Growth and Characterization of GaAs Films from Tris(di-*tert*-butylarsino)gallane

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We report the use of tris(di-*tert*-butylarsino)gallane [$Ga(As(t\text{-}Bu)_2)_3$], a nonstoichiometric, single-source precursor, for the growth of GaAs films. Epitaxial films were grown between 415 and 590 °C in a chemical beam epitaxy reactor operating at 8×10^{-6} Torr. The growth rate and surface smoothness were found to decrease with increasing temperature. Growth rates ranged from 0.1 to 0.042 μm/h. The Ga:As ratio in the deposited films was studied by energy-dispersive spectroscopy, and they were not found to contain any nonstoichiometric Ga or As. Secondary ion mass spectrometry analysis of the films indicated high levels of Si, O, and C, which are impurities in the precursor.

Introduction

Compound semiconductors, like GaAs, have received a great deal of attention due to their superior high-frequency characteristics and unique optical properties when compared to Si.[1] We are studying the growth of GaAs by chemical beam epitaxy (CBE) from single-source precursors. The CBE technique combines advantages of the beam nature of molecular beam epitaxy (MBE) and gas sources of metalorganic chemical vapor deposition (MOCVD).[2] Production of GaAs by CBE has been studied by various researchers.[3–9] These studies have investigated the use of trimethylgallium (TMGa), triethylgallium (TEGa), triisopropylgallium (TIPGa) and triisobutylgallium (TIBGa), arsine and *tert*-butylarsine (TBAs). Problems associated with carbon contamination,[10,11] the pyrophoric nature of group III trialkyl sources, and the high toxicity of group V sources have motivated the search for safer precursors for the growth of compound semiconductors such as GaAs.

We are investigating alternate precursors for the growth of GaAs films to overcome some of the problems associated with conventional compounds. In recent publications we have reported the growth of epitaxial GaAs films from bis(*tert*-butylarsenido)dimethylgallane dimer, [$Me_2Ga(\mu\text{-}As(t\text{-}Bu)_2)]_2$ (**1**), and bis(*tert*-butylarsenido)diethylgallane dimer, [$Et_2Ga(\mu\text{-}As(t\text{-}Bu)_2)]_2$ (**2**).[12,13] The Ga–C bond was found to play a key role in the quality of the films and in the film growth rate; epitaxial films were grown on GaAs when the substrate temperature was high enough to effect complete removal of the Ga–alkyl ligands.[13] Epitaxial films could be grown as low as 400 °C with **2**. Films from **1** and **2** were found to contain significant carbon levels (ca. 10^{19} cm^{-3}).

In an attempt to minimize carbon incorporation, by eliminating Ga–C bonds, and to provide an excess of As to react with Ga adatoms during film growth we have explored the use of tris(di-*tert*-butylarsino)gallane, [$Ga(As(t\text{-}Bu)_2)_3$], as a single-source precursor to GaAs films. Preliminary film growth results[14] indicated that n-type epitaxial film can be grown at 480 °C. In this publication we report the effects of temperature on film growth from $Ga(As(t\text{-}Bu)_2)_3$ and on the properties of the resulting films.

Methods

$Ga(As(t\text{-}Bu)_2)_3$ was prepared by reacting $(t\text{-}Bu)_2AsLi$ with $GaCl_3$. The complete synthesis has been reported.[15] $Ga(As(t\text{-}Bu)_2)_3$ has a vapor pressure of no more than 2×10^{-4} Torr at 150 °C.[16] Ion cyclotron plasma mass spectrometry (ICPMS) analysis of impurities in the precursor is shown in Table 1.

The chemical beam epitaxy system has been described in detail elsewhere.[17] Only the significant features will be elaborated upon here. Undoped, semiinsulating (100) GaAs substrates (Litton, Airtron Division) were used. The

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Table 1. Ion Cyclotron Plasma Mass Spectrometry Analysis of Impurities in $Ga(As(t\text{-}Bu)_2)_3$

element	concentration (ppm)	element	concentration (ppm)
aluminum	0.4	nickel	0.3
iron	0.3	silicon	1.0
lithium	490	zinc	0.9

substrate was glued with indium onto a tantalum foil and was placed on a pyrolytic graphite/pyrolytic boron nitride (PG/PBN) heater that was in turn supported on a copper stage. The temperature was measured by a thermocouple spot welded to the tantalum foil. The thermocouple was calibrated using a pyrometer (the temperature error bars were estimated to be 20 °C). $Ga(As(t\text{-}Bu)_2)_3$ was maintained in a saturator, which consisted of a stainless steel tee, that was in a 150 °C oven. All lines downstream of the oven were also 150 °C to prevent condensation of the precursor. Helium carrier gas was used to facilitate the transport of the precursor into the deposition chamber. Between growth experiments, the pressure in the deposition chamber was maintained at less than 10^{-8} Torr (the ion gauge limit) by a turbomolecular pump. Mass spectral analysis of the background indicated the residual gases to be mainly H_2O, CO, CO_2, and hydrocarbons. The deposition chamber was equipped with a mass spectrometer to ensure that conditions remained steady throughout each film growth experiment.

The copper stage with the GaAs substrate was loaded through a load lock section. After the load lock was pumped down to 1×10^{-7} Torr, the substrate was transferred to the deposition chamber and pretreated. The native oxide on the GaAs wafer surface was removed by heating for 10 min to 500 °C in 100 Torr of H_2 in the reactor.[18] Growth was commenced shortly after the pretreatment (ca. 15 min) and typical growth cycles were 12 h long. The saturator was pumped through the load lock for 15 min before opening it to the deposition chamber. The reactor was maintained at 8×10^{-6} Torr for all film growth experiments. The reactor pressure was based on studies with **1** and **2** that indicated the necessity of operating below 10^{-5} Torr to avoid polycrystalline film growth.[13]

After growth, the film was removed from the reactor and examined by X-ray diffraction using a double-crystal X-ray diffractometer (Cu Kα radiation was used), energy-dispersive spectroscopy (EDS), scanning electron microscopy (SEM), and secondary ion mass spectrometry (SIMS). A portion of the substrate was masked with a tantalum strip during growth. Film thickness was determined by measuring the step height created by the tantalum mask with a profilometer. Electrical and optical property measurements were not conducted due to the high level of unintentional C, O, and Si impurities observed by SIMS.

To ensure that surface pretreatment, wafer handling, and the growth chamber were not significantly contributing to the high impurity levels, a limited number of GaAs films were grown from $Ga(As(t\text{-}Bu)_2)_3$ in an ultrahigh-vacuum (UHV) surface science chamber. A detailed description of this chamber has been given previously.[14] The UHV chamber had a base pressure of 1×10^{-10} Torr. The GaAs wafer was cleaned by sputtering with a 2 keV Ar ion beam and annealing at 475 °C for an amount of time equal to the sputtering time. This procedure has

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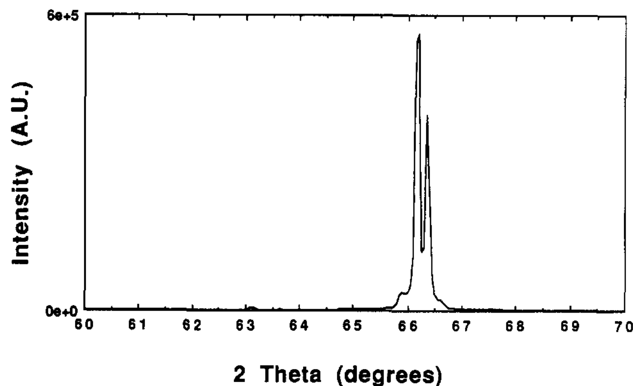

Figure 1. X-ray diffraction of a 1.2-μm film grown at 415 °C.

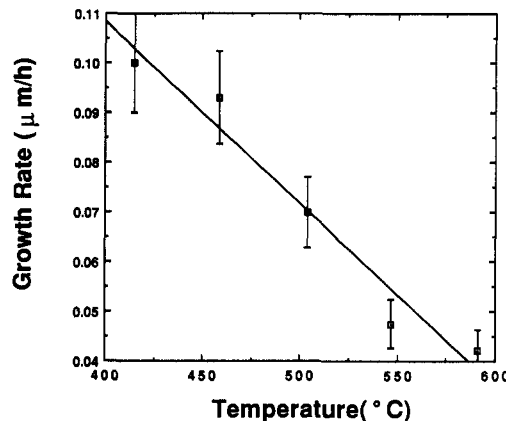

Figure 2. Effect of temperature on the growth rate at 8×10^{-6} Torr.

been shown to produce a Ga-rich GaAs surface.[19] Auger electron spectroscopy was used to verify the surface did not contain carbon or oxygen prior to growth. During growth, the substrate was maintained at 450 °C, the precursor was heated to 100 °C, and the reactor pressure was 1×10^{-7} torr. For film growth in the UHV chamber the precursor was held in a Pyrex ampule that was positioned within 0.5 cm of the substrate surface and the precursor sublimed directly onto the GaAs substrate surface.

Results and Discussion

Film growth from $Ga(As(t\text{-}Bu)_2)_3$ was studied in the temperature range 415–590 °C. The X-ray diffraction pattern of a 1.2-μm-thick film, grown at 415 °C, is shown in Figure 1. The single crystal nature was examined by searching for the (111), (220), and (311) diffraction peaks as they would indicate a polycrystalline nature and could arise only from the film deposited on a (100) GaAs substrate. Only the (200) and (400) GaAs diffraction peaks are observed indicating an epitaxial film was grown. X-ray diffraction analysis showed that films grown over the temperature range studied were epitaxial.

The effect of temperature on growth rate is illustrated in Figure 2. The growth rate decreased from 0.1 to 0.042 μm/h when the substrate temperature was increased from 415 to 590 °C. The cause for the decrease in growth rate with increasing temperature is still being investigated. This could be caused by desorption of an intermediate species formed during precursor decomposition on the surface or

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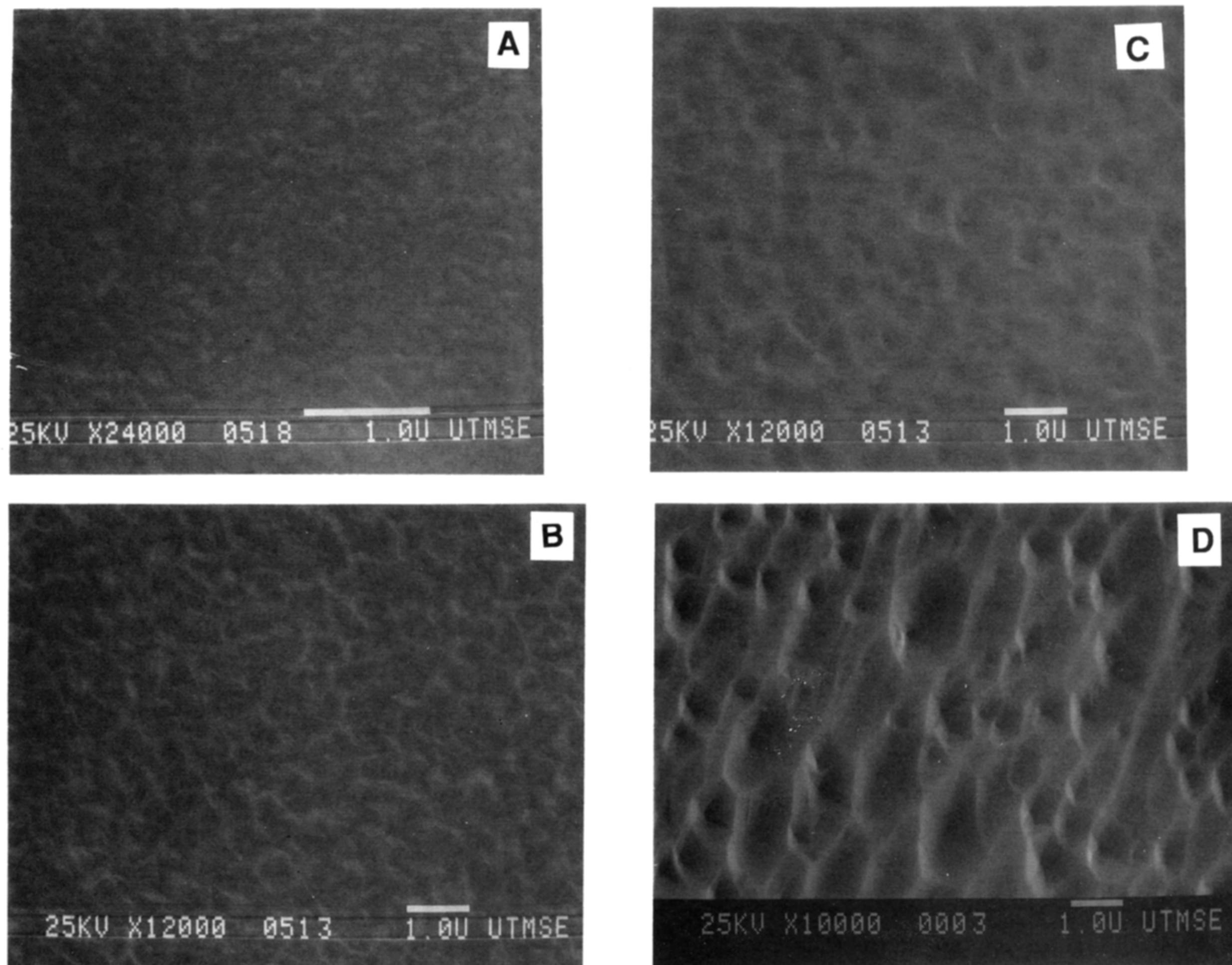

Figure 3. SEM photographs of films grown at: (a) 415 °C, (b) 460 °C, (c) 505 °C, and (d) 550 °C.

by a decreasing sticking coefficient of the precursor. Robertson et al. report an increase in the film growth rate with increasing temperature between 375 and 500 °C and a decrease in the film growth rate with increasing temperature between 500 and 650 °C during GaAs CBE from TEGa and As_2.[20] The increase in growth rate was associated with an increase in reaction rate, while the decrease at higher temperatures was associated with the desorption of diethylgallium radicals. Precedence for reduced sticking coefficients with increasing temperature can be found in the scanning kinetic spectroscopy studies of methanol on Ni(111).[21] Temperature-programmed desorption studies of $Ga(As(t\text{-}Bu)_2)_3$ have shown the physisorbed multilayer to desorb by 25 °C and all the tertiary butyl ligands of the chemisorbed monolayer to react by 300 °C.[22] Furthermore, prolonged exposure of GaAs to $Ga(As(t\text{-}Bu)_2)_3$ at 350 °C followed by programmed heating showed As_2 and As desorption between 420 and 530 °C, revealing that the Ga–As bond of the precursor had broken by 420 °C. The studies reported herein were conducted at temperatures sufficient to cause complete precursor decomposition. The relative importance of a changing sticking coefficient and fragment desorption may be known once the sticking coefficient of $Ga(As(t\text{-}Bu)_2)_3$ is measured as a function of temperature.

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Films grown at 415 and 460 °C had a similar appearance to the substrate; however, films deposited at the higher temperatures had an increasingly grayish appearance. SEM revealed that increasing growth temperature resulted in a greater degree of surface features as illustrated in Figure 3. The surface of the film grown at 415 °C was found to have a nodular appearance with an average feature size of 150 nm. At 550 °C the surface had 150 nm deep pits approximately 1000 nm wide. To determine if pretreatment influenced the surface features, a wafer was pretreated according to the procedure listed in Methods and was examined by SEM; it was featureless, indicating that the substrate pretreatment did not roughen the surface. Precursor properties or impurities, rather than substrate pretreatment or reactor background contaminants are the likely cause of the surface features since films grown with $Ga(As(t\text{-}Bu)_2)_3$ in a MBE chamber also show the same surface features over GaAs substrates that have been annealed at 570 °C under an elemental As flux.[23] The improvement in the morphology observed on lowering the growth temperature could be due to a reduced adatom mobility on the surface.

SIMS profiling of dopants in the films (discussed later) revealed a higher concentration of dopants formed at the substrate film interface than was present in the film. Cross-sectional SEM views of the film at a magnification of 19 000 showed that the roughness features did not propagate to the substrate film interface and there were no features

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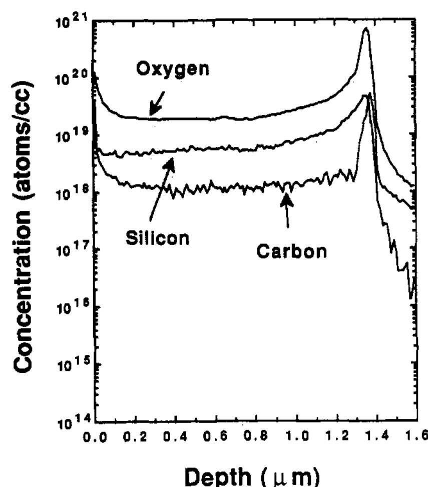

Figure 4. SIMS impurity profile for a GaAs film grown at 8×10^{-6} Torr and 415 °C.

to indicate the location of the film substrate interface. The reason for increasing surface roughness with increasing temperature is not understood. Similar features have been observed by Malocsay et al. using dimethylamine gallane and As_4, who gave no explanation for it.[24] The surface features could somehow be related to the low growth rates at the elevated temperatures and the absence of an As over pressure.

To determine whether $Ga(As(t\text{-}Bu)_2)_3$ co-deposited Ga or As along with the GaAs, the films were examined by EDS. A 10-kV beam energy was selected to minimize the sampling volume.[25] The Lα peaks of Ga and As from a GaAs substrate were used as a standard for the quantitative determination of the Ga:As ratio in the films. Films examined over the entire range of deposition temperature were found to be within 1% of stoichiometry, which is the resolution limit of the instrument. This suggests that it is not necessary for a single source precursor to have 1:1 stoichiometry to deposit GaAs with a 1:1 stoichiometry. The excess As contained in $Ga(As(t\text{-}Bu)_2)_3$ does not incorporate into the film even though it is prebonded to Ga. Also if As desorption is the cause of the rough surface morphology at higher growth temperature (greater than 500 °C), the degree of nonstoichiometry in the film, which produces the roughness is less than 1%.

The impurity levels in the films were examined by SIMS. The AsC, AsSi, and GaO ions were monitored. A typical profile is illustrated in Figure 4 for a film grown at 8×10^{-6} torr. Table 2 summarizes the film properties. The average impurity levels were as follows: O, 3×10^{19} atoms/cm^3; Si, 5×10^{18} atoms/cm^3; C, 6×10^{17} atoms/cm^3 for films grown in the chemical beam epitaxy system. The film grown in the UHV chamber, which has a base pressure of 1×10^{-10} Torr, had similar impurity levels (O, 1.5×10^{19} atoms/cm^3; Si, 2×10^{18} atoms/cm^3, C: 1.5×10^{18} atoms/cm^3). No definite trends in impurity concentrations were observed as a function of substrate temperature. The O and Si impurities in the films originate with the precursor; however, the source of the precursor contamination is not clear at this point. Previous studies have shown the *tert*-butyl ligand to desorb cleanly without carbon deposition from a GaAs surface.[26] Therefore, while the C in the film could be from either the *tert*-butyl ligand or impurities present in the precursor, such as residual solvent from the synthesis, precursor impurities are the likely source.

Table 2. Summary of Film Properties Grown from $Ga(As(t\text{-}Bu)_2)_3$

temp (°C)	pressure (Torr)	growth rate (μm/h)	impurity concentration (atom/cm^3) Si	O	C
415	8×10^{-6}	0.1	7×10^{18}	3×10^{19}	1×10^{18}
460	8×10^{-6}	0.09	5×10^{18}	3×10^{19}	6×10^{17}
505	8×10^{-6}	0.07	6×10^{18}	3×10^{19}	5×10^{17}
550	8×10^{-6}	0.05	3×10^{18}	1.5×10^{19}	3×10^{17}
590	8×10^{-6}	0.04	5×10^{18}	3×10^{20}	2×10^{18}
450	1×10^{-7}	0.1	2×10^{18}	1.5×10^{19}	1.5×10^{18}

The cause of the dopant peak at the film–substrate interface is still being investigated (Figure 4). It is not believed to be due to H_2 pretreatment process as a similar level of dopants was seen on a film where the native oxide was removed by high temperature (600 °C) annealing. We believe that the interface peak is due either to wafer handling resulting in impurities at the initial growth interface or to an artifact of growth. The partial pressure of the precursor decreases from a high value at the start of growth to a steady value after approximately one hour of growth. The dopant profile could be related to the changing flux of molecules at the growing surface. The high impurity levels are not believed to be the primary cause of increasing roughness with increasing temperature since the impurity concentrations were unaffected by the growth temperature while surface roughness clearly increased with increase in temperature.

In summary, epitaxial GaAs films have been grown from $Ga(As(t\text{-}Bu)_2)_3$. The effect of temperature on film growth properties was investigated and studies indicate that lower growth temperatures are beneficial in obtaining higher growth rates and better surface morphology. Purification of the precursor should significantly reduce the impurity levels in the films. The precursor sticking coefficient and As desorption rate are currently being investigated.

Acknowledgment. This work was supported by the Science and Technology Center Program of the National Science Foundation, NSF Grant CHE-8921120. The precursor was prepared by S. U. Koschmieder. The authors acknowledge technical support from H. Isom.

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