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Enhanced efficiency in GaInP/GaAs tandem solar cells using carbon doped GaAs in tunnel junction

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ABSTRACT

Carbon doping of GaAs using CBr4 (carbon tetrabromide) in metal-organic chemical vapor deposition (MOCVD) was investigated to obtain very high and sharp doping profiles required for tunnel junction in tandem solar cells. It was found that the hole concentration increased with decreasing growth temperature and V/III ratio. Hole doping profiles versus distance from the sample surface showed that the hole concentration near the surface was very low in comparison with that far below the surface. As a postgrowth treatment, CBr4 was supplied during the cool down process and produced almost constant hole concentration of 1×10^{20} cm⁻³ regardless of the depth, when CBr₄ flow rate was 9.53 μ mol/min. Based on these results, solar cells were fabricated using both carbon (C) and zinc (Zn) as a p-type dopant. It was shown that C doping exhibits higher efficiency and lower series resistance than those of Zn doping in GaInP/GaAs tandem solar cells.

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1. Introduction

Carbon (C) has been researched extensively as a p-type dopant in GaAs and related materials for applications in electronic and optoelectronic devices such as heterojunction bipolar transistors (HBTs), vertical cavity surface emitting lasers (VCSELs) and solar cells [\[1–3\].](#page--1-0) Doping levels up to 1 \times 10²⁰ cm^{–3} have also been realized with less morphological degradation using metal-organic chemical vapor deposition (MOCVD) [\[4,5\]](#page--1-0). Carbon has lower diffusion coefficient, higher solubility, and smaller memory effect than zinc (Zn) [\[6–8\]](#page--1-0). Thus, in contrast to Zn doping, highly C-doped layers can be obtained during overgrowth with negligible tailing effect [\[9\].](#page--1-0) The low diffusion coefficient and the lack of tailing make C doping more attractive than Zn doping for devices that require highly doped and well-defined p-type doping profiles, such as tunnel junctions [\[3\]](#page--1-0) and HBTs [\[10\].](#page--1-0)

Carbon doping can be performed using two different methods such as intrinsic and extrinsic doping. In intrinsic carbon doping, carbon atoms from the group III precursor, trimethylgallium (TMGa) can be incorporated into the deposited material by reducing the growth temperature and the V/III precursor concentration ratio [\[11–13\]](#page--1-0), which requires a tight control of growth parameters when using arsine $(ASH₃)$ as the group V precursor. On the other hand, carbon atoms can be introduced extrinsically into the depos-

Corresponding author. E-mail address: hogyoungkim@gmail.com (H. Kim). ited material using halomethanes such as carbon tetrachloride $(CCl₄)$, carbon tetrabromide $(CBr₄)$ and carbon bromidetrichloride $(CBrCl₃)$ because they have high doping efficiencies due to weak C–Cl or C–Br bonds [\[14–16\]](#page--1-0). This method makes it easier to control the carbon doping density widely without changing growth conditions such as growth temperature and V/III ratio. High carbon doping levels (>10²⁰ cm⁻³) have been achieved using CCl₄ as a carbon source [\[17\].](#page--1-0) However, a strong reduction of growth rate was observed due to the in situ etching of GaAs by Cl [\[18,19\]](#page--1-0). The reduction in the growth rate of C-doped GaAs was also reported when using CBr₄ due to the HBr etching [\[14\]](#page--1-0). The use of CBrCl₃ was reported by Uchida et al. [\[20\]](#page--1-0) to reduce the etching of GaAs.

When fabricating tandem solar cells, very thin and wide-bandgap tunnel junction is necessary to minimize optical absorption. However, since the tunnel peak current density decreases exponentially with the increase in bandgap energy, it is not easy to obtain low-resistance wide-bandgap tunnel junction. An GaInP tunnel junction has been tried in GaInP/GaAs tandem cell using double heterostructure (DH) to prevent the impurity diffusion (Zn) [\[3\]](#page--1-0). The AlGaAs/GaAs tandem solar cells were reported to reduce the voltage losses effectively across the tunnel junction by incorporation of semimetallic ErAs nanoparticles into the GaAs tunnel junction, where Be and Si were used for p-dopant and ndopant, respectively [\[21\].](#page--1-0) Although lots of research has been done to develop the GaAs-based solar cells, there are relatively few reports on the GaInP/GaAs tandem solar cells using carbon doped GaAs in the tunnel junction. For the present work, we describe

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the carbon doping profiles of GaAs grown by MOCVD under variation of the growth parameters such as $CBr₄$ flow rate, growth temperature, V/III ratio and post-growth treatment. In addition, the conversion efficiency for the GaInP/GaAs tandem solar cells with GaAs tunnel junction using both C and Zn as a p-type dopant is discussed.

2. Experimental

Growth was carried out in a multiwafer MOCVD reactor (AIX2600G3 IC) on semi-insulating GaAs (100) substrates with a misorientation of 2° toward <1 1 1> plane. TMGa and AsH₃ were used as the precursors of Ga and As, respectively. The carrier gas was hydrogen and the reactor pressure was kept at 50 mbar. Carbon doping was achieved using the extrinsic source of $CBr₄$. The CBr₄ bath temperature was maintained at 25 °C. All samples used in this study were grown with a constant TMGa flow rate of 265.05μ mol/min. The total flow rate in the reactor was 58 slm. The influence of three growth parameters such as growth temperature, CBr_4 flow rate and V/III ratio on the hole concentration was first investigated to obtain very high doping levels up to 1×10^{20} cm⁻³. After growth process, AsH₃ was supplied to all samples until the temperature cooled down to 350 \degree C in order to prevent As outdiffusion. Thereafter, the effect of $CBr₄$ flow rate under the cool down process on the hole concentration was studied in order to obtain well-defined carbon doping profiles. The $CBr₄$ flow rate was changed from 0 to 9.53μ mol/min. Electrochemical capacitance–voltage (ECV) measurements were used to determine the hole concentration of carbon doped GaAs layers. Atomic force microscopy (AFM) was used to investigate the surface morphology.

3. Results and discussion

Fig. 1a shows the hole concentration versus $CBr₄$ flow rate. The growth temperature and the V/III ratio were 600 \degree C and 57.25, respectively. When CBr₄ flow rate increases, the hole concentration remains almost constant, although there is a slight increase. Kurpas et al. [\[22\]](#page--1-0) demonstrated that there is a sublinear relationship between hole concentration and $CBr₄$ partial pressure which is expressed as p \propto [CBr₄]^{0.7}. This relation shows that the hole concentration increases linearly at relatively low doping levels and tends to saturate at high doping levels. Watanabe et al. [\[23\]](#page--1-0) investigated the behavior of the hole concentration in carbon doped GaAs grown by MOCVD using $CBr₄$ as a carbon source and concluded that the hole concentration tends to saturate at higher $CBr₄$ flow rates in the very high doping region due to the saturation of carbon incorporation efficiency, not the deactivation of carbon acceptors. The same mechanism can be applied to explain the saturation of the hole doping levels.

Fig. 1b shows the hole concentration as a function of growth temperature. The CBr₄ flow rate and the V/III ratio were kept at 21.43 µmol/min and 57.25, respectively. The growth temperature was varied from 550 to 600 °C. It is clearly observed that the hole concentration was increased by decreasing the growth temperature. Fig. 1c shows the hole concentration versus V/III ratio. The growth temperature and the CBr₄ flow rate were 550 °C and 21.43 μ mol/min, respectively. When the V/III ratio (or AsH₃ flow rate) decreases, the hole concentration increases accordingly and reaches to 1 \times 10 20 cm $^{-3}$. These results imply that the hole concentration increases with decreasing growth temperature and V/III ratio, which are generally observed in the carbon doped p-type GaAs epilayer.

In intrinsic carbon doping, carbon incorporation is possible from the hydrogen radicals generated by the decomposition of TMGa [\[16\]](#page--1-0). When AsH₃ is present, these hydrogen radicals can be present

Fig. 1. Hole concentration as a function of (a) CBr_4 flow rate, (b) growth temperature and (c) V/III ratio, and (d) hole doping profile versus depth for the reference sample that CBr_4 flow was turned off after growth process.

in the form of methane and be desorbed at the GaAs surface, reducing carbon incorporation in GaAs. This mechanism can explain the rapid increase in the hole concentration when V/III ratio decreases. As discussed by Watanabe et al. [\[23\]](#page--1-0), lower growth temperature makes the adsorption coefficient larger and a lower V/III ratio provides more sites for CBr_k to adsorb. Therefore, carbon incorporation can be enhanced further with the presence of $CBr₄$ at low growth temperature and low V/III ratio. In addition, many carbon atoms from hydrogen radicals by TMGa will incorporate with decreasing V/III ratio, increasing hole concentration further.

As discussed above, very high carbon doping $(10^{20} \text{ cm}^{-3})$ could be achieved at the growth temperature of 550 \degree C, the CBr₄ flow rate of 21.43 µmol/min, and the V/III ratio of 16.84, respectively, and these growth conditions were used to investigate the effect of in situ CBr₄ treatment after growth process on the carbon doping profiles. Fig. 1d shows the hole concentration as a function of depth from the surface without supplying $CBr₄$ after growth process (denoted as reference). As the depth increases, the hole concentration increases and reaches to the value of 10^{20} cm⁻³ when the depth is around 150 nm. When making tunnel junction by growing Sidoped n-type GaAs layer on the carbon doped p-type layer, such a doping profile which has quite low doping levels near the p-type GaAs surface cannot be used for the fabrication of tunnel junctions with high performance and low resistance. In this respect, we examined the influence of $CBr₄$ flow rate under the cool down process on the hole doping profiles.

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