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Direct analysis of ultra-trace semiconductor gas by inductively coupled plasma mass spectrometry coupled with gas to particle conversion-gas exchange technique

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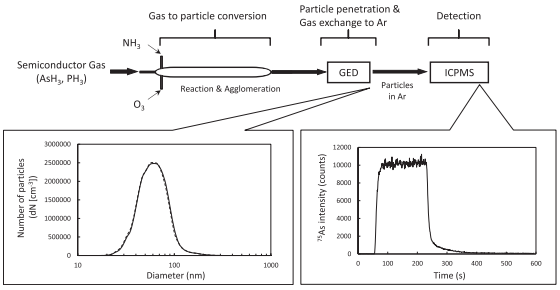
HIGHLIGHTS

- Direct analysis of AsH_3 and PH_3 in ambient air was examined by GPD-GED-ICPMS.
- Particle size distribution of generated particles from GPD was evaluated by SMPS.
- Stable ICPMS signals were obtained with continuous gas introduction.
- Linear regression line was obtained between ICPMS intensity vs gas concentration.
- Sufficiently lower LODs were obtained with respect to required concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

An inductively coupled plasma mass spectrometry (ICPMS) coupled with gas to particle conversion-gas exchange technique was applied to the direct analysis of ultra-trace semiconductor gas in ambient air. The ultra-trace semiconductor gases such as arsine (AsH_3) and phosphine (PH_3) were converted to particles by reaction with ozone (O_3) and ammonia (NH_3) gases within a gas to particle conversion device (GPD). The converted particles were directly introduced and measured by ICPMS through a gas exchange device (GED), which could penetrate the particles as well as exchange to Ar from either non-reacted gases such as an air or remaining gases of O_3 and NH_3. The particle size distribution of converted particles was measured by scanning mobility particle sizer (SMPS) and the results supported the elucidation of particle agglomeration between the particle converted from semiconductor gas and the particle of ammonium nitrate (NH_4NO_3) which was produced as major particle in GPD. Stable time-resolved signals from AsH_3 and PH_3 in air were obtained by GPD-GED-ICPMS with continuous gas introduction; however, the slightly larger fluctuation, which could be due to the ionization fluctuation of particles in ICP, was observed compared to that of metal carbonyl gas in Ar introduced directly into ICPMS. The linear regression lines were obtained and the limits of detection (LODs) of 1.5 pL L^{-1} and 2.4 nL L^{-1} for AsH_3 and PH_3, respectively, were estimated. Since these LODs revealed sufficiently lower values than the measurement concentrations required from

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semiconductor industry such as 0.5 nL L^{-1} and 30 nL L^{-1} for AsH_3 and PH_3, respectively, the GPD-GED-ICPMS could be useful for direct and high sensitive analysis of ultra-trace semiconductor gas in air.

1. Introduction

A semiconductor is widely used for electric and electronics equipment in our living tools such as computer and cellular phone, and the market of the semiconductor industry is huge. The ultra-pure semiconductor gases such as arsine (AsH_3), phosphine (PH_3) and so on, are well known to be used in the synthesis of semiconducting materials related to microelectronics and solid-state lasers. For example, AsH_3 is used to make the compound semiconductors such as GaAs and InAs. The PH_3 is also used as a doping gas for manufacturing compound semiconductors such as InGaP. Small amounts of AsH_3 and PH_3 are also well known to be used as n-dopants for silicon and germanium. On the other hands, these gases show serious toxicity with respect to human being. The exposure of AsH_3 may lead to renal failure and is a recognized carcinogen. The immediately dangerous to life or health concentration (IDLH) cautioned by National Institute for Occupational Safety and Health (NIOSH) is 3 μL L^{-1} [1]. While AsH_3 can be detected by its garlic-like odour at concentrations above 0.5 μL L^{-1}, this is well above the current American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) of 0.005 μL L^{-1} in time weighted average (TWA) [2]. The exposure of PH_3 may also cause acute systematic toxicity and their exposure limits of ACGIH-TLV and IDLH are 0.3 μL L^{-1} and 50 μL L^{-1}, respectively [1,2]. From the toxicity points of view, these gases should be monitored in working and living environments.

In order to control the quality of semiconductor products as well as to estimate the risk concerned with respect to the working and living environment from manufacturing process including exhaust gas, direct and high sensitive analysis as well as real-time monitoring of ultra-trace semiconductor gas in ambient air is required in semiconductor manufacturing facilities.

However, the current analytical techniques for AsH_3 and PH_3 indicated in NIOSH manual of analytical methods are not direct one. The techniques consisted of both sampling and analytical methods such as the sorbent tube and the atomic absorption spectrometry with graphite furnace (GF-AAS) for AsH_3 or the ultraviolet–visible (UV-VIS) spectrometer for PH_3, respectively [3,4]. A gas chromatography (GC) coupled with nitrogen phosphorus detector (NPD) and thermal desorption GC mass spectrometry (TD-GC-MS) were also reported for the analysis of PH_3 in air [5–7]. However, they were not direct analytical methods since the sampling methods such as a cryogenic trap or an adsorbent tube were used. An inductively coupled plasma mass spectrometry (ICPMS) [8,9], which is widely accepted for trace element analysis due to its high sensitivity, multielement capability and wide linear dynamic range, is expected as an effective analytical method, and it was applied for the AsH_3 and PH_3 analysis with a cryogenic trap [10,11]. A hydride generation (HG)-ICPMS can be also applied for trace level of As analysis [12–16]. However, the ICPMS also never perform the direct analysis unless the direct introduction of the gas in ambient air is carried out instead of the sampling method.

In order to achieve direct and high sensitive detections as well as real-time monitoring, a gas to particle conversion-gas exchange technique [17] coupled with ICPMS was newly proposed for direct analysis of ultra-trace metallic compound gas and its figures of merit were successfully demonstrated with respect to metal carbonyl gases such as $Cr(CO)_6$, $W(CO)_6$ and $Mo(CO)_6$ in our previous study [18]. The reaction mechanism of the gas to particle conversion is based on either oxidation of metal carbonyl gas by ozone (O_3) or agglomeration of metal oxide with ammonium nitrate (NH_4NO_3) which is generated by the reaction of O_3 and ammonia (NH_3) gases in a gas to particle conversion device (GPD) [17,18]. To separate the reaction gasses (remaining O_3 and NH_3) as well as non-reacted gases such as nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2) in air from the converted particles, a gas exchange device (GED) [19–27] was used and the particles in argon, otherwise ICP can not be maintained, were directly introduced and measured by ICPMS. Since the technique detects the metallic compound gas directly without sampling methods, it can be applied to the real-time monitoring.

In the present study, we applied the GPD-GED-ICPMS to the direct analysis of semiconductor gases of AsH_3 and PH_3 in ambient air. This is an extended application from our previous study [18], and the analytical capability such as signal stability as well as limits of detection (LODs) and the reaction mechanisms including particle size distribution produced in GPD were examined.

2. Experimental

2.1. Instruments

Fig. 1 shows the schematic diagram of the experimental setup of GPD-GED-ICPMS. The sample gas containing semiconductor gases of AsH_3 and PH_3 in filtered air are introduced into the reaction chamber in GPD where it is mixed with O_3 and NH_3 [17,18]. The 1% O_3 is supplied by an ozonator which is equipped with the GPD. The required NH_3 gas was obtained from 2% ammonia solution prepared from 20% NH_3 solution (Ultrapur, Kanto Chemical Co. Inc., Japan) by bubbling Ar through a PFA bottle. Though the NH_3 gas could be obtained by a gas cylinder, *e.g.*, NH_3 gas diluted in Ar, we chose the NH_3 solution due to its convenience for use as well as flexibility of changing the concentration. The reaction with O_3 and NH_3 provokes the formation of particles which are online transported to the ICPMS through GED (J-Science Labo. Co. Ltd., Kyoto, Japan) [19–27]. Because the GED consists of two concentric glass tubes with pores of 0.07 μm in diameter it acts as a membrane. The introduced air and the remaining gases from the reaction (O_3 and NH_3) are exchanged by Ar introduced as sweep gas into the GED across the membrane. Thus, the particles converted by GPD and stabilized in Ar were introduced directly into the ICPMS. Due to the absence of air, O_3 and NH_3, the ICP can be maintained stably and operated at parameters commonly used in ICPMS. The mixed metal carbonyl gases of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ were obtained by a metal standard gas generator (MSG^2, J-Science Labo. Co. Ltd., Kyoto, Japan) [28,29] for the sake of optimization of support gas for ICPMS as shown in Fig. 1. The measurements of elements were carried out using an Agilent 7500cs ICPMS (Agilent Technologies Inc., Tokyo, Japan) without the use of the collision gas. The size distribution of converted particles, which were introduced into the ICPMS, was also measured by scanning mobility particle sizer, GRIMM SMPS + C systems (GRIMM Aerosol Technik GmbH & Co. KG) as also shown in Fig. 1. The SMPS comprises a condensation particle counter (CPC) as a detector as well as a differential mobility