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A global indicator as a tool to follow airborne molecular contamination in a controlled environment

Abstract The impact of pollutants on production quality in nanotechnology necessitates reduction of contaminant levels in cleanrooms. So, devising a global airborne-pollutant indicator (GAPI) for rapid determination of the level of pollution and its danger to the process is justified. This tool used relative impact weights of the different molecules to quantify the pollution. A calculation of impact weight is proposed in this paper. Impact weights could take into account several characteristics of the molecules (molecular volume, sticking coefficient, ...). They could also be combined to be as close as possible to reality. An example of calculations of the impact of molecular volumes on air quality is given.

Keywords Air quality · Pollutant impact · Cleanroom · VOC · Measurement

Introduction

Much research has been carried out on air quality, particularly indoor air quality, for many years. Some studies have dealt with the effects of contamination on humans (irritation, odour annoyance) [1]. Just as human health and comfort must be taken into account, air quality can also be very important in industrial production.

Controlled environments are used in several applications. For example, to reduce infection rates ventilated operating rooms in orthopaedic surgery require the use of high-efficiency air-particulate filters to remove particles with diameters greater than 0.3 µm [2]. Controlled environments are also used in assisted reproductive technology laboratories. Increases in fertilisation rate and embryo quality are observed with improvement of air quality [3].

In this report, we focussed on the importance of air quality in microelectronics cleanrooms and particularly the danger to the process of airborne molecular contamination.

At the beginning of semiconductor production, only particles are regarded as problems. For example, defects in the Si film caused by metal particle contamination can affect circuit yield [4]. As device geometries based on silicon wafers continue to decrease in size, organic contaminants adsorbed by silicon surfaces are found to be major problems in the process. It has been reported that adsorption of dioctyl phthalate on an hydrophobic surface degrades oxide integrity [4]. Wafer exposure to cleanroom air induced deterioration of gate oxide reliability owing to carbon contamination [5]. Another study [6] showed that organic contaminants adsorbed on the surface of wafers had a significant effect on breakdown charge yield. The effect of the contaminants on the characteristics of the surface of the wafers is determined by the origin and/or the nature of the adsorbed compounds [7]. For example, adsorption of propanol leads to less metal oxide semiconductor degradation than valeric acid [8]. Two solutions are available for reducing contamination of the surface of the wafers—cleaning the surface or increasing air quality.

First, many methods are suggested for cleaning wafer surfaces. For example, efficient removal of organic contaminants from wafers by dry cleaning using

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UV/O_3 and an electron cyclotron resonance plasma is reported in the literature [9]. Another cleaning method uses electrolytic ionised water for the polishing process [10].

Second, improvement of air quality might be a means of protecting the surfaces of wafers. This could be achieved by the use of a microenvironment.

So, methods have been developed for identification and quantification organic contaminants in cleanrooms. Methods [11, 12] proposed include measurement of acidic and basic airborne contaminants in cleanrooms by ion chromatography. Another method is use of multisorbent adsorption/thermal desorption then gas chromatography–mass spectrometry [13].

The main sources of contaminants are process chemicals, cleaning agents, and organic compounds in the air pumped from outside the cleanroom to maintain the laboratory under pressure (atmospheric pollution). Concentrations of VOC (volatile organic compounds) in workplace air have been given in the literature by several authors [13–15]. The number of organic compounds in cleanrooms is so high it is difficult to obtain a rapid assessment of air quality, and the effect of contamination is different for each process. However, not everyone can easily understand the report of analysis done to quantify indoor pollution, this makes an indicator to give a global value of air quality easily understood by non-scientists very desirable. In addition, comparisons of the air quality in different indoor atmospheres can be made very quickly if the same reference is taken. For example, in France, the ATMO index is calculated daily by the monitoring associations. This general composite index profiles the average urban air quality. It is calculated with reference to four pollutants: sulphur dioxide, nitrogen dioxide, ozone and dust particles. This index is based on a 10-point scale (1 for very good air quality, 10 for very bad air quality). Each pollutant is given one of these numbers and the level of the ATMO index is the highest number. This is a simple indicator for informing the public. Our global indicator, GAPI, is more precise and sensitive and takes several impacts into account. This paper deals with the proposition of calculating this air quality indicator which can be applied to all organically contaminated areas such as indoor or industrial atmospheres. An example is shown with the air in cleanrooms used for the production of microelectronic components. Because air contamination values are strongly confidential, they cannot be reported in this paper and the example given is based on bibliographic data.

Experimental

To build this indicator, identification of all the compounds, and their quantification, are required. With these data, a global air quality indicator can be calculated.

Analysis and data collection

Identification and quantification of pollutants are generally performed by gas chromatography and mass spectrometry. Because of the very low levels of contamination in cleanrooms ($\mu g\ m^{-3}$), a preconcentration step might be used if the concentrations are below the detection limit of the detector.

Indicator

The indicator takes into account the concentrations of all the compounds found by analysis. Each concentration is balanced by a coefficient giving the impact of that compound on air quality for the particular application. In each case, a specific indicator can be proposed by an adapted coefficient.

The global airborne pollutant indicator (GAPI) is the sum of all the balanced concentrations and is defined by Eq. (1).

$$\mathrm{GAPI} = \sum_i W_i C_i \tag{1}$$

where C_i is the concentration of pollutant i, and W_i is the impact weight of the contaminant i.

Definition of the impact weight W_i

The impact weight W_i is defined as a characteristic or combination of characteristics of the molecule that can be a problem for the process. For example, the volume of molecules or their sticking coefficients could be regarded as an impact factor.

Calculation of W_i for one impact factor

In this section, two calculations are presented: the impact of molecular volumes and of sticking coefficients.

In nanotechnology, contaminants with a significant size are known to be a potential problem for production because large molecules increase the risk of a printing default. Therefore, volumes might be a relevant impact factor to simulate the danger of each compound to the quality of production. Among the different compounds found in a cleanroom many must be taken into account especially major compounds.

The relative impact coefficient X_i for the volume of molecules is defined as the volume ratio between each molecule and a reference in Eq. (2):

$$X_i = \frac{V_i}{V_{\mathrm{ref}}} \tag{2}$$

where V_i is the volume of molecule i, V_{ref} the volume of the molecule taken as the reference, and X_i the impact weight for molecule i ($X_i \geq 1$)

Volumes were calculated by use of ViewerPro Trial Edition Version 5.0 courtesy of Accelrys, accessible at http://www.accelrys.com

For calculation of X_i the smallest compound is chosen as reference. So, X_i is always greater than 1. Moreover if a molecule with a larger volume is taken as reference, the impact of compounds with a smaller volume must be fixed at 1.

If only the impact of molecular volume X_i is considered, the impact weight W_i is equal to X_i.

Sticking coefficients are the link between the efficiency of adsorption of a given molecule and a given surface [16]. They indicate the probability of a molecule being adsorbed on the surface after contact. These molecules can prevent silicium surfaces from printing and be responsible for the production of poor microelctronic components. In this case, the compound with the lowest sticking coefficient is taken as the reference.

The impact of sticking coefficient Y_i is defined by Eq. (3):

$$Y_i = \frac{\sigma_i}{\sigma_{\mathrm{ref}}} \qquad (3)$$

where σ_i is the sticking coefficient of molecule *i*, σ_{ref} the sticking coefficient of the reference molecule, and Y_i the sticking weight of molecule *i* ($Y_i \geq 1$).

Combination of impact weights

The indicator can depend on one factor only, but many factors are often involved in the danger of pollutants to the process, which is why it should be calculated with several combined impact factors. So, building an indicator that take into account each factor is recommended. A solution is to associate several simple impact weights, as presented in Eqs. (4) and (5):

With two factors,

$$D_i = \sqrt{W_i X_i} \qquad (4)$$

With three factors,

$$M_i = \sqrt{[3]}W_i X_i Z_i \qquad (5)$$

where W_i, is the combined impact weight and X_i, Y_i, Z_i are simple impact factors.

Indicator of mean pollution

All previous calculations give a measure of instant impact but to follow the evolution of air quality in cleanrooms time exposure must be considered. The indicator represents an average value depending on the number of analyses, as shown in Eq. (6).

$$\mathrm{GAPI}_n = \frac{\sum_{t=1}^{n} \mathrm{GAPI}_t}{n} \qquad (6)$$

where *n* is number of analysis per day or during the period of measurement.

Results

An example of application of the indicator is calculated with values from the literature [14]. The factors which can be used include molecular volumes, sticking coefficients, toxicity to humans, ability to produce ozone (based on MIR indicator) [17] or a combination of all these factors or even others that the users of GAPI find important for inclusion in their personal indicator. In the example presented, only the volume impact factor is used. This choice was made because, in this theoretical example, the volume is the only important factor which can change the quality of the product. Propanone is taken as the reference molecule for volume impact. So, the calculated GAPI gives a measure of contamination in propanone equivalents. In Table 1, only compounds with a concentration greater than 2 μg m^{-3} are used to calculate the indicator.

Table 1 shows that a real global concentration of 3,506 μg m^{-3} in the cleanroom has an impact similar to

Table 1 Example of indicator calculation based on volumes

Compound	W_i	Real concentration (μg m^{-3})	C_iW_i
Heptadecane	6.065	3.0	18.2
2,6,8-Trimethyldecane	4.516	2.3	10.4
2,2,6-Trimethyldecane	4.494	3.1	13.8
2,6,7-Trimethyldecane	4.489	2.3	10.3
2,5,5-Trimethyldecane	4.486	2.3	10.3
2,6,6-Trimethyldecane	4.478	2.3	10.3
Hexamethyldisiloxane	3.885	2.0	7.9
Hexadecafluoroheptane	3.558	452.7	1,610.8
Tetradecafluorohexane	3.151	73.2	230.8
Perfluoro-2-methylpentane	3.097	12.7	39.3
Trimethyl(1-methylethoxy) silane	3.041	7.7	23.5
Dodecafluoropentane	2.699	9.6	25.9
Diisopropyl ether	2.487	2.1	5.3
4-Methyl-2-pentanone (MIBK)	2.350	7.9	18.6
2-Hydroxypropanoic acid, ethyl ester	2.350	2.5	5.8
2-Methylpentane	2.294	2.2	4.9
Heptafluorobutanoic acid	2.248	46.4	104.3
Toluene	2.233	4.2	9.4
Methoxytrimethylsilane	2.081	152.0	316.3
Trimethylsilanol	2.036	5.3	10.7
2-Pentanone	2.014	61.0	122.9
1-Hydroxypropanoic acid, ethyl ester	2.010	3.0	6.1
m/*p*-Xylene	2.003	3.1	6.2
n-Pentane	1.981	4.2	8.3
2-Methyl-1,3-butadiene	1.898	3.8	7.1
3-Buten-2-one	1.592	7.3	11.6
2-Butanone (MEK)	1.554	31.9	49.6
2-Propanol (IPA)	1.472	1,527.5	2,249.0
Dichlorodifluoromethane	1.273	3.0	3.8
Tetrahydrofuran	1.181	9.9	11.7
Ethanol	1.146	257.2	294.8
Propanone	1.000	798.6	798.6
GAPI		3,506.4	6,056.7

Concentrations in μg m^{-3} are calculated from ppb level given in [12], common industrial names are given in parentheses

6,056 μg m^{-3} propanone. The increase was about 70%. This result gave an example of the modification of real concentrations in the cleanroom with the danger of that volume to the process. As seen in Table 2 when the indicator is calculated with all the compounds quoted by Kinkead et al. [14], the real concentration was 3,545 μg m^{-3} and the GAPI under these conditions was 6,174 μg m^{-3}. If 2-propanol (IPA) was taken as reference, it means that W_i for IPA is 1.000 and for lower molecules W_i is also fixed at 1.000, GAPI reached 4,510 μg m^{-3}. So, levels of contamination depend on the nature of the reference. When heptadecane and propanone are compared, the impact of heptadecane is six times more important than the impact of propanone. In the same way, comparing two ketones, MIBK and propanone, MIBK is twice as dangerous as propanone to the process because of its volume impact. This potential danger is expressed by the GAPI calculation.

Indicators for several factors could also be devised. Then, classification of the cleanroom is required to say whether wafers produced at the instant of analysis are of good quality. It can also allow, within the framework of the improvement in the quality, the monitoring of the changes in air quality and the decreases in contaminants.

The indicator gives a rapid indication of air quality in the cleanroom, so it is a tool for assessment of air quality in a specific environment and for a specific process. The cleanroom could be classified in terms of danger to a process or of human exposure. This indicator could be a tool to decide if production should be stopped to preserve the quality of wafers.

This tool could be a solution for quantifying pollution at any moment of the day, so air-quality indicators (GAPI$_t$) could be calculated throughout a day. Consequently, mean pollution in the cleanroom might be calculated from GAPI$_n$. This gives an indication of the level of exposure of people working in the cleanroom.

Conclusion

The global airborne pollutant indicator (GAPI) proposed in this article could be used with different levels of complexity, taking into account one or more impact weights for air quality and time exposure. Because this airborne contamination can have a negative impact on production in the cleanroom, GAPI is an efficient tool for following air quality. This example of its application demonstrates well the necessity of being able to make a better estimate of the real impact of air quality Finally, for each type of production, definition of specific limiting values and mean values for the indicator is needed to assess whether or not the level of the contaminant in the cleanroom is acceptable for the quality of production and to determine if workers in the cleanroom reach a fixed limit of exposure to airborne contaminants.

Table 2 Global view of each case of GAPI calculation

	Real concentration (μg m^{-3})	GAPI (μg m^{-3})
All compounds in Ref. 12 with 2-propanol as reference	3,545	4,510
All compounds in Ref. 12 with propanone as reference	3,545	6,174
Compounds in Ref. 12 with $C > 2$μg m^{-3}with propanone as reference	3,506	6,056

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