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LOW COST METAL OXIDE OZONE DETECTOR FOR FOOD PROCESSING

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Abstract

Metal oxide (MO) gas sensors with the potential to operate at ozone concentration levels bellow the critical value of 0.04 ppm set by recognized bodies such as the OSHA and FDA in the USA have been successfully fabricated at IESL/FORTH over the last few years. They have been integrated into a dedicated test chamber equipped with a PATT module and a UV ozone generator, humidity and an air flow meter suitable for food processing tests. Ozone levels are monitored by a combination of a commercial unit and a homemade metal oxide prototype ozone detector. These MO detectors are based on non-stoichiometric InOx thin films grown by dc sputtering. Recent results have shown that films grown at moderate temperatures (~110°C) from a metallic target and in a 100 % oxygen atmosphere exhibit ozone detection levels bellow 0.02 ppm subject to film nanostructure. AFM analyses have shown the contribution of film surface topography to the achieved sensing levels utilizing conductometric techniques.

Introduction

The over $500 billion food processing industry sky-rocked in the USA after the 1997 green light for the use of ozone as “Generally Recognized as Safe” (GRAS) and as an effective disinfectant for a number of products with direct benefits to consumers, the economy and the environment (EPRI report, 1997).

Ozone has gained considerable thrust in the agricultural sector as a replacement for several pesticides including the fumigant methyl bromide banned since 2001 while maintaining its positive impact in agricultural waste management.

Ozone recently got also the approval for use in the U.S. food processing industry as a disinfectant washes or spray to help rid food of dangerous pathogens (bacteria, parasites, fungi, and viruses). When dispersed into water, ozone can kill bacteria – like E.coli – faster than traditionally used disinfectants, such as chlorine (Achen, 2001). Most bottled water is safely treated with ozone, and nearly 200 municipal water treatment plants in the U.S. employ ozone to help cleanse their drinking water. The adoption of ozone technology in food processing depends upon economic competitiveness with existing and emerging technologies that sanitize food, as well as its effectiveness in enhancing food safety.

The food processing industry has faced mounting concerns in recent years about its ability to provide a consistently safe food supply. Food passes through many hands – from growing, picking, boxing, shipping, to final processing – prior to reaching the consumer.

Centuries-old methods of treating food, such as drying, smoking, and use of simple substances like salt, no longer adequately prevents spoilage in today's food marketing system. These methods to prevent contamination can also alter a food's taste.

Food processors have turned to other technologies to both decontaminate and preserve products without substantially changing the appearance, taste, texture, or nutrient content of the food. These methods include steam pasteurization, flash pasteurization, a heating process to kill bacteria in juice; and irradiation, which uses low-dose radiation to treat meats, fruits, vegetables, and spices.

As a non-thermal method of disinfecting food, ozonation reportedly alters taste little, unlike some heat-based steam and flash pasteurization systems that cook the product. Further, in some foods, ozone proponents indicate flavor is enhanced by ozone's ability to neutralize chemicals, pesticides, and bad tastes from gases produced by ripening or decay (Rice, 1984; Razumovski, 1984).

In 1995, the U.S. National Live Stock and Meat Board and various universities conducted a research that showed an ozone wash reduced bacterial contamination on beef carcasses to a level equal to conventional carcass trimming and washing methods.

The strength of the case for using ozone may rest with its versatility and environmental benefits over some existing food sanitizing methods. Ozonated water can be used on food products as a disinfectant wash or spray and can kill some bacteria faster than traditionally used disinfectants, such as chlorine. Ozone also kills viruses, parasites, and fungi. The U.S. Environmental Protection Agency, in conjunction with the Safe Drinking Water Act of 1991, confirmed that ozone was effective in ridding water of hazardous pathogens, including chlorine-resistant Cryptosporidium.

Nowadays, ozone is generally accepted as the strongest oxidant on the market with an oxidizing potential 2.07 compared with 1.57 of its rival chlorine dioxide.

Food products treated with ozone are found to be free of disinfectant residues. Because it is an unstable gas, ozone decomposes in about 20 minutes into simple oxygen, leaving no trace of the ozone disinfectant on the food.

Ozone as a disinfectant in its gaseous state can also be applied to sanitize food storage rooms and packaging materials, which may help to control insects during storage of foods and prevent spoilage of produce during shipping. Gaseous ozone is listed too as an alternative disinfectant for water-sensitive produce, such as strawberries and raspberries in the Guide to Minimizing Microbial Food Safety Hazards for Fresh Fruits and Vegetables (a document forthcoming from FDA and USDA).

Conceivable benefits of adding ozone to air in packinghouses and storage rooms include control of postharvest diseases on fruit, retarding the production of spores from decaying fruit, sanitation of surfaces, and ethylene removal. Both benefit (Pinilla, 1996; Skog, 2001; Palou, 2003) and lack of benefit (Spalding, 1966, 1968) of ozone in air use in fruit and vegetable storage rooms have been reported. Forney (2003) recently reviewed this subject. Some time ago, Schomer and McColloch (1948) summarized the risks and benefits of air ozonation in apple storage. Despite some early drown-backs nowadays ozone treatment is used successfully for the processing of apples by “Tastee Apples” in the U.S. since it reduces the yeast and mold count on the apples so that self-life is extended (EPRI report, 1997). No differences in the physiological properties between treated and untreated fruit were detected.

On the other hand, zone in water is often described as an alternative to hypochlorite as a disinfectant or sanitizer, although they differ in many aspects. Significant advantages of ozone in water are that it decomposes quickly to oxygen, leaving no residue of it and few disinfections by-products, and it has more potency against bacteria, cysts of protozoa, viruses, and fungal spores than hypochlorite (White, 1999). Ozone can oxidize many organic compounds, particularly those with phenolic rings or unsaturated bonds in their structure (Razumovski, 1984). Therefore it can have a role in reducing pesticide residues in process water (Nickols, 1992) and mycotoxins in durable commodities (McKenzie, 1997). These attributes make ozone a good choice when processed water is recycled. However, ozone in water is a dissolved gas and its solubility is relatively low compared to many other sanitizers, typically only about 30 ppm at 20°C. The presence of ozone-reactive compounds in the water, from soil or fruit constituents, can cause a significant ozone demand and cause the concentration to plummet quickly. Pre-conditioning of the water before ozonation, is needed in systems where water is recycled or the source water is of poor quality. In practice, even with high quality water, it is difficult to exceed 10 ppm, and many systems produce 5 ppm or less. However, spores are killed with relatively small doses. A contact time of two minutes in 1.5 ppm ozone killed 95 to 100% of the spores of eight fungi tested, and none survived 3 minutes of contact (Smilanik, 2002). Ozone in water above 1 ppm can liberate ozone to the air that exceeds levels safe to workers, particularly if the water is warm and it passes through high-pressure, small-droplet size nozzles.

As ozone is developing into a major new technology oriented towards solving costly product safety and processing problems, the need for cost-effective tailor made Ozone supply-detection units providing effective solutions to sensitive air quality and environmental control systems is imminent.

However, while ozone production may easily be achieved either in the presence of a UV source or through a low cost discharge system, it is the precise control and accurate monitoring of the produced ozone levels that require the development of reliable supply-detection and control systems. Such systems are of utmost importance for the disinfection process of the products itself as well as for the monitoring of human exposure during the various stages of food processing.

Human exposure to ozone in particular is subjected to international regulations as set by bodies such as OSHA, FDA, CSA, ASHRAE that impose stringent ozone exposure limits in the range of 0.05 to 0.1 ppm. These requirements reflect to a technological challenge for smart ultra sensitive ozone detection systems with reliable operation and detection levels down to or even bellow 0.001 ppm.

Experimental

The test chamber: The chamber contains three main parts the fan, the PATT-module and the sensors as well as humidity and an air flow meter suitable for food processing tests.

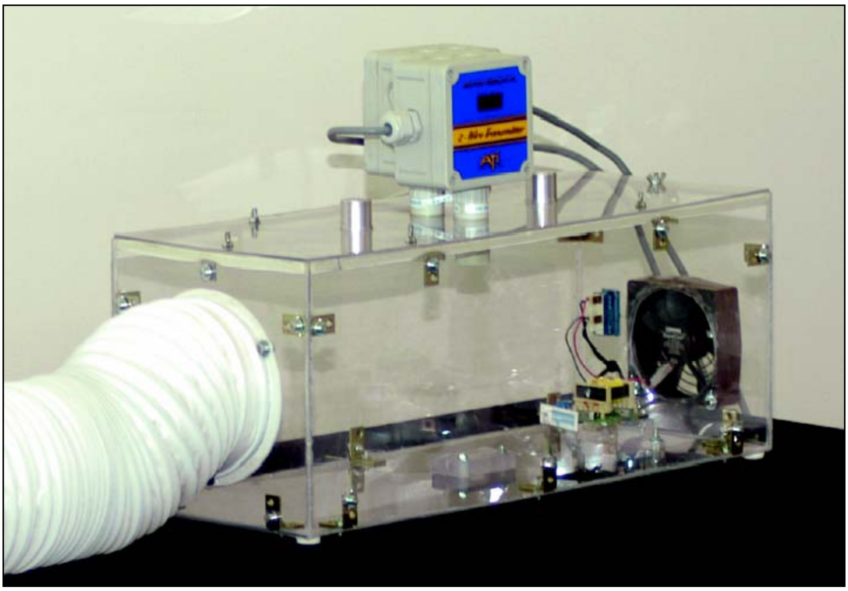

Fig. 1. Testing chamber with fan a PATT module and two sensors

The test chamber with the PATT (Physical Air Treatment Technology) module can be used to generate ozone concentrations up to 4 ppm (without air movement). The PATT module generates plasma between two electrodes by dielectric barrier discharge (DBD). This plasma cracks air molecules and hereby produces ozone (O_3) and molecular oxygen (O) out of Oxygen (O_2). As a by-product of this process different ions are generated. Alternatively, ozone may be generated utilizing a UV pencil lamp with an average intensity of 4 mW/cm^2 at λ = 254 nm. The same UV source is also used for the photoreduction of our InOx films with a film exposure at a distance of 3 cm from the surface. At air velocities from 1m/s to 3 m/s ozone concentrations up to 0.35 ppm are possible. Two commercial sensors for measuring O_2 and O_3 concentrations are mounted to the cover of the testing chamber while a third developed at FORTH provides additional monitoring particularly in the low regime (< .1 ppm) ozone exposures. Such a chamber can be used for a wide variety of measurements, because different kinds of sensors (e.g. temperature, humidity, other gases, etc.) can be mounted and dismounted very easily.

The sensors: Ozone detection levels are monitored by a combination of a commercial unit and a homemade metal oxide (MO) prototype ozone detector. The homemade prototype ozone detector is based on non-stoichiometric InOx thin films grown by dc sputtering. InO_x semiconductor sensors have been successfully used for the detection of oxidizing gases such as O_3 and NO_2 in the concentration range between some ppb and ppm.

Surface properties play an important role in processes occurring at the film-gas interface thus directly influencing the sensor performance. This role is enhanced significantly in the case of nanocrystalline and nanoporous materials due to their large surface-to-volume ratio.

MO semiconductor sensors gained considerable interest over the last decade due to their low cost combined with the ability to be “re-activated” and thus be in an ON state ready for ozone detection, following a fast photoreduction treatment by a low power UV irradiation (Kiriakidis, 2003).

The photoreduction treatment results in an increased conductivity of up to seven orders of magnitude for an InO_x film with thickness of 100nm, while conductivity values as low as $10^{-5}\ \Omega^{-1}\ cm^{-1}$ are obtained by subsequent ozone oxidation. This behavior is completely reversible through many cycles of photoreduction and oxidation treatments as shown in Fig. 2, which illustrates the conductivity versus time at room temperature.

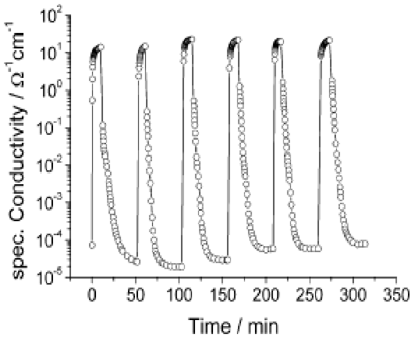

Fig. 2. Photoreduction and subsequent oxidation of InOx films at RT

Conductometric studies have shown that the InO_x films exhibit a characteristic response to ozone even at room temperature after the photoreduction treatment, which triggers the possibility of employing this material as a gas sensitive film, requiring zero or low power battery devices, to operate as portable ozone detectors. Since the sensing mechanism for MO thin films is primarily a surface effect the recent results have shown that films grown at moderate temperatures (~110°C) from a metallic target and in a 100 % oxygen atmosphere exhibit ozone detection levels bellow 0.02 ppm subject to film nanostructure (kiriakidis, 2004). Furthermore, sensing analysis utilizing the Sound Acoustic Wave (SAW) technique (Fekete, 2005) has shown the ability of our films to respond to ozone concentrations down to 0.01 ppm as shown in Fig.3.

AFM analyses have shown the contribution of film surface topography to the achieved sensing levels utilizing conductometric techniques. In the presence of the ionic species on the surface, after UV photoreduction, the electronic concentration in the surface states increases. The surface states concentration is correlated with the roughness and grain size via surface-to-volume ratio. Therefore, the gas sensitivity is direct proportional with the film roughness proving the importance of surface to volume ratio for high sensing applications. Grain radius was found to have the opposite effect on the sensitivity of our films mainly due to the increases of the film stoichiometry controlled by deposition parameters in line with previous results. These sensitivity variations are shown in fig. 4 b and c.

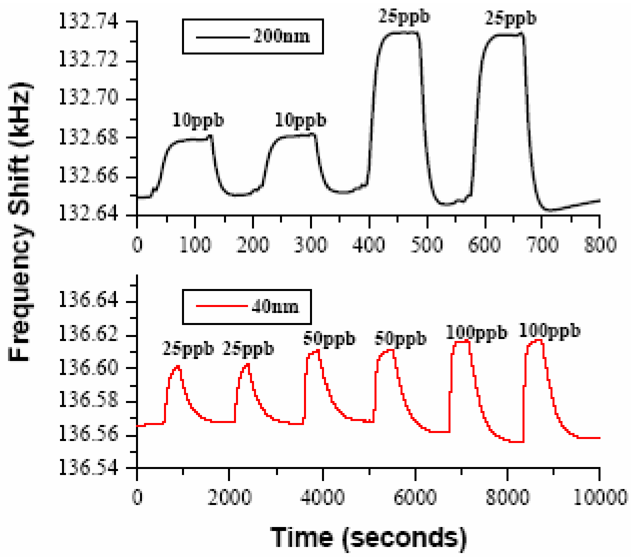

Fig. 3. InOx sensor responses towards ozone at optimal temperatures of 175°C and 230°C

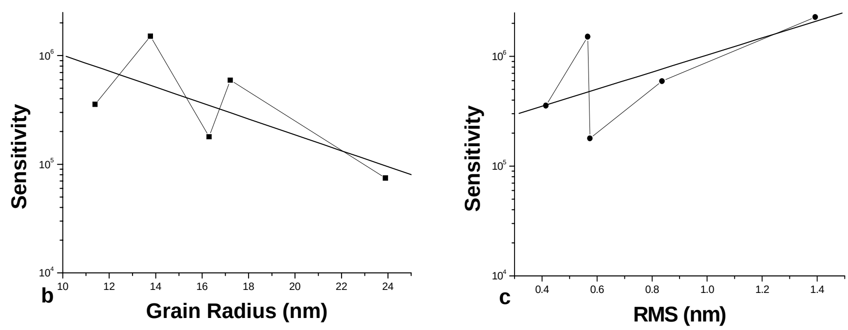

Fig. 4. The film sensitivity vs a) mean grain radius; b) surface roughness

Conclusions

The disinfecting food with ozone is only now emerging. The development of ozone technology in the food processing industry is dependent upon proper safeguards in its use to assure worker safety, economic competitiveness with existing and emerging technologies that sanitize food, as well as its effectiveness in enhancing food safety. Accurate and well-controlled ozone exposure limits must be tailor-made for each food specie-processing set-up while stringent human safety exposure limits require the utilization of ultra sensitive ozone detectors and systems that meet the international standards. The current study on MO ozone detectors has shown that InOx thin films may be utilized for the fabrication of low cost, ultra sensitive and easily "re-activated" ozone sensors operating at room temperature subject to surface properties and growth parameters.

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