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Citation: Applied Physics Letters **57**, 2543 (1990); doi: 10.1063/1.104182 View online: http://dx.doi.org/10.1063/1.104182 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/57/24?ver=pdfcov Published by the AIP Publishing

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## Microwave plasma generation of arsine from hydrogen and solid arsenic

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(Received 28 March 1990; accepted for publication 17 September 1990)

The generation of arsine from the reactions of hydrogen and elemental arsenic in a microwave plasma reactor is described. The arsenic is evaporated from a solid source upstream and carried into the microwave plasma region by a mixture of hydrogen and argon. Stable reaction products, arsine and diarsine, are observed by molecular beam sampled mass spectroscopy along with partially hydrogenated species (e.g., AsH and AsH<sub>2</sub>). The effect of composition and flow rate of the argon/hydrogen carrier gas mixture on the amount of arsine generated is investigated. The arsine production reaches a maximum for an argon-to-hydrogen ratio of unity indicating that metastable argon species act as energy transfer intermediates in the overall reaction. The generation of arsine and diarsine from easily handled solid arsenic by this technique makes it attractive as a possible arsenic source for the growth of compound semiconductors by low-pressure metalorganic chemical vapor deposition.

The toxicity of arsine is a major concern in the growth of GaAs by metalorganic chemical vapor deposition (MOCVD). Being a gas at room temperature, arsine has to be stored in pressurized containers, and the potentially catastrophic consequences of a cylinder leak have prompted the investigation of alternative arsenic sources for MOCVD.<sup>1-3</sup> Since it appears that surface species with As--H bonds are responsible for the scavenging of carbon from the growth surface,<sup>1,2,4</sup> recent studies of alternative arsenic compounds have focused on organoarsenic compounds such as tertiarybutylarsine,<sup>5</sup> diethylarsine,<sup>6</sup> and phenylarsine.<sup>7</sup> Films with reasonable electrical properties, but not equal to those achieved with the use of arsine, have been grown with these precursors.<sup>8</sup> However, their toxicity is within an order of magnitude of that of arsine. In that case, their main advantage is being liquid at room temperature.

A possible alternative approach to the arsine storage problem is the generation of arsine on a demand basis at the point of use. This retains the chemical advantages of using arsine in terms of low carbon incorporation while avoiding storing arsine in pressurized cylinders. Solid arsenic, which is used routinely in molecular beam epitaxy systems, is easy to handle and store, but has not been a useful source in MOCVD,<sup>9</sup> presumably because of the lack of As-H containing species. Thermodynamic restrictions hinder the reaction of arsenic and hydrogen to form arsine by the reaction, As + 3/2  $H_2 \rightarrow AsH_3$ . The standard free energy of formation of arsine,  $\Delta G_{f}^{0}$  is positive, with a value of 16.5 kcal/mole. Equilibrium computations show that a temperature increase shifts the equilibrium away from arsine towards arsenic as reflected by the spontaneous decomposition of arsine at elevated temperatures. We have attempted to circumvent this obstacle by reacting arsenic and hydrogen in a microwave plasma. Similar approaches have been used by Naitoh<sup>10</sup> (1988) to generate phosphine and by Marinace<sup>11</sup> who placed arsenic in a radio frequency discharge. These nonequilibrium plasmas contain excited species, hydrogen radicals,<sup>12</sup> and energetic electrons that make it possible to overcome the barrier for arsine formation.

Diarsines, As<sub>2</sub>H<sub>4</sub> and As<sub>2</sub>H<sub>2</sub>, have been synthesized by Jolly et al.<sup>13</sup> by passing arsine through a radio frequency discharge. Information about the stability of the diarsines is limited. They appear to decompose rapidly to arsine and nonstoichiometric As-H species.<sup>13</sup> Diarsine, As<sub>2</sub>H<sub>4</sub>, has been detected by mass spectroscopy in the pyrolysis of tertiarybutylarsine under conditions relevant to MOCVD.<sup>2</sup> It is also observed in our experiments as described below.

The microwave reactor used to generate arsine is shown in Fig. 1. It consisted of a 13 mm outer diameter  $\times$ 180-mm-long quartz tube. A quartz frit was fused into the tube to provide a support for the solid arsenic while allowing gas to flow through the tube. Arsenic lumps were stacked on this frit in the tube to a height of about 65 mm. A resistive heater was wrapped around the quartz tube, and the temperature of the bed was measured by a type-K thermocouple, located in a quartz thermocouple well in the middle of the bed. An Evenson microwave cavity was placed around the quartz tube immediately downstream of the heated section. The cavity was energized by a 100 W/2.45 GHz power supply. The reactor was operated at low pressure ( $\sim 1$  Torr). A mixture of hydrogen and argon was passed through the generation tube at a flow rate which was controlled by flow controllers. The arsine generation unit was placed in a special MOCVD reactor with molecular beam sampling through a pinhole in the substrate assembly. This system, which has been described previously,<sup>14</sup> allowed sampling with minimal interference from post-sampling gas phase and surface reactions, critical for observing unstable arsenic hydride species. The sample was analyzed by mass spectrometry. Spectra were acquired over a range of masses from 0 to 200 amu, typically at a scan rate of 0.3 amu/s.

The effects of total flow rate and arsenic bed tempera-

0003-6951/90/502543-03\$02.00 © 1990 American Institute of Physics 2543 Appl. Phys. Lett. 57 (24), 10 December 1990 2543

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FIG. 1. Microwave plasma reactor and mass spectrometer system used for generation of arsine. The drawing is not to scale; the microwave reactor has been enlarged.

ture on the arsine generation rate were investigated. These experiments probed the sensitivity of the arsine generation to the As/H<sub>2</sub> ratio. These experiments were carried out at a pressure of 1.0 Torr and a H<sub>2</sub>/Ar ratio of 1.0. The effect of H<sub>2</sub>/Ar ratio on the arsine generation rate was investigated at constant pressure (1 Torr), total flow rate (20 sccm), and bed temperature (310 °C). In all the experiments, the mass spectral data acquisiton was initiated 15 min after temperature and flow controllers had stabilized after a change in set point.

Figure 2 shows typical mass spectral cracking patterns observed in the experiments in the mass ranges 70–85 and 140–165. In the absence of plasma, no peaks are observed in these regions above noise level even at the highest sensitivity of the electron multiplier. The known cracking pattern of arsine<sup>15</sup> is shown in Fig. 2(a) as bars on the same scale after normalization of the parent arsine peak at m/e = 78. The cracking pattern of diarsine, As<sub>2</sub>H<sub>4</sub>, reported by Lum *et al.*<sup>2</sup> is shown in Fig. 2(b) after normalization of the spectrometer sensitivity in Fig. 2(b) is 100 times that in Fig. 2(a). We therefore estimate that As<sub>2</sub> species constitute less than 1% of the total arsenic converted.

No direct calibration of the arsine pattern was possible in the present study since safety considerations precluded



FIG. 2. (a) Cracking pattern of  $AsH_x$  species observed. The known cracking pattern of arsine is overlaid as bars after normalization of the m/e = 78 peak. The experimentally observed spectrum has been offset in the vertical direction for clarity. Pressure = 1 Torr, hydrogen flow rate = 7.5 sccm, argon flow rate = 10 sccm, arsenic temperature = 310 °C. (b) Cracking pattern of  $As_2H_x$  species observed. The cracking pattern of diarsine<sup>2</sup> is overlaid as bars as normalization of the m/e = 150 peak. The experimentally observed spectrum has been offset in the vertical direction for clarity. Pressure = 1 Torr, hydrogen flow rate = 7.5 sccm, argon flow rate = 10 sccm, arsenic temperature = 310 °C.

the use of arsine. However, the concentration of arsine was estimated from published data on the relative ionization cross section of arsine compared to argon,<sup>16</sup> which was present in known quantities. Contributions to this portion of the spectrum from As<sub>2</sub>H<sub>x</sub> species can be neglected since they are only present in very small amounts, as described earlier. In the experiments reported here, 0.5-2% (on a mole basis) arsine is generated depending on the process conditions. Assuming that arsine is the only contributor to the m/e = 78 peak, it is apparent from the cracking pattern that a significant amount ( $\sim 50\%$ ) of the converted arsenic is present as hydride species other than AsH<sub>3</sub>. Thus, we conclude that partially hydrogenated arsenic species (AsH and AsH<sub>2</sub>) are present in significant amounts in the reaction products. A small peak close to m/e = 79remains unassigned.

Examination of Fig. 2(b) shows that  $As_2H_x$  species are also present in the reaction products. The relatively strong signal at m/e = 154 indicates the formation of diarsine

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FIG. 3. (a) Effect of arsenic temperature on concentration of arsine in reaction products. Pressure = 1 Torr,  $H_2/Ar$  ratio = 1.0, total flow rate = 20 seem; (b) Effect of total flow rate through reactor on concentration of arsine in reaction products. Presure = 1 Torr,  $H_2/Ar$  ratio = 1.0, arsenic temperature = 310 °C; (c) Effect of hydrogen/argon ratio on concentration of arsine in reaction products. Pressure = 1 Torr, total flow rate = 20 secm, arsenic temperature = 310 °C.

 $(As_2H_4)$  in the reaction. This parent peak appears somewhat larger than indicated by the overlaid cracking pattern of diarsine. The presence of diarsenic hydride species other than diarsine would have caused the opposite effect, viz. a smaller peak at m/e = 154 than that in the standard cracking pattern. We thus conclude that the primary diarsenic hydride formed in this process is diarsine. Since diarsine decomposes readily on solid surfaces, it may be a more efficient As-H source than arsine in MOCVD. Thus, the plasma activation method may have additional advantages.

Figure 3(a) shows the arsine generation rate as a function of arsenic bed temperature. At constant flow rate and pressure, the arsenic partial pressure downstream of the bed (i.e., in the plasma) increases with temperature. This has the effect of drastically reducing the arsine generation rate. It was observed that at the high arsenic bed temperatures (315 °C) there was a significant amount of solid arsenic depositing on the walls of the quartz tube immediately downstream of the plasma. No deposit was observed in the plasma zone. Thus, it appears that at high As partial pressures, the number of H radicals are insufficient to complete the hydrogenation to AsH<sub>3</sub> and As<sub>2</sub>H<sub>4</sub>. Partially hydrogenated species such as  $As_2H_2$  are known to readily decompose to  $As_2$  and  $H_2$ .<sup>13</sup>

Figure 3(b) shows the dependence of arsine production on total flow rate through the generator. A slight increase in arsine generation is observed as the flow rate is increased. This is consistent with the dependence on bed temperature. An increase in the flow rate leads to a relative reduction in arsenic concentration (analogous to a lower evaporation temperature) and, therefore, an increase in the efficiency of hydrogenation of As to AsH<sub>3</sub>.

Figure 3(c) shows the dependence of the arsine generation rate on the composition of the carrier gas. An optimum composition at a H<sub>2</sub>/Ar ratio around 1 is observed. This suggests that Ar participates in the reaction as an energy transfer medium. At low hydrogen concentrations, the concentration of excited hydrogen species is too low to convert significant amounts of arsenic. As the hydrogen concentration is increased, the concentration of H radicals increases. If argon were not participating in the reaction, an optimum in the AsH<sub>3</sub> production would not be expected. The hydrogen radical concentration would increase monotonically and the AsH<sub>3</sub> production would asymptotically approach the limit of pure hydrogen.

The current apparatus uses a quartz tube to contain the plasma. In hydrogen plasmas, quartz is known to form silane in small quantities. While no significant quantities of silane were observed in this study, the presence of silicon hydride cannot be ruled out. Therefore, sapphire tubes should be used in actual growth studies to avoid potential unintentional silicon doping.

This work was supported by the National Science Foundation (CBT-8351249).

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