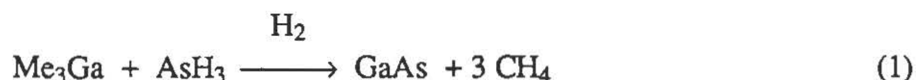
Arsenogallanes - Single Source MOCVD Precursors to GaAs

Shifang Luo Literature Seminar November 27, 1990

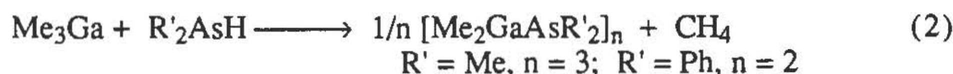
In 1968, Manasevit first demonstrated that thin film GaAs could be grown by contact of a mixture of trimethylgallium (Me_3Ga) and arsine (AsH_3) with a solid surface at 600 to 700 °C in the presence of H_2 (eq. 1) [1].



$$Me_3Ga + AsH_3 \xrightarrow{H_2} GaAs + 3\,CH_4 \quad (1)$$

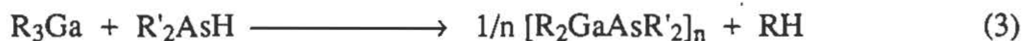
Since then a tremendous amount of study on this Metal-Organic Chemical Vapor Deposition (MOCVD) process has been initiated [2]. Growth of pure thin films with high electron mobility (125,000 - 140,000 $cm^2/V\,s$ at 77K) and low background carrier density ($1 - 5 \times 10^{-14}$ cm^{-3}) has been achieved. This, combined with several other features such as multilayer growth, and large area thin film growth has made the MOCVD process one of the most attractive methods in the GaAs preparation. However, the extreme toxicity of AsH_3 has led to an interest in alternative MOCVD precursors [3] as well as other growth methods such as Liquid Phase Epitaxy (LPE) [4] and Molecular Beam Epitaxy (MBE) [3b, 5] which do not use arsine. In 1988, Cowley and Jones proposed that arsenogallanes could be used as "single source" MOCVD precursors to GaAs [6]. Compared with precursors used in the binary source process, these arsenogallanes have advantages of (1) lower toxicity than AsH_3 and (2) controlled stiochiometry [i.e. either Ga rich or As rich precursors can be prepared if desired].

The chemistry of arsenogallanes was first studied in mid 1960's by Coates when he prepared the first two arsenogallanes through the reaction of trimethylgallium with secondary arsine (eq. 2) [7].

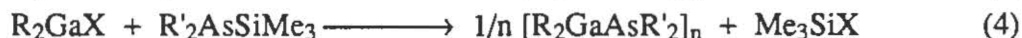


$$Me_3Ga + R'_2AsH \longrightarrow 1/n\,[Me_2GaAsR'_2]_n + CH_4 \quad (2)$$
$$R' = Me,\ n = 3;\ R' = Ph,\ n = 2$$

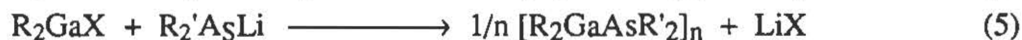
Systematic research began in mid 1980's by Wells, Cowley, Jones et al. [8]. Four methods have been extensively used in the preparation of arsenogallanes: alkane or arene elimination (eq. 3), trimethylsilyl halide elimination (eq. 4), metathesis of a lithium arsenide complex with alkyl gallium halide (eq. 5), and redistribution (eq. 6).



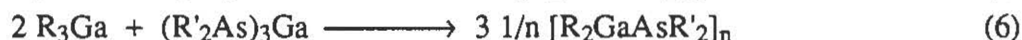
$$R_3Ga + R'_2AsH \longrightarrow 1/n\,[R_2GaAsR'_2]_n + RH \quad (3)$$



$$R_2GaX + R'_2AsSiMe_3 \longrightarrow 1/n\,[R_2GaAsR'_2]_n + Me_3SiX \quad (4)$$

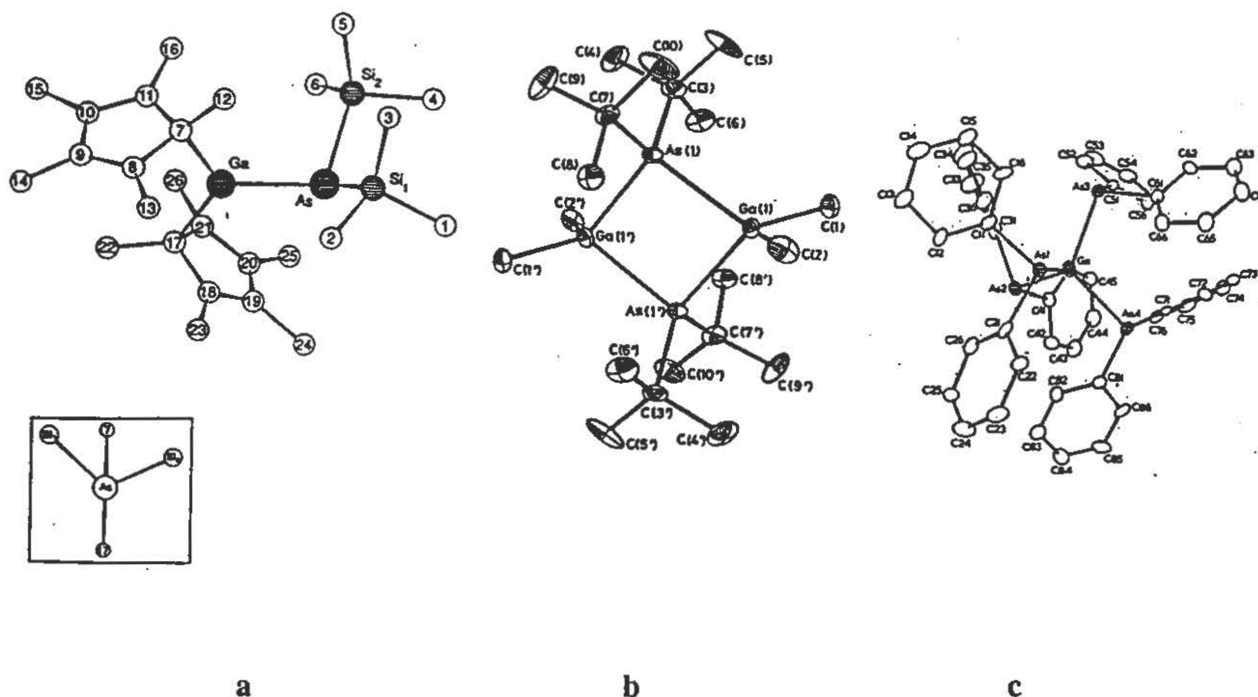


$$R_2GaX + R_2'AsLi \longrightarrow 1/n\,[R_2GaAsR'_2]_n + LiX \quad (5)$$



$$2\,R_3Ga + (R'_2As)_3Ga \longrightarrow 3\,1/n\,[R_2GaAsR'_2]_n \quad (6)$$

The structures of arsenogallanes [$R_2GaAsR'_2$] are strongly dependent on the steric bulk of R and R'. With sterically bulky groups attached to Ga and As, monomeric monoarsenogallanes such as $Cp^*_2GaAs(SiMe_3)_2$ and $Bu^t_2GaAsBu^t_2$ are formed (Figure **a**). With less sterically demanding groups, dimeric or trimeric structures are formed in which $R_2GaAsR'_2$ units are bound together through dative As → Ga bonds (Figure **b**). The $[Ga(AsPh_2)_4]^{1-}$ anion (**c**) is the only molecular model which closely resembles the Ga center in crystalline GaAs. It is interesting that despite the possibility of Ga - As double bonding in these arsenogallanes, no double bonds between Ga and As have been observed thus far. Recently, a compound featuring a double bond between B and As was reported by Power et al. [9].



The first report on the facile decomposition of an arsenogallane to GaAs by Theopold et al. showed that amorphous GaAs could be obtained if $Cp^*_2GaAs(SiMe_3)_2$ was treated with *t*-BuOH at room temperature [10]. By monitoring the reaction with absorption spectroscopy, they claimed the observation of the evolution of nanophase (60 Å) particles of GaAs. A comprehensive CVD study on $[Me_2GaAsBu^t_2]_2$ by Cowley and Jones [11] has showed that the film growth temperature is significantly lower than the temperature used in the binary source MOCVD process. However, residual impurities and polycrystalline nature of the grown films rendered the photoluminescence spectra broad and featureless. No detailed mechanistic studies have been reported thus far, although it has been proposed that ß-H elimination of the *t*-butyl group is the main decomposition route for $[Me_2GaAsBu^t_2]_2$. Studies on the MOCVD of $Bu^t_2GaAsBu^t_2$ support the possibility of a ß - H elimination process [12].

Putting all these studies in perspective, the single source MOCVD process is just at its beginning and there is considerable scope for future research. Recently, the use of trifluoromethyl substituents (CF_3) is attracting increasing attention [3,13]. The stability of the trifluoromethyl group towards thermal cleavage could significantly reduce carbon contamination in the prepared GaAs. Also interesting is the synthesis of single source precursors for the photoenhanced MOCVD process in which, instead of pyrolyzing organometallic precursors at high temperature, photon energy is used to cleave the Ga - C and As - C bonds in the precursors. This avoids the high temperature usually required in the MOCVD process and dramatically reduces the interlayer diffusions in the case of the multilayer growth [14]. Independent of their relevance to MOCVD, these studies in arsenogallane chemistry have made important contributions to the chemistry of Ga and As [15].

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