Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 683-685 S-II-21

Nitridation of Si Substrate Surface during MOCVD Growth of InN

Akio YAMAMOTO, Hiroyuki KITAJIMA, and Mitsunori TSUJINO

Department of Electrical and Electronics Engineering,
Faculty of Engineering, Fukui University,
3-9-1 Bunkyou, Fukui, Fukui 910, Japan

The metalorganic chemical vapor deposition (MOCVD) growth of InN on Si(111) has been studied to realize a new monolithic tandem solar cell composed of InN top cell and Si bottom cell. Relatively well-oriented films is grown only in the limited growth-temperature range, 400-450℃. Compared to those on α-Al_2O_3 substrates, however, grown InN films on Si substrares are of considerably poor quality. The reason for this is the formation of silicon nitride of amorphous phase on Si substrates at a relatively low temperature (~500℃) before and during the growth.

1. INTRODUCTION

Indium nitride (InN) has a direct bandgap of about 1.9eV and wurtzite lattice[1]. For two-bandgap tandem solar cells, the combination of the bandgaps, 1.9eV for InN and 1.1eV for Si, is the optimum to get an conversion efficiency more than 30%[2]. In addition to the merit that InN is a binary material appropriate to large-area cell fabrication, an InN/Si system as a tandem solar cell has advantages that it contains no poisonous elements such as As and uses no toxic gases such as PH_3 in the fabrication process. The key technology to fabricate an InN/Si monolithic tandem cell is heteroepitaxial growth of InN on Si substrates. The lattice mismatch between InN and Si is about 8% for InN(0001)/Si(111), which is comparable to that for an InP/Si system. Heteroepitaxy of InN on Si has not yet been reported althouth the growth on α-Al_2O_3 substrates[3),4)] were carried out.

This paper reports the MOCVD growth of InN on Si with a high molar fraction of NH_3, and shows the surface nitridation of Si substrates at a relatively low temperature (~500°C) before and during the growth, which is a major obstacle in growing heteroepitaxial InN on Si.

2. EXPERIMENTAL

The MOCVD apparatus with a horizontal reactor was used for InN growth. The growth was carried out using trimethylindium(TMI) and NH_3 as source materials and N_2 as a carrier gas. Wafers of Si(111) were used as substrates. The substrates were degreased and etched just before loading into the reactor. The etching procedure consisted of several repitations of oxidation by dipping into a H_2SO_4+H_2O_2 solution and oxide removal by dipping into a HF solution. The substrates were preheated at 1000°C for 10 min in a flowing H_2 just before the InN growth. Wafers of α-Al_2O_3(0001) were also used as substrates for comparison.

Grown InN layers were evaluated with reflection high energy electron diffraction (RHEED), and substrate surfaces treated at a different condition were also examined with RHEED and electron spectroscopy for chemical analysis (ESCA).

3. RESULTS AND DISCUSSION

3.1 Growth temperature dependence of crystalline quality of grown InN films

An InN film with a specular surface is obtained by employing an NH_3/TMI molar ratio more than 10^4 and N_2 carrier gas. Figure 1 shows RHEED patterns from InN films grown at 350, 400 and 500°C on Si(111) substrates and grown at 500°C on an α-Al_2O_3(0001) substrate. In spite of the small lattice mismatch (8%) between InN and Si compared to that (25%) between InN and α-Al_2O_3(0001), poorly oriented InN is grown on Si(111) substrates. The growth of a polycrystalline InN film on a Si substrate at 500°C is not due to an inadequate growth parameters, because a better-oriented film can be grown on an α-Al_2O_3(0001) substrate with the same growth parameters. Dispersion angle for c-axis in RHEED pattern is denoted by $\Delta\theta$ (see in Fig. 1(b)) to show a degree of misorientation for grown films. Figure 2 shows $\Delta\theta$

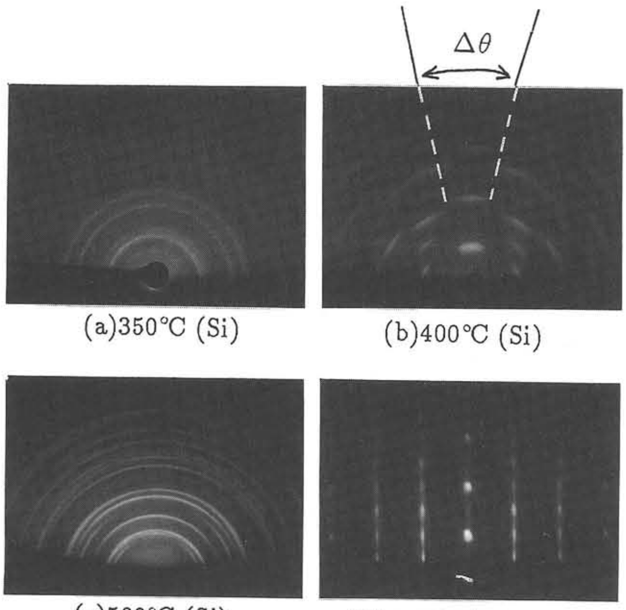


Fig. 1. RHEED patterns for InN films grown on Si(111) and on α-Al_2O_3(0001) substrates at a different growth temperature.

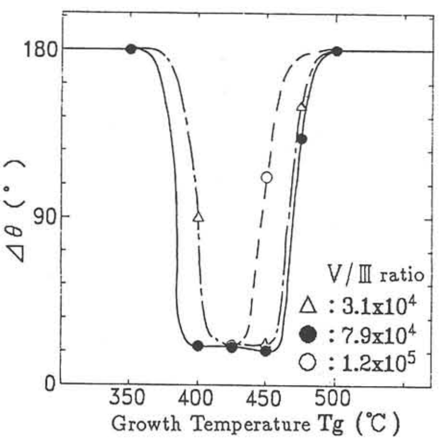


Fig. 2. $\Delta\theta$ (see Fig.1(b)) for films grown on Si(111) as a function of growth temperature T_g.

for films grown on Si(111) as a function of growth temperature T_g. The T_g at which a relatively well-oriented film is grown on Si is limited to the narrow region, 400-450°C. The increace in $\Delta\theta$ for T_g <400 ℃ is believed to be due to the reduced surface migration of deposited species on the substrate. The drastic increace in $\Delta\theta$ for T_g >450℃, on the other hand, is due to the surface nitridation of Si substrates as described below.

Figure 3 shows $\Delta\theta$ for films grown on Si and α-Al_2O_3 by the multi-step method with and without annealing at 600°C for 10 min at the step of the growth. This result shows that the annealing deteriorates the quality of films on Si substrates, while it brings an improvement of crystalline quality for films on α-Al_2O_3 substrates.

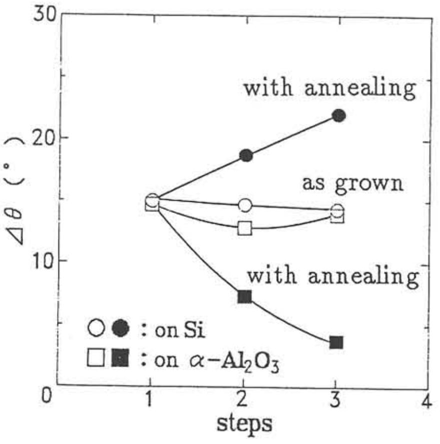
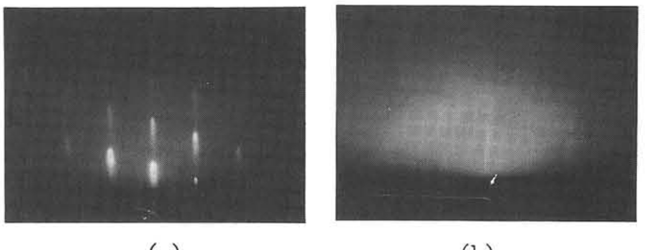


Fig. 3. $\Delta\theta$ for films grown on Si and α-Al_2O_3 by the multi-step method with and without annealing at 600°C for 10 min at the step of the growth.

3.2 Surface analysis of substrates exposed to an NH_3 flow

From the results described above, one can easily suppose that the remarkable difference in InN crystalline quality between Si and α-Al_2O_3 substrates is brought by any difference in substrate surface conditions just before the growth. Figure 4 shows RHEED patterns from Si(111) substrates heated at 1000℃ in H_2 (Fig. 4(a)) and exposed to an NH_3 flow after the heating (Fig. 4(b)). A halo pattern from the substrate exposed to an NH_3 flow (Fig. 4(b)) shows the presence of an amorphous-phase material on the surface.

Figure 5 shows Si 2p spectra for Si substrates exposed to an NH_3 flow at a different temperature (T_{NH_3}) after the heating at 1000℃ in H_2. The peak at 102-103eV in Fig. 5 is originated by Si-N and Si-O bonds. A Si-O bond is thought to be formed by exposing the Si substrates to the air when they are transferred from the MOCVD reactor to the ESCA



(a) (b)

Fig. 4. RHEED patterns from Si(111) substrates heated at 1000°C in H_2 (a) and exposed to NH_3 after the heating at 1000°C (b).

sample chamber. For the sample of T_{NH_3}=900 °C, a silicon nitride film formed is so thick that the oxidation is prevented. The peak positions for samples of T_{NH_3}≈500°C shows that nitridation occures at such a low temprtature by exposing to NH_3 after the heating at 1000 °C in H_2. It is reasonable to consider that the amorphous-phase material detected by RHEED on the NH_3-exposed Si surface (Fig. 4(b)) is a silicon nitride film.

In order to clarify the cause for the improvement of InN crystallinity on the α-Al_2O_3 substrates by the annealing at 600 °C shown in Fig. 3, α-Al_2O_3 surface exposed to NH_3 was analyzed with ESCA. Figure 6 shows N 1s peak intensity detected on α-Al_2O_3 surface exposed to NH_3 at a different temperature T_{NH_3}. The remarkable increase in N amount for T_{NH_3} higher than 700 °C is thought to show the formation of AlN on the α-Al_2O_3 surface. $\Delta\theta$ in RHEED patterns for InN films grown on α-Al_2O_3 exposed to NH_3 at a different temperature (T_{NH_3}) are also shown in Fig. 6. As can be seen in Fig. 6, the formation of AlN brings about an remarkable improvement of InN film quality. This is because AlN has the same lattice structure as InN and the lattice mismatch can be reduced from 25% for InN/α-Al_2O_3 to 13% for InN/AlN.

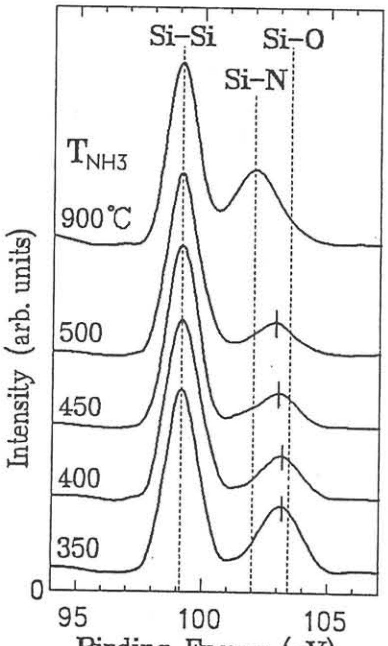


Fig. 5. ESCA spectra for Si 2p from Si substrates exposed to NH_3 flow at a different temperature T_{NH_3}.

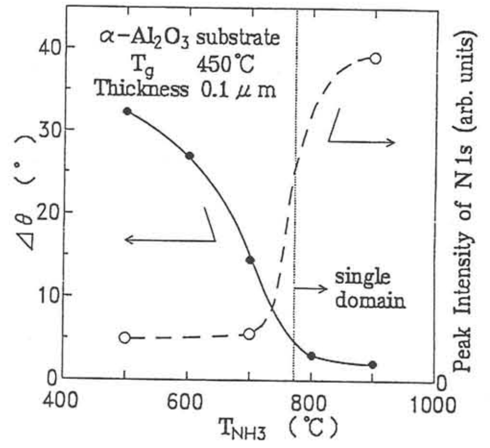


Fig. 6. Peak intensity of ESCA N 1s spectra for α-Al_2O_3 surface exposed to NH_3 at a different temperature T_{NH_3}. $\Delta\theta$ for InN films grown on NH_3-exposed α-Al_2O_3 is also shown as a function of T_{NH_3}.

4. CONCLUSION

We have studied the MOCVD growth of InN on Si(111) and on α-Al_2O_3 for comparison. It was found that nitridation of the substrates had important effects on the quality of grown InN films. For Si(111) substrates, the formation of silicon nitride of amorphous phase on their surface at a relatively low temperature (~500°C) before and during the growth is a difficulty in growing heteroepitaxial InN films. Nitridation of α-Al_2O_3, which results in the formation on AlN, is favorable for the InN growth because AlN has the same lattice as InN and the lattice mismatch is reduced

ACKNOWLEDGEMENTS

The authors would like to express their thanks to Prof. A. Hashimoto for usefull discussions and to Prof. M. Takashima for the ESCA analysis. This work was supported in part by the Scientific Research Grant-in-Aid for Energy Research No.04203217 from the Ministry of Education, Science and Culture, and by the Murata Science Foundation.

REFERENCES

1) K.Osamura, S.Naka, and Y.Murakami, J.Appl.Phys., 46, (1975) 3432.
2) M.E.Neil and A.M.Barnett, IEEE Trans. Electron Devices, ED-34, (1987) 257.
3) L.A.Marasina, I.G.Pichugin, and M.Tlaczala, Krist.Tech., 12, (1977) 541.
4) A.Wakahara and A.Yoshida, Appl.Phys.Lett., 54, (1989) 709.