

Plasma-Assisted MOCVD Growth of GaAs/GaN/GaAs Thin-Layer Structures by N-As Replacement Using N-Radicals

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GaAs/GaN/GaAs thin-layer structures were grown for the first time by plasma-assisted low-pressure MOCVD. GaN layers were formed by exposing the surfaces of GaAs epitaxial layers to nitrogen-radical fluxes. When the N amount exceeded that in one-monolayer-thick GaN, the GaN/GaAs interfaces deteriorated drastically. Low-temperature photoluminescence from the structures suggests that the GaN layer thickness is self-limited to one monolayer and that the excess nitrogen atoms form GaN clusters in underlying layers. The one-monolayer-thick GaN embedded in GaAs shows intense photoluminescence, whereas the GaN cluster is non-radiative, probably because of the defects caused by the large lattice-mismatch between GaN and GaAs.

Introduction

GaN is a widegap semiconductor and one of the promising materials for blue or ultraviolet light emitting devices. Because the lattice structure of GaN is usually hexagonal, heterostructures with other cubic compound semiconductors may be difficult to create. Although cubic GaN has been grown on GaAs substrates¹⁻⁴⁾, and will be used in the integration of GaN and GaAs devices, the optical or electrical characterization of the GaN/GaAs heterointerface has not yet been reported, probably because the roughness caused by the many facets at the interface⁵⁾ makes the necessary experiments difficult. GaAs may be required to be grown on GaN for the integration, however, growth of GaAs on GaN has not been reported yet. GaN can be used as a mask for selective growth of GaAs⁶⁾, indicating that GaAs is not preferentially grown on GaN and that the GaAs growth on GaN is difficult.

The growth of GaAsN alloys, which may be widely applicable in electronic devices using semimetallic layers as well as in light emitters covering entire visible spectrum, has been reported recently⁷⁻¹¹⁾. The nitrogen concentration in these alloys has so far been limited to low levels, and one possible way to increase nitrogen concentration is by growing thin-layer superlattices: $(\text{GaAs})_m(\text{GaN})_n$. This requires GaAs growth on GaN layers and flat interfaces between GaAs and GaN.

This paper reports the first success of the growth of GaAs/GaN/GaAs thin-layer structures by plasma-assisted low-pressure metalorganic chemical vapor deposition (MOCVD). A novel method for controlling radical supply precisely is proposed. Photoluminescence (PL) from the structures is also described.

Experimental

GaAs/GaN/GaAs thin-layer structures were grown by plasma-assisted low-pressure MOCVD using N

radicals from N_2 gas, which is a better N-precursor than is NH_3 ¹¹⁾. The reactor and the gas-flow sequence for growing the structures is shown schematically in Fig. 1. A water-cooled stainless-steel chamber is pumped by a combination of a mechanical booster and a rotary vacuum pump. This allows MOCVD growth at the very low pressure of 30 Pa. Low pressures are required for plasma operation and efficient supply of reactive species (such as radicals) to a substrate.

A downstream-type plasma-cracking cell, irradiated with 2.45 GHz microwaves at a maximum power of 260 W, was used to supply N radicals. In conventional method, a pressure of about 300 Pa, which is too high for stable downstream operation, is necessary to ignite plasma in the cell and it takes about 20 seconds to stabilize the chamber pressure at the growth condition. Furthermore, the amount of radicals supplied during plasma-ignition procedure is neither controllable nor reproducible. This makes short-duration radical-supply impossible.

To control the radical supply precisely, a novel method is proposed. Argon gas is introduced into the cell and Ar plasma is ignited prior to the growth of a GaAs buffer layer. Because of the short lifetime of ions in a gas phase, Ar ions are not supplied to the substrate. No difference between the characteristics of undoped GaAs layers grown with and without Ar plasma was found. When N_2 is introduced into the Ar plasma, N_2 molecules immediately dissociate because of collisions with Ar ions, and N plasma is thus ignited without increasing pressure or increasing microwave power. N radicals are created in the plasma and supplied to the substrate surface. This method enables the radical supply to be controlled easily and precisely: the N-radical supply is started and stopped simply by opening and closing a valve, and the amount of radicals is controlled by adjusting the flow rate of N_2 gas. In this study, Ar plasma was ignited before the thermal cleaning of the

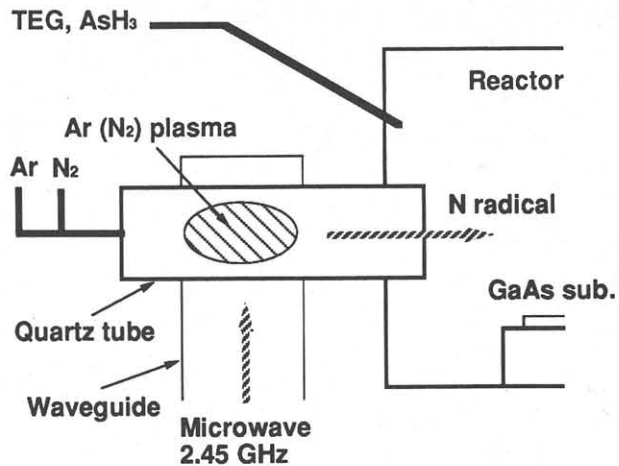
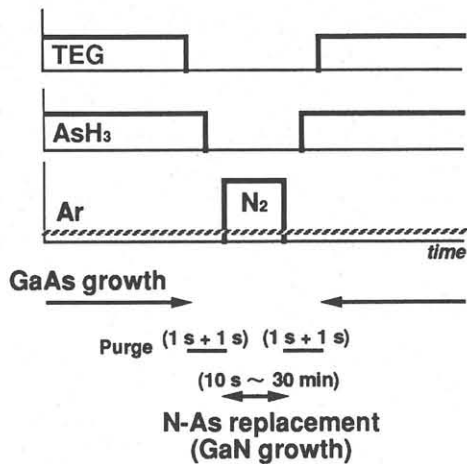


Fig. 1 Schematics of the growth reactor and gas-flow sequence for growing GaAs/GaN/GaAs structures.

GaAs substrate surfaces.

The structures were grown on (100) GaAs substrates. The typical growth temperature and pressure were 500°C, where the desorption of surface As atoms have a lifetime of about 30 s^{-12} , and 30 Pa. Triethyl-gallium (TEG) carried by H_2 carrier gas, uncracked AsH_3 , and plasma-cracked N_2 were used as Ga, As, and N sources, respectively. GaN layers were formed by exposing As-stabilized surfaces of GaAs epitaxial layers to N-radical fluxes. Arsenic atoms are replaced by N atoms, forming GaN thin-layers on GaAs buffer layers. 250-nm-thick GaAs cap layers were grown on the GaN layers.

The structures were characterized by x-ray diffraction (XD), secondary ion mass spectrometry (SIMS) using N-implanted GaAs as a standard sample, and low-temperature (10 K) PL using a He-Ne laser (632.8 nm) as an excitation source and a cooled Ge diode as a detector.

Results and discussion

The SIMS analysis of the structures gave very narrow N-concentration profiles with full width at half maximum values of as small as 20 nm. The profiles were integrated to obtain the total amount of N in each structure, and the concentration is shown in Fig. 2 as a function of the N-radial exposure time. The value for the exposure time of 10 s is almost equal to (or slightly less than) $6.3 \times 10^{14} \text{ cm}^{-2}$, which is the number of the sites in a (100) atomic plane in GaAs, thus indicating that the surface As atoms are easily replaced by the N atoms at 500°C and that one-monolayer (ML)-thick GaN was grown. The N concentration increases with the exposure time, but this increase is not linear, indicating that the replacement of the As atoms in the second or deeper As-plane is slower than those at the surface.

Since the GaN layers in the structures were very thin, no separated peaks from the GaN layers were observed in XD. The XD pattern of the structure with the N-radical exposure time of 10 s is shown in Fig. 3. The clear fringe on both sides of the GaAs substrate peak indicates that the GaN/GaAs interface and the surface are very flat. A structure with less N also showed a clear fringe, although of lower amplitude of the fringe, because there is less strain in the structure. The structures with more than 1 ML's worth of N showed no fringes

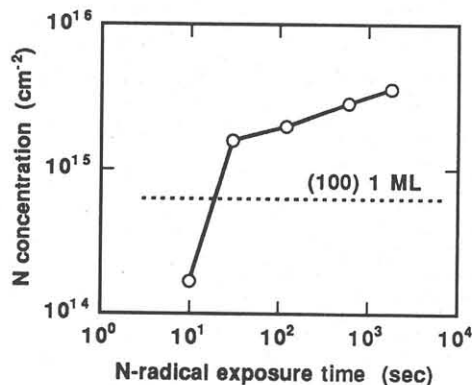


Fig. 2 Total nitrogen amounts in GaAs/GaN/GaAs structures by integrating the SIMS depth profiles.

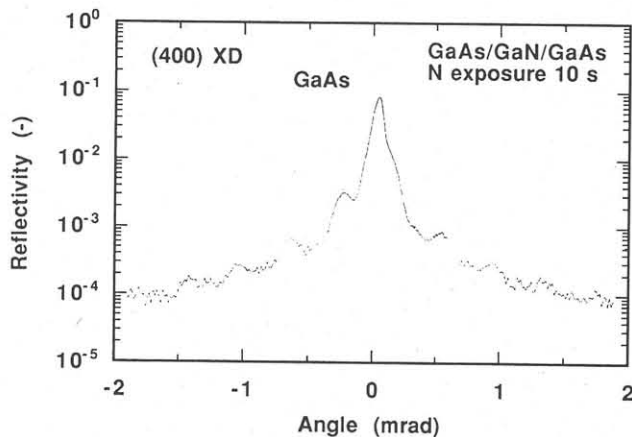


Fig. 3 X-ray diffraction pattern from a GaAs/GaN/GaAs structure whose N-radical exposure time is 10 seconds.

in XD, indicating the interface flatness had deteriorated.

PL spectra from the structures are shown in Fig. 4 together with the spectrum from GaAs not exposed to N-radicals. Deep emission at 1.43 eV appears as separated peaks in (b), (c) and (e) and as a shoulder peak in (d). The PL intensity of the 1.43-eV peak increases linearly with the excitation intensity, suggesting that the peak represents an excitonic emission like the emission from quantum wells. The PL peak intensities of the 1.49-eV peak (carbon in GaAs) and the 1.43-eV peak are shown in Fig. 5. The intensity of the 1.49-eV peak drastically decreases at exposure times longer than 120 s. The intensity of the 1.43-eV peak decreases gradually with increasing exposure time. The decrease of the PL intensities and the disappearance of the XD fringes suggest that GaN layers thicker than 1 ML deteriorate the qualities of the GaN/GaAs interfaces and the GaAs cap layers.

Because of the strong electronegativity of N atoms, a GaN layer in GaAs attracts electrons. The 1.43-eV peak is probably due to the excitonic emission from the 1-ML-thick GaN. The surface As atoms are easily replaced by N atoms and this replacement occurs two-dimensionally, thus, forming 1-ML-thick GaN. When the replacement of the surface As-layer is completed, N radicals start to replace As atoms of the second As-layer from the surface. Because of the large lattice-mismatch between GaAs and GaN, the replacement of As atoms situated lower than the second layer cannot be two-dimensional and GaN clusters may be formed. Because of the large lattice-mismatch between GaAs and GaN, these GaN clusters may be the source of defects causing the rough interface and the low PL intensity from the cap layers. The broad peak at about 1.38 eV in Fig. 4 (d) is probably due to GaN clusters whose size is small enough not to create defects.

Conclusion

GaAs/GaN/GaAs thin-layer structures were grown for the first time by plasma-assisted low-pressure MOCVD. GaN layers were formed by exposing As-stabilized surfaces of GaAs epitaxial layers to N-radical fluxes. When more than 1 ML of As atoms were replaced by N atoms and the amount of N exceeded that in 1-ML-thick GaN, the GaN/GaAs interfaces deteriorated. Low-temperature PL from the structures suggests that the two-dimensional growth of GaN layer is limited to 1-ML and that the excess N atoms form GaN clusters in underlying layers. The 1-ML-thick GaN layer embedded in GaAs showed intense PL at 1.43 eV, whereas the GaN cluster is non-radiative, probably because of the defects caused by the large lattice-mismatch between GaN and GaAs.

The author wishes to thank Drs. Naoki Kobayashi, Yoshiji Horikoshi, and Tatsuya Kimura for their fruitful discussions and continuous encouragement.

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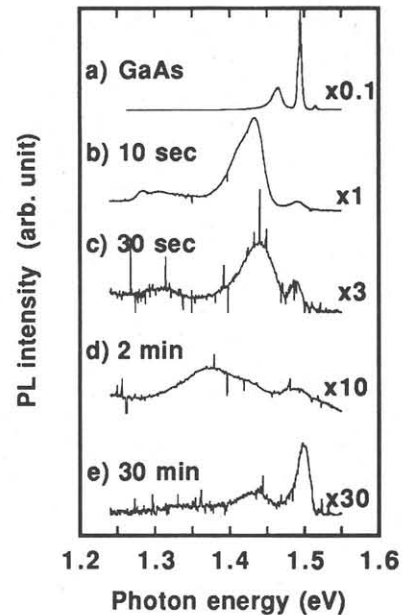


Fig. 4 Photoluminescence spectra measured at 10 K.
a) GaAs without N-radical exposure.
b)-e) GaAs/GaN/GaAs structures.

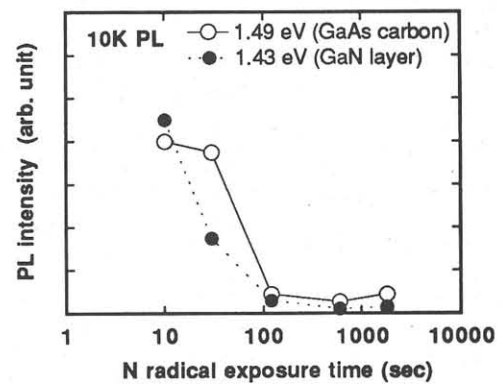


Fig. 5 Photoluminescence peak intensities as a function of the N-radical exposure time.

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