INTRODUCTION

Trace levels of organic contaminants that can be present in process gases due to intrinsic impurities or component out gassing are potentially incorporated into semiconductor devices during film growth. Device performance can be adversely affected by these impurities. A newly developed inorganic based purifier material removes these non-methane carbon-containing compounds from reactive and non-reactive processes gases to sub-ppb levels, similar to the best heated getter technology.

BACKGROUND

To date, commercial purifier materials that operate at room temperature have a very limited potential for removal of non-methane hydrocarbons from reactive and non-reactive gas matrices. The increasing purity requirements in the semiconductor industry for new processes such as silicon epi or front-end etch, however, creates a demand for the purification of even trace levels of organic species in the process chamber.

FINDINGS

An inorganic based high surface area material was modified and purified to guarantee emission free service even in reactive gas service. Emission free performance of the material was verified by passing ultra clean gases through the purifier bed and studying the effluent stream with APIMS, GC-DID, and FTIR. The absence of even ultra low emissions is one of the key requirements in any new purifier development, especially in reactive gas service. An example is the release of toxic carbonyl components from nickel and iron metal-containing CO purifiers.

Hydrocarbon removal efficiency and capacities of the new material were evaluated in inert and ammonia matrix. APIMS measurements with C4 and C6 challenges indicated efficiencies below the detection limits of the instrument (low ppt levels). The capacity of ~15 l/l purifier material is sufficient to guarantee hydrocarbon free gases even with small bed volumes, since carbon containing species are typically not found in high quantities in semiconductor-grade gases. Measurements in ammonia were used as an example to demonstrate the performance in a reactive matrix gas. Aliphatic and aromatic hydrocarbons challenges in the ppm range were removed below the detection limits of the FTIR and GC-DID instruments (low ppb range) used for the studies. Even at temperatures above 200 °C, the materials has a strong affinity for the adsorbed hydrocarbon impurities and no release was found.

High efficiency for other impurities such as moisture were also verified. Limited capacities for those impurities, however, due to the specific design of the material for hydrocarbon removal, suggest the combination with traditional purifier materials such as organometallic resins to obtain a purifier bed that removes typical atmospheric oxygenated contaminants as well as hydrocarbon species.

Hans Funke, Dan Fraenkel, Jon Welchans, David Lawrence, Mark Raynor, and Virginia Houlding
Matheson Tri-Gas, Inc., Advanced Technology Center, 1861 Lefthand Circle, Longmont, CO 80501
A new non-methane hydrocarbon purifier that operates at room temperature was developed from a high surface area inorganic material. The purifier removes hydrocarbons from inert matrices below the detection limits of APIMS. Measurements in ammonia matrix showed efficiencies below the detection limits of FTIR and GC-DID. The material has high capacities and can be used as a stand-alone purifier or in combination with other purifier materials to obtain a universal purifier bed.
New Purifier Material for Removal of Trace Organic Contaminants from Process Gases

Hans Funke, Dan Fraenkel, John Welchhans, Dave Lawrence, Mark Raynor, and Virginia Houlding

Matheson Tri-Gas, ATC Longmont

Trace hydrocarbon impurities - from where?

• source gases (cylinders, raw material)
• system component outgassing
  (Pump Oil, MFC’s, valves, lines...)

Why are they problematic?

decreased device performance in Si processes
  • poly-Si, Si$_3$N$_4$, well formation, field oxides, EPI-Si, Al deposition, ...
  • carbon as dopant?
Current Purifier Technologies

organometallic resins
  - HC's not removed
functionalized inorganic supports
  - HC's not removed
oxide based inorganic materials
  - NM-HC's removed
heated Getters (e.g. Zr/Fe/V-based)
  - All HC's removed

n-Hexane Removal Efficiency (N₂ matrix, APIMS)

- 5 ppb challenge
- 0.6 ppb challenge
- ~5 ppb challenge
- 6300 ppb (6.3 ppm) challenge
- 630 ppb challenge
- 49 ppb challenge
n-Hexane Removal Capacity
(86 ppm Challenge, N₂ matrix, APIMS)

[Graph showing n-Hexane concentration over time]

Capacity ~ 15 l/l

Aromatics Removal from Contaminated N₂ Stream

[Graph showing APIMS response over time]

HC purifier

m/z=106

m/z=78
APIMS Spectra Comparison:
New HC Purifier vs. Heated Getter

- low level HC contaminated N₂
- heated getter
- hydrocarbon purifier
- heated getter - hydrocarbon purifier

Ethylbenzene Removal from NH₃ (FTIR)

- bypass
- D/L ~50 ppb through carbon bed

Mark Raynor, Matheson Tri-Gas - Slide 7
Mark Raynor, Matheson Tri-Gas - Slide 8
n-Butane Removal from NH₃ (FTIR)

Summary

- new inorganic NM-hydrocarbon purifier
- inert and reactive process gases
- high surface area - high capacity (15 l/l C₆)
- operates at room temperature
- stand-alone or combined w/ other materials
- high efficiency verified for C₄ and C₆