

200001608-9

1 21 MAR 2000

Title

Method of Detecting Amines in the Sub Part Per Billion Range

Related Applications

This application is related to copending U.S. patent application, serial no.09/283437 , filed on the same day, entitled "SUB PART PER BILLION AMINE DETECTION APPARATUS" assigned to the present assignee and which is incorporated by reference in its entirety.

Field of the invention

This invention is directed to the detection of ambient air constituents in the parts per billion range in real time and more particularly to the detection of amines, in situ, on a parts per billion scale in real time.

BACKGROUND OF THE INVENTION

In different experimental and industrial processing environments, especially those associated with the use and manufacture of deep UV photoresists, the presence of some substances, gaseous or liquid, whether the substances be byproducts or not, can have a detrimental effect on the desired

chemical processes being undertaken. Alternately, ambient environmental conditions, whether they be transitory or continuous, could adversely affect the processing environment.

For example, certain segments of the semiconductor industry have moved to using certain types of photoresists (resists) in the processing of semiconductor wafers. One class of resists, called Deep UV (DUV) resists have become more popular as feature size on wafers decreases. Generally, DUV resists are resists that are photoactive in the spectrum of light of $< 300 \text{ nm}$. DUV resists can have variable specific chemical forms. However, they tend to share a common characteristic that enhances their viability. DUV resists tend to be acid based and the presence of bases or compounds that can act like bases reduces their photoactivity. The presence of amines, RNH_x , in a processing environment can cause decreases in the photoactivity of DUV resists when the concentrations are as little as 6 parts per billion (ppb). It can be difficult to isolate and detect the source of RNH_x contamination in a manufacturing environment. The human skin can emit RNH_x as high as parts per million. Therefore an operator waving their ungloved hand near the resist could cause an adverse reaction. Alternatively, there could be a small long term contamination point in a small, specific area of the processing environment that could cause the adverse reactions. It is difficult, costly, slow and sometimes nearly impossible to

try to determine the location of the source and extent of RNH_x contamination during any one interval, even when a disaster/ line down situation occurs.

Traditionally, manufacturers have used a series of very large, very expensive filters for the clean room air to "prevent" contamination. The filters are changed at manufacturer defined intervals, usually without knowledge of whether the filters are still effective, or if not, when they lost their effectiveness. Typically, testing involves sampling vials that are left in the processing area for a user defined period of time. The vials are removed and sent to a lab. Testing has in the past consisted of sending the water samples with the trapped ambient air to labs that can measure RNH_x concentrations in the sub ppb range. The testing is very time consuming (24 - 36 hours after receipt of samples) and a finding of contamination means that product produced during the interval between sample collection and results, often 36 - 48 hours, might be contaminated. There is no way to know how much of the product, if any, is contaminated. Also, the sample collection method typically gives an average reading over the interval that the sample was being collected. With this technique it is extremely difficult to tell whether a sudden amine concentration spike or a lower, more continuous amine site is responsible for the reading obtained from the testing labs.

One of the difficulties with doing a real time, in situ test for the concentrations of RNH_x is that one of the more common forms of RNH_x present in the processing environment is NH_3 . Using one of the more popular methods of measurement, mass spectrometry, might not render adequate resolution at the sub ppb level in this instance. NH_3 , with an atomic weight of 17, has a peak that is located in the same mass channel as the peak for OH^+ , which effectively masks the NH_3 . Since H_2O forms OH^+ at much higher concentrations in the environment, and the signal from the sub ppb levels of NH_3 are effectively masked.

There are methods that measure the concentration of amines indirectly. Methods to determine amine concentration include a method whereby amines, particularly NH_3 , (a first gas) are converted to NO (a second gas) and then converted to a final gas, NO_2^* , where NO_2^* is in an excited state and the quantity of that gas is measured by, for example, the light emission. The level of the final gas is then monitored. While this method can be an effective way of monitoring the level of amines, there can be limitations associated with the method. If the second gas itself is also present before the conversion then the measurement is a combination of the background NO (second gas) concentration and the amine (first gas) concentration. The exact amount of amine in the system is never known. Using this information can lead to situations where a processing operation is interrupted

unnecessarily or prematurely. Especially in situations where only one of the first and second gas is detrimental to the process.

An unnecessary interruption can occur when the concentration of amine is low and the concentration of the second gas is high. The system is unable to distinguish between a high reading caused by high amine concentration and a high reading caused by a high second gas concentration (and a low amine concentration) so the process is interrupted even when the process might not have been affected by the actual amine concentration. For example, for illustrative purposes only, if each 1 part per billion (ppb) of amine converts to 1 ppb of the second gas and 6 ppb of amine could cause a detrimental effect, then 6 ppb of the second gas could contain enough amine to cause a detrimental effect. However, it should be intuitive that 6 ppb of the second gas could also be caused by 1 ppb of amine and 5 ppb of the second gas itself. In this case, any interruption of the process would be premature unnecessary and costly. It is also important to note that the catalyst and temperature used to convert amine to NO can also convert NO₂ to NO. Since NO₂ and NO both exist in the ambient air, the converted NO is the sum of the concentrations of amines and NO and NO₂. Thus there remains a need for a method for calculating the part per billion concentrations of amine specifically in the processing system.

Summary of the Invention

It is therefore an object of the present invention to provide a method for measuring the concentration of ambient air constituents on the part per billion level. It is also an object of the present invention to provide a method for measuring the concentration of amines in the part per billion range. It is a further object of the present invention to provide a method for measuring the concentration of amines in the part per billion range in the presence of OH^+ .

In accordance with the above listed and other objects, we claim a method of determining an airborne gaseous constituent concentration in a gaseous compound having at least three constituents, comprising the steps of:

- a. converting at least a first gaseous constituent of a first gaseous compound to a second gas in a first converter in a first conversion;
- b. converting at least a third gaseous constituent of the first gaseous compound to a second gas in a second converter in a second conversion;
- c. measuring a first concentration of the second gas after the first conversion;

- d. measuring a second concentration of the second gas after the second conversion.

Description of the Preferred Embodiments

Since airborne amines are present and can be introduced in many ways (i.e. by human skin) in concentrations far greater than the detrimental limit in processing environments, especially DUV lithography area, they must be closely monitored. As stated earlier, since it is difficult to directly measure amines at such low concentrations in real time and in situ it is necessary to determine the concentration of amines indirectly. For purposes of illustration only, amine will first be converted to nitric oxide (NO), as part of the Oswald process, shown below:



There are a number of ways that the concentration of NO (g) can be determined. However, using only equation (1) we cannot determine the concentration of amines because there is no reference point. Therefore we must also measure the concentration of NO without converting the amines and compare the values, because NO₂ is also present in the processing environment. The NO₂ will be converted to NO during the same

interval that the amines are being converted to NO.

In a typical processing environment containing at least RNH_x , NO_2 , and NO, the concentration of amines (RNH_x) can be represented by the following series of equations:

$$[\text{RNH}_x] = [\text{NO}_y] - [\text{NO}_x] \quad (2)$$

$$[\text{NO}_x] = [\text{NO}_2] + [\text{NO}] \quad (3)$$

$$[\text{NO}_y] = [\text{RNH}_x] + [\text{NO}_2] + [\text{NO}] \quad (4).$$

In order to calculate NO_y and NO_x , using equations (3), and (4), it is necessary to have a process which converts NO_2 to NO without converting amines to NO. Generally, the processing steps for the method are given below:

- 1) extract amines, NO_2 and NO from the ambient processing environment
- 2) convert amines and NO_2 to NO in a first chemical reaction (equation 4), preferably in a first catalytic converter
- 3) convert ambient NO_2 to NO in a second chemical reaction (equation 3) where the amines are kept intact, preferably in a second catalytic converter
- 4) measure the amount of NO from the first chemical reaction, which preferably gives the total

concentration represented by $[\text{NO}_y]$

- 5) measure the amount of NO from the second chemical reaction, which preferably gives the total concentration represented by $[\text{NO}_x]$
- 6) compare the amount of NO from the first chemical reaction to the amount of NO from the second chemical reaction, which preferably will give the absolute value of $[\text{NO}_y] - [\text{NO}_x]$.

The measurement in steps 4 and 5 can be done by any means known in the art, including chemiluminescence, where the NO is converted to an excited NO_2^* molecule and the resulting emitted photons are measured.

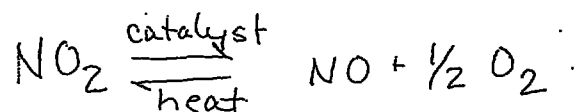
CONVERSION OF AMINES AND NO_2 TO NITRIC OXIDE

In a preferred embodiment, the amine in the gas stream enters a catalytic converter, for example an array of stainless steel tubing having a sufficiently large surface area for a sufficient amount of amine molecules to be converted, which is heated to about 800C. The reaction in equation (1) will occur. Additionally at that temperature, the NO_2 present will convert to NO. The reaction sequence is shown below in the next section. Typically, the temperature necessary to drive the $\text{NO}_2 \rightarrow \text{NO}$

reaction is lower than the temperature which drives the amine - NO reaction. However, it is difficult to give a temperature for the conversion since the conversion is a function of the temperature and the catalyst chosen. In a preferred embodiment, the conversions would take place in an ECOPHYSICS, AG of Dürnten Switzerland catalytic converters.

CONVERSION OF NO₂ TO NITRIC OXIDE

NO₂ can be converted to NO at a lower temperature in the presence of a catalyst.



There are any number of ways that the information can be used to determine the concentrations of amines. For all embodiments discussed infra, the first conversion will be performed in accordance with equation (3) identified supra. The second conversion will be performed in accordance with equation (4) identified supra.

In a first embodiment, at predetermined user defined intervals only the reaction associated with equation (4) would be performed, yielding a "processed" NO reading. Once the processed

NO reached a concentration that could contain a detrimental amount of amine then the reaction associated with equation (3) be performed at a second user defined interval to monitor the concentration of amines. It is not possible in this embodiment, using the method of the instant invention, that the calculated amount of amine be at a detrimental level without the level of "processed" NO being at least equal to the corresponding level. For example, if 6 ppb of amine is detrimental to processing and 1 ppb of amine converted to 1 ppb of NO, then it is not possible that the concentration of amine is at a detrimental level if the concentration of "processed" NO is less than 6 ppb.

In another embodiment, at user defined intervals, reactions performing the conversions identified in equations (3) and (4) would be carried out, preferably simultaneously. The difference between equations (3) and equations (4) (see equation 2 supra) would be determined and the absolute value of the result would be the concentration of amines. The operator could then react when the concentration of amines exceeded a user predefined threshold value.

While the invention has been described in terms of specific embodiments, it is evident in view of the foregoing description that numerous alternatives, modifications and variations will be apparent to those skilled in the art. Thus, the invention is

intended to encompass all such alternatives, modifications and variations which fall within the scope and spirit of the invention and the appended claims.



We claim:

1. A method of determining an airborne gaseous constituent concentration in a gaseous compound having at least three constituents, comprising the steps of:
 - a. converting at least a first gaseous constituent of a first gaseous compound to a second gas in a first converter in a first conversion;
 - b. converting at least a third gaseous constituent of the first gaseous compound to a second gas in a second converter in a second conversion;
 - c. measuring a first concentration of the second gas after the first conversion;
 - d. measuring a second concentration of the second gas after the second conversion.
2. The method according to claim 1 further comprising the step of comparing the concentration of the second gas after the first conversion to the concentration of the second gas after the second conversion.



3. The method according to claim 1 wherein the first and second conversion comprise catalytic conversions.
4. The method according to claim 1 further comprising the step of calculating the concentration of at least one of the first or the third constituent after the step of comparing.
5. The method according to claim 1 wherein the first constituent is also converted during the second conversion.
6. The method according to claim 5 wherein the third constituent is not converted during the first conversion.
7. The method according to claim 6 wherein the first gaseous constituent is NO_2 .
8. The method according to claim 7 wherein the third gaseous constituent is an amine.
9. The method according to claim 8 wherein the second gas is NO .



10. The method according to claim 1 wherein the step of measuring the first concentration comprises converting the second gas to a fourth gas.

11. The method according to claim 1 wherein the step of measuring the second concentration comprises converting the second gas constituent to a fourth gas.

12. The method according to claim 10 wherein the step of measuring the first gaseous concentration comprises measuring the light emissions.

13. The method according to claim 11 wherein the step of measuring the second gaseous concentration comprises measuring light emissions.

14. The method according to claim 10 wherein the step of measuring the second gas concentration comprises converting the second gas to a fourth gas.

15. The method according to claim 14 wherein the step of measuring the first gaseous concentration comprises measuring light emissions.



16. The method according to claim 15 wherein the step of measuring the second gaseous concentration comprises measuring light emissions.

17. The method according to claim 16 wherein the fourth gas is the second gaseous constituent.

18. The method according to claim 1 wherein the second gas is a constituent of the first gaseous compound.

19. A method of determining an airborne gaseous constituent concentration in a gaseous compound having at least a first and a second gaseous constituent, comprising the steps of:

a. determining the concentration of a second gaseous constituent of a first gaseous compound;

b. converting at least a first gaseous constituent of the first gaseous compound to the second gaseous constituent of the first gaseous compound in a first converter in a first conversion;

c. measuring the concentration of the second gaseous



14 constituent after the first conversion;

20. The method according to claim 18 further comprising the step of comparing the concentration of the second gaseous constituent after the first conversion to the concentration of the second gaseous constituent prior to the first conversion.