Abatement of waste gases and water during the processes of semiconductor fabrication

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Abstract:The purpose of this article is to examine the methods and equipment for abating waste gases and water produced during the manufacture of semiconductor materials and devices. Three separating methods and equipment are used to control three different groups of electronic wastes. The first group includes arsine and phosphine emitted during the processes of semiconductor materials manufacture. The abatement procedure for this group of pollutants consists of adding iodates, cupric and manganese salts to a multiple shower tower (MST) structure. The second group includes pollutants containing arsenic, phosphorus, HF, HCl, NO_2, and SO_3 emitted during the manufacture of semiconductor materials and devices. The abatement procedure involves mixing oxidants and bases in an oval column with a separator in the middle. The third group consists of the ions of As, P and heavy metals contained in the waste water. The abatement procedure includes adding $CaCO_3$ and ferric salts in a flocculation-sedimentation compact device equipment. Test results showed that all waste gases and water after the abatement procedures presented in this article passed the discharge standards set by the State Environmental Protection Administration of China.

Keywords: waste gases; waste water; abatement; pollutant;semiconductor

Introduction

The rapid development of the electronic industry has brought about new pollution. Numerous laboratories and factories emit increasing amount of untreated wastes to the environment. Typical air-borne pollutants include such as arsine, phosphine, hydrogen chloride, sulfur dioxide, sulfur trioxide, nitric oxide, nitrogen oxide, fluohydric acid, sulfuric acid, nitric acid and other pollutants containing arsenic or phosphorus and so on. Water-borne pollutants include poisonous substances containing arsine, phosphorus and their compounds, ammonia nitrogen, detergents, Cu, Cr, or Cd containing pollutants. These toxic emissions present serious threats to the atmosphere and water resources.

Metallorganic vapor phase epitaxy(MOVPE) is the most important epitaxy production technique. It has been commonly utilized to grow materials for the device fabrication, such as laser diodes, light emitting diodes, heterojunction bipolar transistors (HBT) and heterojunction field effect transistors (HFETs). MOVPE is attractive because it can produce high quality superlattices and quantum wells, and the technique can be relatively easily put into production. However, poisonous gases, particles, and waste solutions are discharged during the MOVPE process.

1   Abatement of arsine and phosphine during the manufacture of semiconductor materials

1.1   Equipment and procedure

A multiple shower tower(MST) was connected to the exhaust pipe of MOVPE to transform various species of arsenic into AsO_4^{3-}, and phosphorous into PO_4^{3-} through chemical reactions in three stages. The flowchart and MST structure for arsenic and phosphorus abatement are shown in Fig.1(a) and (b), respectively.

Tail gas containing AsH_3, PH_3 and their compounds are let into the oil separator (1) to remove oil and increase abatement efficiency. If pressure in 1 exceeds allowable limit for any reason, the gas would go firstly into the pressure protection tank (2), then into the activated carbon absorbing device (3), and

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trigger the high pressure alarm (4). Under normal pressure, the tail gas will be pumped into the KIO_3, KI and H_2SO_4 solution in the 1st stage treatment tank (5), where the majority of AsH_3 and PH_3 is absorbed. The tail gas, with much of its AsH_3 and PH_3 stripped, moving upward into the 1st stage reverse spray column 5, is showered by the solution drawn from the same tank (5).

This technology has been used in practice for the treatment of tail gases during MOVPE, MBE, CBE and other processing of GaAs and InP.

1.2 Results and discussion

1.2.1 Abatement solutions choice

A thermodynamic study (Yang, 1992; Barin, 1991; Dean, 1985) has demonstrated that the main forms for arsenic in MOVPE tail gases are As_4, AsH_3, As_2 and As, and for phosphorus are P_4, PH_3, P_2 and P. According to this study, the most effective chemicals and concentrations were determined to abate As and P in tail gases through a series of tests and simulations. For this purpose gas samples prepared by adding AsH_3 (99.99%) and PH_3 (99.99%) into high purity hydrogen, were analyzed by high temperature hydrogen reduction gas chromatography to determine As and P concentrations before and after spray-absorption. The experimental for high temperature hydrogen reduction gas chromatography conditions were as follows: (1) Reduction system: reducing H_2 flow =
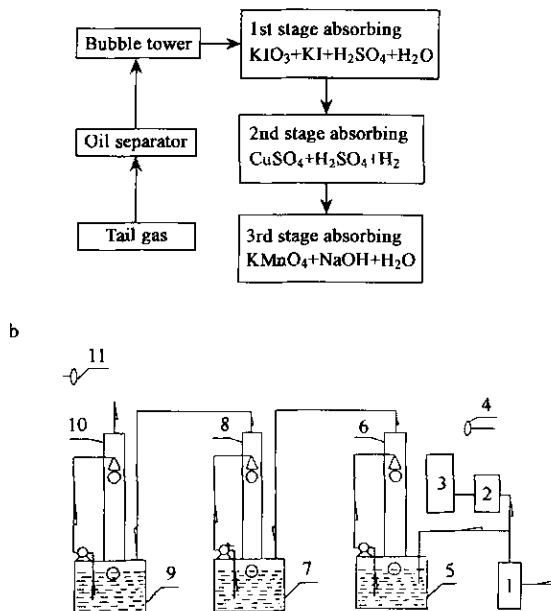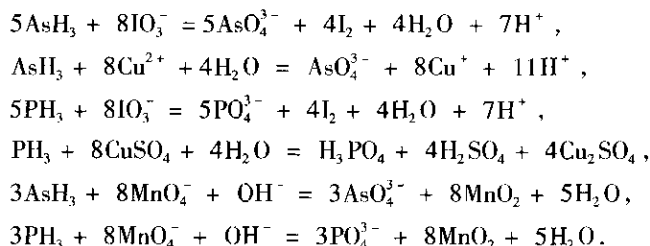
Fig.1   Multiple shower tower for arsenic and phosphorus abatement:
(a) flow chart; (b) schematic diagram of equipment
1.oil separator; 2.pressure protection tank; 3.activated carbon absorbing device; 4.high pressure alarm; 5.1st stage treatment tank; 6.1st stage counter-current-spray column; 7.2nd stage treatment tank; 8.2nd stage counter-current-spray column; 9.3rd stage treatment tank; 10.3rd stage counter-current-spray column; 11.monitor/alarm device

158 ml/min, carrying H_2 flow = 4.0 ml/min mixing chamber temperature = 760℃. (2) Gas chromatography system: carrying air flow = 57 ml/min, flame H_2 flow = 238 ml/min, air flow 1 = 92 ml/min, air flow 2 = 182 ml/min , detector temperature = 100℃. The results are shown in Table 1.

Table 1 shows that the most effective treatment outcome occurred when iodate, copperate, and manganate were used in various acid and alkaline medium. Major chemical reaction equations for As and P are as follows:

$$5AsH_3 + 8IO_3^- = 5AsO_4^{3-} + 4I_2 + 4H_2O + 7H^+ ,$$

$$AsH_3 + 8Cu^{2+} + 4H_2O = AsO_4^{3-} + 8Cu^+ + 11H^+ ,$$

$$5PH_3 + 8IO_3^- = 5PO_4^{3-} + 4I_2 + 4H_2O + 7H^+ ,$$

$$PH_3 + 8CuSO_4 + 4H_2O = H_3PO_4 + 4H_2SO_4 + 4Cu_2SO_4 ,$$

$$3AsH_3 + 8MnO_4^- + OH^- = 3AsO_4^{3-} + 8MnO_2 + 5H_2O ,$$

$$3PH_3 + 8MnO_4^- + OH^- = 3PO_4^{3-} + 8MnO_2 + 5H_2O .$$

<p style="text-align:center">Table 1   Comparison of different solutions for As and P abatement [*]</p>

No.	Solution	As and P concentration, mg/m³				Abatement effectiveness, %	
		Before treatment		After treatment			
		As	P	As	P	As	P
1	Sat. KIO₃ + Sat. KI	0.61	0.052	0.04	0.003	93.4	94.2
2	4% KIO₃ + 0.4%. KI + 1% H₂SO₄	0.91	0.135	0.05	0.005	94.5	96.2
3	5% HIO3	0.11	0.04	0.01	0.003	90.9	92.5
4	0.5% CuSO₄ + 1% H₂SO₄	0.93	0.08	0.06	0.004	93.5	95.0
5	2 and 4 in series	0.94	0.19	0.04	0.006	95.7	96.8
6	1% KMnO₄ + 1% NaOH	0.69	0.06	0.05	0.004	92.8	93.3

* As and P concentrations were determined by gas chromatography and colorimetry both methods agree well with each other; the experimental conditions for high temperature hydrogen reduction gas chromatography were as follows: (a) reduction system: reducing H_2 flow = 158 ml/min, carrying H_2 flow = 4.0 ml/min mixing chamber temperature = 760℃; (b) gas chromatography system: carrying air flow = 57 ml/min, flame H_2 flow = 238 ml/min, air flow 1 = 92 ml/min, air flow 2 = 182 ml/min, detector temperature = 100℃.

As and P concentrations were determined by gas chromatography and colorimetry both methods agree well with each other.

Judging from the effectiveness and cost, we use 4% KIO_3 + 0.4% KI + 1% H_2SO + H_2O, 0.5% $CuSO_4$ + 1% H_2SO_4, and 1% $KMnO_4$ + 1% NaOH + H_2O as the first, the second and the third stage absorbing solution, respectively.

1.2.2   Abatement methods

Various abatement methods for tail gases containing arsenic and phosphorus during MOVPE process were evaluated. The arsenic and phosphorus concentration were determined by high-temperature hydrogen reduction gas chromatograph (Wen, 1997). Table 2 shows the arsenic and phosphorus concentration in tail gases treated by single bubbling, single absorption and bubbling plus spray absorptions. The arsenic and phosphorus abatement effects before and after treatment are listed in Table 3 and 4, respectively.

The results showed that after abatement P and As concentration in tail gas are well below the National Discharge Standard and the abatement efficiency is high. The high efficiency of abatements is due to the multiple shower tower structure and the use of iodate, copperate and manganate in various acid and alkaline medium. Conventional abatement technology for tail gases involves chemical solution to absorb AsH₃ and PH₃ (Brookman, 1988). A typical method is simply to pass the gas through the solution. Another method is to pump to the gas upward through a column and spray it into the solution. In our MST, a technology combining the two

<p style="text-align:center">Table 2   Comparison of various tail gas absorption methods [*]</p>

	Untreated	After single bubbling	After single spray absorption	After bubbling plus spray absorptions
As conc. in tail gas, mg/m³	0.91	0.15	0.12	0.05
As abatement effectiveness, %		83.6	86.8	94.5
P conc. in tail gas, mg/m³	0.135	0.05	0.03	0.005
P abatement effectiveness, %		63.0	77.8	96.3

*. Determined by gas chromatography as in Table 1

<p style="text-align:center">Table 3   Arsenic abatement effectiveness determined by colorimetry and gas chromatography</p>

Sample No.	Before treatment, mg/m³		After treatment, mg/m³		Abatement effectiveness, %	
	A [*]	B [**]	A [*]	B [**]	A [*]	B [**]
1	0.61	0.69	0.041	0.040	93.2	94.2
2	0.49	0.51	0.030	0.040	93.9	92.2
3	0.91	0.93	0.046	0.042	94.9	97.5
4	0.26	0.31	0.033	0.038	87.3	87.7
5	0.32	0.33	0.04	0.048	87.5	88.1

A [*]. colorimetry   B [**]. gas chromatography

methods is used to effectively remove AsH_3, PH_3, and other pollutants. Moreover, the oil separator located in front of the bubble tower separates gas from oil resulting in more effective abatement during the next step.

The MST is able to treat tail gas containing AsH_3 and PH_3 of concentration below 1 mg/m^3.

Table 4 Phosphorus abatement effectiveness

Sample No.	1	2	3	4	5
Before treatment, mg/m^3	0.052	0.091	0.048	0.047	0.130
After treatment, mg/m^3	< 0.003	0.004	< 0.003	0.004	0.004
Abatement effectiveness, %	> 94.2	95.6	> 93.8	91.5	96.9

2　Abatement of waste gases containing As, P, HF, HCl, NO_2 and SO_3 during semiconductor processes

2.1　Equipment

Waste gases containing As, P, HF, HCl, NO_2 and SO_3 are treated by basic solution containing $KMnO_4$ or H_2O_2. After that, arsenic, phosphorus and other acid radical ions are abated through the oxido-reduction.

An oval spray-absorption tower with a mid-separator was used for above mentioned purpose. This makes a concurrent flow on one side and a counter-current flow on another side for gas and solution. Because of this, the contact area and the time between gas and solution could be aggrandized and prolonged.

The construction of the equipment is shown in Fig.2.

According to the results concerning the selection of absorbers and considering the variety of effluents from laboratories and factors concerning cost and performance, three kinds of absorbers for treating As. P and other kinds of acid gases have been chosen. They are 0.2%—0.5% $KMnO_4$ + 0.5%—1% NaOH, 0.5%—1% NaOH and 0.2%—0.5% H_2O_2 + 0.5%—1% NaOH. After treatment the quality of the discharged gases have meet National Discharge Standards.

2.2　Results and discussion

After treatment the pollutant concentrations were analyzed. The arsenic and phosphorus were determined by gas chromatography and the other anions by ion chromatography (Wen, 1998).

The experimental conditions for ion chromatography are as follows: separation column, IonPac-AS4A; sensitivity of conductometer, 1 μs; volume of sample, 100—480 μl; eluent solution flow rate, 3 ml/min; regenerating solution flow rate, 2.8 ml/min.

The experimental conditions for As and P determination by gas chromatography were the same as in paragraph 1.2. The analyzed results are shown in Table 5.

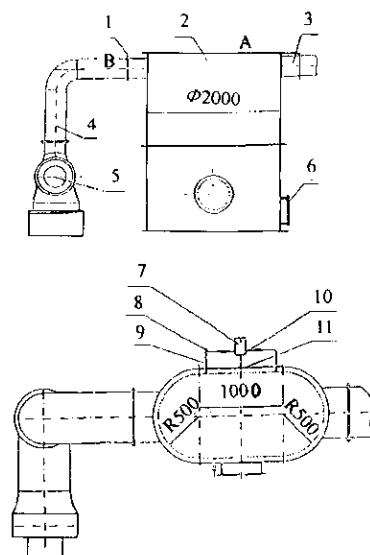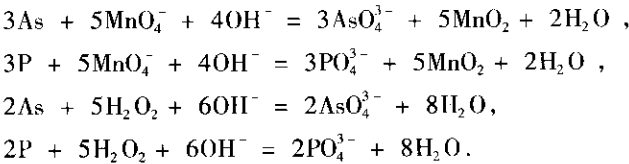The representative chemical reactions are as follows:

Fig.2　Equipment of oval spray-absorption plate tower

1. rectangular flange; 2. spray-absorber; 3. vent; 4. inlet; 5. ventilator; 6. water level indicator; 7. pump for chemicals; 8. 90° connector; 9. connector; 10. valve; 11. pipe for chemicals

$$3As + 5MnO_4^- + 4OH^- = 3AsO_4^{3-} + 5MnO_2 + 2H_2O ,$$

$$3P + 5MnO_4^- + 4OH^- = 3PO_4^{3-} + 5MnO_2 + 2H_2O ,$$

$$2As + 5H_2O_2 + 6OH^- = 2AsO_4^{3-} + 8H_2O,$$

$$2P + 5H_2O_2 + 6OH^- = 2PO_4^{3-} + 8H_2O.$$

HF, HCl, H_2SO_4, HNO_3 and H_3PO_4 are neutralized with alkali in spraying liquid to form NaF, $NaCl$, Na_2SO_4, $NaNO_3$ and Na_3PO_4, respectively.

Table 5 shows that the pollutant concentrations after treatment meet the National Discharge Standards GB16297— 96. The oval spray-absorption tower with a mid-separation conjunction with basic solution containing $KMnO_4$ and H_2O_2 proved to be effective for abatement of waste gases during semiconductor processes.

The high efficiency of abatement is partly due to the construction of the oval spray-absorption tower. The construction makes a concurrent flow on one side and a counter-current flow on another side for gas and solution. Because of this, contact area and time between gas and solution could be aggrandized and prolonged. Moreover, within this oval spray-absorption tower gas can flow smoothly beneath the mid-separator. The resistance is very low, only 3.72 Pa, being about 1/5 of the resistance of the linking pipe between two towers in series. Thus, the tower can treat waste gas very well even though the tower is not too high and

Table 5   Comparison of Pollutant concentration before and after treatment[*]

Pollutant concentration	Before treatment, mg/m³	After treatment, mg/m³
Cl^-	0.23—2.4	0.037
F^-	0.56—0.91	0.010
SO_4^{2-}	0.2—3.1	0.082
NO_3^-	0.88	0.07
Arsenic	0.32	0.04
Phosphorus	0.13	0.09

[*]. The experimental conditions for Cl^-, F^-, SO_4^{2-} and NO_3^- by ion chromatography are as follows: separation column: IonPac—AS4A, sensitivity of conductometer = 1 μs, volume of sample = 100—480 μl, eluent solution flow rate = 3 ml/min, regenerating solution flow rate = 2.8 ml/min

The experimental conditions for As and P determination by gas chromatography are the same as Table 1.
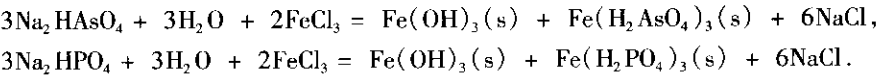
the lower velocity blast can work well. In the oval spray-absorption tower there are many nozzles spraying water crosswise, so there is no dead corner in this tower. The water velocity is less than 2 m/s in an empty tower. The pressure drop is 400 Pa per meter of fillings. The selected blast has a rotation speed of 2900 r/ min, and stands temperature as high as 120℃. Its pressure fits the resistance of the tower well. In contrast with it, the usual motors have a rotation speed of 1450 r/min and stands temperature < 50℃, and its pressure does not fit the resistance of the tower. The parameters of selected corrosion-resistant fiberglass pump are as follows: flux of 12.5—18.0 m³/h, lift of 18—14.3 (m), 2900 r/min, power of 2.2 kW. The pump can transport all kinds of corrosive liquids with temperature of 120℃.

3   Waste water treatment

3.1   Principle

Coprecipitation takes place by the action of neutralization in conjunction with flocculation. According to this principle, $Fe(OH)_3$ precipitates by adjusting pH value to 8—10 and adding Fe^{3+} flocculent. At the same time ions of As, P and heavy metals should be absorbed on the surface of precipitated solid. Small particles in turn agglomerate becoming large precipitates.

The chemical reactions take place according to following equations:

$$3Na_2HAsO_4 + 3H_2O + 2FeCl_3 = Fe(OH)_3(s) + Fe(H_2AsO_4)_3(s) + 6NaCl,$$

$$3Na_2HPO_4 + 3H_2O + 2FeCl_3 = Fe(OH)_3(s) + Fe(H_2PO_4)_3(s) + 6NaCl.$$

3.2   Equipment

Specially designed flocculation-sedimentation compact device is made of erosion-resistant steel. In this device there is a slant-pipe settlement device, in which the slant pipes are installed with an angle 60^0.

Water flows upward with a velocity of 0.5 mm/s while sludge falls down the slant pipes. Its sedimentation efficiency is 5—6 times higher than that of conventional methods.

The flocculation-sedimentation flowchart and the compact device is shown in Fig.3.

3.3   Results and discussion

The concentrations of heavy metals including Cu, Ba, Cd, Cr, total As and P, chemical oxygen demand (COD) by $K_2Cr_2O_7$ oxidation, biochemical oxygen demand (BOD) by cultivation for five days, suspended solid (SS), linear alkyl benzene sulfonate (LAS), ammonia nitrogen ($NH_3 - N$) and pH values before and after waste water treatment are shown in Table 6. The National Waste Water Discharge Standard GB 8978—96 is also listed for comparison in Table 6, which shows that the pollutant concentrations in waste water after the treatment meet the National Waste Water Discharge Standard.

According to our experiment, the method can be applied to waste water containing COD < 500 mg/L, BOD < 300 mg/L, SS < 100 mg/L, LAS < 20 mg/L, As < 30 mg/L, P < 10 mg/L, F < 5 mg/L, and heavy metal < 15 mg/L. The enhancement of abatement efficiency by using the flocculation-sedimentation device with a slant settlement pipe is due to the following factors. Firstly, the flocculation-sedimentation device with a slant settlement pipe has a larger surface than that of a conventional one. Secondly, the effective height of sedimentation for this device is higher than that for a conventional one. Calculation results showed that the surface and effective height is increased by a factor of 1.75 and 2.9—3.5, respectively, for waste water rate of 10 m³/h. The resultant sedimentation efficiency is $1.75 \times (2.9 - 3.5) = 5 - 6$ times higher than that of conventional sedimentation device.
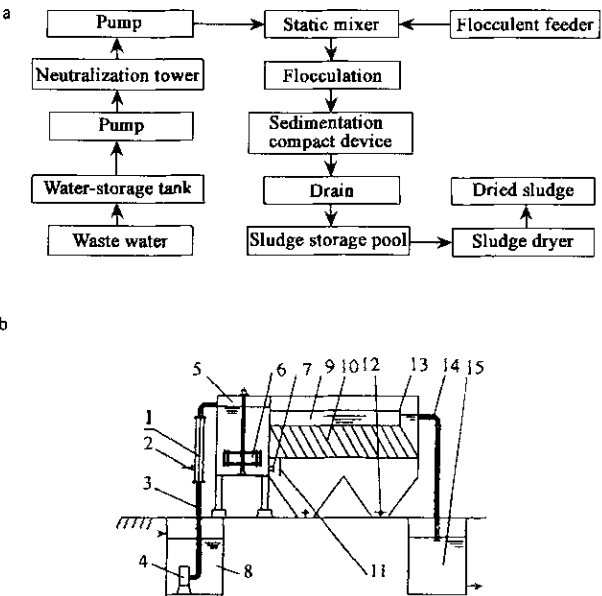
a

b

Fig.3 Flocculation-sedimentation compact device
(a) flow chart; (b) schematic diagram of device
1. static mixer; 2. inlet for chemicals; 3. inlet pipe; 4. submerged pump; 5. reaction pool; 6. agitator; 7. inlet port; 8. regulating pool; 9. slant-pipe sedimentation pool; 10. fiber glass slant pipes with hexagonal cross section; 11. water distributor; 12. pipes with holes for removing sludge; 13. triangle weir plate; 14. outlet pipe; 15. water pool

Table 6   Comparison of pollutant concentration before and after waste water treatment

No.	Impurity	Concentration, mg/L		National Waste Water Discharge Standard, mg/L First class
		Before abatement	After abatement	
1	Cu	0.0214	0.018	0.5
2	Ba	0.254	0.096	/
3	Cd	0.00050	0.000072	0.1
4	Cr	0.0069	0.0017	1.5
5	Total As	5.42	0.103	0.5
6	Total P	1.2	0.4	/
7	COD_{Cr}	45.7	20.0	60
8	BOD_5	29.7	10.2	20
9	F^-	0.58	0.31	10
10	SS	28.3	9.3	20
11	LAS	0.032	0.023	5
12	$NH_3 - N$	2.84	0.53	15
13	pH	6.8	7.1	6—9

References:

Barin I, Knacke O, Kubachewski O, 1991. Thermochemical properties of inorganic substances [M]. Berlin: Springer.

Brookman R P, Flaherty E, Weadock D K, 1988. Semiconductor International[J]. Oct. 88—93.

Dean J A, 1985. Lange's handbook of chemistry[M]. 13th ed. McGraw-Hill Book Co.

The Chinese National Discharge Standards, 1996. GB 16297—1996[S].

The Chinese National Discharge Standards, 1996, GB 8978—1996[S].

Wen R M, Liang J W, Zhou S J *et al*., 1997. Measurement of trace phosphorus in dichlorosilane by high-temperature hydrogen reduction-gas chromatography [J]. J Chromatogr A, 757: 319—323.

Wen R M, 1998. Determination of trace anions in high purity gases in semiconductor process [J]. J Chromatogr Sci[J], 36:579—582.

Yang H, Liang J W, 1992. Thermodynamic and fluid dynamic analysis of GaAs MOVPE process [C]. Proceedings of the 1st Pacific Rim international conference on advanced materials and processing (Shi C D, Scott A, Eds). TMS. 541—545.