 0.89 μmol/min, (b) Growth temperature = 700ºC, and CCl_4=0.89 μmol/min.

4. CONCLUSION

In summary, the effect of CCl_4 on the growth rate (etch-back) of AlGaAs:C has been investigated. It was found that the etchback is strongly dependent on the growth temperature and the CCl_4 flow rates. The mechanism leading to a reduction of growth rate is caused by the formation of GaCl and $GaCl_3$. In addition, the hole concentration in AlGaAs:C is much higher than in GaAs:C at the same growth condition (growth temperature=700 C,CCl_4 flow

=0.89µmol/min) with the etchback rate in $Al_{0.6}Ga_{0.4}As$:C slower than in GaAs:C. This is due to the $AlCl_3$ being less volatile than $GaCl_3$.

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