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°C. Compared to those on α-Al2O3 substrates, however, grown InN films on Si substrates 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°C) before and during the growth.

1. INTRODUCTION

Indium nitride (InN) has a direct bandgap of about 1.9eV and wurtzite lattice. 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%. 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 PH3 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 although the growth on α-Al2O3 substrates were carried out.

This paper reports the MOCVD growth of InN on Si with a high molar fraction of NH3, 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 NH3 as source materials and N2 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 repetitions of oxidation by dipping into a H2SO4+H2O2 solution and oxide removal by dipping into a HF solution. The substrates were preheated at 1000°C for 10 min in a flowing H2 just before the InN growth. Wafer of α-Al2O3(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 NH3/TMI molar ratio more than 104 and N2 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-Al2O3(0001) substrate. In spite of the small lattice mismatch (8%) between InN and Si compared to that (25%) between InN and α-Al2O3(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-Al2O3(0001) substrate with the same growth parameters. Dispersion angle for c-axis in RHEED pattern is denoted by Δθ (see in Fig. 1(b)) to show a degree of misorientation for grown films. Figure 2 shows Δθ

683
Fig. 1. RHEED patterns for InN films grown on Si(111) and on \( \alpha\text{-Al}_2\text{O}_3(0001) \) 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 increase in \( \Delta \theta \) for \( T_g < 400 \) °C is believed to be due to the reduced surface migration of deposited species on the substrate. The drastic increase in \( \Delta \theta \) for \( T_g > 450 \) °C, 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 \( \alpha\text{-Al}_2\text{O}_3 \) 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 \( \alpha\text{-Al}_2\text{O}_3 \) substrates.

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 \( \alpha\text{-Al}_2\text{O}_3 \) 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°C 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°C 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.
sample chamber. For the sample of $T_{NH_2}=900^\circ C$, a silicon nitride film formed is so thick that the oxidation is prevented. The peak positions for samples of $T_{NH_2}=500^\circ C$ shows that nitridation occurs at such a low temperature 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 $\alpha$-Al$_2$O$_3$ substrates by the annealing at 600°C shown in Fig. 3, $\alpha$-Al$_2$O$_3$ surface exposed to NH$_3$ was analyzed with ESCA. Figure 6 shows N 1s peak intensity detected on $\alpha$-Al$_2$O$_3$ surface exposed to NH$_3$ at a different temperature $T_{NH_2}$. The remarkable increase in N amount for $T_{NH_2}$ higher than 700°C is thought to show the formation of AlN on the $\alpha$-Al$_2$O$_3$ surface. $\Delta \theta$ in RHEED patterns for InN films grown on $\alpha$-Al$_2$O$_3$ exposed to NH$_3$ at a different temperature ($T_{NH_2}$) 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/$\alpha$-Al$_2$O$_3$ to 13% for InN/AlN.

![Fig. 5. ESCA spectra for Si 2p from Si substrates exposed to NH$_3$ flow at a different temperature $T_{NH_2}$](image)

![Fig. 6. Peak intensity of ESCA N 1s spectra for $\alpha$-Al$_2$O$_3$ surface exposed to NH$_3$ at a different temperature $T_{NH_2}$. $\Delta \theta$ for InN films grown on NH$_3$-exposed $\alpha$-Al$_2$O$_3$ is also shown as a function of $T_{NH_2}$](image)

4. CONCLUSION

We have studied the MOCVD growth of InN on Si(111) and on $\alpha$-Al$_2$O$_3$ 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 ($\sim 500^\circ C$) before and during the growth is a difficulty in growing heteroepitaxial InN films. Nitridation of $\alpha$-Al$_2$O$_3$, 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.

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REFERENCES