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MOVPE Growth and Characterization of InPN Alloy Semiconductor Films

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Introduction

III-V compound semiconductors containing small amount of nitrogen, known as “dilute nitrides”, have been of interest in recent years. In the family of III-V nitrides, InPN has been little studied partially due to small nitrogen incorporation (<1%) [1]. One and only published MOVPE growth of InPN films was carried out in N_2 carrier gas [2]. In this work, InPN films have been grown on InP (001) substrates by MOVPE in H_2 carrier gas. The influence of the carrier gas type, nitrogen and phosphor precursor flow rate, growth temperature and pressure on the InPN growth has been investigated.

Experimental

The InP or InPN films were grown on semi-insulating (001)-oriented InP substrates in H_2 carrier gas. Trimethylindium (TMI), tertiarybutylphosphine (TBP) and dimethylhydrazine (DMHy) were used as In, P and N precursors, respectively. An rf-heated horizontal-type reactor was designed to increase the effective precursor supply by feeding the precursors through a capillary extending near to the substrate, as shown in Fig. 1. At a reactor pressure of 60 Torr, an InP buffer layer was grown on an InP (001) substrate at 575°C with [TBP]/[TMI]=55, and then the InPN epilayer was grown. For the growth of InPN films, the growth temperature, growth pressure, [TBP]/[TMI], [DMHy]/[TMI] were varied in the ranges of 440°C~480°C, 30Torr~120Torr, 20~30, 350~1000, respectively. The N content in the InPN films was estimated by fitting the 2θ-ω (004) HRXRD profiles with a dynamic simulation. Photoluminescence experiments were carried out at 10K. The sample was illuminated by the 514.5 nm light from an argon ion laser, and the PL signals were detected at the exit of a 1200 lines/mm monochromator by an InGaAs photodiode.

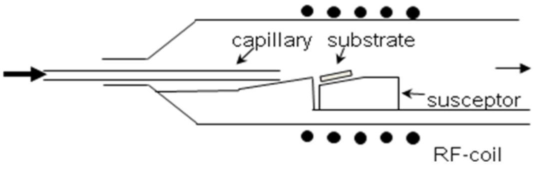

Fig. 1　Separate-supply method reactor with the capillary extending to the susceptor region

Results and discussion

Fig. 2 shows the PL spectra of InP films grown with and without DMHy precursor supplied. These three samples were grown when TMI precursor was fed through the capillary to the InP substrate. Peak 1, which reaches maximum at 1.41eV, corresponds to free-excitonic transition in InP. Peak 2 (1.37eV) is related to shallow dopant optical transition, and Peak 3 (1.33eV) originates from LO phonon replica

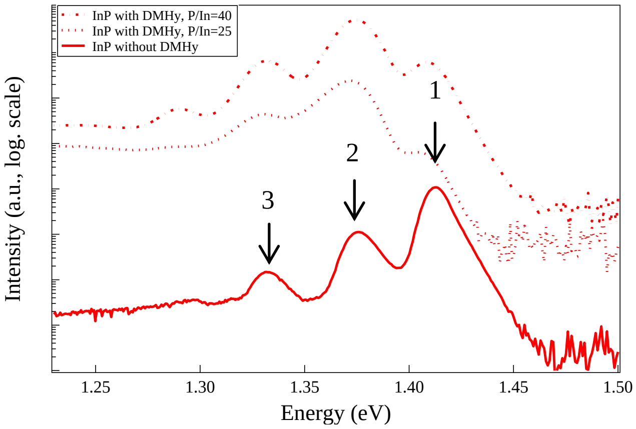

Fig. 2. PL spectra of InP films with and without DMHy supplies

of Peak 2. With the introduction of DMHy supplies to the InP growth, the strongest peak switches from Peak 1 to Peak 2. This fact indicates that most of the dopant, considered to be carbon, which associates with the luminescence of Peak 2 is from DMHy molecules. Another fact is that by XRD measurement, N atoms were not incorporated into the two InP samples grown with DMHy supplied. It is concluded that after the pyrolysis of DMHy molecules, a part of C atoms are incorporated into InP films while almost all the N atoms escape from the surface of the samples.

For the growth of InPN films, the precursor fed through the capillary was changed from TMI to DMHy in order to increase the effective supply of DMHy. In this condition, an InPN film with highest N content of 0.04% was obtained when the growth temperature, growth pressure, [TBP]/[TMI] and [DMHy]/[TMI] were 460°C, 60Torr, 25 and 115, respectively. This growth condition is the central condition for the investigation of growth condition dependence of InPN growth. Fig. 3 shows the AFM surface images of the InPN films grown in the H_2 and N_2 carriers with other growth parameters kept identical. Compared with the InPN film grown in N_2 (RMS: ~50nm), that grown in H_2 yields an atomically-smooth surface (RMS: ~0.6nm). The 2θ-ω (004) HRXRD profiles of these two InPN samples are shown in Fig. 4. With the carrier gas changed from N_2 to H_2, the N composition decreases from 0.18% to 0.04%. This may be due to the fact that the vapor-phase boundary layer over the substrate in N_2 ambient is thinner than that in H_2 ambient, because N_2 has less thermal conductivity, higher viscosity as well as larger density [3].

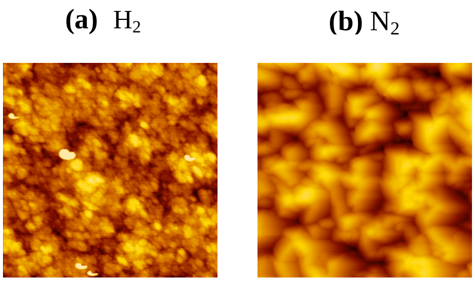
(a) H_2 **(b)** N_2

Fig. 3. AFM images of InPN grown in H_2(a) and N_2(b)

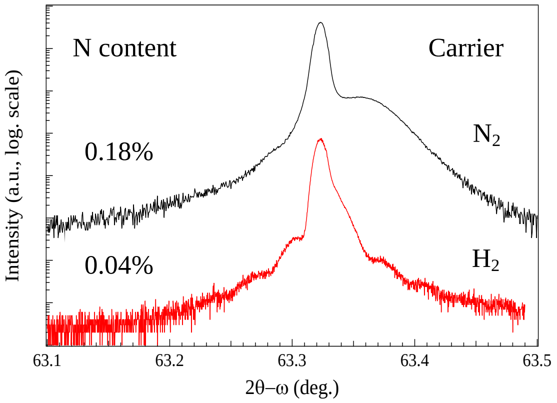

Fig. 4. XRD 2θ-ω (004) profiles of InPN grown in H_2 and N_2

The growth of InPN films was attempted with [DMHy]/[TMI] varied from 47 to 133, and other growth parameters kept the same as those in the central growth condition of InPN, shown in Fig. 5(a). When [DMHy]/[TMI] is 47, 80, 115, the N content of InPN films is 0.02%, 0.03%, and 0.04%, respectively. This fact indicates that N incorporation can be increased by increasing the N precursor supply. However, N atoms are not incorporated into InP with [DMHy]/[TMI] more than 133, and the surface RMS also increases remarkably. This may be due to the fact that oversupply of N precursor prevents the introduction and migration of P atoms, facilitating In droplet formation on the sample surface.

Fig. 5(b), (c), (d) show the dependence of N content and surface RMS of InPN films on [TBP]/[TMI], growth pressure and temperature, respectively. The phenomenon that N content increases with the decrease of V/III and growth temperature, which is common for other III-V-N alloy, is verified in InPN. However, at a temperature as low as 440°C or [TBP]/[TMI] as low as 20, the N atoms can not be incorporated into InP lattice. A low temperature or [TBP]/[TMI] makes In supply rich, facilitating In droplet formation. The In droplets worsen the crystal quality and surface morphology, impeding the N incorporation.

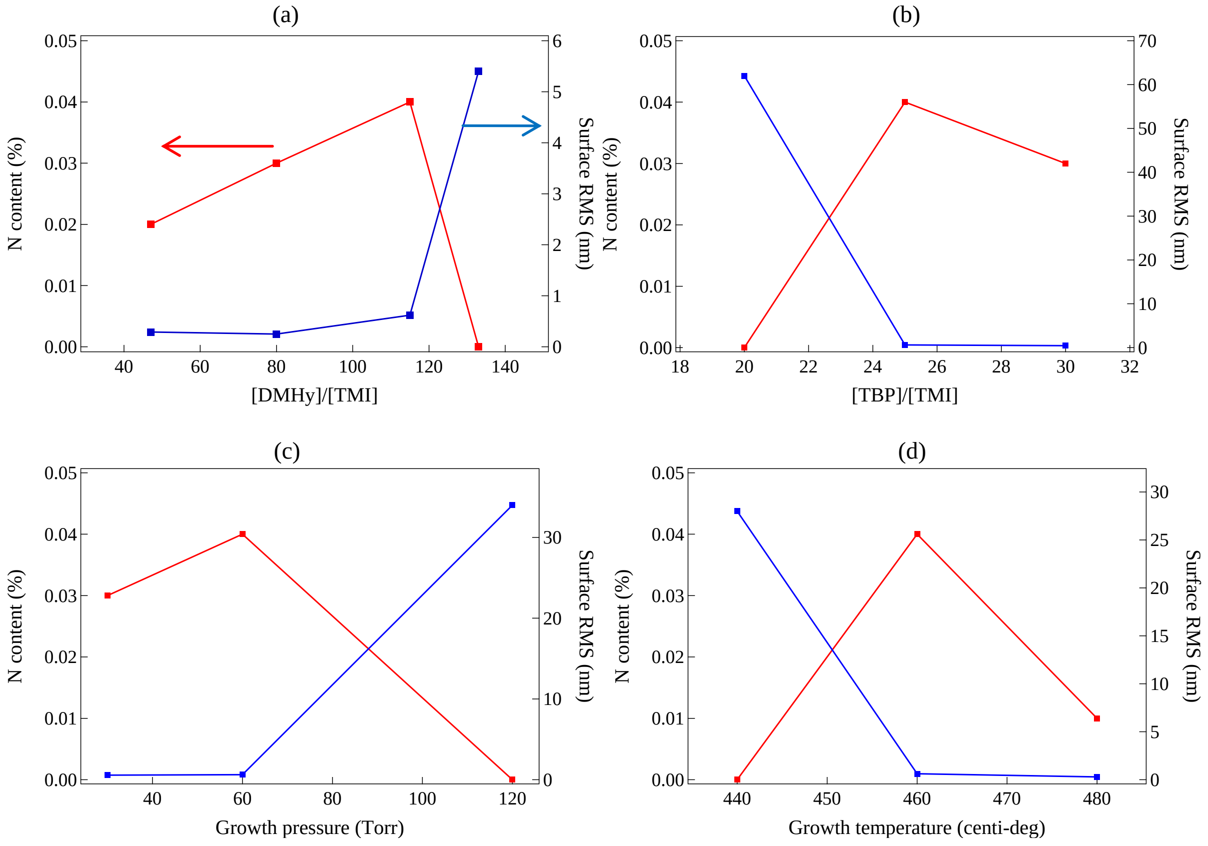

Fig. 5. Dependence of N content and surface RMS of InPN films on [DMHy]/[TMI] (a), [TBP]/[TMI] (b), growth pressure (c) and growth temperature (d)

Conclusion

An InPN film with highest N content of 0.04% was obtained in H_2 carrier gas. Dependence of N content and surface morphology of InPN films on the carrier gas type, growth temperature, growth pressure, [TBP]/[TMI] and [DMHy]/[TMI] has been investigated. Unless In droplets form on the film surface, low growth temperature, low [TBP]/[TMI] and high [DMHy]/[TMI] benefit N incorporation into InP.

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学会発表

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4. 第 72 回応用物理学会学術講演会　「MOVPE Growth and Characterization of InPN Films」