

# Vapor etching of GaAs and AlGaAs by CH<sub>3</sub>I

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(Received 11 November 1991; accepted for publication 13 January 1992)

With the objective of developing an improved process for *in situ* etching of GaAs-based materials in organometallic vapor phase epitaxy reactors, GaAs wafers and Al<sub>x</sub>Ga<sub>1-x</sub>As epilayers have been etched with CH<sub>3</sub>I vapor in a horizontal reactor operated at atmospheric pressure with H<sub>2</sub> or He carrier gas. For a H<sub>2</sub> flow rate of 2.1 s lpm, etching temperatures from 400 to 625 °C, and CH<sub>3</sub>I mol fractions ( $y_{\text{CH}_3\text{I}}$ ) from 0.0012 to 0.015, the measured GaAs etch rate  $r$  (in Å min<sup>-1</sup>) is given by  $r = k_0 y_{\text{CH}_3\text{I}}^{0.83} \exp[-45(\text{kcal mol}^{-1})/RT]$  with  $k_0 = 3.2 \times 10^{16}$  Å min<sup>-1</sup>. The value of  $k_0$  depends on the type of carrier gas, flow rate, total pressure, and reactor geometry. The etch rate appears to be controlled mainly by the decomposition of CH<sub>3</sub>I to CH<sub>3</sub> and I, for which the activation energy has been reported to be 43.5 kcal mol<sup>-1</sup>. The etch rate of Al<sub>x</sub>Ga<sub>1-x</sub>As epilayers with  $x$  up to 0.7, which was measured at 480 °C with  $y_{\text{CH}_3\text{I}} = 0.015$ , does not depend on Al content. The surface morphology of etched GaAs wafers improves with decreasing temperature. Specular surfaces are maintained at temperatures below 500 °C for etch depths up to 5000 Å.

Development of a more satisfactory process for vapor etching of GaAs and AlGaAs alloys in organometallic vapor-phase epitaxy (OMVPE) reactors could significantly advance the technology available for fabricating optoelectronic devices. The use of such a process for *in situ* wafer patterning and cleaning could lead to improvements in the performance of devices grown by OMVPE. In addition, an effective *in situ* etching process would permit OMVPE to be employed more conveniently in the fabrication of GaAs/AlGaAs devices, such as buried heterostructure and distributed feedback diode lasers, that require two epitaxial growth steps interrupted by a patterning/etching step. Currently, the employment of OMVPE for such devices is limited because the oxide formed on AlGaAs surfaces exposed to air prevents high-quality regrowth.

Studies of the vapor etching of GaAs by HCl,<sup>1-4</sup> AsCl<sub>3</sub>,<sup>2,5-7</sup> HBr,<sup>8</sup> and AsBr<sub>3</sub>,<sup>9</sup> and of AlGaAs by HCl<sup>10,11</sup> have been reported. In all cases, etching temperatures above 750 °C were required in order to maintain specular surface morphology. Dopant and/or alloy interdiffusion occurring at such high temperatures could degrade the performance of some types of devices. Furthermore, HCl and HBr are corrosive gases that could cause system contamination. Consequently, *in situ* vapor etching is infrequently used in OMVPE processing.

Initial experiments were recently reported<sup>12</sup> on the vapor etching of GaAs substrates with an alternate etchant, methyl iodide (CH<sub>3</sub>I), that is potentially useful in OMVPE systems because it is liquid at room temperature, has a suitable vapor pressure, and is noncorrosive. It was found that featureless surface morphology can be maintained with this etchant at temperatures of only 450 to 500 °C. A

more detailed study has now been made of the etch rate as a function of temperature, CH<sub>3</sub>I concentration, and flow rate for GaAs substrates and for Al<sub>x</sub>Ga<sub>1-x</sub>As epilayers with  $x$  up to 0.7. Over this range of compositions, the etch rate is found to be independent of Al content.

The etching experiments were performed in a horizontal reactor operated at atmospheric pressure with H<sub>2</sub> or He as the carrier gas. Gaseous H<sub>2</sub> from a liquid H<sub>2</sub> source was used without further purification, while He was purified in a titanium furnace for gettering O<sub>2</sub>. Methyl iodide was obtained at 99% purity and in some cases was further purified by one or two distillations through a column packed with molecular sieve under an atmosphere of high purity He to remove traces of H<sub>2</sub>O. The purity of the CH<sub>3</sub>I did not appear to influence the etch rate. When unpurified material was used, however, iodine remaining in the bubbler corroded the stainless-steel lines in the vicinity of the bubbler. The total flow rate through the reactor ranged from 0.5 to 5 s lpm. By flowing part of the carrier gas through the CH<sub>3</sub>I bubbler maintained at temperatures between 2 and 18 °C, values of CH<sub>3</sub>I concentration  $y_{\text{CH}_3\text{I}}$  ranging from 0.0012 to 0.03 mole fraction could be obtained.<sup>13</sup>

The GaAs samples were Si-doped  $n^+$  (100) wafers that were partially masked with silicon nitride. The AlGaAs samples were nominally undoped 2- $\mu\text{m}$ -thick epilayers that were grown on a GaAs substrate by OMVPE in a separate reactor, capped with 500 Å of GaAs to prevent Al oxidation, and then partially masked with silicon nitride. Before CH<sub>3</sub>I etching, each sample wafer was first degreased by successive rinses in trichloroethylene, acetone, methanol, and deionized water, then placed in concentrated H<sub>2</sub>SO<sub>4</sub> for 1 min under moderate agitation, rinsed in deionized water, placed in concentrated HCl for 1 min under moderate agitation, rinsed again in deionized

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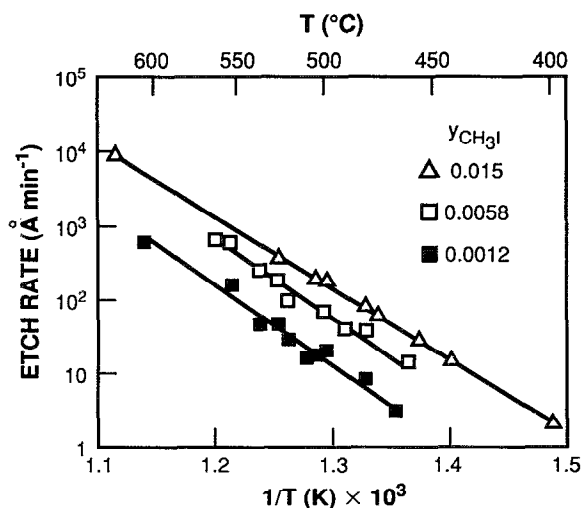


FIG. 1. Etch rate of GaAs as a function of temperature for three concentrations of  $\text{CH}_3\text{I}$  in  $\text{H}_2$  carrier gas at a flow rate of 2.1 s lpm.

water, and finally dried with  $\text{N}_2$  gas. The wafer was then placed on a Mo susceptor in the etching reactor. The reactor was purged with  $\text{H}_2$  for 30 min, the susceptor was heated to the desired etching temperature (as measured with a thermocouple), and  $\text{CH}_3\text{I}$  was switched in for a given length of time. The reactor was then purged with  $\text{H}_2$  and cooled to room temperature. The silicon nitride mask was removed from GaAs samples by etching with HF and from AlGaAs samples by  $\text{CF}_4$  plasma etching. The step height was then measured with a mechanical stylus, and the etch rate was found by dividing the step height by the exposure time. The morphology of the etched surfaces was evaluated by Nomarski interference microscopy.

Figure 1 shows the measured etch rate  $r$  of GaAs as a function of reciprocal absolute temperature for susceptor temperatures from 400 to 625 °C and  $y_{\text{CH}_3\text{I}}$  values of 0.0012, 0.0058, and 0.015 mole fraction in  $\text{H}_2$  carrier gas at a flow rate of 2.1 s lpm. For  $y_{\text{CH}_3\text{I}} = 0.015$  mole fraction,  $r$  increased from 2.5  $\text{\AA min}^{-1}$  at 400 °C to 9000  $\text{\AA min}^{-1}$  at 625 °C. For each  $\text{CH}_3\text{I}$  concentration, a good fit to the data is given by a straight line whose slope corresponds to an activation energy of  $45 \pm 2 \text{ kcal mol}^{-1}$ . Using He instead of  $\text{H}_2$  as the carrier gas decreased  $r$  by a factor of 1.5 but did not affect the activation energy.

Figure 2 shows the dependence of  $r$  on  $y_{\text{CH}_3\text{I}}$  at 480, 500, and 525 °C, again with  $\text{H}_2$  carrier gas at a flow rate of 2.1 s lpm. For each susceptor temperature, the data are well fitted by a curve given by the expression  $r = \text{const} (y_{\text{CH}_3\text{I}})^n$ , where the reaction order  $n = 0.83 \pm 0.03$ . The sublinear dependence of  $r$  on  $y_{\text{CH}_3\text{I}}$  contrasts with the superlinear dependence of etch rate on etchant concentration that is observed for the etching of GaAs with HCl (Ref. 1) and  $\text{AsCl}_3$  (Ref. 6).

The data of Figs. 1 and 2 can be represented by the expression

$$r = k_0 y_{\text{CH}_3\text{I}}^{0.83} \exp[-45(\text{kcal mol}^{-1})/RT] \quad (1)$$

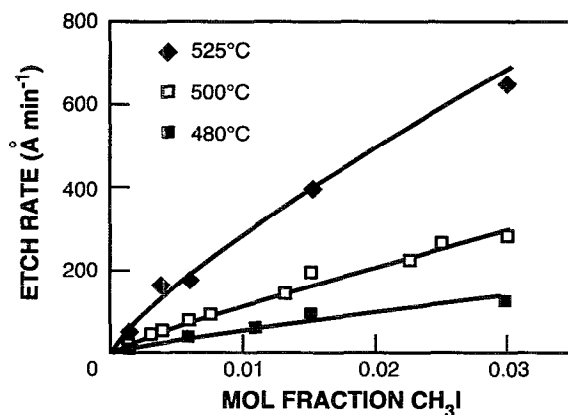


FIG. 2. Etch rate of GaAs at three temperatures as a function of  $\text{CH}_3\text{I}$  concentration in  $\text{H}_2$  carrier gas at a flow rate of 2.1 s lpm.

with  $k_0 = 3.2 \times 10^{16} \text{ \AA min}^{-1}$ . The activation energy for the unimolecular gas-phase decomposition of  $\text{CH}_3\text{I}$  to  $\text{CH}_3$  and I is reported to be 43.5  $\text{kcal mol}^{-1}$  (Ref. 14). The agreement between this value and the activation energy of 45  $\text{kcal mol}^{-1}$  in Eq. (1) indicates that the decomposition reaction is the principal rate-controlling step in the etching process, although the slightly sublinear dependence of  $r$  on  $y_{\text{CH}_3\text{I}}$  indicates that the etching rate is also influenced by some other factor. The value of  $k_0$  in Eq. (1) depends upon a number of experimental conditions, including reactor geometry, total gas pressure, carrier gas species, and carrier gas flow rate. The reduction in  $r$  obtained by changing the carrier gas from  $\text{H}_2$  to He was noted above. Figure 3 shows the dependence of  $r$  on  $\text{H}_2$  flow rate for  $y_{\text{CH}_3\text{I}} = 0.015$  mole fraction and a susceptor temperature of 485 °C. The value of  $r$  decreases from 190  $\text{\AA min}^{-1}$  at 0.5 s lpm to 70  $\text{\AA min}^{-1}$  at 5 s lpm. The data are fit by a power law expression with an exponent of  $-0.44$ . By decreasing the residence time of the  $\text{CH}_3\text{I}$  molecules in the high-temperature region adjacent to the susceptor, an increase in flow rate tends to reduce the decomposition rate and therefore the etching rate, as observed. To explain the quantitative dependence of  $r$  on flow rate, it is also necessary to take account of the effect of the flow rate on the temperature profile in the gas phase<sup>15</sup> and on the thickness of the dif-

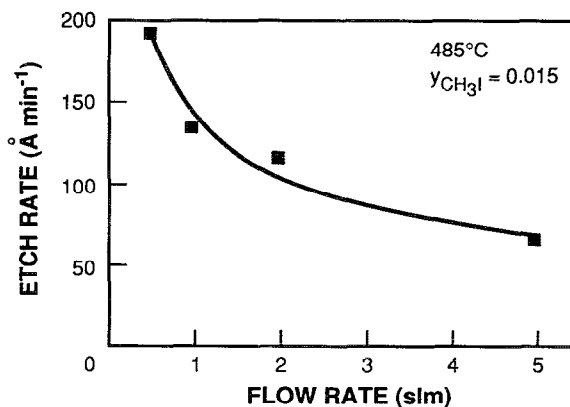


FIG. 3. Etch rate of GaAs vs flow rate of  $\text{H}_2$  carrier gas for  $\text{CH}_3\text{I}$  mol fraction of 0.015 and temperature of 485 °C.

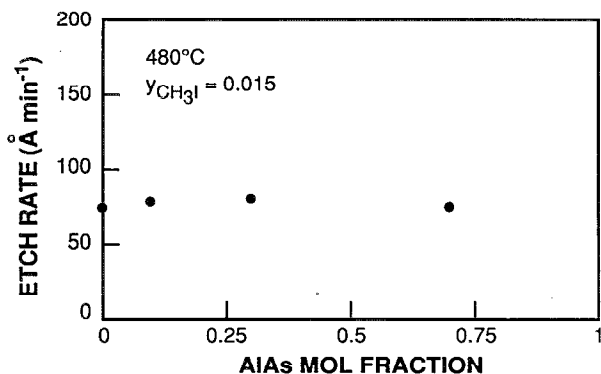


FIG. 4. Etch rate of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  vs  $x$  for a temperature of  $480^\circ\text{C}$  and  $\text{CH}_3\text{I}$  mole fraction of 0.015 in  $\text{H}_2$  carrier gas at a flow rate of 2.1 s lpm.

fusion boundary layer adjacent to the wafer surface,<sup>16</sup> which influence the  $\text{CH}_3\text{I}$  decomposition rate and the rate at which the decomposition products are transported to the surface.

In a series of experiments to investigate the etching of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloys with  $\text{CH}_3\text{I}$  vapor, a GaAs control wafer and epilayers with  $x = 0.1, 0.3, \text{ or } 0.7$  were etched at  $480^\circ\text{C}$  with  $y_{\text{CH}_3\text{I}} = 0.015$  mole fraction and a  $\text{H}_2$  flow rate of 2.1 s lpm. As shown in Fig. 4, under these conditions  $r$  was the same over the entire composition range. This result is consistent with control of the etching rate by the gas-phase decomposition of  $\text{CH}_3\text{I}$  and transport of the decomposition products to the sample surface, rather than by the surface chemical reaction with GaAs or AlGaAs. In contrast, it was found in previous studies<sup>10,11</sup> that the rate of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  etching with HCl vapor decreased with increasing Al content.

Some but not all of the GaAs etching experiments discussed above yielded surfaces that were smooth and featureless as observed by Nomarski interference microscopy. In these and supplementary experiments on surface morphology, it was found that the morphology generally improved with decreasing temperature for fixed  $y_{\text{CH}_3\text{I}}$  and depth, and with increasing  $y_{\text{CH}_3\text{I}}$  for fixed temperature and etch depth. Specular surface morphology was maintained at temperatures of  $480^\circ\text{C}$  and below for etching times up to 1 h (depths up to  $0.9\ \mu\text{m}$ ) and at  $500^\circ\text{C}$  for times up to 15 min (depths up to  $0.5\ \mu\text{m}$ ). Above  $520^\circ\text{C}$ , surfaces were generally degraded in times as short as 5 min (depths up to  $0.35\ \mu\text{m}$ ).

In conclusion, GaAs wafers and AlGaAs epilayers have been etched with  $\text{CH}_3\text{I}$  vapor at temperatures from  $400$  to  $625^\circ\text{C}$  in a horizontal reactor operated at atmospheric pressure. The etch rate has an activation energy of  $45\ \text{kcal mol}^{-1}$ , decreases with increasing total gas flow rate, and is independent of Al content. These observations

indicate that the principal rate-controlling step is the unimolecular decomposition of  $\text{CH}_3\text{I}$  in the gas phase, although they do not establish what decomposition product(s) are responsible for the etching reaction. Specular surface morphology has been obtained at etching temperatures below  $500^\circ\text{C}$ , considerably lower than those required to obtain specular GaAs surfaces with any other vapor etchant. On the basis of these results, it is believed that etching with  $\text{CH}_3\text{I}$  vapor is a promising process for *in situ* treatment of GaAs/AlGaAs structures in OMVPE reactors. In further experiments on the development of *in situ* technology, which will be described elsewhere,<sup>17</sup> it has been found that GaAs epilayers with specular surfaces and excellent photoluminescence properties can be grown on GaAs surfaces etched with  $\text{CH}_3\text{I}$  vapor, and that the level of contamination with C or other elements at the regrowth interface is essentially the same as the level in structures grown without  $\text{CH}_3\text{I}$  etching.

The authors would like to acknowledge V. Diadiuk for technical discussion and  $\text{CF}_4$  plasma etching, and C. H. Anderson, M. K. Connors, D. F. Kolesar, and D. M. Tracy for technical assistance. Helpful discussions with R. A. Brown and Critical reading of this manuscript by A. J. Strauss are also acknowledged. This work was sponsored by the National Science Foundation and by the Department of the Air Force.

- <sup>1</sup>R. Bhat, B. J. Baliga, and S. K. Ghandi, *J. Electrochem. Soc.* **122**, 1378 (1975).
- <sup>2</sup>R. Bhat and S. K. Ghandi, *J. Electrochem. Soc.* **125**, 771 (1978).
- <sup>3</sup>M. Heyen and P. Balk, *J. Cryst. Growth* **53**, 558 (1981).
- <sup>4</sup>C. Pelosi, G. Attolini, and G. Salviati, *Mater. Chem. Phys.* **9**, 139 (1983).
- <sup>5</sup>R. Bhat and S. K. Ghandi, *J. Electrochem. Soc.* **124**, 1447 (1977).
- <sup>6</sup>B. El Jani, J. C. Grenet, M. Guittard, and B. Senouci, *J. Cryst. Growth* **58**, 381 (1982).
- <sup>7</sup>B. El Jani, M. Guittard, J. Cl. Grenet, and P. Gibart, *J. Cryst. Growth* **60**, 131 (1982).
- <sup>8</sup>E. I. Givargizov and R. A. Babasian, *J. Electron. Mater.* **9**, 883 (1980).
- <sup>9</sup>T. F. Keuch, E. Marshall, G. J. Scilla, R. Potemski, C. M. Ransom, and M. Y. Hung, *J. Cryst. Growth* **77**, 539 (1986).
- <sup>10</sup>M. Nido, I. Komaziak, K. Kobayashi, K. Endo, M. Ueno, T. Kamejima, and T. Suzuki, *IEEE J. Quantum Electron.* **QE-23**, 720 (1987).
- <sup>11</sup>K. Shimoyama, M. Katoh, M. Noguchi, Y. Inoue, H. Gotoh, Y. Suzuki, and T. Satoh, *J. Cryst. Growth* **93**, 803 (1988).
- <sup>12</sup>C. W. Krueger, M. Flytzani-Stephanopoulos, R. A. Brown, and C. A. Wang, presented at Electronic Materials Conference, Santa Barbara, CA, 27–29 June, 1990.
- <sup>13</sup>Vapor pressure data for  $\text{CH}_3\text{I}$  obtained from CRC Handbook of Chemistry and Physics, 60th ed., edited by R. C. Weast (Chemical Rubber, Boca Raton, FL, 1979), p. D-203.
- <sup>14</sup>K. Saito, H. Tahara, O. Kondo, T. Yokubo, T. Higashihara, and I. Murakami, *Bull. Chem. Soc. Jpn.* **53**, 1335 (1980).
- <sup>15</sup>D. I. Fotiadis, M. Boekholt, K. F. Jensen, and W. Richter, *J. Cryst. Growth* **100**, 577 (1990).
- <sup>16</sup>M. R. Leys and H. Veenliet, *J. Cryst. Growth* **55**, 145 (1981).
- <sup>17</sup>C. A. Wang, C. W. Krueger, and M. Flytzani-Stephanopoulos, *J. Electron. Mater.* **21**, 299 (1992).