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THE USE OF TRIS(TRIMETHYLSILYL)ARSINE TO DEPOSIT GaAs BY OMCVD

by

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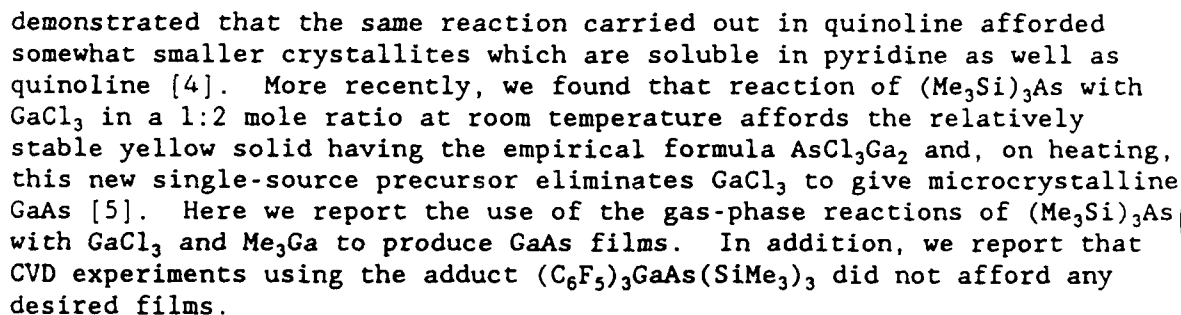
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Chemical vapor deposition experiments using $(\text{Me}_3\text{Si})_3\text{As}$ with either GaCl_3 or Me_3Ga at ambient pressure have produced films of GaAs on Si and semi-conducting GaAs substrates. The films have been characterized by X-ray diffraction and Auger electron spectroscopy, and each have small amounts of C and O impurities. No desired films were deposited from $(\text{C}_6\text{F}_5)_3\text{GaAs}(\text{SiMe}_3)_2$ at 500°C and low pressures.

In 1986, we reported the initial use of silylarsines to prepare gallium-arsenic compounds via metathetical elimination of a silyl halide [1] and, during the ensuing years, we exploited the utility of this type of reaction to prepare a number of novel gallium-arsenic systems [2]. As a part of these studies, it was also demonstrated that dehalosilylation reactions could be used to prepare AlAs, GaAs, and InAs [3]; thus, reactions between $(\text{Me}_3\text{Si})_3\text{As}$ and MX_3 ($\text{M} = \text{Al}, \text{X} = \text{Cl}$; $\text{M} = \text{Ga}, \text{X} = \text{Cl}$ or Br ; $\text{M} = \text{In}, \text{X} = \text{Cl}$) proceed at relatively low temperatures according to equation 1. Subsequently, Alivisatos *et al.* reported that GaAs nanocrystals are produced in experiments using GaCl_3 , and they also



Tris(trimethylsilyl)arsine was synthesized according to published procedures [6]. Gallium trichloride, purchased from Alfa, Inc., was sublimed prior to use. Trimethylgallium was purchased from Alfa, Inc. and used without further purification. The adduct $(C_6F_5)_3GaAs(SiMe_3)_3$ was prepared [7] by combining $(Me_3Si)_3As$ (0.438 g, 1.49 mmol) with $(C_6F_5)_3Ga \cdot OEt_2$ [8] (0.960 g, 1.49 mmol) in 80 mL of benzene in a 250-mL one-necked round-bottomed flask equipped with a Teflon valve. Following removal of the mother liquor from the crystals which formed after 2 days, the latter were dissolved in benzene and the two solutions combined. Removal of the volatiles in vacuo afforded $(C_6F_5)_3GaAs(SiMe_3)_3$ as a white powder containing a very small amount of yellow impurity (1.19 g, 1.380 mmol, 92.8% yield), mp 209-213°C (dec., brown gas-evolving liquid).

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sublimes $\sim 155^\circ\text{C}/10^{-5}$ Torr; ^1H NMR (C_6D_6) δ -0.090 (s, Me_3Si), -0.009 (s, Me_3Si), 0.112 (s, Me_3Si), [9].

Chemical vapor deposition experiments using two separate precursors were carried out in a vertical Pyrex reactor at atmospheric pressure with H_2 as a carrier gas. Precursors were stored in Pyrex bubblers connected to a mixing manifold and individual flowmeters by stainless steel flexible tubing. A flow rate of $150\text{ cm}^3/\text{min}$ was used for $(\text{Me}_3\text{Si})_3\text{As}$ and GaCl_3 and $10\text{ cm}^3/\text{min}$ for Me_3Ga . Hydrogen diluent was introduced in the mixing manifold at a rate of 1 liter/min. Heat tape was used to warm the bubblers of $(\text{Me}_3\text{Si})_3\text{As}$ (102° - 103°C) and GaCl_3 (41° - 42°C), their transport lines, and the mixing manifold. Trimethylgallium was kept at -12°C (v.p. ~ 31 Torr [10]) and the transport line at ambient temperature. Silicon and GaAs substrates were cleaned as described previously [11], and the Si was subsequently etched in 48% HF for 5 minutes, followed by rinsing with distilled water and drying under a stream of N_2 . Substrates were placed on an inductively heated graphite susceptor at 400°C for GaCl_3 and 500°C for Me_3Ga .

Deposition experiments with $(\text{C}_6\text{F}_5)\text{GaAs}(\text{SiMe}_3)_3$ were done in a vertical Pyrex reactor under low pressure. The precursor was heated under a dynamic vacuum and sublimed or carried in a stream of Ar across the substrate mounted on a heated block.

X-ray diffraction data were obtained on a Philips 12045 diffractometer using a Cu K α radiation tube. Auger spectra were recorded on a Physical Electronics Ind. Model 10-155 spectrometer with a 3 kV beam energy and a current density of $\sim 4\text{ mA}/\text{cm}^2$.

RESULTS AND DISCUSSION

Deposition of GaAs using $(\text{Me}_3\text{Si})_3\text{As}$ and GaCl_3 in our reactor occurred in the presence of a visible white vapor and appeared to be influenced by substrate temperature and relative amounts of precursors used. A film of GaAs with nonuniform thickness and poor morphology was deposited on etched Si at 400°C during 1 1/2 hr. Thickness measurements by profilometry along one edge of a masked area gave an average value of $8000\text{ \AA}$. The X-ray diffraction pattern contained peaks with d values of 3.252, 1.984, and $1.702\text{ \AA}$, which were consistent with various orientations of GaAs [12]. The Auger spectrum of an Ar-sputtered sample contained peaks at 1054 eV and 1210 eV characteristic of the LMM lines of Ga and As respectively. The peak-to-peak ratio of the As to Ga lines was 0.56 in comparison to a measured value of 0.58 for an n-doped sample of GaAs and 0.63 from a published spectrum [13]. The spectrum also contained very weak peaks at 272 eV and 505 eV corresponding to the KLL lines of C and O respectively. No evidence of Si or Cl was found within the detection limits of the spectrometer. Additional deposition experiments at a substrate temperature of 500°C or with GaCl_3 at ambient temperature and 60°C gave no evidence of GaAs. In all instances, a yellow-brown solid formed in the manifold exit tube going into the reactor.

The use of Me_3Ga produced thicker, more uniform films of GaAs, but still with poor morphology. Contrary to the behavior of the $(\text{Me}_3\text{Si})_3\text{As}$ - GaCl_3 system, no white vapor was observed in the reactor during deposition and no residue remained in the mixing manifold. The X-ray diffraction pattern contained peaks with d values of 3.276, 2.002, 1.705, and $1.702\text{ \AA}$, which were also in good agreement with those for GaAs [12]. The Auger spectrum of an Ar-sputtered sample contained Ga and As peaks at 1047 and 1203 eV respectively with an average As to Ga ratio of 0.37, indicating a Ga-rich film. This is not surprising in view of the considerable difference in volatiles of $(\text{Me}_3\text{Si})_3\text{As}$ and Me_3Ga and the difficulty in regulating low mass flows in our reactor. The Auger spectrum also contained a very weak C and a weak O peak. As in the GaCl_3 system, no evidence for Si was found.

In a related experiment, an attempt was made to deposit GaAs on a Si substrate in vacuo using the adduct $(C_6F_5)_3GaAs(SiMe_3)$. No films were obtained with a substrate temperature of 500°C at pressures of 1×10^{-5} Torr without a carrier gas. Those results are similar to the behavior of $(C_6F_5)_3GaAsEt_3$ as reported by Maury, et al. [14].

In summary, we have demonstrated in principle the growth of GaAs using $(Me_3Si)_3As$ as an alternate source of As with $GaCl_3$ and Me_3Ga . These initial films are of poor quality but nevertheless offer encouragement for further investigation. The adduct $(C_6F_5)_3GaAs(SiMe_3)_3$ does not yield GaAs at 500°C and low pressures.

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REFERENCES

1. C.G. Pitt, A.P. Purdy, K.T. Higa, and R.L. Wells, *Organometallics* 5, 1266 (1986).
2. W.K. Holley, R.L. Wells, S. Shafieezad, A.T. McPhail, and C.G. Pitt, *J. Organomet. Chem.* 381, 15 (1990), and references cited therein.
3. R.L. Wells, C.G. Pitt, A.T. McPhail, A.P. Purdy, S. Shafieezad, and R.B. Hallock, *Chemistry of Materials* 1, 4 (1989); *Chemical Perspectives of Microelectronic Materials*, Materials Research Society Symposium Proceedings 131, 45 (1989), Materials Research Society, Pittsburgh, Pennsylvania.
4. M.A. Olshavsky, A.N. Goldstein, and A.P. Alivisatos, *J. Am. Chem. Soc.* (in press).
5. J.D. Johansen, R.L. Wells, R.B. Hallock, A.T. McPhail, and C.G. Pitt, *Abstr. Papers*, 200th Nat. Meeting Am. Chem. Soc., Washington, DC, INOR 507 (August 1990).
6. V.G. Becker, G. Gutekunst, and H.J. Wessely, *Z. Anorg. Allg. Chem.* 462, 113 (1980).
7. All manipulations were carried out in a nitrogen-filled Dri-Lab using Schlenk apparatus or on a vacuum line. $(Me_3Si)_3As$ is an air-sensitive liquid with a very disagreeable odor and should be handled with the assumption that it is toxic.
8. J.L. Pohlman and F.E. Brickman, *Z. Naturforsch.* 20b, 5 (1965).
9. These characterization data compare favorably to those recorded for an authentic sample of $(C_6F_5)_3GaAs(SiMe_3)_3$. Elemental analysis (C,H) and a crystal structure were also obtained for the adduct as initially isolated from a different reaction mixture [R.L. Wells, C.G. Pitt, A.T. McPhail, J.D. Johansen, and R.B. Hallock, *Abstr. Papers*, SE-SW Comb. Reg. Meeting Am. Chem. Soc., New Orleans, LA, INOR 269 (December 1990).]
10. O. Kayser, H. Heinecke, A. Brauers, H. Lüth, and P. Balk, *Chemtronics* 3, 90 (1988).

11. A.D. Berry, R.T. Holm, M. Fatemi, and D.K. Gaskill, J. Mater. Res. 5, 1169 (1990).
12. Joint Committee on Powder Diffraction Standards File Card No. 32-389.
13. R. Ludeke and L. Esaki, Surface Sci. 47, 132 (1975).
14. F. Maury, A. El Hammadi, and G. Constant, J. Crystal Growth 68, 88 (1984).

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