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Effects of gas-flow sequences on the self-limiting mechanisms of GaAsN films grown by atomic layer epitaxy

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ABSTRACT

We adapted the atomic layer epitaxy (ALE) technique to grow GaAsN thin films. The effects of the gas flow sequences used on the self-limiting mechanism (SLM), the N incorporation ratios, and the concentrations of residual impurities were investigated. A pulse of the N precursor (monomethylhydrazine) was added after that of the Ga precursor (trimethylgallium) or the As (trisdimethylaminoarsenic) precursor, which were part of the conventional sequence used for the growth of GaAs films via ALE. If it was noticed that the SLM was in effect, the N precursor was supplied on the Ga- or As-terminated surface (the corresponding sequences and their resulting films are labeled as *On-Ga* and *On-As*, respectively). The *On-As* film exhibited rough surfaces, nonuniform N concentration, and disordered lattices owing to defects. On the other hand, in the case of the *On-Ga* sequence, GaAsN films with high-quality crystals were grown with the SLM in effect and the concentration of N being a few percent. The concentrations of the residual impurities (C and H) in the *On-Ga* film were low. This demonstrated that the *On-Ga* sequence was effective for growing GaAsN thin films on precisely controlled surfaces using the ALE technique.

1. Introduction

(In)GaAsN is being explored for use as a material for multijunction solar cells such that they exhibit a conversion efficiency of more than 45% [1]. However, the electrical characteristics of (In)GaAsN, such as its minority carrier lifetime and carrier mobility deteriorate significantly with the addition of even a small amount of N to GaAs. This deterioration is considered to originate from N-related point defects and/or fluctuations in the distribution of N [2–7]. It has been shown recently that GaAsN films grown via chemical beam epitaxy (CBE) have higher minority carrier lifetimes and higher carrier mobilities than those formed using other growth techniques [8,9]. It is believed that these improvements are related to differences in the N-incorporation process that takes place during CBE and those that occur during the other growth techniques. Films grown via CBE are sensitive to the morphological characteristics of the growing surface, such as steps and terraces. This is so because precursors react only on the growth surface, owing to their long mean free path by the low growth pressure, and the reactions of N precursors with the substrate are weaker than that of N-radicals. These factors suggest that the control of the structure and morphology of the growth surface are of critical importance to the N-incorporation processes, which should help modify the electrical properties of GaAsN films.

To control the morphology of the growth surface during the growth of GaAsN films precisely, we adapted the atomic layer epitaxy (ALE) technique, since by using this technique, it is possible to control the growth surface with single-atomic-layer accuracy because of a self-limiting mechanism (SLM) [10]. As a first step, it was necessary to find the growth conditions for fabricating GaAsN films with the SLM in effect. During growth using conventional ALE, atoms of Group III and V elements are alternately supplied, resulting in the formation of corresponding single films (i.e., incomplete or half monolayers), respectively. In the case of GaAsN, the layer of Group V elements consists of As and N atoms. These atoms and their precursors have different reaction rates on the growth surface [11]. Furthermore, these atoms may even be substituted by each other [12]. All these processes should modify the conditions under which the SLM is in effect. In addition, these processes also effect the concentration of N in GaAsN films, which plays an important role in controlling the band-gap energy of the films. The mechanisms for the incorporation of the N precursor also modify the concentrations of residual impurities, which are usually introduced along with N atoms [13,14].

Therefore, in this study, as first step in the growth of GaAsN films on precisely controlled surfaces by the ALE technique, the effects of gas flow sequences on the SLM, N-incorporation ratios, and concentrations of residual impurities were determined.

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2. Experimental details

In this study, GaAs and GaAsN films were grown by ALE on semi-insulating GaAs(001) substrates. The Ga, As, and N precursors used in the study were trimethylgallium (TMGa) ($Ga(CH_3)_3$), trisdimethylaminoarsenic (TDMAAs) ($[N(CH_3)_2]_3As$), and monomethylhydrazine (MMHy) ($H_3N_2CH_3$), respectively. Hydrogen was used as both the carrier and the purge gas. ALE was performed through a technique called pulsed-jet epitaxy [10]. The gas and precursors were introduced from the bottom and allowed to escape through the top of the reactor using high-capacity vacuum pumps. The reactor structure was designed to allow for the smooth, vortice-free flow of gas. The substrate was positioned in a fast stream of hydrogen gas emitted from a jet nozzle in order to prevent the thermally decomposable source molecules in the stagnant layer from being deposited on the substrate surface. The exchange of the precursors was achieved using a pressure-balanced vend-and-run gas manifold.

The GaAs substrates (14×16 mm^2) were loaded into the reactor through a load-lock chamber and were then thermally annealed under a flow of the As precursor at 550 °C for 5 min to remove the native oxide from the substrates. After the GaAs substrates had been thermally cleaned, GaAs or GaAsN thin films were grown on them using alternating supplies of the precursors. The pulse durations for the Ga and As precursors were fixed at 4 and 10 s, respectively. The growth temperature was varied from 480 to 520 °C. The fluxes of the Ga and As precursors with respect to the substrate surface (i.e., their flow rates per unit area) were such that the growth rates of the Ga and As monolayers were 0.33 ± 0.05 and 0.80 ± 0.05 monolayers (ML)/s, respectively. These were determined from the rate of growth of the GaAs films grown under Ga- and As-poor conditions, respectively. In total, the amounts of the Ga and As precursors that were supplied to the substrate surface during each cycle were such that 1.2 and 8 MLs of Ga and As, respectively, formed during each cycle. The sequence of the flow of the precursors in the case of the growth of GaAs films in the absence of an N precursor is shown in Fig. 1a (The samples grown by this sequence are labeled as *GaAs*). To grow the GaAsN films, a pulse of the N precursor was added to the sequence of the Ga and As pulses and a H_2 purge, as shown in Fig. 1b and c. If it was noticed that the SLM was in effect during these sequences, the pulse of the N precursor was incorporated and N precursor molecules supplied to the Ga- and As- terminated surfaces (*On-Ga*, and *On-As*, respectively). As discussed later in detail, the surfaces of the *On-As* films were rough. The reason for this roughening of the surfaces was considered to be the desorption of As atoms from the substrate surfaces during the N precursor pulse or the exchange of N and As atoms at the surface. To verify whether this was the case, the N precursor pulse was substituted with a H_2 pulse and a GaAs film (*Long-H_2*—the pulse sequence for this film is shown in Fig. 1d) was grown instead. The duration of the N pulse was fixed at 10 s. The exact flux of the N precursor was not evaluated. However, it was estimated to be of the same order or lesser than that of the As precursor, as discussed in the Results section. To grow the GaAs(N) films, their corresponding pulse sequence was repeated 350 times. When the SLM was in effect in each sequence, the thickness of the formed films was 350 ML, which corresponded to 100 nm. For comparison, a GaAsN film was grown via the metal-organic vapor-phase epitaxy (MOVPE) method under the simultaneous supply of all the precursors (the film is labeled as *MOVPE* and shown in Fig. 1e). For the *MOVPE* film, the duration of the growth process was 1400 s. This was the same as the total period for which the Ga precursor was supplied during the sequences.

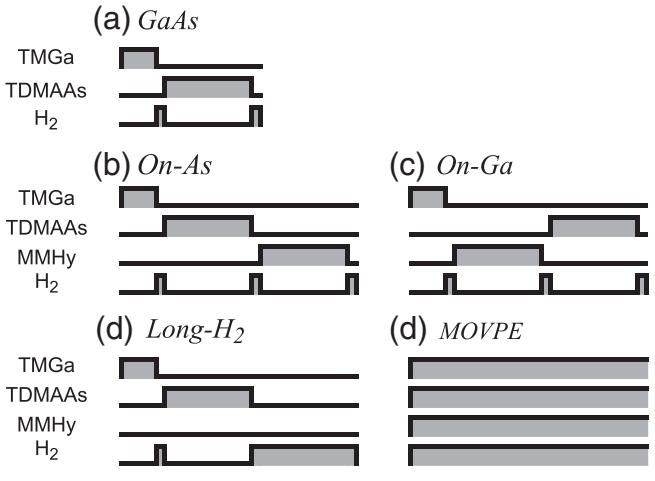

Fig. 1. Gas flow sequences used in this study for growing the GaAs and GaAsN films. Details of the sequences are given in the text.

The morphologies and thicknesses of the grown films were determined from their surface and cross-sectional images taken using scanning electron microscopy (SEM), which was performed with a Hitachi S-5500 system; the operating voltage was 30.0 kV. The N concentrations of the GaAsN films were estimated from their lattice constants measured via X-ray diffraction (XRD) analyses performed using a PANalytical X'Pert PRO instrument. The conventional two theta-theta configuration was employed and Cu Kα1 radiation was used. The crystal quality in the case of each film was also evaluated by XRD. Since some XRD patterns of the GaAsN films exhibited fringe peaks, the thicknesses of these films were calculated from the periodicity of the fringe peaks and were compared with those estimated from their SEM images. The growth per cycle of each film was calculated from the total thickness of the film and the total number of cycles used. This value was considered the growth rate of the films (ML/cycle). The concentrations of the residual impurities (C and H) in the grown films were determined using secondary ion mass spectroscopy (SIMS). The SIMS-based measurements were performed by Evans Analytical Group.

3. Results and discussion

The images of the surfaces of the various films grown using the different sequences are shown in Fig. 2. The *GaAs* and *On-Ga* films had smooth surfaces and uniform thicknesses, irrespective of the growth temperatures (images of the films grown at 480 °C and 520 °C are not shown here). Defects were observed on the surfaces of the *On-As* and *Long-H_2* films. The defect densities in the case of both these films types were of the same order at each growth temperature. The defects observed on the surfaces of the *Long-H_2* films were oval shaped and similar to those often observed in GaAs films grown by molecular beam epitaxy [15,16]. It is generally assumed that these oval-shaped defects are formed owing to the presence of contaminants on the substrate surfaces prior to the epitaxy process and by particles present in the reaction chamber [16]. However, this was not the case here, since the defects were observed only in the *Long-H_2* films. In addition, it was found that the defect density increased with an increase in the growth temperature. Thus, we concluded that the surface defects observed in the *Long-H_2* films were due to the availability of As atoms during the formation of the films being low. In other words, As atoms were desorbed from the substrate surfaces during the H_2 pulse. In the case of the *On-As* films, the depth and width of the defects on the surfaces of the films were larger than those of the *Long-H_2* films. Therefore, the surface roughness of the *On-As* films could be attributed not only to the desorption of As but also to exchange reactions between the As and N atoms. The films grown via the *MOVPE* mode were small grained, and the crystal orientation of these grains was random. Thus, it was surmised that the growth parameters investigated in this study were not suitable for the epitaxial growth of GaAsN films.