Technology

Removal of Ultratrace Total Organic Contamination (TOC) in Inert Purge Gas Using NANOCHEM® INX-Plus Purifier: Low ppt Quantification of TOC by Preconcentration-GC/MS Technique

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Ultra high purity purge gases are required for advanced lithography processes such as Extreme Ultraviolet Lithography (EUVL) in order to prevent contamination of the imaging optics. In this work, a NANOCHEM® INX-Plus purifier designed for removing Total Organic Contamination (TOC) is evaluated with the aim of removing TOC in argon gas to low ppt levels. To achieve this, an ultratrace analytical method using a preconcentration-GC/MS technique has been developed with a lower detection limit of <1ppt for TOC (amu >100). Removal of 500 ppt TOC (amu >100) in argon gas to less than 1 ppt is demonstrated with the NANOCHEM® INX-Plus purifier by monitoring the outlet of the purifier with the preconcentration-GC/MS unit.

1. Introduction

EUVL technology is the front runner for next generation critical dimension imaging to pursue Moore's law. The leading semiconductor foundries have ramped up the use of EUVL tools rapidly in the last few years and the demand for tools will keep growing.

Organic and/or particulate contamination can not only negatively impact the lifetime of the imaging optics, but also result in defects in the transferred image[1-2]. For these reasons, ultra high purity inert purge gases are required to prevent contamination of the imaging optics in EUVL tools. Specifically, to ensure gas purity, point-of-use purifiers are typically installed in the gas supply system upstream of the optics compartment. Thus, a point-of-use purifier with the capability of removing TOC in purge gases to low ppt levels is necessary.

In this work, we discuss and present results on an ultratrace analytical method using a preconcentration-GC/MS technique and the performance of a NANOCHEM® INX-Plus purifier for removal of TOC in argon gas.

2. NANOCHEM® Purifier[3)]

NANOCHEM® purifiers have led the semiconductor industry in state-of-the-art gas purification technology since the early 1980's. NANOCHEM® purifiers have proven to remove impurities to the lowest levels in the industry, typically below the lower detection limits of the most sophisticated instrumentation. For many gases, ppt levels of H_2O, O_2, CO_2, and CO are achieved. Purifier end point detection is also available for many applications. For point-of-use requirements, NANOCHEM® purifiers are suitable for ensuring gas purity at the process tool if installed on the gas stick immediately before the MFC or the chamber.

Fig. 1 NANOCHEM® point-of-use purifier

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3. Ultratrace TOC Analysis

3.1 Experimental

The experiment was performed using a BTEX (benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene) gas standard as a benchmark for TOC. The experimental equipment used to analyze BTEX in argon gas is shown in Fig. 2. The BTEX standard was diluted to 12.5, 18.75 and 25.0 ppt (vol.) for the method evaluation. After the dilution, BTEX was trapped in the preconcentration unit. Finally, the trapped BTEX components were transferred to the cryo-focusing trap at the front of the GC column, and then injected into the GC/MS. The detection limit, repeatability and linearity for BTEX injections were evaluated.

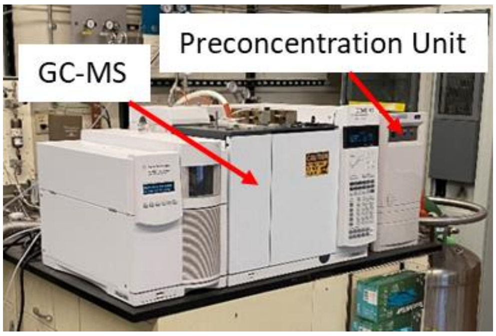

Fig. 2 Preconcentration-GC/MS system

3.2 Results

The Total Ion Current (TIC) chromatogram resulting from a 25.0 ppt BTEX sample is shown in Fig. 3. It shows that all BTEX components are detected with sufficient signal-to-noise. The detection limit of toluene (amu =92.14) calculated using peak height and the baseline noise level, is less than 2 ppt. The detection limit of ethylbenzene (amu =106.17) also calculated using peak height and the baseline noise level, is less than 1 ppt. Good linearity of R^2 >0.99 and good reproducibility of <5 % relative standard deviation are achieved for all BTEX components. In summary, the detection capability of 2 ppt for TOC (amu <100) and 1 ppt for TOC (amu >100) were demonstrated with the preconcentration-GC/MS technique.

In our previous work[4], the existing hydrocarbon purifier only evaluated challenge concentrations down to the detection limit of the APIMS analyzer. However this preconcentration-GC/MS technique enables expanded analytical capability to low ppt levels to prove the performance of purifier products.

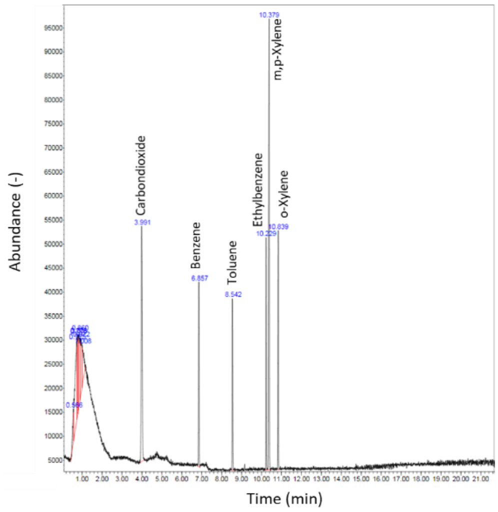

Fig. 3 Chromatogram resulting from 25.0 ppt of BTEX

4. Purifier Material Testing

4.1 Experimental

The NANOCHEM® INX-Plus purifier (WK-75F) was prepared and installed in the system shown in Fig. 4. BTEX as a benchmark of TOC can be flowed via either the bypass or the purifier lines. The purifier material was tested according to the following procedure at room temperature. To make the calibration curve for low ppt levels and verify the challenge concentration, the BTEX standard was diluted with the manifold and flowed via the bypass. The actual challenge concentration in argon gas was analyzed by the preconcentration-GC/MS system. For the purifier testing, the challenge stream was switched from the bypass to the purifier. The purifier material was tested over a period of 24 hours at 100 sccm to determine the efficiency of removing TOC in argon gas. Once the testing was completed, the challenge stream was switched from the purifier to the bypass to verify the challenge concentration again.

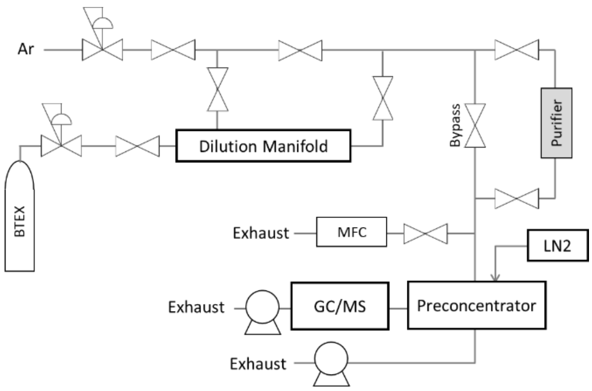

Fig. 4 Schematic of the manifold used to test purifier material performance for removing TOC

4.2 Results

The four calibration points including the blank (purified argon gas) and the concentration of ethylbenzene as an example of BTEX during the efficiency testing, is shown in Fig. 5. The calibration points show good detection and reproducibility at low ppt levels. The initial concentration of ethylbenzene in argon gas prior to the purification was about 505 ppt. After switching the challenge stream through the purifier, the outlet concentration of ethylbenzene and the other BTEX components were less than the detection limit and maintained the efficiency for 6 hours of testing on this day. The outlet concentration remained below the detection limit on the following day while the challenge concentration was held constant. After that, the challenge stream was switched from the purifier to the bypass, and the challenge concentration of ethylbenzene was verified to be about 506 ppt. From these data, the purifier material tested shows the removal efficiency of <2 ppt for TOC (amu <100) and <1 ppt for TOC (amu >100).

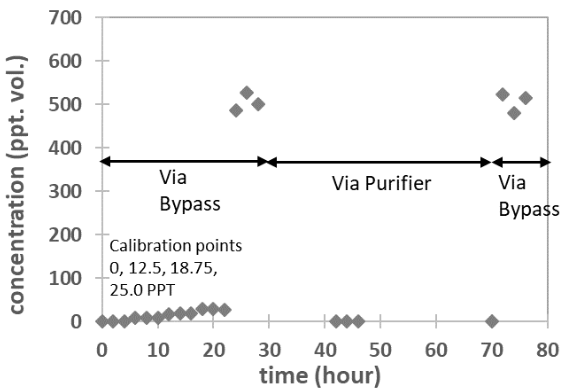

Fig. 5 Ethylbenzene concentration in argon gas during the purifier material efficiency testing

5. Conclusions

An ultratrace analytical method using a preconcentration-GC/MS technique has been developed. This state-of-the-art method shows a detection limit of less than 1 ppt for TOC (amu >100) and sufficient accuracy. In addition, it has been used to show that the NANOCHEM® INX-Plus purifier is capable of removing TOC (amu >100) in argon gas to less than 1 ppt, which is a very positive outcome. The results meet the chemical cleanliness requirement for purge gas purity used in EUVL tools. Therefore the NANOCHEM® INX-Plus purifier can be proposed as an ultra high purity point-of-use purifier for EUVL technology.

Reference

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2) Tyler R. Mowll, et al., *Extreme Ultraviolet (EUV) Lithography IV Volume 8679*, SPIE, 86792D1-86762D6, 2013
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4) Hans Funke, Mark Raynor, et al., *SEMI Technical Symposium Innovation in Semiconductor Manufacturing*, SEMICON West, 733-739, 2001