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Relationship between the growth rate and Al incorporation of AlGaN by metalorganic chemical vapor deposition

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ABSTRACT

The growth rate and its relationship with growth conditions of AlGaN alloy films by metalorganic chemical vapor deposition (MOCVD) are investigated. It is found that both parasitic reaction and competitive adsorption play important roles in determining the growth rate and Al incorporation in AlGaN. Low reactor pressure can weaken parasitic reactions, thus increasing the Al composition. In addition, a decrease of absolute amount of Ga atoms arriving on the substrate may lead to a lower Ga competitive power, and then a higher Al content in AlGaN film.

1. Introduction

The investigations on Al incorporation in AlGaN have been emphasized for many years due to the wide applications of AlGaN-related devices, especially for the ultraviolet photodetectors which can be used in secure space-to-space communication, solar ultraviolet monitoring and so on [1–5]. It is known that a high quality of the material is necessary for AlGaN-related devices [6]. Moreover, a suitable Al content in the alloy is also very significant in determining the device performances. There has been a certain number of papers about the growth rate and Al composition of AlGaN [7]. However, due to the difficulty of growing AlGaN materials with high Al content [8], it is necessary to study the optimization of factors that influence the Al incorporation. Especially it is an interesting topic to investigate the relationship between the growth rate and Al incorporation during metalorganic chemical vapor deposition (MOCVD) growth. In this paper it is found that both parasitic reaction of gas source precursors in the vapor phase and competitive adsorption of Al and Ga atoms have essential effects on the Al incorporation in AlGaN. It is found that a reduced amount of Ga atoms which arrive on the substrate surface may lead to a higher Al incorporation.

2. Experimental procedure

All investigated AlGaN epilayers are prepared by the two-step growth method on *c*-plane sapphire substrate by MOCVD. The ammonia (NH_3), trimethylgallium (TMGa), trimethylaluminum (TMAl) are used as N, Ga and Al sources, respectively. The growth process is as follows: firstly a low temperature GaN buffer layer is deposited on the substrate, then a high-temperature GaN epilayer follows. Afterwards the AlGaN layer is grown on the GaN template layer at 1060 °C. The *in situ* optical reflectance measurement is employed to monitor the growth process of AlGaN. The growth parameters such as reactor pressure, TMAl flux and TMAl + TMGa flux are adjusted separately during the growth, and their influences are examined in order to understand the growth mechanism and the effects of parasitic reaction and competitive adsorption. The triple-axis X-ray diffraction (TAXRD) measurements of samples are performed to study the Al incorporation under different growth circumstances.

3. Results and discussion

The *in situ* optical reflectance measurements can provide information such as growth rate and surface conditions, etc. [9,10]. Fig. 1 shows the growth rate of (Al)GaN as a function of the reactor pressure under different TMAl fluxes, i.e. at 0, 6 and 15 μmol/min

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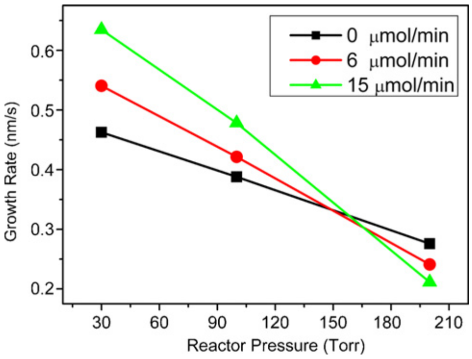

Fig. 1. The measured growth rate of AlGaN versus reactor pressures. The flux of TMAl adopted in the growth is 0, 6 and 15 μmol/min, respectively, while TMGa flux is fixed as 56.32 μmol/min.

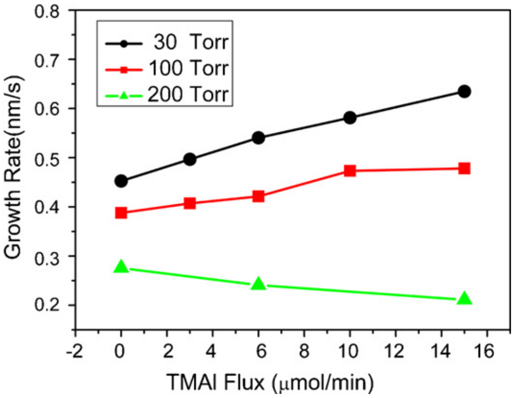

Fig. 2. The measured growth rate of AlGaN versus TMAl flux. The reactor pressures adopted in the growth are 30, 100 and 200 Torr, respectively while TMGa is fixed as 56.32 μmol/min.

respectively, while TMGa flux is fixed as 56.32 μmol/min. It is shown that the AlGaN growth rate declines as reactor pressure increases. This result is reasonable because a higher reactor pressure may enhance parasitic reaction and further reduce the growth rate of AlGaN [7,11]. It has been reported that parasitic reaction of TMAl has a great influence on Al incorporation into the film [7]. We compare three specific samples which were grown at a fixed TMAl flux of 6 μmol/min, but the reaction pressure is different. The X-ray diffraction result (not shown here) indicates that the Al content of AlGaN films grown under 30, 100 and 200 Torr (1 Torr = 133.32 Pa), is 20%, 17% and 13%, respectively. It is understood that the increasing parasitic reaction with increasing pressure causes a decline of Al atoms arriving on the growth surface [12], which in turn reduces the Al content in the alloy film. A close inspection of Fig. 1 indicates that the growth rate of (Al)GaN decreases slower with increasing reactor pressure, when the TMAl flux is 0 μmol/min, while the slope of growth rate dependence becomes steeper if the TMAl flux is raised to 6 μmol/min, and the growth rate decreases even more rapidly if the TMAl flux is as high as 15 μmol/min, indicating that the parasitic effect is more serious for the growth process with higher TMAl flux. In fact, it has been shown that the parasitic effect between TMAl and NH_3 is more serious than that between TMGa and NH_3, thus it has a stronger influence on AlN growth than on GaN growth [12,13]. It is noted that from the data of Fig. 1 when the reactor pressure is 200 Torr, an interesting phenomenon appears, i.e. the growth rate of AlGaN (with a TMAl flux) is even lower than GaN (TMAl flux = 0). We assume that the growth rate of AlGaN alloy is the sum of the growth rates of AlN and GaN. When TMAl flux is zero, the film growth rate equals that of GaN. According to the above assumption, when a TMAl flux is added, the growth rate of AlGaN should be the growth rate of GaN adding that of AlN. It means that if the growth rate of GaN is the same as at zero TMAl flux, the growth rate of AlGaN at 6 μmol/min TMAl flux should be higher than the growth rate of GaN. Indeed we have seen a reversed result, i.e. the AlGaN growth rate becomes even smaller. It may be caused by so-called competitive adsorption effect between AlN and GaN growth and is needed to clarify further. Therefore, we have carried out the following experiments in order to make the understanding of this interesting phenomenon clearer.

The relationship between AlGaN growth rate and TMAl flux is more directly shown by the curves in Fig. 2, where the reactor pressure values adopted in the growth processes is 30, 100 and 200 Torr, respectively, while TMGa flux is fixed as 56.32 μmol/min. It is found that as the TMAl flux goes up, the growth rate of AlGaN alloy increases when the reactor pressure is as small as 30 Torr. However, the growth rate increases slowly or remains almost unchanged with the increasing TMAl flux when the reactor pressure is raised to 100 Torr, and it instead turns to decrease when the reactor pressure is 200 Torr. The following analysis of growth rate-determining mechanism is still based on the assumption that the AlGaN growth rate should be the growth rate of GaN adding that of AlN, but there is an important influence of the parasitic reaction as well as the competition between adsorbtion of Al and Ga atoms and their incorporation into the film.

When the reactor pressure is 30 Torr, the parasitic reaction is very weak, the AlN growth rate increases with increasing flux of TMAl while the growth rate of GaN might be unchanged or only slightly reduced due to the competition effect, thus resulting in a rise of growth rate. When the reactor pressure is raised to 100 Torr, the parasitic reaction is still not so important, and the AlN growth rate increases slowly with increasing TMAl flux while the GaN growth rate might drop also slowly, and this can explain why the total AlGaN growth rate stays approximately unchanged with increasing TMAl flux. However, when the reactor pressure is raised to 200 Torr, the parasitic reaction of AlN become severe, but the AlN growth rate may still slightly rise a little with increasing TMAl flux as reported in [11]. It means the AlGaN growth rate may be reduced due to the parasitic effect of TMGa at the reactor pressure of as high as 200 Torr. A reduced amount of Ga atoms arriving on the substrate, it which in turn leads to a weaker Ga competitive power and then result in a decrease of GaN growth rate. Therefore, the total growth rate of AlGaN is reduced with increasing TMAl flux as shown in Fig. 2.

According to the above-mentioned analysis, we put forward a postulation that when the total number of Al and Ga atoms go up with a fixed Al/Ga ratio, the increasing number of Ga atoms arriving on the surface may lead to a stronger competitive ability of Ga atoms, so in turn the Al content in the alloy drops. The experimental result supporting this postulation is as follows.

In this experiment, the reactor pressure value adopted in the AlGaN growth is 100 Torr, which can ensure a much weaker parasitic reaction than what happens at a higher pressure of 200 Torr. The absolute amount of Ga atoms arriving on the surface can be adjusted by changing the total TMAl + TMGa flux with a fixed Al/Ga ratio by using a fixed TMAl/TMGa ratio of 3/28.16. In Fig. 3, as the total TMAl + TMGa flux increases, the AlGaN growth rate increases rapidly. There is approximately a linear relation of 1:1 between growth rate and source flux, demonstrating that the parasitic reaction has very little effect on AlGaN growth. From Fig. 4, the ω–2θ XRD curves at (0 0 0 2) plane of three AlGaN epilayers grown on GaN templates are shown when the flux of TMAl is 3, 6, and 15 μmol/min, respectively. It is clearly seen that the peak distance between AlGaN alloys and GaN substrates becomes shorter with increasing total TMAl + TMGa flux, which indicates that although TMAl/TMGa ratio is unchanged, the lattice constant of AlGaN film

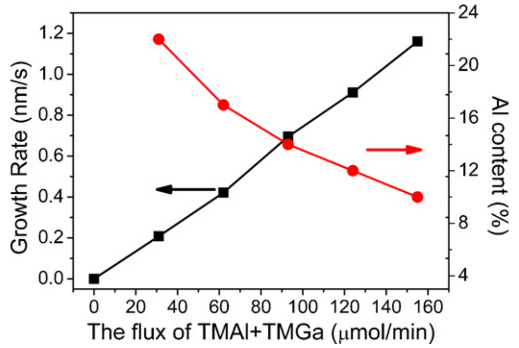

Fig. 3. The measured growth rate and Al content versus the flux of total TMAl + TMGa flux. The reactor pressures adopted in the growth is 100 Torr and the TMAl/TMGa ratio is fixed as 3/28.16.

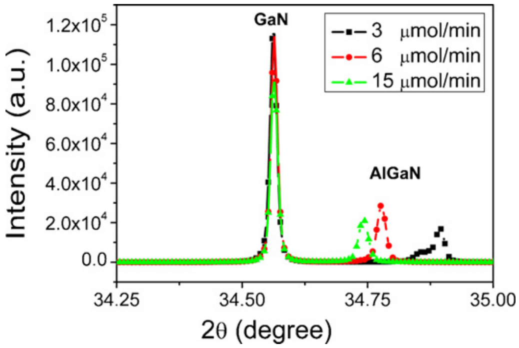

Fig. 4. The XRD ω–2θ curves at (0 0 0 2) plane of AlGaN epilayers grown on GaN templates with varying TMAl flux of 3, 6, and 15 μmol/min, the corresponding Al content of AlGaN is 22%, 17%, and 10%, respectively.

goes up. In other words, Al content in AlGaN film has been reduced. The detailed information of Al content has been calculated and the corresponding data points are shown in Fig. 3. It is seen that when TMAl flux is 3, 6, and 15 μmol/min, the corresponding Al content in AlGaN is 22%, 17% and 10%, respectively, i.e. the Al content decreases with increasing TMAl flux. The Al content changes in an opposite direction in comparison to the increase of TMAl flux, which is in line with our previous analysis that the incorporation of Al atoms suffers a very strong competition from Ga atoms. When pressure of MOCVD system is not too high, or the influence of parasitic reaction may be less important, the number of Ga atoms which arrive on the growth surface increases. The Ga competitive power grows stronger in comparison with Al atoms under this growth circumstance. More Ga atoms participate into the growth process, which leads to a higher Ga incorporation ratio and a lower Al composition. Based on the above discussions, it is concluded that the Al composition will be severely influenced by the competition effect between the Ga and N atoms arriving to the film surface. The condition of reactor pressure, TMAl/TMGa ratio, and the flux of TMAl + TMGa should be carefully chosen in order to gain AlGaN with a demanded Al content.

4. Summary

The growth rate and its influences on Al incorporation in AlGaN film grown by MOCVD are investigated. It is found that both parasitic reaction and competitive adsorption effects play significant roles in determining the Al content of AlGaN. It is shown that a lower reactor pressure can suppress parasitic reactions, thus increasing the growth rate and Al content of AlGaN. A decrease of Ga atoms arriving on the growth surface may be helpful to gain AlGaN alloy films with higher Al content.

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