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Growth of InN pillar crystal films by means of atmospheric pressure halide chemical vapor deposition

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Preparation of InN thin films has been examined using an atmospheric pressure halide chemical vapor deposition technique. It was found that the quality of the InN pillar crystal film grown on a Si(100) substrate is significantly dependent upon the ratio of $NH_3 : InCl_3$ used as source materials. Hall mobility decreases as the $NH_3 : InCl_3$ ratio is decreased, while the carrier concentration increases. This is explained in terms of the formation of nitrogen vacancies. A decrease of the $NH_3 : InCl_3$ ratio causes the increase of nitrogen defects in the InN film. This also increases the number of electrons being trapped by the defects, while their mobility is reduced because of the electrons being scattered at the vacancies.

1. Introduction

Blue light emitting diodes with Ga-rich InGaN as the active layer are already on the market. Also, a violet laser has been developed recently with nitrides as well. If the light emitting region is to be extended to red with the same constituents, In-rich InGaN and/or InN are promising candidates. This would bring the advantage over the present GaAs-based light emitting devices of the elements used being non-toxic. However, there are only a few papers dealing with this material[1,2] because In-rich InGaN and InN are difficult to grow epitaxially. They have extremely large dissociation pressures so that it is said that a large ratio (more than 1000) of nitrogen source to group III (In and Ga) source is necessary to grow the films.

We have already reported that atmospheric pressure halide chemical vapor deposition (AP-HCVD) is an appropriate technique for the preparation of InN films.[3,4] Advantages of this method are as follows: (a) the film is formed by a simple reaction of gaseous $InCl_3$ with NH_3 under atmospheric pressure; (b) there is no need to post-anneal; and (c) high-purity $InCl_3$ is cheap compared with other compounds, such as $In(CH_3)_3$ and $In(C_2H_5)_3$, used for molecular beam epitaxy (MBE) and metal–organic chemical vapor deposition (MOCVD).

In this paper we report the results of an investigation into the growth of hexagonal InN on a Si(100) substrate by means of

Table 1 Typical growth conditions

Substrate	Si(100)
$InCl_3$ partial pressure/atm	4.6×10^{-3}
NH_3 partial pressure/atm	9.2×10^{-2}–2.8×10^{-1}
Carrier gas	N_2
Total flow rate/cm^3 min^{-1}	750
Growth temperature/°C	650

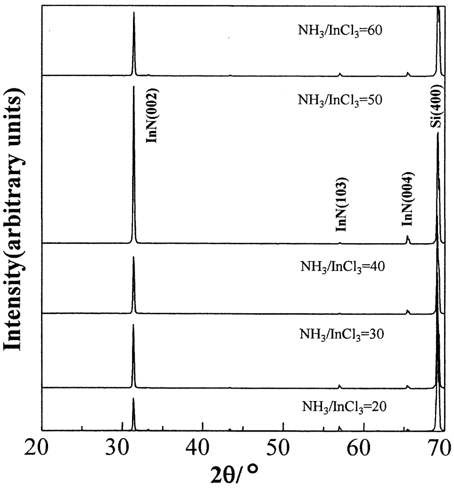

Fig. 1 X-ray diffraction profiles of the films grown at various $NH_3 : InCl_3$ supply ratios.

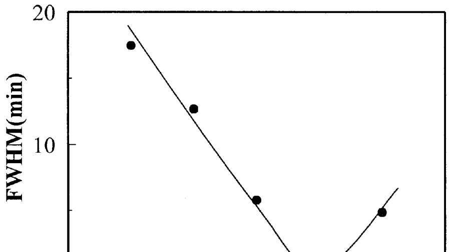

Fig. 2 FWHM of the (0002) diffraction line for the obtained hexagonal InN films as a function of the $NH_3 : InCl_3$ ratio.

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AP-HCVD with varying $NH_3:InCl_3$ ratios. The structure, surface morphology and electrical properties of the resulting InN thin films are examined.

2. Experimental

The horizontal quartz reactor used in this study is the same as that described earlier.[3,4] Thin films of InN were grown on a Si(100) substrate under atmospheric pressure. The substrate was an n-type Si(100) wafer with 0.05 Ω cm. $InCl_3$ in a source boat was evaporated at a temperature of 250 °C, and supplied to the growth zone by purified N_2 carrier gas. The partial pressures of $InCl_3$ and NH_3 were adjusted independently by varying the flow rates of the carrier gas. Typical experimental conditions are summarized in Table 1.

The crystallographic structure of the deposited InN films was

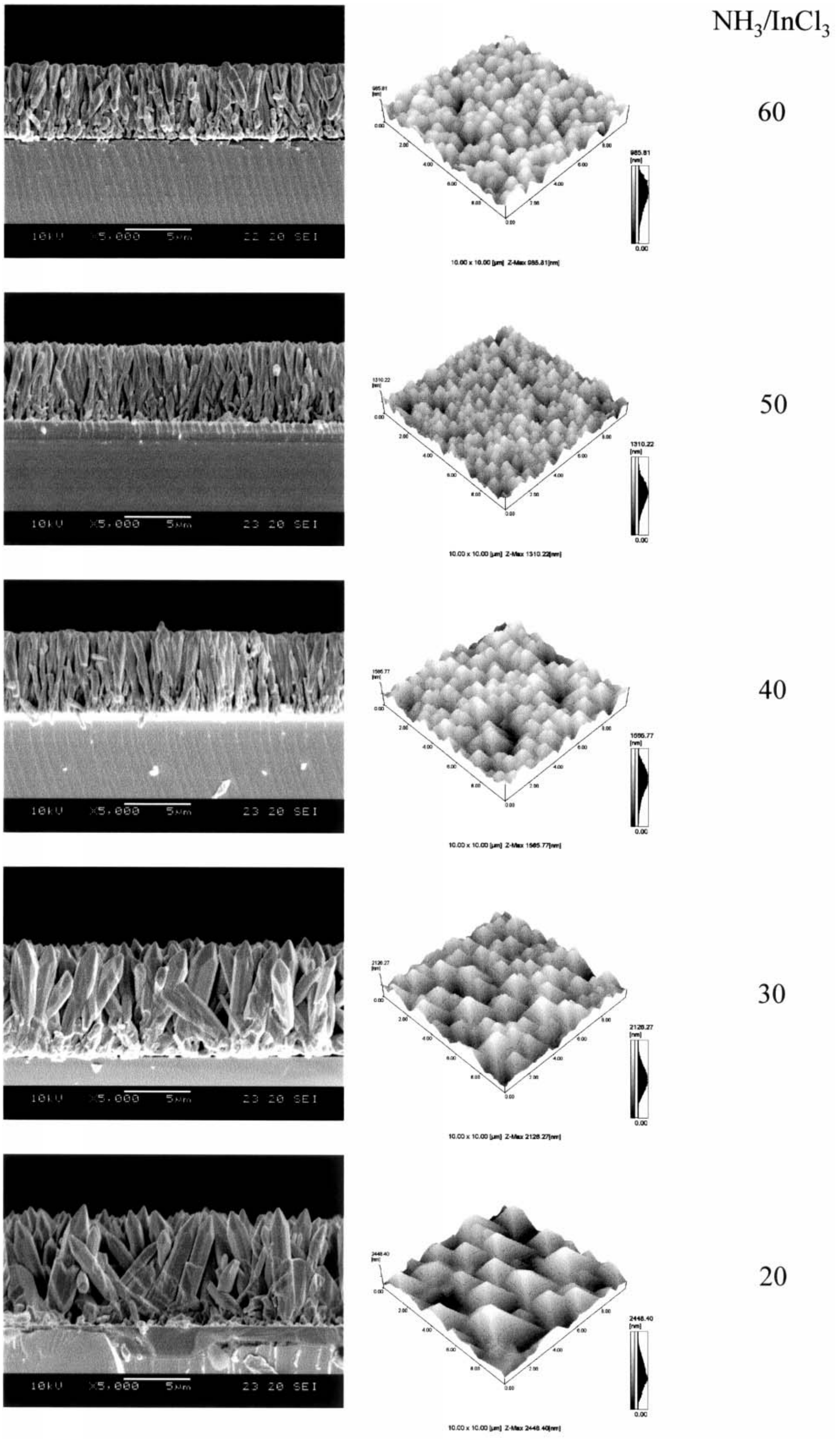

Fig. 3 SEM and AFM images of the InN films grown at various $NH_3:InCl_3$ ratios.

examined by a Rigaku RINT 2000 X-ray diffractometer. Their crystallinity was assessed by a double crystal X-ray diffraction technique. The film thickness and surface morphology were evaluated by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. XPS spectra were measured using a Shimadzu XRTOS-XSAM 800 X-ray photoelectron spectrometer. Electrical properties were measured using the Van der Pauw method.[5]

3. Results and discussion

Fig. 1 shows X-ray diffraction profiles of the films grown at various $NH_3:InCl_3$ ratios, in which the growth rate was a constant of about 10 μm h^{-1}. It is seen that all the thin films obtained show an intense diffraction line at 31.2°, which is assigned to the (0002) diffraction of InN with a hexagonal structure. Another line at 69.2° is due to the (400) diffraction of the Si substrate. This implies that the InN films grow epitaxially at an $NH_3:InCl_3$ ratio of 20–60. It should be note that the intensity of the diffraction peak at 31.2° varies with the $NH_3:InCl_3$ ratio.

The lattice constant of the obtained InN thin films was calculated to be 5.697 Å utilizing the observed (0002) diffraction. The estimated value is slightly smaller than the reported one of 5.7033 Å for the bulk InN powder.[6] This reduction is probably due to nitrogen vacancies formed in the film because the N_2 equilibrium pressure over InN is high at a growth temperature of 650 °C.[1,2] Fig. 2 shows the FWHM of the (0002) diffraction line for the obtained hexagonal InN films as a function of the $NH_3:InCl_3$ ratio. The FWHM values of the (0002) diffraction line for the InN films were measured by a double crystal X-ray diffraction technique. As is evident from Fig. 2, the FWHM decreases with increasing $NH_3:InCl_3$ ratio, reaches a minimum and then gradually increases. A minimum FWHM value of 1 min was obtained at $NH_3:InCl_3 = 50$.

Fig. 3 shows the SEM cross-section micrographs and AFM images of the InN films grown at various $NH_3:InCl_3$ ratios. From the SEM micrographs in Fig. 3 it is immediately obvious that the deposited InN films consist of hexagonal pillars with diameters of between 0.5 and 1 μm depending on the $NH_3:InCl_3$ ratio. Interestingly, they are standing on the surface of the substrate. The AFM images in Fig. 3 show that the surface of InN films has rough morphology of the order of 100 nm, which is consistent with the shape of the pillar crystals found by SEM. As the $NH_3:InCl_3$ ratio is increased from 20 to 50, the density of the pillar crystals increases significantly, while their size decreases drastically. This is a clear indication of the fact that the growth process depends on the $NH_3:InCl_3$ ratio.

Fig. 4 shows the Hall mobility and carrier concentration of the InN films grown at various $NH_3:InCl_3$ ratios. All of the InN films prepared showed n-type conduction. It can be seen that the Hall mobility increases with increasing $NH_3:InCl_3$ ratio up to 50 and then gradually decreases. Regarding carrier concentration, it shows a minimum at $NH_3:InCl_3 = 50$ where the Hall mobility is maximum. This implies that the optimum $NH_3:InCl_3$ ratio to prepare high quality InN film is 50. It is thought that the decrease of Hall mobility and increase of carrier concentration occurring on both sides of $NH_3:InCl_3 = 50$ are due to an increase in the number of vacancies. The Hall mobility and carrier concentration obtained for the InN films prepared at $NH_3:InCl_3 = 50$ are similar to those reported by others.[7]

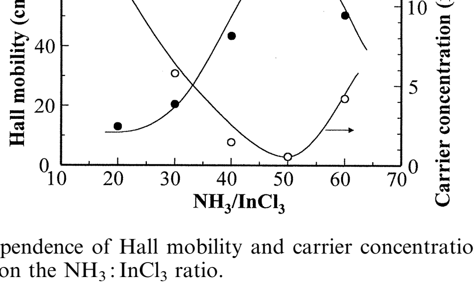

Fig. 4 Dependence of Hall mobility and carrier concentration of the InN film on the $NH_3:InCl_3$ ratio.

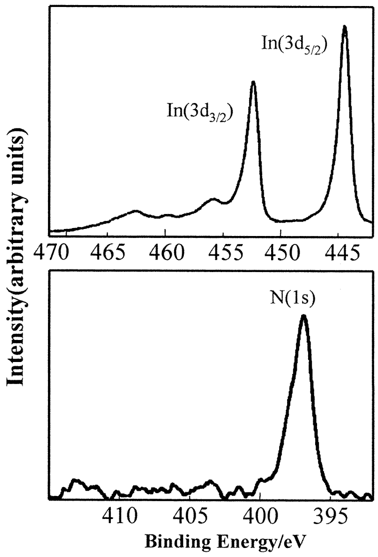

Fig. 5 Representative XPS spectra of the InN film prepared at an $NH_3:InCl_3 = 50$.

The indium and nitrogen contents of the InN film were determined by XPS. Fig. 5 shows the representative XPS spectra of the as-deposited InN films. It can be seen that the peaks assigned to N(1s), In($3d_{2/3}$) and In($3d_{5/2}$) appear at binding energies of 396.8, 452.3 and 444.7 eV, respectively. The relative peak-height ratio of N(1s) to In(3d) of the obtained InN film at $NH_3:InCl_3 = 50$ is similar to those reported for bulk InN.[8] For this reason it is deduced that the resulting films have a stoichiometry close to In : N = 1 : 1. Free carriers being present in InN films ranging from 1×10^{-20} to 13×10^{-20} cm^2 V^{-1} s^{-1} are possibly due to native defects of nitrogen vacancies. Also, it was found that no peak assigned to carbon, chlorine and oxygen is observed for the InN films prepared in this study so that their contents are less than 1 atom%, implying that there is little contamination of these elements.

4. Conclusions

Thin films of the InN pillar crystal were grown on a Si(100) substrate in a hot-wall reactor by the AP-HCVD technique using $InCl_3$ and NH_3. The effect of their supply ratio was investigated regarding the crystal quality of the hexagonal InN formed. From X-ray diffraction, SEM and AFM observations it was clarified that the growth process of InN films is strongly dependent on the $NH_3:InCl_3$ ratio. Variations of the Hall mobility and carrier concentration against the $NH_3:InCl_3$ ratio suggest that the best quality of InN film is obtained at $NH_3:InCl_3 = 50$. Nitrogen vacancies increases on both sides of the $NH_3:InCl_3$ ratio.

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