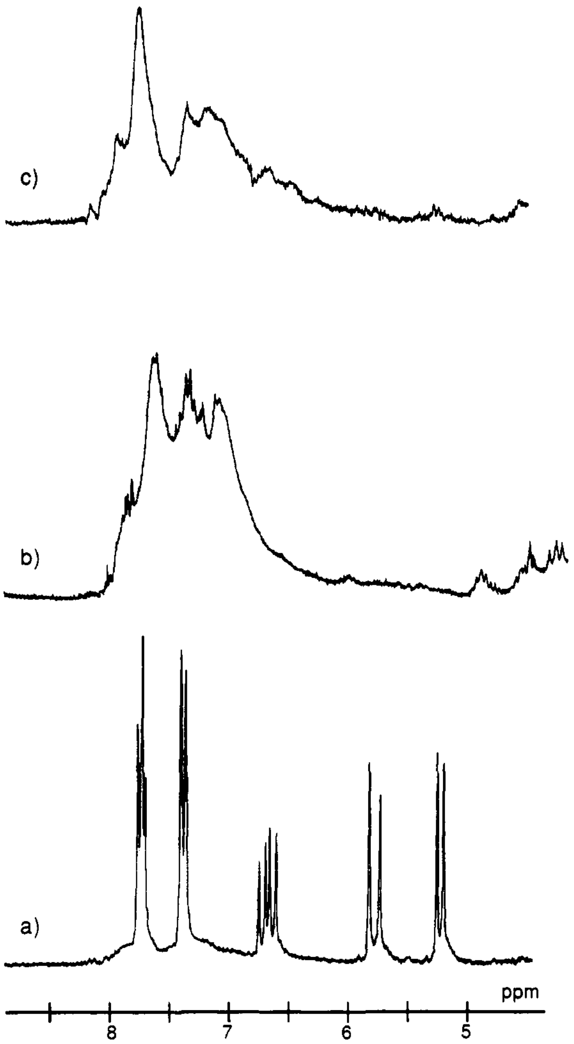

Figure 5. ^1H NMR spectrum of SiW11Si(styryl) based polymers: (a) $SiW_{11}Si$(styryl) monomer; (b) polymer, AIBN (8% ratio), DMSO, 60 °C; polymer yield 100%; (c) polymer, POB (6% ratio), PC, 80 °C; polymer yield 100%.

6. It is characteristic of a reversible reduction of the polymetalate structure, with two successive one-electron processes.[15] Upon UV irradiation, these solutions turn blue. Their visible spectrum is characterized by a wide absorption band in the visible–near-IR range centered upon 1000 nm. Such behavior is characteristic of a intervalence transition W^{5+}–W^{6+} in mixed valence polymetalates.[16] Therefore, the electrochemical or photochemical behavior of the POM active molecules do not depend on their spatial proximity inside these mixed organic inorganic polymers.

Transparent thin films can be deposited from these POM–polymeric solutions, on different kinds of substrates (glass, plastics, metals). They turn reversibly to blue upon UV irradiation or electrochemical reduction.

These mixed organic–inorganic structures present interesting materials for electrode modification in heterogeneous catalysis, electrocatalysis, and photochromic and electrochromic devices. In order to increase the polymerization yield, the structure, and the mechanical properties of the material, copolymerization of the modified oxopolymetalate and organic monomer, such as methyl methacrylate or styrene, was investigated.

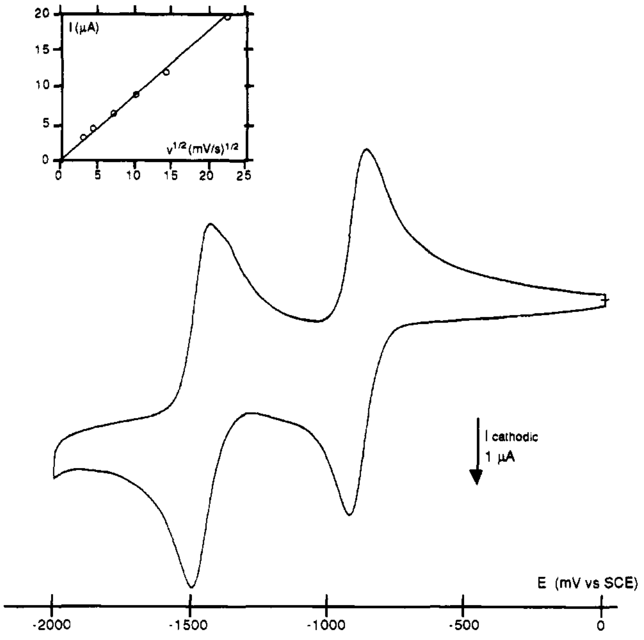

Figure 6. Cyclic voltamogram of $SiW_{11}Si$(methacryl) polymer (10^{-3} M) in DMF/Bu_4NBF_4 (10^{-1} M), scanning rate 100 mV/s. (polymerization conditions, POB (2% ratio), DMF, 90 °C; polymer yield, 70%). The inset shows the dependence of the cathodic peak current upon (scan rate)$^{1/2}$ [diffusion process].

Acknowledgment. This work was supported by the CNRS (URA 1383) and by the University of Paris XI. Sincere thanks are due to F. Perez for chemistry advice, J. Maquet for CP-MAS NMR experiments, and Drs. C. Sanchez and B. Cabane for helpful discussions.

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Growth of Epitaxial (100) GaAs Films Using the Single-Source Precursor $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$

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Received August 9, 1991
Revised Manuscript Received October 17, 1991

Considerable attention has been directed recently at finding alternatives to the traditional sources used to produce III–V compound semiconductor films, trimethyl and triethyl group 13 molecules, and group 15 hydrides.[1] This has been motivated by the toxic nature of the hydrides and the pyrophoric nature of the group 13 sources. In addition, the thermal stability of the hydrides imposes the need for a high growth temperature (ca. 650–700 °C) during chemical vapor deposition (CVD). As a consequence of the high growth temperature, an excess of the hydride must used to maintain a sufficient overpressure since this prevents the group 15 component from prefer-

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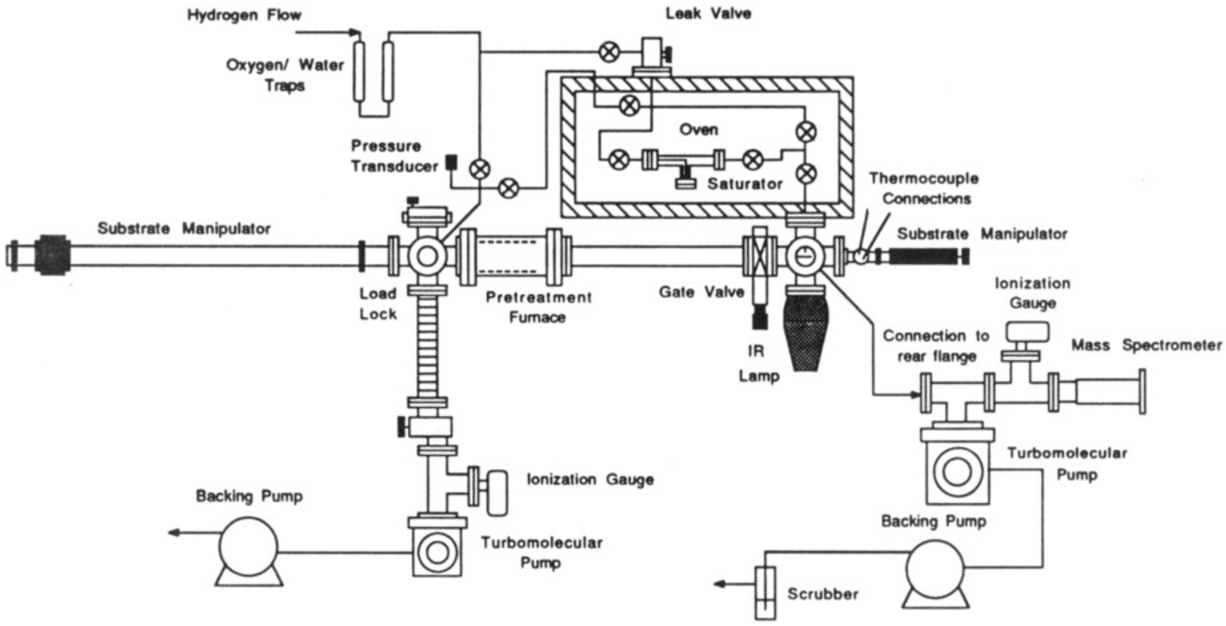

Figure 1. Schematic of the chemical beam epitaxy system.

entially evaporating. Films can be grown at lower temperatures (ca. 550 °C), but an excess of the hydride is still required because only a small fraction of it decomposes at these temperatures.[2]

We are studying the feasibility of film growth at temperatures near 500 °C using single-source organometallic compounds of the general structure $(L_2MEL'_2)_x$ where M and E are the group 13 and 15 atoms, respectively, L and L′ are alkyl ligands such as methyl, ethyl, isopropyl, and *tert*-butyl, and x is 2 or 3. In previous publications we reported the growth of polycrystalline GaAs from $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$.[3,4] Here we report the epitaxial growth of GaAs on a (100) GaAs substrate using $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ as the only source in a chemical beam epitaxy (CBE) reactor. A more complete discussion of the relationships between precursor structure and film properties when using $(L_2GaAsL'_2)_x$ will be forthcoming.

The films were grown in the system shown schematically in Figure 1. The load–lock/preparation chamber and a main deposition chamber were pumped by turbomolecular pumps. The deposition chamber, a standard six-way stainless steel vacuum cross made from 3.81-cm o.d. tubing, was maintained at less than 10^{-8} Torr. During film growth the chamber pressure, measured near the entrance to the turbomolecular pump, was typically 5×10^{-6} Torr. The precursor was maintained at 135 °C, and hydrogen was used as a carrier gas to facilitate transport into the chamber. The precursor flowed through a 1.3-cm i.d. tube and exited 0.75 cm from the surface of the substrate. A mass spectrometer (UTI 100C) was used to monitor the gas composition in the reactor to ensure that constant conditions were maintained throughout the deposition process. The substrate (1 cm × 1 cm) was placed on tantalum foil (1.7 cm × 1.7 cm) and heated from below by an infrared spot heater; this enabled growth at temperatures up to 550 °C.

Undoped, semiinsulating (100) GaAs substrates (Litton, Airtron Division) were used. They were ultrasonically degreased in trichloroethylene and methanol and then etched for 5 min in an 8:1:1 solution of H_2SO_4:H_2O_2:H_2O. They were then rinsed in deionized water, blown dry, and loaded into the preparation chamber. The preparation chamber was first evacuated to 1×10^{-6} Torr and then backfilled with 100 Torr of H_2 gas. The wafers were then heated to 500 °C for 10 min to react away the oxides.[5] The chamber was again evacuated, and the wafer was transferred into the growth chamber.

Epitaxial films were grown at substrate temperatures ranging from 475 to 550 °C. Films grown at 450 and 425 °C were polycrystalline. GaAs could not be deposited from $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ at 400 °C. Films grown at 5×10^{-6} Torr appeared mirrorlike while films deposited at 1×10^{-5} Torr exhibited areas of haziness. Growth rates were determined by profilometry and found to be 0.2 μm/h in the temperature range 475–550 °C with a saturator temperature of 135 °C and a pressure of 5×10^{-6}. At lower substrate temperatures the growth rate was a function of substrate temperature. Growth rates larger than 0.2 μm/h could be obtained by increasing the saturator temperature and/or the hydrogen carrier gas flow rate. Increasing the carrier gas flow rate also had the effect of raising the reactor pressure. The growth efficiencies could not be determined because the delivery rate of the precursor to the reactor has not been characterized. Figure 2 presents a representative single-crystal, X-ray diffraction pattern (Cu $K\alpha$ radiation) for the films grown under the conditions listed above. The (400) diffraction peaks at 2θ of 66.08° ($K\alpha_1$) and 66.26° ($K\alpha_2$) for a 2.0-μm film (Figure 2A) are nearly identical to the (400) peaks for the substrate (Figure 2B). A diffraction peak was also seen at 2θ of 31.85° corresponding to the (200) GaAs reflection. In a previous paper[3] we reported (111) oriented polycrystalline films from $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$; no (111) diffraction peaks were observed for the conditions reported herein.

The films are p-type with room-temperature Hall effect measurement of the epitaxial films yielding carrier concentrations of 2×10^{18}–5×10^{19} cm^{-3} and mobilities of 54–94 cm^2/V s. Figure 3 presents a 4 K photoluminescence spectrum of a 2.0-μm film grown at 500 °C and 5×10^{-6}

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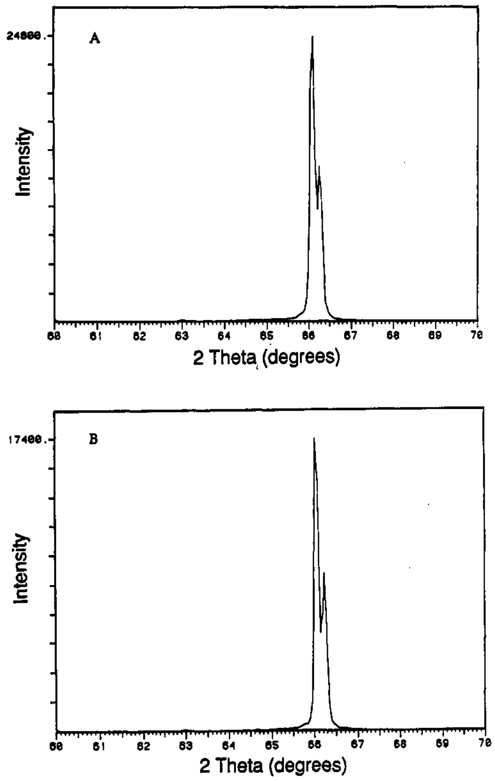

Figure 2. Single-crystal, X-ray diffraction pattern (A) for a 2.0-μm-thick film grown at 1×10^{-5} Torr and 475 °C and (B) for the (100) GaAs substrate.

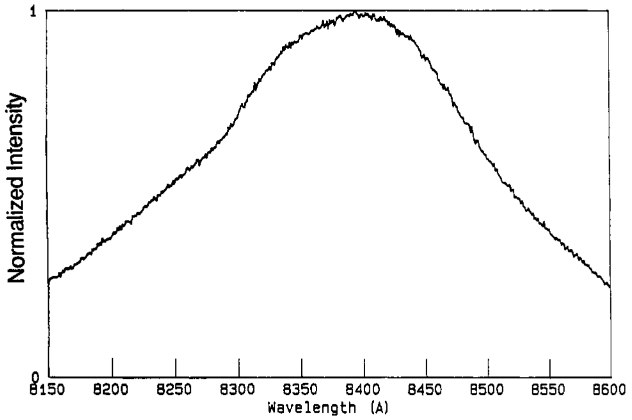

Figure 3. Photoluminescence spectra (4 K) of a 2.3-μm-thick film grown at 5×10^{-6} Torr and 500 °C.

Torr. The spectrum exhibits a single broad peak at 840 nm which arises from high concentrations of silicon and carbon in the film.[6] Inductively coupled plasma mass spectroscopy analysis of the precursor showed a high concentration (1000 ppm) of silicon. The silicon in the precursor probably originated from the stopcock grease used on the synthesis glassware. Steps have been undertaken to eliminate the use of stopcock grease during precursor synthesis. The carbon likely originated from the methyl ligands of the precursor. Several groups have investigated the use of $Ga(Me)_3$ and $Ga(Et)_3$ in CBE studies with both arsine and solid arsenic sources.[7] The films grown with $Ga(Me)_3$ typically contained greater than 1×10^{19} carbon atoms cm^{-3} whereas films grown from $Ga(Et)_3$ contained 10^{14}–10^{16} carbon atoms cm^3. Experiments are underway with $[Et_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ to determine how ligand structure and reactivity affect carbon impurity levels in the films.

Previous film growth studies[3] with $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ were conducted at pressures of 1×10^{-4} Torr. A significantly lower growth pressure was used herein, and it led to epitaxial films from the same precursor and at similar (500 °C) temperatures. We suspect that the lower pressure is necessary to eliminate prereaction of the precursor in the heated transfer line and/or in the gas region above the heated substrate. The role of prereaction in film crystallinity is currently under study.

Acknowledgment. This work was supported by the Army Research Office (Contract DAAL03-89-K-0164) and the Science and Technology Center Program of the National Science Foundation (Grant CHE-8920120). We also thank our colleagues in the Department of Chemistry at the University of Texas at Austin, Professors A. H. Cowley and R. A. Jones, for their input. The precursor used in this study was prepared by M. A. Mardones and J. W. Nail. The PL spectra were obtained by J. G. Neff.

Registry No. GaAs, 1303-00-0; $[Me_2Ga(\mu\text{-}t\text{-}Bu_2AS)]_2$, 106417-80-5.

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Rapid Synthesis of GaP and GaAs from Solid-State Precursors

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Received September 5, 1991
Revised Manuscript Received October 21, 1991

The III–V compound semiconductors GaAs and GaP are well-known for their use in optoelectronic devices.[1] Bulk samples of these materials have been precipitated from solution and prepared by the decomposition of single-source solid-state precursors. Amorphous materials are typically made from solution. Cumberbatch and Putnis produced gallium arsenide by bubbling arsine through gallium nitrate solutions,[2] Byrne et al. reacted a monomeric arsinogallane with *tert*-butyl alcohol to produce GaAs,[3] and Lawrence made both GaAs and GaP in organic solutions from reactions between metal– or pnictide–tris(trialkylsilyl) derivatives and pnictide– or metal–trihalides, respectively.[4] Wells et al. used $GaCl_3$ and $(Me_3Si)_3As$ to both prepare bulk GaAs directly[5] and indirectly form the single-source precursor $AsCl_3Ga_2$, which upon heating decomposed to GaAs and $GaCl_3$.[6] Cowley et al. decomposed $[t\text{-}Bu_2Ga(\mu\text{-}AH_2)]_3$, where A = P or As, to form

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