

Ozone as Airborne Molecular Contamination (AMC) in semiconductor manufacturing

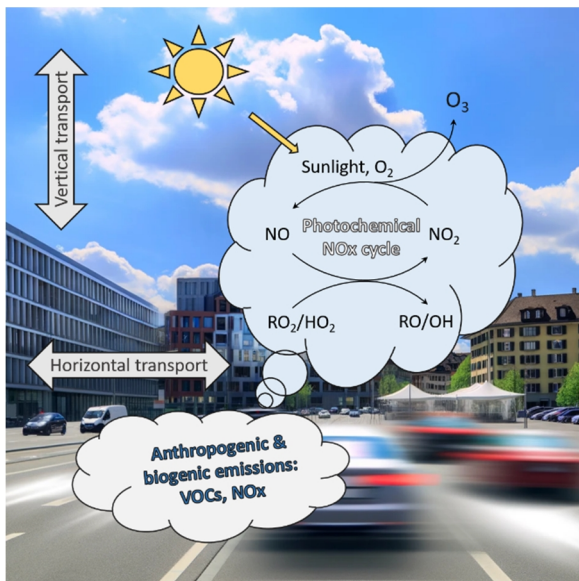
New filter materials
with long-term stable removal performance

Technical report 2403001



Ozone (O_3) is a strong oxidising agent that is formed daily in the near-surface layers of the atmosphere under the influence of UV light from solar radiation in a NO_x /VOC-assisted cycle in the presence of abundant atmospheric oxygen (O_2). [Fishman & Crutzen, 1978; Finlayson-Pitts & Pitts, 2000; Seinfeld & Pandis, 2016].

In an environment in which NO_x (nitrogen oxides, $NO + NO_2$) and oxidisable hydrocarbons are present, the build-up rate is significantly controlled by the radiation intensity and the relative concentrations of NO_x and VOCs. The build-up rate is well researched and the contributions to it are well described by reaction equations and model calculations. [e.g. Crutzen, 1971, Finlayson-Pitts & Pitts, 2000]



Schematic: Lower atmosphere (tropospheric) ozone generation; NO_x /VOC/ O_3 cycle

With decreasing or absent UV radiation (sunset), the formation rate drops below

the loss rate for ozone. The ozone concentration in the lower atmosphere decreases again. This is due to loss reactions in the NO_x cycle, in particular the rapid loss reaction of ozone with nitrogen monoxide ($NO + O_3 = NO_2 + O_2$), as well as other reactions in which the reactive and unstable ozone molecule acts as an oxidising agent and is consumed. Of particular importance here is the contact of ozone-containing air masses with the ground or other surfaces where the loss takes place. [e.g. Jacob, 2000].

Due to the combination of the above-mentioned formation and depletion processes, it is not surprising that ozone concentrations in the ambient air generally show a strong day-night difference, with peak values of up to 100 - 150 ppb, in the early afternoon and at the same time potentially low values of 10 - 15 ppb, before sunrise in the morning. [Monks et al., 2015].

Examples of typical ozone concentrations in Switzerland during the summer months are shown by outdoor air measurements at the NABEL stations (Figure 1) and in the vicinity of the artemis control AG laboratory in the greater Zurich area, Switzerland. The parallel measurements of ozone, NO and NO_2 (NO_x) show the interaction of ozone concentrations, the morning entry of NO into the cycle and the distribution of NO and NO_2 over the course of the day (Figure 2). Figure 3 shows past ozone measurement values from the fresh air supply of a prototype production facility for nanoelectronic materials with partial fresh air filtration.

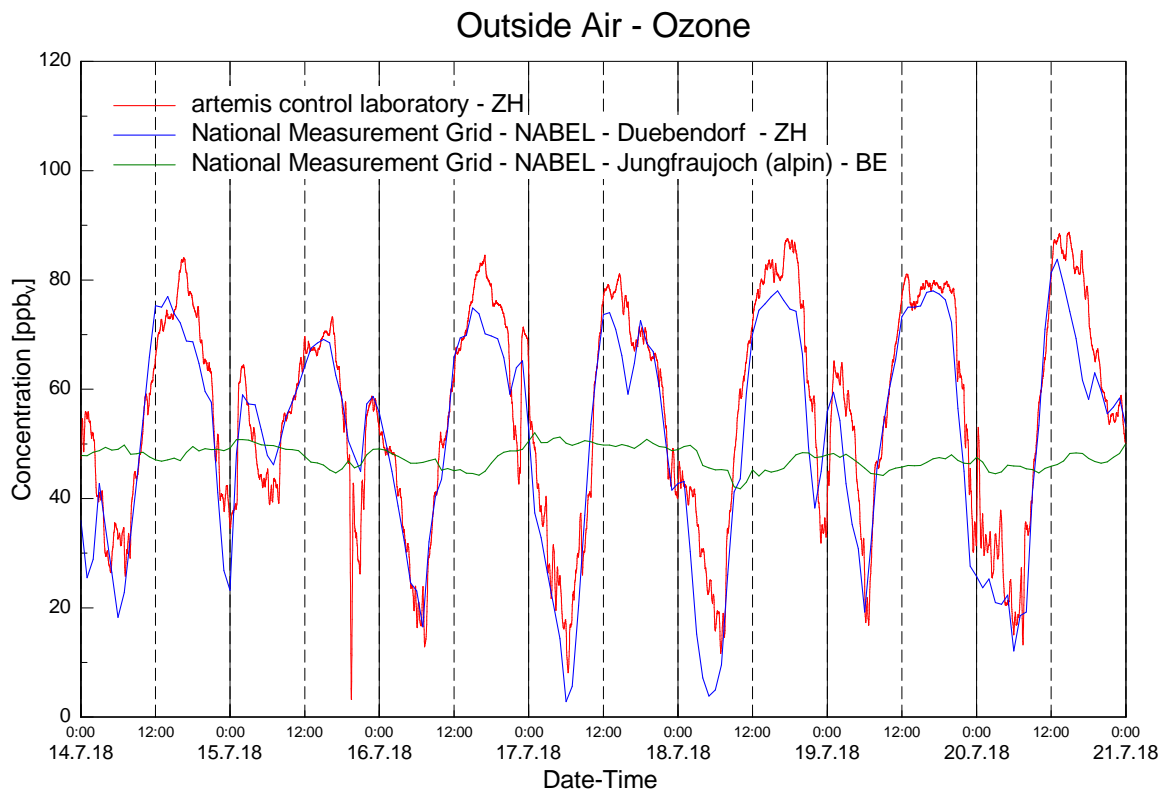


Figure 1: Ozone in outdoor air - typical concentration values & daily variations in the summer months in Europe - examples at the NABEL measuring stations in Switzerland and at the laboratory of artemis control AG, ZH, Switzerland

One can subjectively assume that the ground-level ozone values and the daily peak concentrations are highest in the tropics due to the high number of "sunny days". This is correct insofar as the seasonal fluctuations in solar radiation and UV intensity are lower in the tropics than in higher latitudes in the northern or southern hemisphere. [Cooper et al., 2014, Monks, 2000] However, in late spring and early summer - i.e. around the so-called solstice - the day length and duration of light irradiation in the respective hemisphere is generally considerably longer than at the same time in the tropics. If, in addition to this long irradiation period, a high radiation output under a clear sky meets a favourable NO_x /VOC

mix, the peak ozone concentrations in the high latitudes quickly exceed the typical average daily peaks in the tropics. [Monks, 2000].

In addition, favourable micrometeorological conditions, such as low air movement during the night or low NO inputs, can mean that the ozone formed during the day is not broken down at night and a "base" of 30 - 40 ppb_v remains, on which ozone formation continues to build up the next day (see also *Figure 3*). A similar mechanism led to a significant net increase in ground-level ozone production during the COVID-19 lockdown in eastern China, for example. [Chen et al, 2021].

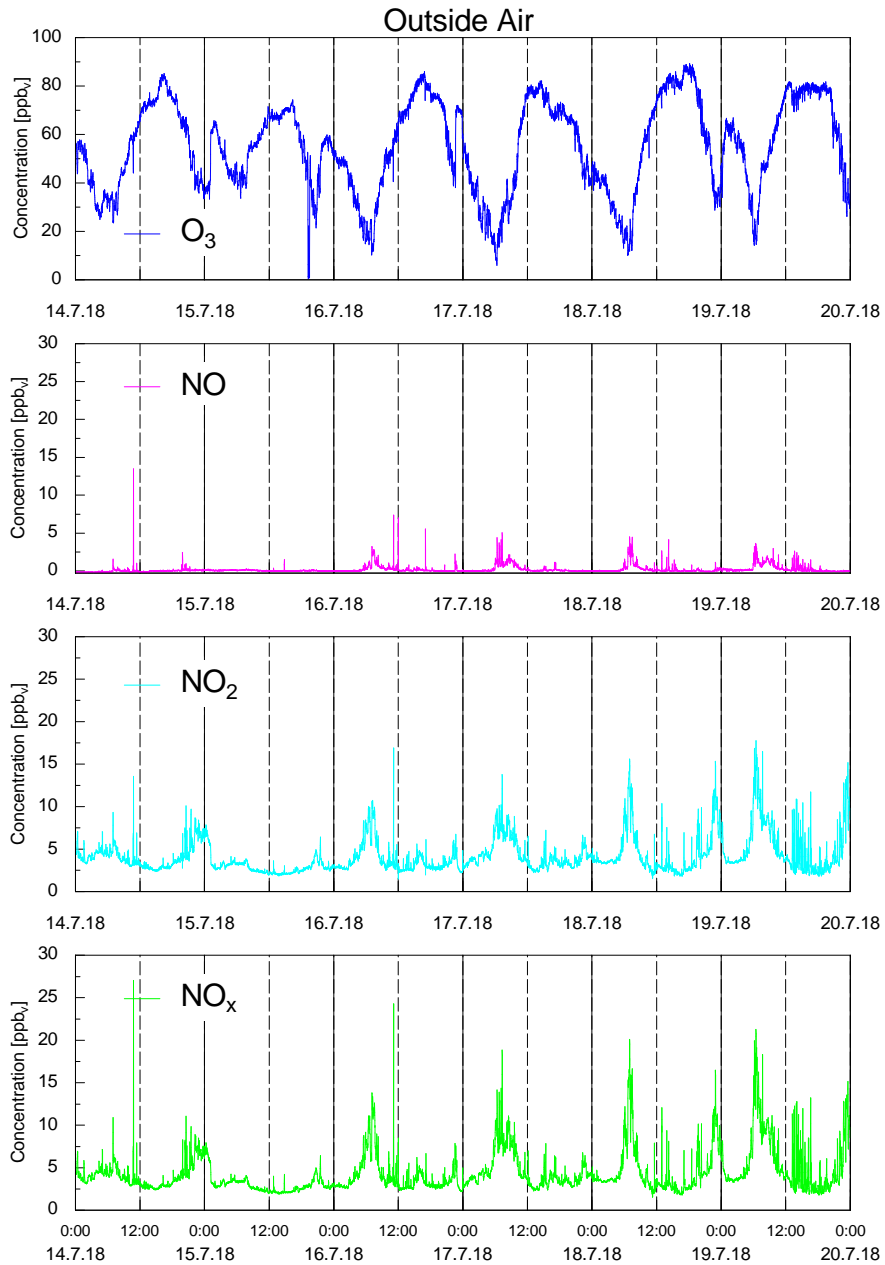


Figure 2: Parallel measurements of ozone, NO and NO₂ (NO_x) at the laboratory of artemis control AG, Zurich region, Switzerland. The curves show the interactions of the ozone concentrations, the morning entry of NO into the cycle and the distribution of NO and NO₂ over the course of the day.

In these situations, it is not uncommon for regional ozone limit values to be exceeded [Monks et al., 2015], which are set and issued taking into account the effects on the respiratory system, especially in older people or people with impaired health [Bell et al., 2005, Jerrett et al., 2009]. If the limit values are exceeded, people at risk are advised to avoid strenuous outdoor activities and to stay indoors instead. This is due to the generally lower ozone concentrations indoors, where practically only loss reactions take place.

The manufacturing processes in nanoelectronics can also be affected by ozone in the ambient air of the nanoelectronic structure and its oxidising effect. [Park et al., 2001]

This is easiest to understand for the still young and small field of polymer electronics or organic polymer conductors and semiconductors. This is because the basic structure of polymer conductors are conjugated polymer main chains, which consist of a strictly alternating sequence of single and double bonds. The polymers therefore have a delocalised

("mobile") electron system, which enables semiconductor properties and, after chemical doping, conductivity.

However, unsaturated (C=C) double bonds are favoured points of attack for the oxidising agent ozone and lead to oxidative chain breakage as part of "ozonolysis" and thus to destruction of the (conductive) polymer.¹ [Petrick & Dubowski, 2009] Depending on the type of conductive polymer and its processing and storage process, ozone concentrations of > 5 ppb_v in the ambient air are already classified as process-critical and damaging.

In silicon-based semiconductor technology, the effect of ozone (in addition to other oxidising agents) is held responsible for the unwanted, uncontrolled formation of silicon oxide layers on pure Si surfaces. Native metal surfaces of easily oxidisable metals are also classified as affected.

Park et al. (2001) report on a Si-O growth of 0.015 - 0.07 Angström/minute when exposed to ozone in the concentration range of 20 - 200 ppb_v. This Si-O growth leads to an unwanted change in the capacitive properties of a storage cell and should be avoided.

¹ Ozone initiated polymer cleavage was already observed in the 19th century on chemically unstabilised natural rubber/rubber. Other redox reactions with ozone have been used, for example, in

electrochemical processes to probe the vertical distribution of ozone in the atmosphere, see references in [Kames & Schmidt, 1992].

Means for limiting ozone concentrations in the cleanroom air

The main process for the formation of ozone is the photolytic formation in the outside air described above. The main source of ozone in the cleanroom air is the entry of outside air into the cleanroom through the make-up air system. Localised source reactions for ozone from the use of UV light or high voltage can occur in the cleanroom, but these are limited.

With daily peak values of 60 - 150 ppb_v in the outside air over several hours, active ozone separation from the make-up air is required in order to comply with threshold values of no more than 5 ppb_v.

It is true that an ozone content of e.g. 60 ppb_v in the outside air does not immediately lead to a corresponding concentration in the cleanroom due to the limited fresh air rate of 5-7% of the recirculated air rate. This is prevented - in addition to the wall loss of ozone in the air duct system - by further back reactions and low exchange rates and loss reactions in the recirculated air circuit. Typically, in a cleanroom without active ozone separation, a peak forms within two hours after such peak occurred on the level curve in the outside air.

The use of AMC filters in the make-up air system is recommended to reduce the ozone content in the make-up air. In state-of-the-art outdoor air systems for cleanrooms for the production of nanoelectronics, at least one and preferably two stages are usually provided for cleaning the make-up air from AMC.

However, the focus is often on reducing and stabilising the levels of acids or acid formers, organic and organosilicon air constituents and alkaline components.

For the filtering removal of ozone from the air, the mechanism is generally used which, in addition to the reactive loss with NO, represents the main loss pathway in the outside air. This is the reactive loss with surfaces and the re-formation of ozone to oxygen.

An AMC filter based on activated carbon is commonly regarded as a filtering system with a large surface area. As a highly porous material, activated carbon does indeed have an "inner surface area" of 900 - 1200 m² /g of sorbent. Activated carbon suitable for trace gas filtration has a system of transport pores and micropores that are easily accessible to a small, mobile molecule such as ozone.

In indicative laboratory tests, almost all state-of-the-art AMC filters based on activated carbon have therefore proven to be suitable. In such tests, filtration efficiencies of >98% can be easily demonstrated for short periods on new filters and at elevated concentrations. These tests are often also carried out at very high ozone concentrations and extrapolated in terms of "capacity performance" via the size of a dose in ppb_vh to a usable period of use under typical outdoor air pollution.

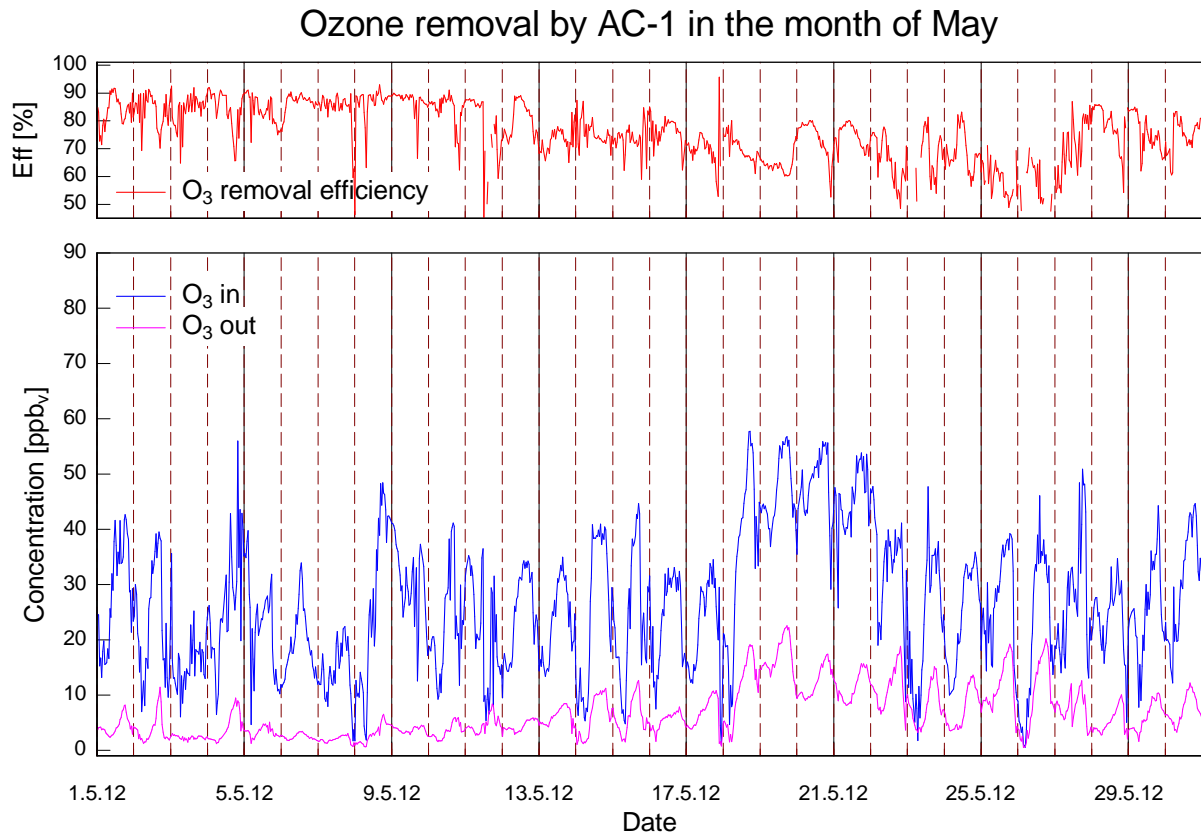


Figure 3: Tracking the measured ozone values ("O₃ in" in the outside air, "O₃ out" on the downstream side of the filter barrier) and ozone removal on an outside air system equipped with type AC-1 filters (nanoelectronic material pilot production). The days with constantly increased concentrations of ozone in the outside air lead to the formation of a "base" of approx. 40 ppbv, which also remains at night, resulting in a "memory effect" and reduced performance for ozone separation for this filter type (AC-1). The effect is reversible but undesirable, as the course of outdoor air concentrations cannot be actively influenced or predicted.

Unfortunately, separation efficiencies found in tests designed in this way often do not materialise in practice. The reason for this lies in the combination of the separation mechanism and the performance requirements for lower but periodically occurring peak concentrations in practice.

Comparative investigation of AMC filter systems for the separation of ozone - material variants and service life

The loss of ozone on solid surfaces is, among other things, a recombination to oxygen ($2 \text{ O}_3 \rightarrow 3 \text{ O}_2$) as well as a reaction with substances on the surfaces in the sense of a sorptive reaction.

A reaction with the material of the surface itself or a combination of the mechanisms mentioned can also occur.

Accordingly, it is clear that there are materials and surfaces that degrade very little ozone and are used in this sense (glass, PTFE [Cano-Ruiz et al., 1993]) as well as materials that degrade ozone efficiently and continuously (e.g. heated ozone filters with metal/metal oxide structures on systems and appliances).

In the field of AMC filtration, it only makes sense to use systems that guarantee that the concentration in the out-flow area of the filter is permanently below the limit values of 2 - 5 ppb, at low, but dynamically changing concentrations

without added thermal power and taking into account other AMC present in the air. The systems should be free of by-products, e.g. from the removal of ozone.

Table 1 shows a comparison of the initial separation efficiency of ozone on four AMC filters. The AMC filters AC1 - AC4 have in common that the sorption material in the base body is activated carbon. The characteristics of the inner surfaces of the activated carbons are different.

For comparison, the separation of ozone on AMC filters made of functional polymers (FP-B and FP-A) is shown, which - in line with expectations and the material design - should not and do not show any separation of ozone.

Table 1: The initial separation efficiency of ozone on various AMC filters, the AC ("activated carbon") types are all based on activated carbon composite materials, the FP ("functional polymer") types on porous organic polymer structures

	AC-1	AC-2	AC-3	AC-4	FP-B	FP-A
Entry [ppb] _v	10-75	10-75	10-75	10-75	10-75	10-75
Outlet [ppb] _v	1-15	1-5	1-4	1-5	10-75	10-73
Distance	90-70%	96-85%	98-94%	96-90%	0%	0-2%

Table 2: The ozone removal efficiency of AMC filters after only 6`000 ppb_vh input dose

	AC-1	AC-2	AC-3	AC-4	FP-B	FP-A
Entry [ppb] _v	10-75	10-75	10-75	10-75	10-75	10-75
Outlet [ppb] _v	10-20	1-5	1-4	1-5	10-75	10-73
Distance	90-60%	96-80%	98-94%	96-84%	0%	0-2%

In a continuation of the investigations, we show the behaviour of various AMC filters under a continuous controlled cyclic day-night load in a long-term test under realistic operating conditions (Figures 4 and 5).

It can be seen that the AMC filter type AC-2, a filter with the target application "VOC & Condensables", initially achieves a high separation efficiency under realistic test conditions, which can guarantee

compliance with the < 5 ppb_v criterion. This picture changes after prolonged use of - in this test - three months under consistently high exposure (corresponds to a total dose of approx. 100'000 ppb_vh). The

separation efficiency decreases and no longer complies with the limit value at peak concentrations (compare "as new" and "aged" states in Figure 4).

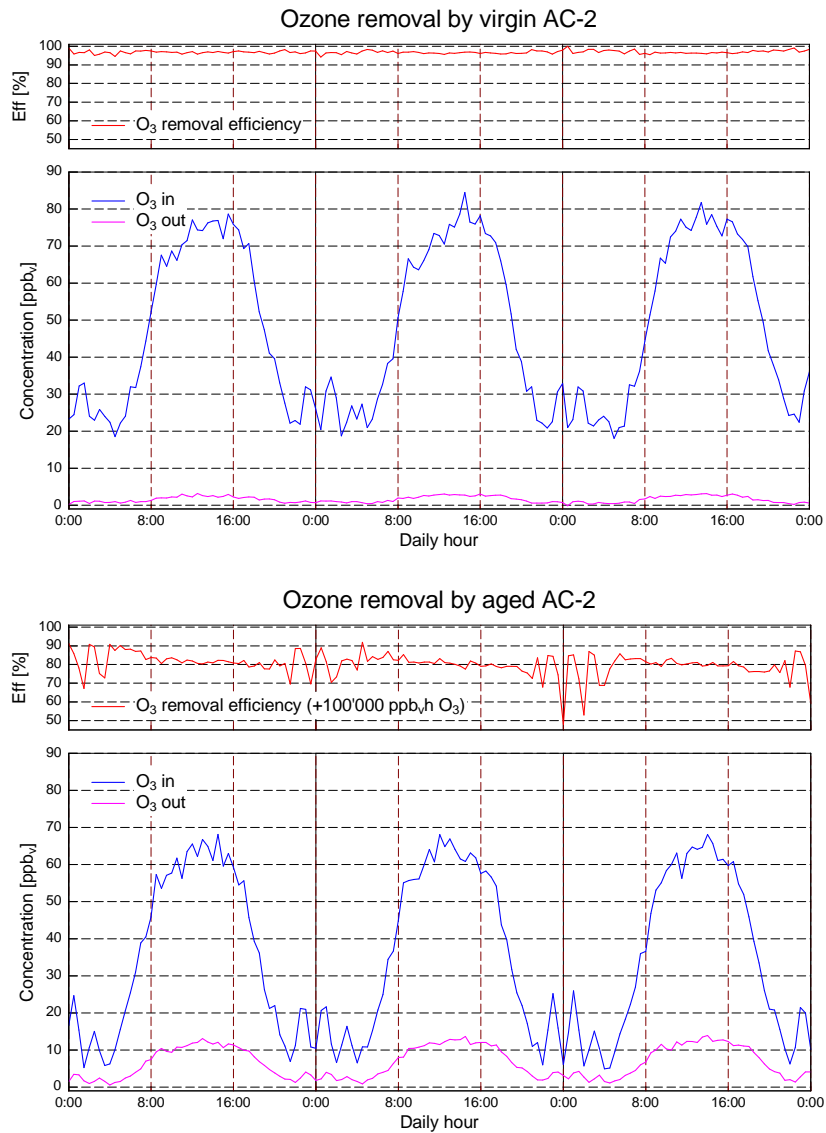


Figure 4: Comparison of initial removal efficiency of ozone at the AMC filter AC-2 with the removal efficiency of this filter in the aged state (up to a dose of 100'000 ppb_vh ozone)

At the same time, the separation efficiency determined compared to the input concentration decreases again at lower concentrations. This is particularly the

case in the periods of decreasing concentration that follow the daily peak load. We attribute this behaviour to a temporary saturation of the reactive surface when

the reaction is inhibited, which can be regarded as a "memory effect". The filter retains an influence from the previous phase, which proportionally prevents the

decomposition of newly inflowing ozone of lower concentration and leads to a measurable reduction in the spontaneous ozone output.

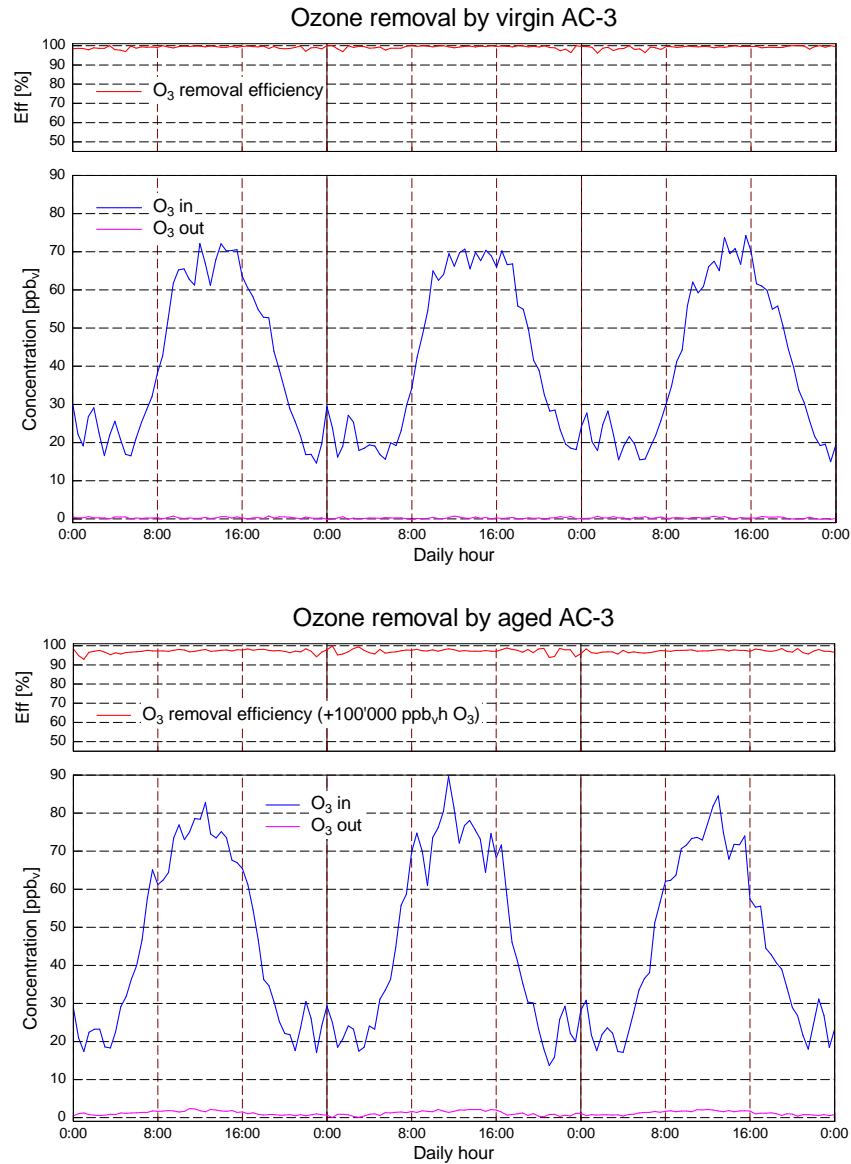


Figure 5: Comparison of initial removal efficiency of ozone at the AMC filter AC-3 with the removal efficiency of this filter in the aged state (up to a dose of 100'000 ppb,h ozone)

The "memory effect" is a basic characteristic of many common activated carbon types and has been repeatedly observed during the operation of AMC filters. This occurs in particular where no specific ma-

terial selection is required and implemented for the criterion of stable ozone separation. (See the example of the use of AC-1 for a fresh air supply (pilot plant nanoelectronics) in figure 3).

In comparison, the AMC filters of type AC-3 (and AC-4) do not show this undesirable characteristic - neither after a longer period of operation nor in detailed temporal resolution of the performance in a phase of increasing or decreasing ozone input concentrations. A progressive inhibition of the reaction is not recognisable and is based on the specific material selection adapted to the task (Figure 5).

When analysing and investigating AMC filters used in cleanroom operation (operation in outdoor air systems, imposition of different AMC sum loads determined by the local conditions of the system design, the natural and imposed AMC sources in the environment), the investigations described above can be confirmed throughout.

The filter type AC-2 - a filter designed for the treatment of VOC & Condensables - experiences a loss of VOC separation efficiency during system operation under the influence of organic & inorganic AMC and ozone, which, expressed as a percentage, occurs primarily during peak

loads and in periods with high ozone levels during the day/night cycle. In relation to the assessment of performance at lower concentrations, the filter appears "used up" and "no longer effective". However, it can be shown that the removal efficiency increases again some time after these episodes. However, as the duration and frequency of the episodes cannot be predicted and influenced, safe compliance with the cleanroom limits cannot be guaranteed with AC-2, VOC & Condensables filters alone.

In comparison, the loss of separation efficiency with filter type AC-3 is low to undetectable even after more than 18 months of continuous operation. The use of this filter type enables compliance with the requirement for a low outlet-side concentration at all times and under all foreseeable circumstances. For AMC filters based on the AC-3 and AC-4 filter materials, these performances are stated, specified and guaranteed by artemis control AG in the product information. Such AMC-filters can be recognised by the user by their product codes.

Conclusions

Ozone (O₃) is an airborne molecular contaminant (AMC) in a number of process steps in semiconductor production, which leads to the unwanted and uncontrollable formation of oxide layers. In the case of polymer conductors, the effect of ozone can lead to chain scission and a reduction in conductivity.

For the reasons mentioned, there are specific specifications for the maximum tolerable ozone concentration in the cleanroom air or in the process system for a large number of processes and storage situations, in which the material properties and cycle times of the processes are taken into account.

The tolerable limit values for ozone concentrations in the process are generally in the range of a few ppb_v, but in any case far below the typical concentrations in the outside air in sunny weather.

As the source of ozone concentrations in cleanrooms is essentially the ambient air or fresh air supply, the control of ozone concentrations often begins with the AMC filtration of the fresh air and can be extended to cleanroom zones or specific process systems.

Although almost all porous materials such as activated carbons, zeolites, etc. show a reduction effect against the unstable ozone molecule in orientating and short-term material tests. However long-term effects, such as the "memory

effect to elevated peak exposure" cannot be ruled out on a short-term test scenario.

Further long-term effects, such as a passivating change of the surfaces can also not be identified by short-term tests. These long-term effects can remain unnoticed for a long time, but lead to a sudden drop in separation efficiency in phases of increased continuous load and, in the worst case, to a violation of the specified process limit values. These violations can occur spontaneously and disappear again due to the aforementioned cause, leading to a "phantom phenomenon" and causing many distraction and uncertainties regarding the process stability. Basically AMC filters for the broadband separation of VOC & Condensables from the air are not long-term stable AMC filters for ozone.

The use of specific sorbents with modified and stabilised surfaces in AMC filters specified in this way prevents the aforementioned loss of performance. If the operating instructions are followed, this leads to compliance with the process limit values over a very long operating period and over a wide range of inlet concentrations including daily peaks.

artemis control offers AMC filters that are specially designed for the task of efficient and long-term stable ozone reduction from the air.

Please contact us if you require further information, advice or an AMC filter solution for this task.

About artemis control

artemis control is a leading provider of contamination control solutions, including AMC filters, particulate filters and analytical services for the semiconductor and general nanotech industries. artemis control is ISO 9001:2015 certified and has manufacturing, customer service and/or research facilities serving key global locations in these industries. For more information, please visit www.artemis-control.com

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