Indium-modified growth kinetics of cubic and hexagonal GaN in molecular beam epitaxy

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The kinetics changes in the growth of GaN induced by the presence of In segregated on the surface have been investigated *in situ* by using reflection high energy electron diffraction intensity oscillations. Two types of surfaces have been studied, namely, Ga-polar (0001) wurtzite, and (001) zinc blende. It has been found that In influenced both Ga and N surface kinetics, leading to a change in the growth rate associated with a change in the amount of Ga and N effectively available for the GaN growth. © *1999 American Institute of Physics.* [S0021-8979(99)07820-2]

I. INTRODUCTION

Although ternary $Ga_xIn_{1-x}N$ alloys constitute the active layer of blue light emitting diodes and blue lasers, the prediction of their composition is still a challenging issue for the crystal growers. As a matter of fact, it has been shown by various authors that the maximum In concentration strongly depends on the growth temperature of the ternary alloy, more indium being incorporated for lower temperature. However, for large In concentration, phase separation was found to occur, with the expected consequence that the *real* concentration of $Ga_xIn_{1-x}N$ alloys in the active zone of devices is poorly estimated, rather consisting of a mixture of In-poor and In-rich zones in which the excitons are strongly localized.[1–3] The phase separation is believed to result from the insolubility of In in GaN for typical growth temperature in metalorganic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE).[4] Actually, some experimental evidence of phase separation was already demonstrated,[5] especially for MOCVD grown samples.[6,7] As concerns MBE which is basically a nonthermodynamical equilibrium growth process at low temperature, it is not possible to predict phase separation effects with respect to these thermodynamical considerations.

One of the main advantages of MBE resulting from the low pressure in the growth chamber is the possibility to measure the growth rate *in situ* by means of reflection high energy electron diffraction (RHEED) intensity oscillations. Taking advantage of the RHEED technique, the aim of the present article was to *in situ* determine the influence of In on the growth of GaN in molecular beam epitaxy. Actually, we have previously shown that, for a high enough growth temperature, In acts as a surfactant, not being incorporated but modifying the GaN growth kinetics, which results in improved structural and optical properties.[8] We demonstrate further in the present work that the growth rate of both cubic and hexagonal phase GaN is modified in presence of In. As a consequence of this result, we show that the *in situ* determination of the In concentration in $Ga_xIn_{1-x}N$ alloys through growth rate measurement using RHEED oscillations must be carefully considered, being directly affected by the kinetical changes associated with the presence of In.

II. EXPERIMENTS

The growth was performed in a commercial MECA 2000 chamber equipped with effusion cells for Ga and In and with a radio frequency (rf) plasma cell from the EPI company for N. Two types of substrates were used: (i) MOCVD GaN on sapphire for the growth of Ga-polarity hexagonal GaN, (ii) cubic SiC deposited by MOCVD on (001) Si for the growth of (001) cubic GaN. After a standard degreasing procedure, (i) the GaN MOCVD substrate was In bonded on a Mo sample holder (molyblock), whereas (ii) the SiC substrates were diped in HF and rinsed in deionized water before bonding onto a molyblock. Whatever the type of substrate, it was *in situ* outgassed at 700 °C prior to the MBE growth. Note that the substrate temperature was measured using a thermocouple carefully shielded from direct heating by the hot filament of the heater. The thermocouple was in mechanical contact to the molyblock using a spring to ensure a good reproducibility of the temperature measurement.

Unless stated, all experiments reported below were carried out at a substrate temperature, T_s, of 700 °C. This substrate temperature was high enough to ensure that *no indium could be incorporated.* This was checked by Rutherford backscattering spectroscopy (RBS). It was found that the indium content in the layers was lower than the detection limit of 10^{-4}, meaning that the growth rate changes which were observed could not be assigned to In incorporation.

Other features common to all experiments were the rf power (300 W) and the N_2 flux in the plasma cell (0.5 sccm), allowing us to compare to some extent the results of various experimental runs, as will be discussed below.

Figure 1(a) shows the GaN growth rate variation as a function of the Ga cell temperature in the case of Ga-polarity (0001) wurtzite GaN. Without In, two regimes are observed: (i) below $T_{Ga}=1020$ °C, the growth rate increases as a function of the Ga cell temperature, as an indication that the growth is Ga limited (N-rich regime), (ii) above T_{Ga}

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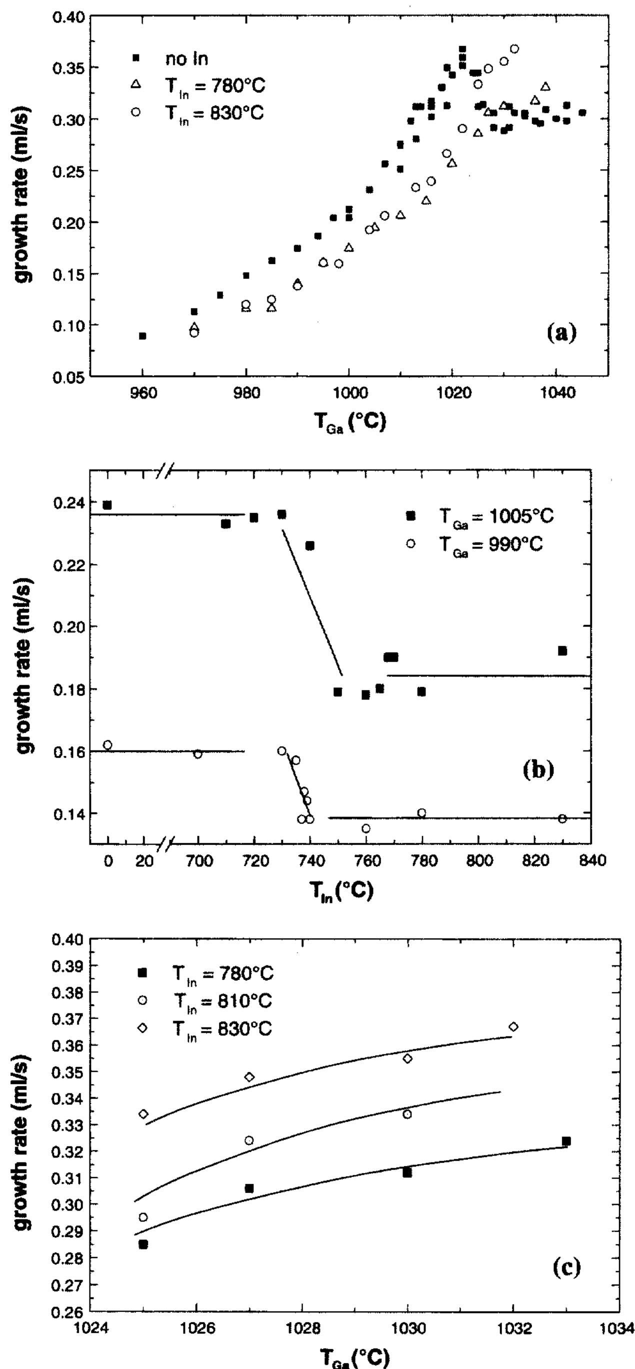

FIG. 1. (a) Variation of the GaN growth rate as a function of the Ga cell temperature for a hexagonal Ga-polarity (0001) surface. Closed squares: without In. Open symbols: in the presence of In, as indicated in the figure. (b) GaN growth rate change as a function of the In cell temperature in the N-rich regime for fixed Ga flux. T_{In}=740 °C corresponds to an In flux of about 5% of the Ga flux required for Ga/N stoichiometry. (c) GaN growth rate change as a function of the In cell temperature in the Ga-rich regime. Note that a In cell temperature of 830 °C corresponds to an In flux of about 40% of the Ga flux at Ga/N stoichiometry. In all cases, the error bar on the growth rate value is ±0.015 ML/s.

= 1030 °C, the growth rate is stable for increasing Ga cell temperature, as an indication that the growth is N limited (Ga-rich regime). The peak underlying the transition between the two regimes is assigned on one hand to the formation of Ga droplets, as will be discussed below, and on the other hand to an increased probability of N desorption in the Ga-rich regime with respect to the N-rich regime.

The effect of In was found to be very different in the two regimes. In the N-rich regime, the GaN growth rate was constant as a function of the In flux, followed by an abrupt *decrease*, as shown in Fig. 1(b). Note that, based on beam equivalent pressure measurements, the In cell temperature of 740 °C to which the abrupt transition is observed corresponds to an In flux of roughly 5% with respect to the Ga flux. For In cell temperatures higher than 750 °C, the GaN growth rate was constant. The onset of the growth rate decrease was found to be very weakly dependent on the Ga flux whereas the amplitude of the growth rate jump increases with the Ga cell temperature.

By contrast, in the Ga-rich regime, the GaN growth rate was found to increase continuously as a function of the In flux. This is illustrated in Fig. 1(c) which is an enlargement of Fig. 1(a) in the 1024–1034 °C range for the Ga cell temperature and for various In cell temperatures. Note that the In fluxes required to observe the effect are about one order of magnitude higher than those responsible for the effect observed in the N-rich regime. Interestingly, it should be noted that the maximum GaN growth rate value measured when increasing the In flux was found to be roughly equal to the value of about 0.36 monolayers (ML) s^{-1} measured at the maximum of the peak observed in the growth rate variation as a function of the Ga flux for T_{Ga}= 1020 °C without In.

As far as the Ga-rich or N-limited plateau regime is concerned, the increase in the growth rate in the presence of In can only be assigned to an increase of the amount of N atoms available for the GaN growth since RBS demonstrated that no In was incorporated. This observation first allows us to infer that a significant fraction of N atoms physisorbed on the surface are not used for the growth. Second, it consistently indicates that the desorption of N is limited in the presence of In. As a matter of fact, N atoms are bound to the Ga-polarity (0001) GaN surface by only one bond and exhibit three dangling bonds. It is reasonable to assume that these weakly bound N atoms can, to a certain extent, diffuse on the surface and recombine to form N_2 molecules. In this scheme, the role of In is tentatively viewed as passivating the N dangling bonds, with the consequence that the N+N recombination is made more difficult. Hence, the growth rate is increased in the plateau regime because more N is available for the growth. However, as the In–N bond is unstable at 700 °C, this finally leads to the exchange with a Ga atom. At this point, it is worth noting that this model is supported by previous experiments tending to establish that the metastable N–In bond is responsible for the GaN growth kinetics changes observed in the presence of In (Refs. 8, 9). In particular, we have shown that the basal plane stacking faults density was considerably reduced in the presence of In, which was interpreted as resulting from a dramatic increase in Ga diffusion length in the N-rich regime, provided that the N dangling bonds were passivated by In (Ref. 8).

As far as the N-rich regime is concerned in the present experiments, a decrease of the GaN growth rate has been observed in the presence of In (see Fig. 1). As a matter of fact, this growth rate decrease may result either from the increasing probability to form Ga droplets in the presence of

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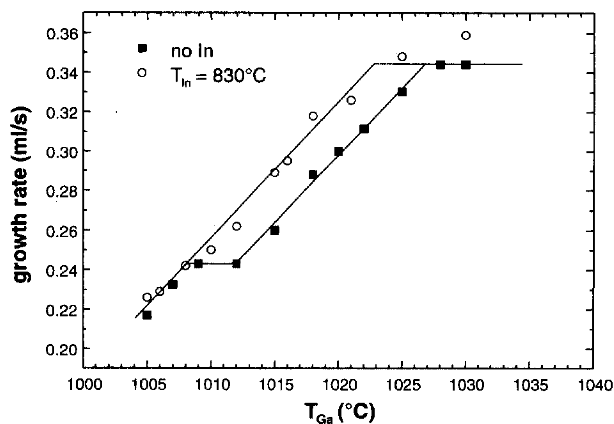

FIG. 2. Variation of the GaN growth rate as a function of the Ga cell temperature for a cubic (001) GaN surface. Closed squares: without In. Open circles: in the presence of In (T_{In}=830 °C). The error bar on the growth rate value is ±0.015 ML/s.

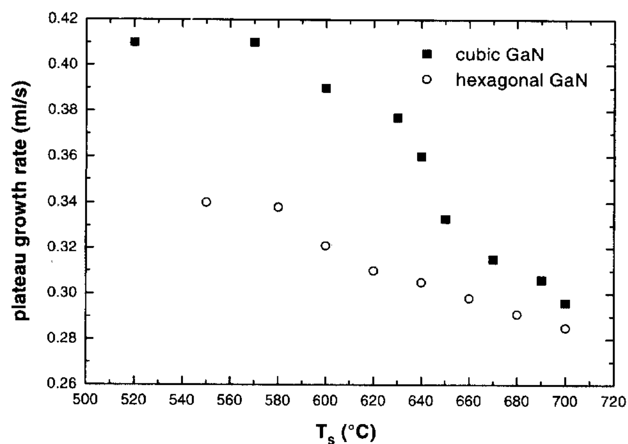

FIG. 3. Variation of the growth rate in the plateau regime as a function of the substrate temperature for a (001) cubic GaN surface (closed squares) and for a Ga-polar (0001) hexagonal GaN surface (open circles). The error bar on the growth rate value is ±0.015 ML/s.

In or from a decrease in the Ga sticking coefficient although it is difficult at this stage to decide between these two hypothesis.

In addition to the case of Ga-polar (0001) wurtzite GaN, that of (001) cubic GaN was also investigated. As shown in Fig. 2, two regimes are still observed in the absence of In, namely, a Ga-rich and a N-rich regime. In the N-rich regime, an inflexion in the growth variation was observed for $T_{Ga} \approx 1010\,°C$. Again, it was assigned to the formation of Ga droplets, leading to a slope change in the growth rate variation.

In the presence of In, a growth rate increase was observed, for $T_{Ga} > 1010\,°C$ in the N-rich regime. If one assumes that the anomaly in the growth rate variation observed at $T_{Ga} \approx 1010\,°C$ in the absence of In is associated with the formation of Ga droplets, the effect of In should be to delay the Ga droplet formation, with the consequence that more Ga is available for growth, resulting in a larger growth rate. Note that for $T_{Ga} < 1010\,°C$, In has no effect on the growth rate, consistent with the hypothesis that Ga droplets are not formed in this Ga flux range value.

It is remarkable that In has no effect in the N-limited (Ga-rich) regime. This suggested that the N bonds-passivating effect of In invoked above to explain the results on the Ga-polarity surface are irrelevant in the case of cubic (001) GaN. Next, it also suggests that the growth mechanisms responsible for the existence of a plateau regime are not the same for hexagonal and cubic material. In order to check this hypothesis, the variation of the growth rate in the plateau regime was measured as a function of the substrate temperature for both Ga-polarity and cubic surface in the absence of In. The results are shown in Fig. 3. Whereas a relatively weak temperature dependence of the growth rate plateau value was observed for the Ga-polarity (0001) surface between 550 and 700 °C, a stronger variation was found in the case of the (001) cubic surface. The saturation limit was about 0.34 and 0.41±0.015 ML/s for the hexagonal and cubic case, respectively.

A first conclusion of this experiment is that hexagonal and cubic surfaces behave quite differently, possibly due to the difference in the number of dangling bonds for N or Ga, depending on the surface under consideration. It should be recalled that the growth rate in the plateau regime is N limited. Then, the results in Fig. 3 suggest that the sticking coefficient and/or the desorption probability of N atoms are thermally activated in both hexagonal and cubic case but with a rather different activation energy value. Correlatively, it appears that the In-induced N-passivating process which was found to efficiently compete with the N desorption process in the hexagonal case is uneffective in the cubic case.

At this point, it is worth recalling that the incorporation site density is expected to be $\sqrt{3/2}$ times larger for (0001) hexagonal surface than for (001) cubic surface. As a consequence, for a similar N flux and sticking coefficient, the growth rate is expected to be $\sqrt{3/2}$ times smaller for the hexagonal surface with respect to the cubic one. Then, when comparing in Fig. 3 the maximum growth rate value in the hexagonal case (0.34±0.015 ML/s measured at 560 °C) with the maximum growth rate value in the cubic case (0.41±0.015 ML/s measured at 520 °C), it is experimentally found that their ratio is about 0.83±0.05, consistent with the expected value of 0.866.

III. CONCLUSION

In conclusion, we have demonstrated that the GaN growth kinetics is deeply influenced by the presence of indium. For substrate temperatures high enough to ensure that no In was incorporated, drastic growth rate modifications were found to be induced by the presence of In. The effect of In was found to depend on the metal/N ratio value during the growth. It led either to the passivation of the N dangling bonds resulting in a decrease of the N desorption rate (case of Ga-polarity (0001) GaN surface in the N-limited plateau regime) or to a decrease of the amount of Ga available for the growth due to a mechanism still to be identified (case of Ga-polarity (0001) GaN surface in the Ga-limited regime). By contrast, the N desorption process was found to be weakly affected by the presence of In in the case of

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(001) GaN surface. In this case, it was suggested that the Ga droplet formation was inhibited in the presence of In.

As a whole, it appears remarkable that the effect of In is drastically dependent on the surface structure under consideration, i.e., (0001) hexagonal or (001) cubic. Nevertheless, whatever the type of growing surface, the results reported in this article demonstrate that In can be viewed as a surfactant modifying the surface kinetics of the material without being incorporated. We wish to emphasize an important practical consequence of our study: it clearly establishes that the *in situ* determination of the composition of GaInN alloys by means of RHEED oscillations measurements must be cautiously considered. As a matter of fact, we have found that even at temperature lower than 700 °C very important errors in the prediction of the alloy composition can be made if neglecting the surfactant effect of In.

ACKNOWLEDGEMENTS

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