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Epitaxial Gallium Arsenide from Trimethyl Gallium and Arsine

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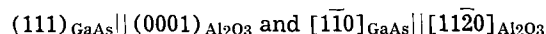
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Gallium arsenide is used in devices such as Gunn oscillators, high-voltage varactors, lasers, tunnel diodes, etc. Epitaxial techniques are being developed in which gallium arsenide with controlled doping is deposited from the vapor or liquid phase on gallium arsenide as well as sapphire substrates. Most deposition techniques reported to date use some form of transport mechanism *via* a halide (1). Relatively high volatility and the absence of any transport agents (such as HCl) make trimethyl gallium an attractive source of gallium for the vapor growth of GaAs. For instance, trimethyl gallium has a vapor pressure of 0.25 atm at room temperature, compared to 3.4×10^{-36} atm for gallium and 0.49 atm for GaCl₃ (2). Manasevit and Simpson (3) have reported on the use of organometallics in the preparation of III-V compounds. Manasevit has also reported on some structural aspects of the single-crystal growth of GaAs on a number of single-crystal, insulating, oxide substrates (4). In this communication, use of trimethyl gallium for the growth of epitaxial GaAs on gallium arsenide and sapphire substrates is reported.

A conventional horizontal rf heated reactor having a graphite susceptor was used. The substrates used were semi-insulating GaAs of (100) orientation and sapphire of (0001) orientation. The sawed GaAs substrates were lapped with 5 μ alumina powder and chemically polished to remove 75 μ from the depositing surface. The chemical etchants used were conc H₂SO₄: 30% H₂O₂ : H₂O :: 5:1:1. X-ray topography of the polished wafer indicated that the polished surface is damage free. Sapphire substrates were mechanically polished and annealed in H₂ for 2 hr at 1400°C prior to film growth. The trimethyl gallium [(CH₃)₃Ga] sources were used as received from the supplier (typical purity in ppm: Si 50 to 100; Cu, Ag, Ca, Pb, and Na < 1; Mg 1). Palladium-purified hydrogen was bubbled through the trimethyl gallium and was reacted with arsine (AsH₃) to form the epitaxial GaAs layer. The resistivity, the net carrier concentration, and the mobility of these films were measured by van der Pauw technique (5). Examination by reflection and transmission electron diffraction and microscopy was used to assess film perfection. The layers and substrates were also analyzed by a spark source mass spectrometer.

Figure 1 shows a diffraction pattern of a GaAs film grown on GaAs substrates having an (100) orientation. The film was grown at about 700°C using (CH₃)₃Ga and AsH₃ with partial pressures of 7.5×10^{-4} atm and 1.0×10^{-2} atm, respectively. Depending on gas velocity, the growth rate of the films was varied from 0.69 to 0.11 μ /min. The film from which Fig. 1 was obtained

was grown at 0.11 μ /min and the resulting surface of the epitaxial layer was extremely smooth and free of any visible defects. Transmission electron microscopy examinations of the films were compared to those obtained from layers grown by a conventional AsCl₃-Ga-H₂ system; the appearance of the deposits from the two systems is comparable. Films produced by both processes were found to contain isolated amorphous precipitates. The study of these defects is in progress and the results will be reported subsequently. Figure 2 show an electron diffraction pattern of a GaAs film grown under conditions identical to that of Fig. 1 but on a sapphire substrate. The films were epitaxial, the orientation relationship between film and substrate being



All the films grown on GaAs substrates were n-type with a net carrier concentration of 2.6×10^{17} to 9.0×10^{17} atoms/cm³ and a mobility of 1740 to 2550 cm²/V sec. Most of the films grown on sapphire were found to be n-type (however, hot-probe analysis was not always definitive), with one of the best films having a net carrier concentration of 6.5×10^{17} atoms/cm³ and a mobility of 2480 cm²/V sec. The layers were analyzed by a spark source mass spectrometer and the results are compared in Table I with those from a semi-insulating GaAs substrate as well as with epitaxial GaAs from a AsCl₃-Ga-H₂ system.

It should be emphasized that the impurity concentrations listed here are essentially surface concentra-

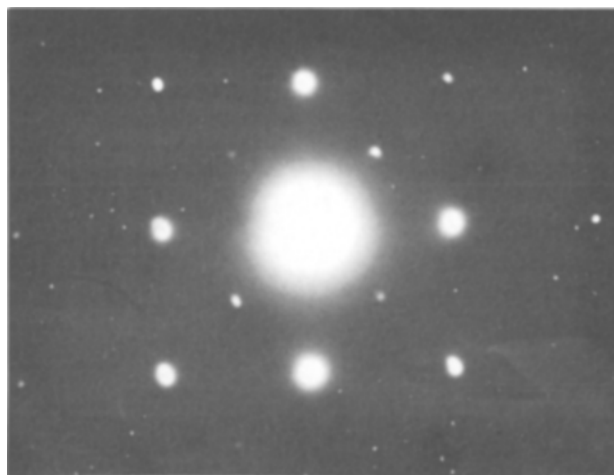


Fig. 1. Transmission electron diffraction pattern of GaAs films grown on semi-insulating GaAs substrate of (100) orientation.

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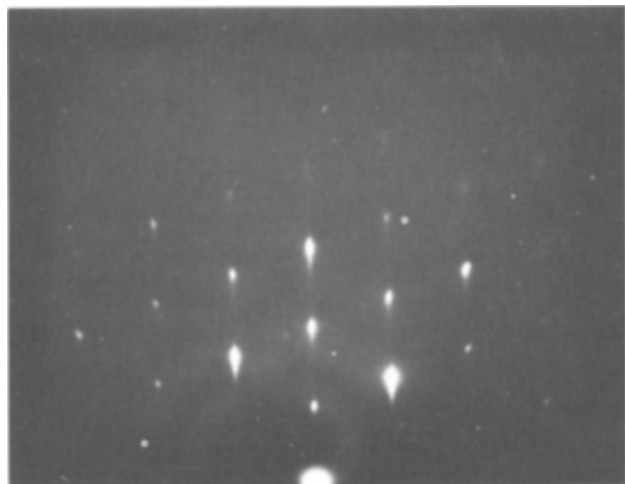
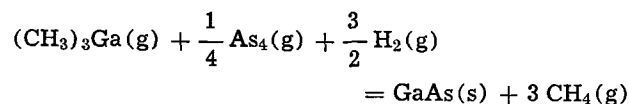


Fig. 2. Reflection electron diffraction pattern of GaAs films grown on sapphire substrate of (0001) orientation; (111)GaAs || (0001) Al₂O₃, [110] GaAs || [1120] Al₂O₃.

tion in the case of epitaxial layers and might therefore contain some adsorbed impurities difficult to clean. The impurity concentrations in the substrate material, however, are more reliable since the entire epitaxial layer was sparked off before analysis. Since the carbon contamination level in the present system is comparable with the AsCl₃-Ga-H₂ system, it appears that the carbon contamination from the trimethyl gallium is probably insignificant. Metallographic examination of the surface of the epitaxial layers also supports this view. Carbon contamination from TMG is also unlikely from thermodynamic considerations. The over-all reaction may be written as



The CH₄ formed may decompose to give graphite and hydrogen. At 1000°K, for example, the equilibrium partial pressure of CH₄ for the reaction

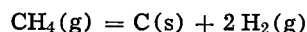


Table I. Impurity concentrations in GaAs in ppm

Element	Layers from (CH ₃) ₃ Ga-AsH ₃ -H ₂ system	Layers from AsCl ₃ -Ga-H ₂ system*	Semi-insulating GaAs substrate
C	238.4	100-569	8.79
N	1.78	Not detectable	0.07
O	220.4	307-1042	0.52
Si	4.46	—	0.19
S	1.47	Not detectable	0.27
Fe	1.60	Not detectable	Not detectable
Cu	2.24	Not detectable	Not detectable
Zn	0.89	Not detectable	Not detectable

* The GaAs layer grown in the AsCl₃-Ga-H₂ system had a net carrier concentration of 1.1×10^{16} atoms/cm³ and a mobility of 3400 cm²/V sec.

is 9.7×10^{-2} atm which is considerably above the (CH₃)₃Ga partial pressures used for growth of GaAs. Therefore, CH₄ will not decompose to graphite.

In summary, the epitaxial GaAs produced from trimethyl gallium and arsine is of good quality metallurgically, but requires some improvement in purity. The electrical parameters such as mobility and net carrier concentrations of GaAs on sapphire are comparable with those of GaAs grown on semi-insulating GaAs substrates.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1970 JOURNAL.

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