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Microwave plasma removal of sulphur hexafluoride

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ABSTRACT

Sulphur hexafluoride (SF_6) gas is a common pollutant emitted during the plasma etching of thin films and plasma cleaning chemical vapor deposition (CVD) production processes used in the semiconductor industry. In this paper a method using microwave (2.45 GHz frequency) plasmas sustained at atmospheric pressure for the abatement of SF_6 is investigated experimentally for various gas mixture constituents and operating conditions, with respect to its ability to decompose SF_6 to less harmful molecules. The destruction and removal efficiencies (DRE) of plasma abatement of SF_6 at concentrations between 1.7 and 5% in nitrogen in the presence of water vapor were studied as a function of the total gas flow rate and microwave power. Water vapor proved to be an effective source of free radical species that reacts with the radicals and ions resulting from SF_6 fragmentation in the plasma and also, it proved to reduce the process by-products. It was measured that ~25% of the initial SF_6 is converted to SO_2. Destruction and removal efficiencies of SF_6 up to 99.9% have been achieved.

1. Introduction

Air pollutants may be considered primary – emitted directly into the air – or secondary pollutants that are formed in the air by chemical and/or photochemical reactions on primary pollutants. The formation of secondary pollutants, such as tropospheric ozone and secondary aerosols, from primary pollutants such as SO_2, NO_x, NH_3 and volatilic organic compounds (VOCs) is strongly dependent on climate and atmospheric compositions [1].

Amongst air pollutants, an important category consists of greenhouse gases, gases that affect the planet's heat balance. These gases can contribute to the greenhouse effect both directly and indirectly. Direct effects occur when the gas itself is a greenhouse gas like water vapor, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and ozone (O_3).

Indirect radiative forcing occurs when chemical transformations of the original gas produce other greenhouse gases, when a gas influences the atmospheric lifetimes of other gases, and/or when a gas affects atmospheric processes that alter the radiative balance of the earth. Very powerful greenhouse gases that are not naturally occurring include perfluorocompounds (hereafter PFC), e.g. SF_6, CF_4, CHF_3, NF_3, C_2F_6. At present, the largest use of PFC (a few hundred tonnes per year) is by the semiconductor industry [2]. Amongst them SF_6 is the most potent greenhouse gas with the highest global warming potential (GWP_{100} = 23,900) and an atmospheric lifetime of 3200 years [3] making SF_6 highly dangerous if exhausted to the atmosphere. SF_6 emissions vary depending on a number of factors: gas used, type/brand of equipment used, company-specific process parameters, number of SF_6-using steps in a production process and whether abatement equipment has been implemented. Generally, process tools consume from 15 to 60% of influent SF_6 depending on the chemical used and the process application (etch or CVD) [4,5]. It follows that the waste gases will contain 40–85% of the input amounts of SF_6 so to further reduce emission levels, process optimization, alternative chemicals, capture/recycling and effluent abatement are all being considered. Also, before the exhaust gas is vented to the atmosphere, an abatement device is often provided to treat the exhaust gas. The abatement device converts the more hazardous components of the exhaust gas into species that can be readily removed from the exhaust gas, for example by conventional scrubbing and/or can be safely exhausted to the atmosphere.

This paper is concerned with the effective decomposition of SF_6 using a high pressure microwave (2.45 GHz frequency) plasma induced and sustained within a resonant cavity.

2. Considerations of gas abatement using atmospheric pressure plasmas

At the present time, the only field-proven technique for treating SF_6-containing exhaust streams is thermal, either by direct thermal oxidation or catalytic oxidation. In thermal treatment the object is to transfer heat to the exhaust stream with either electrical resistance losses or burning fuel providing the original source

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of heat. This method is indirect and can be somewhat fuel or electricity intensive. It is within this context that, over the past 10 years or more, atmospheric pressure plasmas have been increasingly promoted as a technology for a number of applications in the area of pollution abatement and it is intended to improve on some of the shortcomings of thermal systems. Atmospheric pressure plasmas have a big advantage over low-pressure plasma due to the fact that atmospheric plasmas do not require a containment vessel, hence allowing continuous processing on a large scale.

It is by now well established that optimal mixtures of some particular reactants can be produced in a weakly ionized medium only if the electron temperature is much greater than the ion and gas temperatures. Previous research on SO_2/NO_x removal from flue gas showed that a minimum electron temperature $T_e \approx 10$–15 eV was required to produce significant yields of active species such as OH radicals and monoatomic nitrogen and oxygen while if the gas temperature (T_g) was allowed to increase towards equilibrium values, recombination would reduce the concentration of the active species more rapidly than the desired reactions could take place [6,7]. It appears that only in the non-equilibrium state with $T_e \gg T_g$ can the desired reactions proceed at an appreciable rate. Furthermore, many chemical reactions rates can be greatly increased if the reactants are in excited vibrational states that would not be populated to an appreciable extent in an equilibrium plasma [8]. Therefore, there is a growing interest in using non-equilibrium plasmas for different chemical applications. In addition, for gas cleaning applications, such plasmas do not require additional fuel material as per combustion technologies, since they generate high energy electrons capable of forming reactive free radicals that facilitate the decomposition process, whilst maintaining relatively modest ambient temperatures.

Physically, non-thermal equilibrium in atmospheric pressure discharges is a relatively marginal solution. In practice there are three excitation concepts to generate such discharges. To date, environmental applications have been using mainly corona or dielectric barrier discharge (DBD) systems. However, these concern essentially low concentrations (10–100 ppm) in medium to high air flows (10–1000 m^3/h). Electron densities in corona or DBD plasmas hardly exceed 10^{11} cm^{-3} in streamers and 10^9 cm^{-3} in homogeneous volume [9–11]. In practice, this is totally insufficient to achieve appropriate PFC conversion rates in the typical conditions that prevail at the exhaust of a primary vacuum pump, namely 0.3–0.5% relative concentrations in 20–50 L/min nitrogen or air.

Microwave (MW) plasma differs significantly from other plasmas, exhibiting many interesting properties. For example, the electron density and temperature is higher in MW plasma than in radio-frequency or dc plasmas, so its reactivity is expected to be higher. The reason of this being the fact that at high frequencies, only light electrons can follow the oscillation of the electric field. This way they gain energy and collide mainly by elastic collisions with both the molecules to be abated and the carrier gas. At atmospheric pressure, microwave plasmas exhibit homogeneous densities of 10^{12}–10^{15} cm^{-3} and therefore seem much more attractive for effluent abatement in the aforementioned flow and concentration conditions [9]. In addition, a large number of inelastic electron-neutral collisions result in very efficient dissociation at relatively high concentrations of the gas to be abated. Such inelastic collisions proceed continuously preventing the reformation of the initial molecules. Microwave plasmas can be excited inside resonant cavities, within waveguide microwave circuits or by means of surface wave field applicators [12,13].

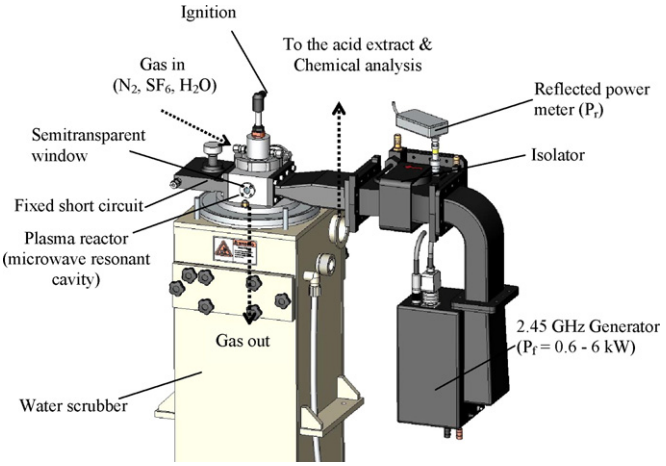

Fig. 1. Schematic of the experimental system.

3. Experimental

3.1. Microwave and plasma set-up

The microwave system used to initiate and create the discharge is shown in Fig. 1. It consists of a microwave generator (power supply and magnetron) with the power output adjustable from 0.6 to 6 kW at a frequency of 2.45 GHz, a water cooled isolator (maximum rating of 6 kW) with crystal detector for reflected power measuring, a rectangular waveguide, a single-mode microwave cavity and a microwave short circuit designed with a stub tuner to compensate for any changes in impedance loading, thus optimizing power transfer from the source to the gas to be abated.

The plasma source in this investigation is based on a single-mode microwave rectangular cavity with an internal volume $V = 120$ cm^3 within which the active zone of the plasma discharge is enclosed [14–16]. The resonant cavity enables highly efficient coupling of microwave radiation to the plasma, due to careful design such that a standing wave is established at a precise point in the enclosure. The cavity is made from a section of a standard WR340 waveguide that at 2.45 GHz frequency operates in the fundamental mode, yielding TE_{10} mode for the cavity. The electric field distribution is represented in Fig. 2(1).

A very accurate texture of all surfaces and the choice of stainless steel as material for the plasma reactor is not only a requisite to minimize wall losses and to maximize the quality factor Q of the single-mode microwave rectangular cavity but also to ensure sufficient reliability of the plasma reactor exposed to the highly energetic and corrosive plasma in fluorinated nitrogen and water vapor.

Microwaves are fed into a WR340 waveguide which is tapered to raise the electric field in front of the coupling section of the cavity. The discharge is operated at atmospheric pressure; the breakdown is initiated and maintained by the field enhancement inside the resonator cavity from power levels as low as 600 W. Microwaves with a frequency of 2.45 GHz are fed into the plasma reactor resulting in a high field concentration in the middle of the cavity—Fig. 2(2). In this region, the plasma is ignited and heated. Several kilowatts can be injected into the plasma. The breakdown and subsequent behaviour of the plasma is observed visually through the semitransparent window of the resonant cavity as well as by recording the value of the reflected power.