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Reduction of In Composition in Heavily Zn-Doped InAlGaAs Layers Grown at Low Temperature by Metalorganic Chemical Vapor Deposition

Haruki Yokoyama, Takuya Hoshi, Naoteru Shigekawa, and Minoru Ida

NTT Photonics Laboratories, Atsugi, Kanagawa 243-0198, Japan

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Growth of heavily Zn-doped InAlGaAs at low temperature (560 °C) by metalorganic chemical vapor deposition (MOCVD) is investigated. The lattice constant contracts and the growth rate decreases with increasing dithylzinc (DEZn) flow rate. To clarify the reason, the growth rates of InAs, AlAs, and GaAs components are examined. The growth rates of AlAs and GaAs components are almost constant; only that of InAs dramatically decreases when the DEZn flow increases. This indicates that the incorporation of In is suppressed by the DEZn supply. The doping behavior during the growth is well fit by the surface adsorption-trapping model, which suggests that excess Zn atoms on the growth surface induce the reduction of the InAs component.

1. Introduction

InAlGaAs quaternary alloy lattice-matched to InP is a very attractive material because its band gap can be controlled from 0.76 eV (InGaAs) to 1.48 eV (InAlAs). Moreover, the composition control of InAlGaAs is easier than that of InGaAsP, which enables a similar band-gap engineering because the precise composition control of volatile group-V elements is not necessary. Meanwhile, Zn is widely used as a p-type dopant for III–V compound semiconductors. Therefore, Zn-doped InAlGaAs has also been applied in the fabrication of electronic and optoelectronic devices, such as heterojunction bipolar transistors (HBTs),[1] laser diodes (LDs),[2] and photodetectors.[3] However, it is well known that heavy Zn doping in III–V compound semiconductors results in abnormal Zn diffusion through the kick-out process induced by the group-III interstitials.[4] Although an effective way to suppress this diffusion is to reduce the growth temperature, Lin *et al.* studied Zn-doped InGaAs layers grown at low temperature (550 °C) by metalorganic chemical vapor deposition (MOCVD) and reported that the In composition decreases with increasing diethylzinc (DEZn) flow rate.[5] They described the possibilities of the promotion of triethylgaliium (TEGa) decomposition and suppression of trimetylindiumu (TMIn) decomposition, but it has not been clarified which reaction is dominant. However, for the practical use of heavily Zn-doped InAlGaAs layers grown by MOCVD, a fuller understanding of the growth process is necessary because adequate composition control is essential for the fabrication of device structures.

This paper systematically studies the growth rate and composition of heavily Zn-doped InAlGaAs layers grown at low temperature by MOCVD. The lattice constant contracts and the growth rate decreases with increasing DEZn flow rate. The changes of the InAs, AlAs, and GaAs components in the InAlGaAs layers indicate that only the incorporation of In is suppressed by the DEZn injection. To explain this phenomenon, the effects of excess Zn on the growth surface are discussed.

2. Experimental Procedure

The MOCVD growth was carried out using a close-coupled showerhead reactor. The epitaxial layers were grown on (001) oriented semi-insulating Fe-doped InP wafers. The group-III sources were TMIn, trimethylaluminum (TMAl), and TEGa. Group-V sources were 100% arsine (AsH_3) and 100% phosphine (PH_3). The p-type dopant was DEZn. The growth time, temperature, and pressure were 900 s, 560 °C, and 125 mbar, respectively. The carrier gas was hydrogen and its flow rate was kept at 20 slm. The wafer temperature was monitored by a LayTec EpiTT *in-situ* monitor system calibrated by the eutectic point of AlSi.

After growth, the cleaved wafers were partially masked using a photoresist. Then, the area without the photoresist was etched to the substrate with a selective wet chemical etchant. The film thickness was determined by measuring the step height using a surface profiler after the photorsist had been removed. The hole concentration and mobility were measured by the van der Pauw method at room temperature. The lattice constant and band gap were determined by double-crystal X-ray diffraction (DCXD) and photoluminescence (PL) spectroscopy measurements. The Zn concentration in the InAlGaAs layer was analyzed by secondary ion mass spectroscopy (SIMS). To examine the In, Al, and Ga composition in the InAlGaAs layer, we performed X-ray photoelectron spectroscopy (XPS). To determine the composition, we used a standard undoped InAlGaAs sample whose composition was calibrated from the band gap and lattice constant.

3. Results and Discussion

Figure 1 shows the hole and Zn concentration as a function of the DEZn flow rate. At lower DEZn flow rates, the hole concentration increases as the DEZn flow rate increases. However, at higher DEZn flow rates (more than 0.1 sccm), saturation occurs. The maximum hole concentration was about 1.1×10^{19} cm^{-3}, while the Zn concentration in the InAlGaAs layer measured by SIMS was about 1.8×10^{19} cm^{-3} (open circle in Fig. 1). Although some of the Zn atoms may occupy interstitial sites because the Zn concentration is slightly higher than the hole concentration, the suppression of Zn incorporation into the InGaAlAs layer would result in the saturation of hole concentration at higher DEZn flow rates. A similar result has also been obtained for the growth of Zn-doped InGaAs.[6]

The relationship between mobility and hole concentration in Zn-doped InAlGaAs is shown in Fig. 2. It is found that InAlGaAs has intermediate characteristics between InGaAs and InAlAs. Yoon *et al.* studied Be-doped InAlGaAs layers grown by molecular beam epitaxy (MBE) and reported that the mobility data lie between InGaAs and InAlAs.[7] They also described the possibility that the presence of a higher level of deep traps results in the lower mobility in the Al-

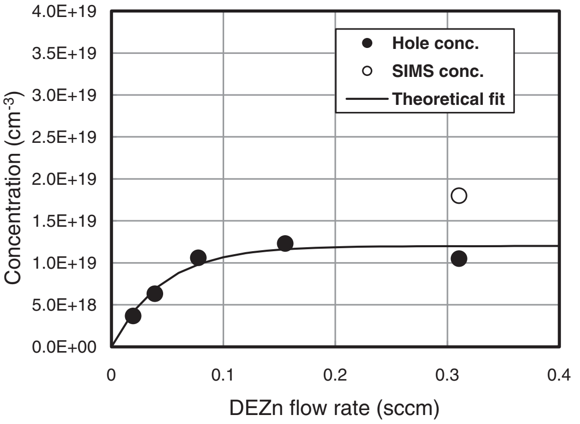

Fig. 1. Hole and Zn concentration as a function of DEZn flow rate. Closed circles and the open circle indicate the hole concentration and Zn concentration, respectively. The solid curve is a theoretical fit using eq. (8).

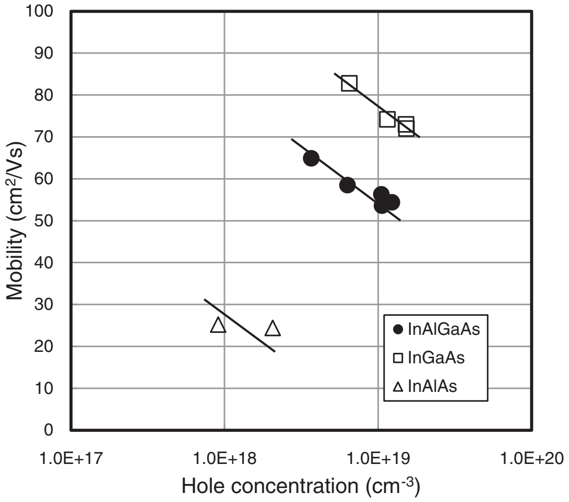

Fig. 2. Relationship between mobility and hole concentration in Zn-doped InGaAs, Zn-doped InAlAs, and Zn-doped InAlGaAs layers.

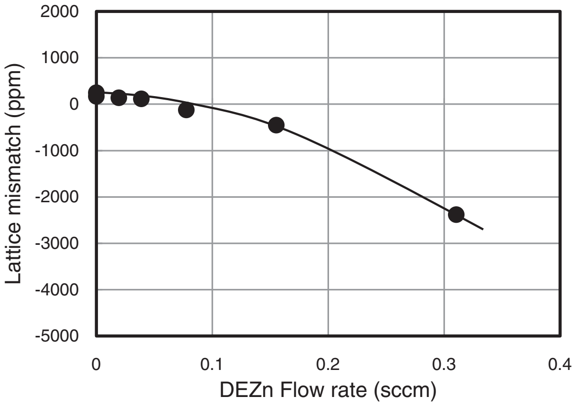

Fig. 3. Relationship between lattice mismatch and DEZn flow rate in Zn-doped InAlGaAs layers.

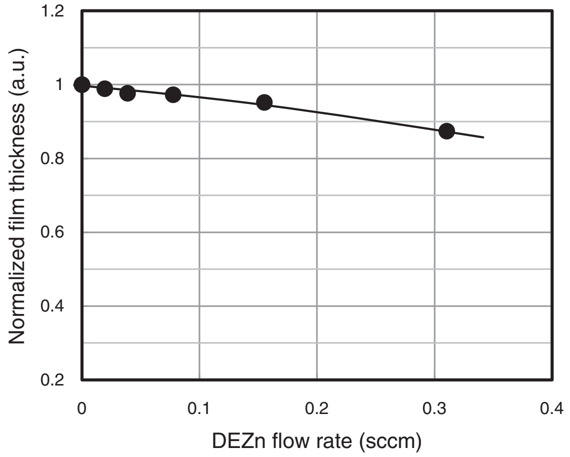

Fig. 4. Normalized film thickness of the InAlGaAs layer as a function of DEZn flow rate.

containing materials. The energy gap of undoped InAlGaAs grown under the same growth condition was around 0.9 eV. This means that our InAlGaAs layer can be used as a transparent p-type contact layer to 1500-nm wavelength, which is used for fiber-optic communications. The mobility of InGaAsP, whose band gap is 0.9 eV, is about 20% smaller than that of InAlGaAs. In addition, the maximum hole concentration of InGaAsP is about half as large as that of InAlGaAs. Therefore, it is conceivable that InAlGaAs is more suitable as a low-resistance contact layer than InGaAsP.

The lattice mismatch between the Zn-doped InAlGaAs layer and InP was also examined. In Fig. 3, the lattice mismatch becomes larger with increasing DEZn flow rate. In this work, the (+) or (−) sign of lattice mismatch means the dilation and contraction of the lattice constant compared to the lattice constant of InP. The covalent radius of Zn ($r = 1.31$ Å) is larger than that of Ga ($r = 1.26$ Å), Al ($r = 1.26$ Å), and As ($r = 1.18$ Å) and smaller than that of In ($r = 1.44$ Å).[8] Therefore, if Zn is incorporated at group-III sites and especially if it replaces In, the lattice constant of the Zn-doped InAlGaAs layer will decrease as the hole concentration increases. However, it continuously decreases even though the hole concentration saturates as shown in Fig. 1. Furthermore, Zn incorporation of more than 10^{20} cm^{-3} will be necessary in order to change the lattice constant. Therefore, we conclude that the contraction of the lattice constant is not due to the effect of substitutional Zn.

Figure 4 shows the normalized film thickness as a function of DEZn flow rate. The film thickness gradually decreases as the DEZn flow rate increases. To clarify the reason, we analyzed the solid compositions of In, Al, and Ga in InAlGaAs layers using XPS. Figure 5 shows the changes of x and y in $In_{1-x-y}Al_xGa_yAs$. The x and y for the undoped InAlGaAs layer are 0.104 and 0.363, respectively, and they increase to 0.116 and 0.398 at the DEZn flow rate of 0.31 sccm. From the film thickness in Fig. 4 and solid composition in Fig. 5, we calculated the growth rates of InAs, AlAs, and GaAs components. Figure 6 shows the normalized growth rates of InAs, AlAs, and GaAs components as a function of DEZn flow rate. The growth rates of AlAs and GaAs are almost constant but that of InAs dramatically decreases with increasing DEZn flow rate. This indicates that the suppression of In incorporation is the main reason for the lattice constant contraction and growth rate decrease. Moreover, the reduction of the InAs component with increasing DEZn flow rate was also observed for heavily

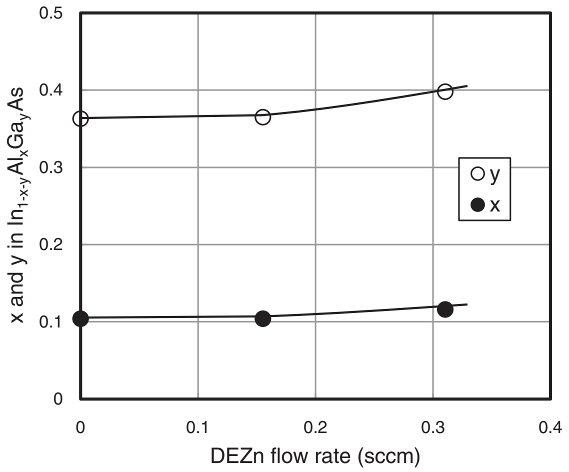

Fig. 5. The x and y in Zn-doped $In_{1-x-y}Al_xGa_yAs$ layer as a function of DEZn flow rate.

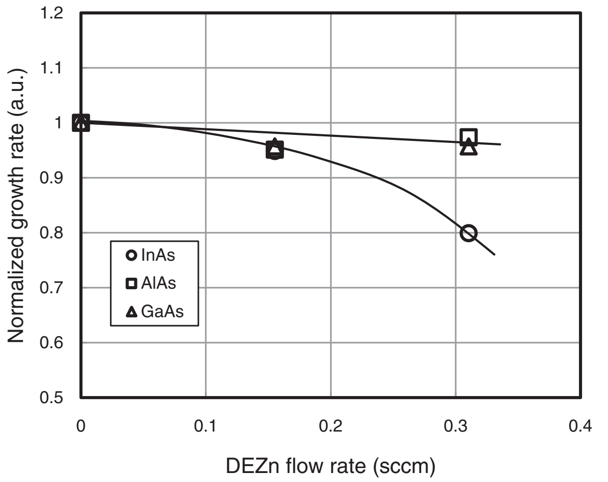

Fig. 6. Normalized growth rate of InAs, AlAs, and GaAs components as a function of DEZn flow rate.

Zn-doped InGaAs (maximum hole concentration: 2×10^{19} cm^{-3}). Although we do not have data for InAlAs and InAlGaAs with different compositions, we believe the same phenomenon takes place because Zn-doping scarcely affects the growth rates of AlAs and GaAs components in Fig. 6.

There are two possible reasons for the reduction of In composition: Suppression of TMIn decomposition and enhancement of In desorption from the growth surface. It has been reported that the pyrolysis of DEZn occurs by β-hydride elimination reactions:[9)]

$$\mathrm{Zn(C_2H_5)_2 \rightarrow ZnH_2 + 2C_2H_4}, \tag{1}$$

$$\mathrm{ZnH_2 \rightarrow Zn + H_2}, \tag{2}$$

$$\mathrm{C_2H_4 + ZnH_2 \rightarrow Zn + C_2H_6}. \tag{3}$$

Butler *et al.* has proposed the following reactions for the TMIn decomposition under the condition of low-pressure and hydrogen atmosphere:[10)]

$$\mathrm{In(CH_3)_3 \rightarrow In(CH_3)_2 + CH_3}, \tag{4}$$

$$\mathrm{CH_3 + H_2 \rightarrow CH_4 + H}, \tag{5}$$

$$\mathrm{CH_3 + CH_3 \rightarrow CH_4 + CH_2}, \tag{6}$$

$$\mathrm{CH_3 + In(CH_3)_3 \rightarrow CH_4 + In(CH_3)_2CH_2}. \tag{7}$$

The effect of DEZn on the suppression of TMIn decomposition would be small because ethane and ethene are not generated by the decomposition of TMIn. Moreover, if the suppression of TMIn decomposition were the main reason, not only the growth rate of InAs but also that of AlAs would have to decrease because the activation energy of TMAl decomposition is much higher than that of TMIn. We assume that TMIn decomposes completely during InAlGaAs growth because it is well known that the decomposition of TMIn starts at a very low temperature (350 °C).

Next, we consider a second possibility — enhancement of In desorption from the growth surface. It has been reported that the doping behavior of a heavily Zn-doped InP layer can be well fit by a surface adsorption-trapping model.[11)] In this model, only Zn atoms captured by surface defects have a chance of being buried into the bulk when the growth of the next layer commences. The hole concentration (N_{Zn}) is given by

$$N_{\mathrm{Zn}} = 2N_{\mathrm{S}}^{*} \frac{1 - e^{-\beta \Delta t X}}{a}, \tag{8}$$

where N_{S}^{*} is the density of the adsorption centers, Δt is the growth time for one atomic layer, X is the DEZn carrier gas flow rate, and a is the lattice constant. The parameter, β, can be expressed as $\beta = N_{\mathrm{S}}^{*}/N_{\mathrm{S}}^{0} a_{\mathrm{C}} \delta(\tau_{\mathrm{C}}/\Delta t) C$, where N_{S}^{0} is the surface atomic density, a_{C} is the capture cross-section, τ_{C} is the life time of adsorption, and C is the flux factor, which is equal to the number of DEZn molecules impinging on a unit area of the substrate surface per 1 sccm flow of the carrier gas. The trapping process of the adsorbed Zn is taken into account by a δ function. As shown in Fig. 1, the experimental result can be well fit with the calculated curve using eq. (8). Although it is obvious that eq. (8) reduces to $N_{\mathrm{Zn}} = 2N_{\mathrm{S}}^{*}/a$ for large values of X, under such growth conditions, a large number of Zn atoms which are not captured by the adsorption centers exist on the growth surface. Since the Zn atoms basically incorporate into the group-III sites, the excess Zn atoms on the surface compete with the group-III atoms during the growth of heavily Zn-doped InAlGaAs. Moreover, this competition occurs easily with In atoms because the binding energies of Ga–As and Al–As are much higher than that of In–As. However, the competition with Al and Ga may occur rarely because it seems that AlAs and GaAs components slightly decrease in Fig. 6. Meanwhile, during growth, Zn atoms are unlikely to incorporate directly into the normal growth sites because all possible zinc-arsenic compounds, $ZnAs_2$, $ZnAs_4$, and Zn_3As_2, are volatiles. For the MBE growth of Zn_3As_2, it has been reported that Zn_3As_2 is rapidly desorbed at temperatures above 360 °C.[12)] Moreover, for Zn_3As_2 growth by atmospheric-pressure MOCVD, no growth occurred at 600 °C.[13)] Therefore, it is presumed that the excess Zn atoms on the growth surface result in the reduction of the InAs component and that they desorb again without a chance of being buried into the bulk lattice. Although the growth parameters, such as growth temperature and growth rate, would affect the competition between Zn atoms and group-III atoms, further investigation is required to clarify the details.

4. Conclusions

We investigated the growth of heavily Zn-doped InAlGaAs at low temperature by MOCVD. The lattice constant contracted and the growth rate decreased with increasing DEZn flow rate. From the changes of the InAs, AlAs, and GaAs components in the InAlGaAs layers, it was clarified that the incorporation of In is suppressed by the DEZn supply. The effect of DEZn on the suppression of TMI decomposition would be small. We showed that the doping behavior during the growth is well fit by the surface adsorption-trapping model, which suggests that the excess Zn atoms on the growth surface induce the reduction of InAs component.

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