The Effect of Unprecracked Hydride on the Growth and Carbon Incorporation in GaAs Epilayer on GaAs(100) by Chemical Beam Epitaxy

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Received October 28, 1994

We have grown GaAs epilayers by chemical beam epitaxy (CBE) using unprecracked hydrides and metalorganic compounds *via* a surface decomposition process. This result shows that unprecracked arsine (AsH_3) or monoethylarsine (MEAs) can be used in chemical beam epitaxy (CBE) as a replacement of a precracked AsH_3 source in CBE. It was also found that the uptake of carbon impurity in epilayers grown using trimethylgallium (TMG) with unprecracked AsH_3 or MEAs was significantly reduced compared to that in epilayers grown by CBE process employing TMG and arsenics produced from precracked hydrides. We propose a surface structural model suggesting that the hydrogen atoms play an important role in the reduction of carbon content in GaAs epilayer. Intermediates like dihydrides from hydride sources were also considered to hinder carbon atoms from being incorporated into the epilayers or to remove other carbon containing species on the surface.

Introduction

The use of precursors which do not require a high-temperature cracking cell appears attractive for conveniences related with chemical beam epitaxy (CBE) and metalorganic molecular beam epitaxy (MOMBE) growth processes.[1] It has been attempted to grow GaAs by using TMG and undecomposed arsine in an ultrahigh vacuum system.[2] However, it turned out difficult to grow GaAs using this technique because cracking of arsine into arsenic at the substrate surface alone may be negligible and thus not sufficient for achieving growth at the temperatures below 570 ℃.[1,3,4] An explanation of the earlier results[2] was that the arsine (AsH_3) injection capillary might be accidentally heated by radiation from the hot susceptor leading to a partial decomposition of the arsine.[3] This observation suggested that arsine must first be precracked at high temperatures in a cracking cell prior to growth to be used in the CBE process. Moreover, the use of arsenics does not provide a proper chemical reaction which can reduce the carbon contamination anticipated to result from the decomposition of carbon-containing metalorganic compound at the growing surface.

In the CBE or MOMBE growth of epitaxial layers, hydrogen has been recognized to play an important role in obtaining high quality materials. It has been shown repeatedly that the use of arsine and elemental Ga produces high quality GaAs epilayers;[5,6] this was considered to be due in part to the hydrogen ambient resulting from the thermal cracking of arsine in the cell. Furthermore, the partially cracked species of arsine were demonstrated to be responsible for the improved GaAs characteristics at low arsine cracking temperatures.[7] In addition to the use of hydrogen atoms attached to precursors for the growth of high-quality GaAs, it has been also demonstrated that a hydrogen ambient[8] and the introduction of ionized hydrogen[9] during GaAs growth significantly reduce the incorporation of carbon and oxygen in the epilayer.

In this study, we have investigated the feasibility of growing GaAs using unprecracked arsine, monoethylarsine (MEAs), TMG, and triethylgallium (TEG). We paid special attention to the role of hydrogen atoms dissociated from hydrides in the reduction of carbon incorporation in the GaAs epilayers grown by this method. This study showed conclusively that GaAs epilayer can be grown using TMG or TEG coupled with unprecracked arsine or MEAs under ultrahigh vacuum condition. It was also suggested that the hydrogen atoms from thermally decomposed arsine on the surface play an important role in the reduction of carbon in the epilayers.

Experimental Procedure

The growth experiments were conducted in a CBE chamber which has been also used in our earlier works.[10] The UHV growth chamber is evacuated with a 510 *l*/s turbomolecular pump and a titanium sublimation pump. The pumping system maintained the growth chamber at a pressure of less than 3×10^{-10} Torr after the system was baked out for 48 hours at 150 ℃. The gas flux was adjusted by means of a high-precision automatic pressure controller which is essentially a closed-loop operated UHV leak valve. Metalorganic compound and hydride gases were injected into the growth chamber and directed towards the substrate through stainless steel tubes without carrier gases. The temperature at the end of tube was 118 ℃ when the substrate temperature was maintained at 610 ℃ for 2 h. This eliminates the possibility of decomposition of hydrides and metalorganic compounds in the gas tube. The substrate temperature was monitored by an infrared pyrometer. Commercially available "super-cleaned" Cr-doped semi-insulating GaAs(100) wafers (2° off towards the nearest (110) plane) were used as substrates without any pre-cleaning process. After a 1.5 cm×1.5 cm substrate was mounted on an In-free molybdenum block, it was introduced into the load-lock chamber. Prior to grow-

This paper is dedicated to professor Woon-Sun Ahn in honor of his retirement.

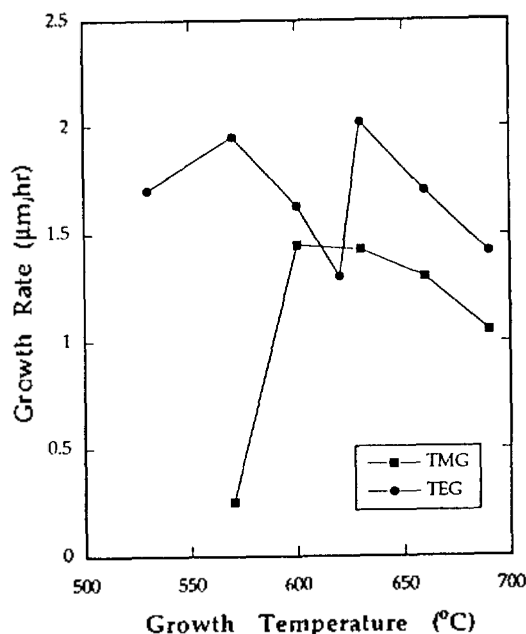

Figure 1. Effect of growth temperature on the GaAs growth rates using unprecracked AsH_3 with TMG (V/III=10, P=1.2×10^{-4} Torr) and TEG (V/III=20, P=1.2×10^{-4} Torr).

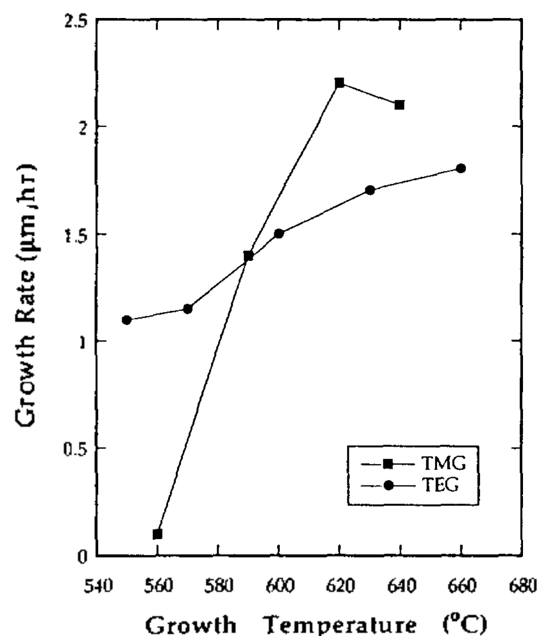

Figure 2. Effect of growth temperature on the GaAs growth rates using unprecracked MEAs with TMG (V/III=10, P=5.5×10^{-5} Torr) and TEG (V/III=20, P=5.7×10^{-4} Torr).

th, the substrate and sample holder were outgased at 200 ℃ in the growth chamber for 15 min. The pre-growth annealing in the growth chamber was carried out at a temperature of 630 ℃ for 15 min under an AsH_3 pressure of 10^{-4} Torr to obtain a clean surface. The gas pressure in the chamber during growth was in the range from 10^{-5} to 10^{-4} Torr depending upon the V/III ratio. Layer thickness was measured by scanning electron microscopy (SEM) on stained and etched cleavage planes. The samples were inspected by optical microscope and SEM for the evaluation of their morphology. Low temperature photoluminescence (PL) and Hall measurements at room temperature were also made for optical and electrical characterization of grown epilayers.

Results and Discussion

SEM and optical micrographs of GaAs epilayers showed that gallium droplets are formed on the surface at low temperature, which gradually disappear with increasing substrate temperature resulting in a mirror-like surface. The formation of gallium droplets is attributed to an insufficient supply of arsenic in the formation of GaAs on the surface. It was also found that the morphology improves rapidly and a mirror-like surface is obtained from TMG- and TEG-grown epilayers with increasing V/III ratio at high substrate temperature.

Figure 1 represents the temperature-dependent GaAs growth rates obtained from the samples grown with unprecracked AsH_3 coupled with TMG and TEG. The growth rate with TMG as shown in Figure 1 is divided into three regions. Below 600 ℃, the growth rate is believed to be limited by the decomposition process of TMG on the surface. Between 600 and 630 ℃, the temperature is high enough to completely dissociate all the TMG resulting in a constant growth rate with increasing temperature. Above 630 ℃, the gradual decrease in growth rate is considered to be caused by the desorption of gallium atoms or partially cracked TMG. The growth rate with TEG, however, has two humps as shown in Figure 1. Our observation is similar to an anomalous temperature dependence of growth rate of GaAs grown by CBE using TMG and arsine.[11] Similarly, the anomalous behavior of growth rates with TEG, which is shown in Figure 1, may also be explained by a growth model which assumes that TEG is decomposed into two different forms of reaction intermediates (partially cracked TEG), resulting in the two humps in the growth rate in the presence of surface hydrogen atoms from unprecracked arsine.

Figure 2 represents the temperature dependent growth rates of GaAs grown using MEAs with TMG and TEG. The growth rates with TMG in Figure 2 seem to be similar to the growth rates at low temperature, which were observed in the case of growth of GaAs using TEG[12] or TMG.[13] The growth rate with TEG, however, increases gradually with increasing substrate temperature presumably due to the low decomposition temperature of TEG as illustrated in Figure 2. Whereas the growth rate with TMG is very small at a low growth temperature of 550 ℃, a growth rate of about 1 μm/h can be obtained at the same temperature when TEG is used as gallium source. All materials obtained by growth with MEAs and TMG exhibited p-type background doping of 10^{15}-10^{17} cm^{-3} with a mobility of 230-330 $cm^2/V\cdot sec$ at 300 K. The hole concentrations in TMG-grown samples decreased as substrate temperature increased, which suggests that carbon containing species may drastically desorb from the growth surface with increasing substrate temperature. Epilayers grown with TEG were mostly semi-insulating with p-type background doping of less than 10^{14} cm^{-3}. At the growth temperature of 600 ℃ and V/III ratio of 5, n-

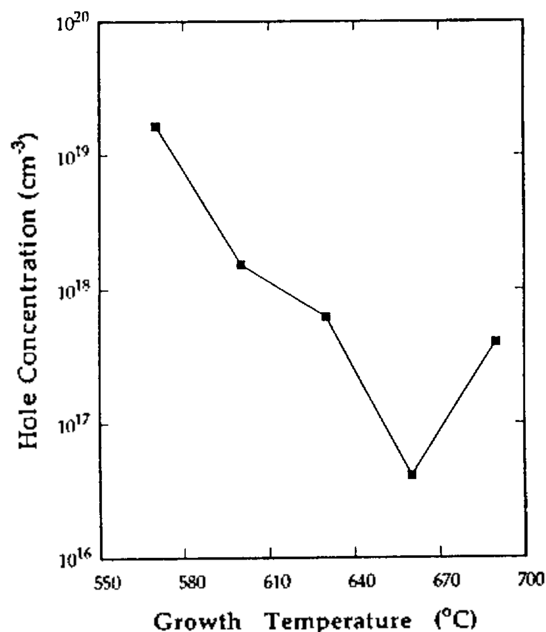

Figure 3. Temperature-dependent hole concentrations in GaAs films grown with AsH_3 and TMG (V/III=10, $P=1.2\times10^{-4}$ Torr).

type background doping of 4.9×10^{15} cm^{-3} with a mobility of 4290 cm^2/V sec at 300 K was measured in TEG-grown epilayer. These values indicate that the samples are moderately compensated.

The carrier concentration and the corresponding Hall mobility were obtained from van der Pauw measurements at room temperature. The thicknesses of the grown layer were in the range of 2-3 μm. The hole concentrations of samples grown by AsH_3 and TMG are in the range of 10^{16} to 10^{19} cm^{-3} as shown in Figure 3. Below 660 ℃, the hole concentrations decrease with increasing substrate temperature, which suggests that carbon-containing species drastically desorb from the growth surface with increasing growth temperature. Above 660 ℃, however, the hole concentration increases, which may be mainly due to the incorporation of carbon atoms in arsenic sites on the growth surface at high temperature. The cause for this reason may be due to the desorption of arsenic atoms from the surface at high substrate temperature, then creating arsenic vacancies and finally allowing carbon to occupy arsenic sites. The different temperature dependence of carbon incorporation, which results in shaped curve, has been also reported for AlGaAs[14] suggesting that the carbon incorporation is dominated by the different mechanisms in the different temperature regimes. As shown in Figure 3, the carbon impurity concentrations measured in our samples are significantly lower by 2-3 orders of magnitude than those reported in other studies[15,16] where CBE was employed for the growth of GaAs using arsenics obtained from precracked arsine. This result may be explained by an observation that high temperature exposure to AsH_3 consumes the CH_2 adsorbate, apparently by hydrogenating them back to CH_3 groups to desorb.[17,18] It is often thought that AsH_3 facilitates the removal of adsorbed CH_3 *via* CH_4 formation[19,20] thus leading to a reduction in carbon doping, even though attempts to directly monitor CH_4 production via a surface reductive elimination process have failed.[21,22]

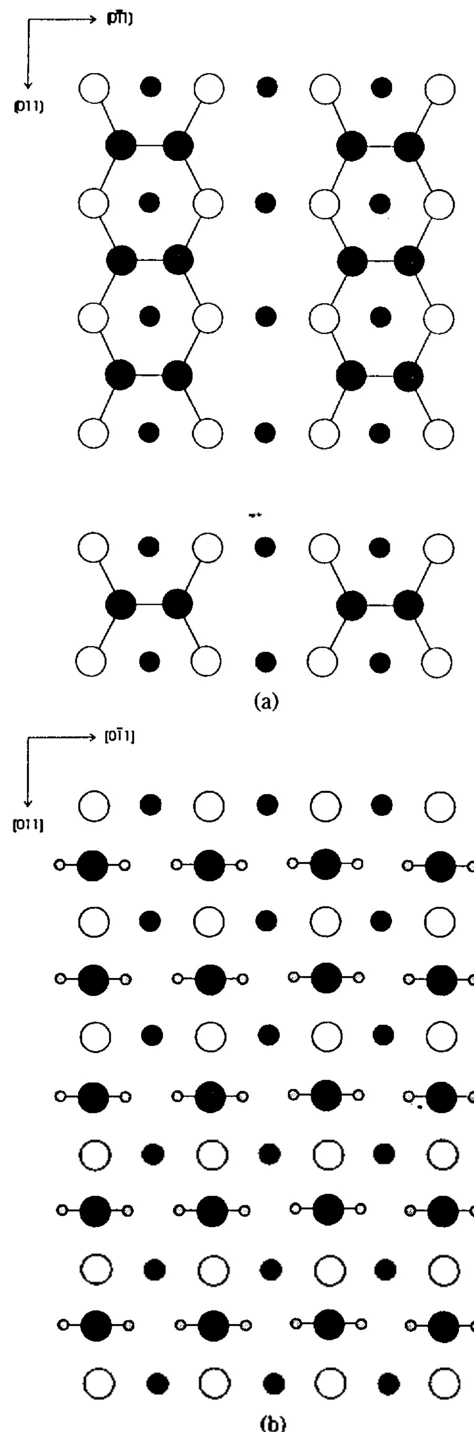

Figure 4. Planar view of GaAs(100): (a) As-rich GaAs(100)-(2×4) surface unit cell. The As atoms form three dimers per unit cell. The dimer vacancy exposes four Ga atoms in the second layer. Large filled circles: As in the top most layer; Open circles: Ga in the second layer; Small filled circles: As in the third layer. (b) hydrogen or subhydride passivated GaAs(100) surface where hydrogen atoms are inserted into the arsenic dimers. Large circles with two small shaded circles: AsH_2; Open circles: Ga in the second layer; Small filled circles: As in the third layer.

The significant reduction of carbon impurities in GaAs epi-

layers by CBE using unprecracked hydride gases as shown in Figure 3, may also be explained by carbon incorporation processes on the surfaces with different structures which are formed by two different arsenic sources supplied during growth. A coherent growth mechanism for molecular beam epitaxy (MBE) on III-V(100) surfaces in general and the GaAs(100) surface in particular under arsenic overpressure has been proposed by Farrell *et al.*[23] This model for the growth mechanism is based on experimental results from reflection high energy electron diffraction (RHEED) intensity ocillations,[24] high resolution electron energy loss spectroscopy studies,[25] angle-resolved photoemission and low energy electron diffraction (LEED) investigations[26] of the atomic structure of the GaAs(100)-(2×4) reconstructed surface as shown in Figure 4(a). In CBE growth of GaAs, organogallium compound is used as group III source instead of solid elemental Ga source used in MBE. Therefore, arsenic-rich GaAs (100) surface structure which is similar to the one shown in Figure 4(a) is also expected to be formed in CBE under arsenic overpressure. In this case of CBE, carbon atoms or carbon containing species dissociated from the metalorganic compounds can be easily trapped in the area of missing dimers as well as the area between arsenic dimer rows as shown in Figure 4(a), which results in the higher carbon concentration in the epilayer than that by MBE. However, in CBE process using unprecracked hydrides which is used in this study, hydrogen atoms from surface hydrides are believed to be inserted into As-dimer bonds producing a hydrogen passivated GaAs(100) surface which is schematically shown in Figure 4(b). Subhydride species such as dihydrides generated from MEAs or arsine may also produce the same surface structure which is shown in Figure 4(b). Then, the hydrogen passivated arsenic-rich GaAs(100) surface structure formed under an arsine overpressure has hydrogen atoms which can prevent the carbon atoms or carbon-containing species from being incorporated into subsurface layer. Such hydrogens can also react with carbon species forming the stable hydrocarbon compounds such as methanes which easily desorb from the surface. In this study, we have shown that it is possible to grow GaAs by CBE using unprecracked hydrides and metalorganic compounds as source materials. It is also suggested that the hydrogen atoms and subhydrides dissociated from hydrides may play an important role in the reduction of carbon incorporation in the GaAs epilayer grown by this method.

Conclusion

We have shown that AsH_3 and MEAs without precracking can be used in the growth of GaAs by CBE using TMG and TEG via a surface decomposition process. Three temperature-dependent regions of growth rates by TMG were observed. The growth rates by TEG, however, produced an anomalous dependence on the growth temperature showing two humps, which are indicative of two hydride intermediates. Growth of GaAs epilayers was also successful at fluxes compatible to that of precracked arsine together with TMG and TEG. This points to the fact that a sufficient amount of arsenics is produced by the thermal and catalytic decomposition of hydrides adsorbed on the GaAs surface. We propose a surface structural model suggesting that a significant drop in hole concentration results from the efficient removal of carbon-containing species by surface hydrogens or partially decomposed hydrides from the adsorbed hydrides. Intermediates like AsH_2 from AsH_3 or MEAs are also considered to passivate GaAs substrate and to supply hydrogen atoms during growth, which may remove carbon containing species as CH_3 or CH_4.

Acknowledgment. This work has been supported by Korea Telecom and by the Ministry of Communications, Korea.

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Selective Functionalization of Calix[6]arene

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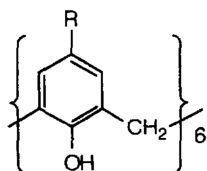
Received October 31, 1994

Calix[6]arenes are selectively dialkylated at the lower rim and further functionalized by the aminomethylation and Claisen Rearrangement reactions. Dialkylation was conducted by the reaction of calix[6]arene and alkyl halides such as benzyl bromide, allyl bromide, ethyl bromoacetate, propyl bromide, and methyl iodide under the carefully controlled reaction conditions. Aminomethylation was carried out with the treatment of disubstituted calix[6]arene and secondary amine in the presence of formaldehyde. Claisen rearrangement reaction of the *O*-diallylcalix[6]arene produced the *p*-diallylcalix[6]arene.

Introduction

Calixarenes[1] are cavity-containing macrocyclic compounds which have a tremendous attention recently as an attractive host molecule. Particularly calix[6]arenes have a very suitable cavity for the complexation of various aromatic compounds such as anthracene, pyrene,[2] and fullerene[3] and also the functionalized calix[6]arenes were found to bind certain metal ion[4] selectively. Functionalization of calix[6]arene usually is more complicated than that of calix[4]arene due to several factors including the bad solubility and the variety of conformational isomers. Particularly selective functionalization of calix[6]arene could be difficult task to achieve. So far a few examples[5-7] were reported as a reliable selective functionalization procedure of calix[6]arene.

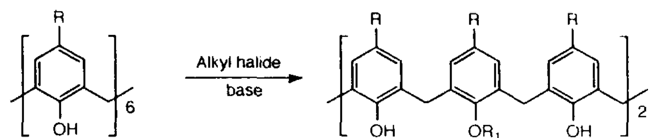
Here we report a selective functionalization of calix[6]arene. We expanded Gutsche's dibenzylation of *p-tert*-butylcalix[6]arene to the general dialkylation procedure of *p-tert*-butylcalix[6]arene as well as calix[6]arene. Also aminomethylation[8] and Claisen rearrangement reactions[9] of dialkylated calix[6]arenes were carried out.



1a R = $C(CH_3)_3$
1b R = H

Results and Discussion

Dialkylation of *p-tert*-Butylcalix[6]arene[10] and Calix[6]arene[11]. Gutsche and Kanamathareddy[6] reported that *p-tert*-butylcalix[6]arene **1a** is selectively dibenzylated with the reaction of *p-tert*-butylcalix[6]arene and benzyl bromide in the presence of Me_3SiOK as a base. We found that **1a** reacted not only with benzyl bromide but with the various alkyl halides such as allyl bromide, ethyl bromoacetate, and propyl bromide in the presence of base to give a corresponding disubstituted calix[6]arenes. Also calix[6]arene **1b** was found to react with the various alkyl halides in the presence of base to yield the dialkylated calix[6]arenes. The various dialkylated calix[6]arenes were prepared in moderate to high yield as shown in Scheme 1.



1a R = $C(CH_3)_3$
1b R = H

2a R = $C(CH_3)_3$, R_1 = $CH_2CH{=}CH_2$
2b R = $C(CH_3)_3$, R_1 = $CH_2CH_2CH_3$
2c R = $C(CH_3)_3$, R_1 = CH_2CO_2Et
2d R = H, R_1 = $CH_2C_6H_5$
2e R = H, R_1 = $CH_2CH{=}CH_2$
2f R = H, R_1 = $CH_2CH_2CH_3$
2g R = H, R_1 = CH_2CO_2Et
2h R = H, R_1 = CH_3

Scheme 1. Dialkylation of Calix[6]arene.

Typical dialkylation procedures are as followed. Treating **1a** with 2.8 equivalents of allyl bromide in the presence of 6 equivalents of Me_3SiOK in THF-DMF for 3.5 h produced the diallylated **2a** in 61% yield after recrystallization from $CHCl_3$-hexane. The ^1H NMR spectrum of **2a** showed a singlet at 8.13 ppm arising from the 4 hydroxy protons, three singlets at 7.07, 7.00, and 6.98 ppm arising from the 12 aromatic protons, 2 : 1 ratio of two singlets at 3.83 and 3.75 ppm arising from the 12 bridge methylene protons, and 2 : 1 ratio of two singlets at 1.20 and 1.10 ppm for the 54 *tert*-butyl