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Control of arsenic pollution from waste gases during fabrication of semiconductor

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Abstract— The abatement technology of toxic arsenic pollution during fabrication of semiconductor materials and devices has been studied.

Keywords: Semiconductors; arsenic; pollution; abatement.

1 Introduction

The development of high technology has caused in a deteriorating environmental pollution. For example, many kinds of toxic gases are used for fabrication of semiconductor materials and devices. Many of these speciality gases are flammable, explosive, readily hydrolyzable, and with very low value of IDLH (immediately dangerous to life or health), therefore the pollution control of them is difficult. Due to the continued expansion of electronic industry, the chemical pollution becomes severe. We analysed the waste gases from a certain region for last eight years and the data showed that the arsenic concentration in atmosphere from less than 0.001 mg/m^3 in 1984 increased to 0.12 mg/m^3 in 1992. These mean that the toxic arsenic emissions from plants increase rapidly and cause serious pollution.

2 Arsenic pollution during fabrication of semiconductor compounds

Methods used for fabrication of semiconductor compounds are horizontal Bridgman method, liquid encapsulated Czochralski method (LEC), molecular beam epitaxy (MBE), chemical beam epitaxy (CBE), liquid phase epitaxy (LPE), vapor phase epitaxy (VPE) and metalorganic vapor phase epitaxy (MOVPE). During above mentioned processes, the following sources and dopants are used: elements including As, P, Ga, Al and In, chlorides including $AsCl_3$, PCl_3; hydrides including AsH_3, PH_3, H_2Se. H_2S; metalorganics including $Ga(CH_3)_3$, $Ga(C_2H_5)_3$, $Al(CH_3)_3$, $Al(C_2H_5)_3$, $Zn(CH_3)_2$, $In(C_2H_5)_3$ and $Zn(C_2H_5)_2$. In addition to these a wide variety of chemicals and organic solvents are used for semiconductor compounds fabrication. All these hazardous materials may be emitted into atmosphere along vent tubes with tail gases, causing serious environment pollution. We will illustrate the process taking MOVPE as an example.

MOVPE is a kind of newly developed technology for growth of electronic materials including III-V and II-VI compounds and high temperature superconductor films. MOVPE technology is able to grow high purity materials with abrupt transition region and good uniformity. High quality quantum well and super lattice materials can be grown and high speed electronic devices, lasers and detectors can be fabricated successfully by MOVPE.

During MOVPE process product and unreacted gases are emitted as effluent gases.

The total reaction is

$$Ga(CH_3) + AsH_3 \longrightarrow GaAs + CH_4 \ ,$$

$$In(CH)_3 + PH_3 \longrightarrow InP + CH_4 .$$

The detail of reaction is (Schlyer, 1977)

$$Ga(CH_3)_3 \xrightarrow{\text{substrate surface}} Ga(CH_3)_3^* \ ,$$

$$AsH_3 \xrightarrow{\text{substrate surface}} AsH_3^*,$$

$$Ga(CH_3)_3^* + AsH_3^* \longrightarrow (CH_3)_2GaAsH_2 + CH_4,$$

$$(CH_3)_2GaAsH_2 \longrightarrow (CH_3)GaAsH + CH_4 \ ,$$

$$(CH_3)GaAsH \longrightarrow GaAs + CH_4 \ .$$

As a rule, the excess quantity of AsH_3 is used, therefore effluent gases contain AsH_3, CH_4, H_2Se (dopant) etc. Arsenic compounds can steady exist in atmosphere as vapor or aerosol. The equipment of MOVPE is shown in Fig. 1.

3 Abatement process design

Generally the abatement technologies used in the world are wet scrubbers including spray tower, packed tower etc, dry adsorption including adsorption and chemisorption, combustion and decomposition.

Twofold abatement for toxic gases released from semiconductor were used in this study.

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* Means condensed form on substrate surface.

First step: Thermal decomposition and absorption with $KMnO_4$ + NaOH or H_2O_2 + NaOH solution.

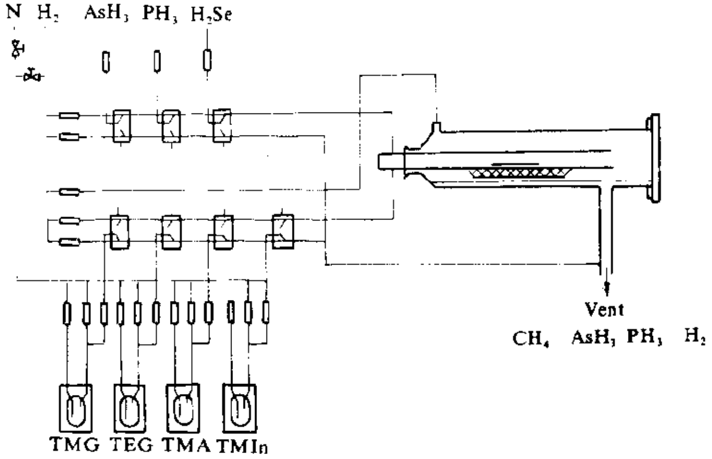

Fig.1 The equipment of MOVPE (sketch map)

Second step: Abatement of gases from the first step by using spray-packed tower in which the scrubbing liquid flows in opposite direction to the flow of waste gas. Three kinds of scrubbing liquids were used for various waste gases. The spray-packed tower is effective for controlling of vapors containing acid radicals, such as F^-, Cl^-, SO_4^{2-}, PO_4^{3-} and AsO_4^{3-}. Satisfied results were obtained with these methods.

According to the standard issued by Beijing Environmental Protection Agency, the acceptable level of emission is equal to or less than 0.04 mg/m^3 near a chimney exit being 42 meters high. In the first phase experiment, the effluent gases have been treated by different scrubbing liquid, e.g. $KMnO_4$, KOH, KIO_3, H_2SO_4, H_2O_2 and solid activated charcoal adsorbent. The concentration of AsH_3 were analyzed before and after abatement.

4 Results of AsH_3 abatement by different types of scrubbers

The results of first phase experiment are shown in Table 1.

Considering the high priced HIO_3, difficulty of charcoal activation and low abatement effectiveness of H_2SO_4, in the second phase we have designed an abatement process by using ten spray-packed towers. The scrubbing liquids are $KMnO_4$, H_2O_2, NaOH and their mixing solution.

Table 1 Comparison of AsH_3 abatement with different types of scrubbing materials

Scrubbing materials	AsH_3 concentration, mg/m^3 Before	After	Abatement percentage, %
1. 5% $KMnO_4$ + 1% NaOH	2.54	0.03	98
2. 5% H_2O_2 + 1% NaOH	0.42	0.03	92
3. 2% NaOH	0.49	0.022	95.4
4. 5% HIO_3	0.11	0.01	90.7
5. 1 + 2 in series	6.54	0.038	99.4
6. Activated charcoal and $KMnO_4$ + NaOH	0.172	0.01	94.7
7. Activated charcoal	0.018	0.01	44
8. 2% H_2SO_4	0.44	0.32	27

The flow chart of abatement by using ten spray towers is shown in Fig.2.

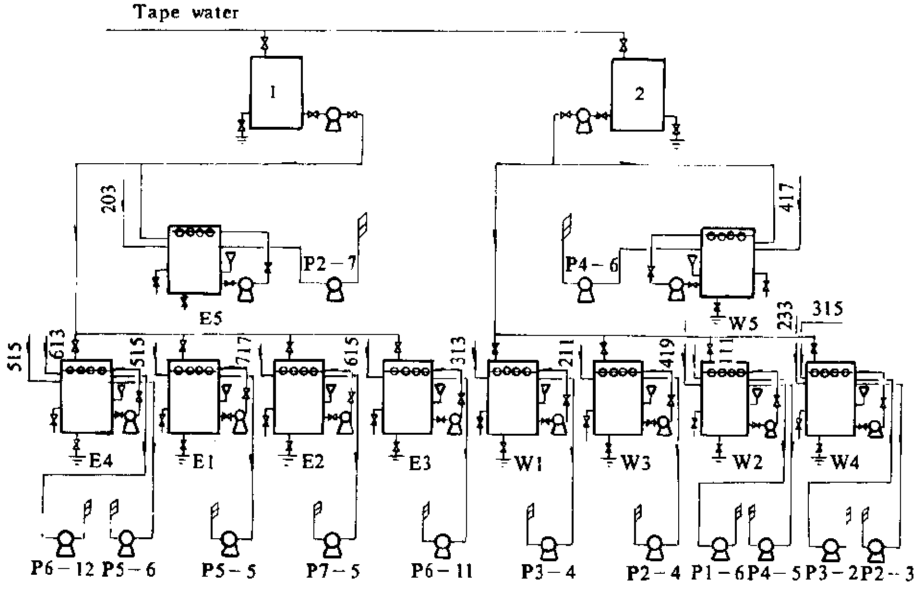

Fig. 2 Flow chart of abatement by using ten spray-packed tower (sketch map)
1.2: solution box

The result of arsenic abatement by using ten spray-packed towers are shown in Table 2.

Table 2 **Abatement effectiveness by using ten spray-packed towers**

		Tower number				
		W1	W2	W3	W4	W5
Conc. of As.	Before	0.46	0.23	0.01	0.18	0.324
$\mathrm{mg/m^3}$	After	0.016	0.04	<0.01	0.025	0.034
Abatement percent, %		96.5	81.7		86.1	89.4
		E1	E2	E3	E4	E5
Conc. of As,	Before	<0.01	<0.01	0.31	0.175	0.164
$\mathrm{mg/m^3}$	After	<0.01	<0.01	0.021	0.011	0.023
Abatement percent, %				93.2	93.7	85.9

The data showed that after abatement the concentration of arsenic satisfied the standard of acceptable level of emission.

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