Contaminant gas removal using thin-film Ti electrode microdischarges

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We report a method for the selective chemisorption of oxygen and nitrogen in sealed cavities utilizing microdischarges between thin-film Ti electrodes. The method is used to remove contaminating air from both inert and organic gas environments, reducing the nitrogen and oxygen concentrations by factors of 50 and 16, respectively. A microchip-based optical emission spectroscopic sensor is used to monitor the purification. The purification improves the ability of the optical emission sensor to detect carbon by a factor of 8. The method has been tested at temperatures between 23 and 200 °C. © *2009 American Institute of Physics*. [doi:10.1063/1.3226679]

Plasma-based spectroscopic chemical sensing is widely used for the identification of numerous chemical species. Its use with gas chromatographs[1,2] can enhance selectivity. However, its practical utility in microsystems is often limited by strong background emissions that are caused by contaminating gases, e.g., nitrogen, that are present in the inert carrier gas, e.g., helium. Further, the nitrogen may react with carbon-containing gases in the mixtures undergoing analysis. Even trace contamination can dominate emission spectra and prevent the detection of target gases.[1–4] As cavity volumes are reduced to the microscale, contaminating nitrogen is increasingly problematic. It can be introduced by even small amounts of parasitic leakage, such as outgassing from surfaces or diffusion through the cavity walls. To reduce the effect of nitrogen, macroscale optical emission sensors utilize gas purifiers.[1,5] An effective on-chip purification method would be valuable in contexts other than spectroscopic sensing as well, for example, in maintaining inert gas environments in sealed packages that are essential for a variety of micromachined sensors and actuators.[6]

Currently, microscale environments can be purified using nonevaporable getters (NEGs). NEGs are included in sealed environments in strips or pellets and remove gases through oxide formation, hydride formation, and surface chemisorptions.[7] While they work on both the macroscopic and microscopic scale and have no moving parts, NEGs typically operate at pressures less than 100 Pa. Additionally, their operation is temperature dependant, requiring a high temperature activation step to remove surface oxide layers, which causes outgassing. Activation is performed by annealing the package or by Joule heating the NEG strip. Standard getters are activated at temperatures of 300–550 °C.[8–10] Thin-film titanium has been used; however, it requires activation at 300 °C.[11]

Given the operating temperature limitations of current purification methods, the use of on-chip microdischarges to sputter Ti from thin-film electrodes is an attractive option for the controlled purification of gas microenvironments. (Portions of this article appear in conference abstract form in Ref. 12). Microdischarges have high temperature electrons and ions, which allow them to operate over a wide range of temperatures.[13] In related work, microscale-sputter-ion pumps have previously been utilized to reduce the pressure in sealed packages,[14] but have not been developed to purify inert gas environments.

In this effort, we use dc or pulsed dc microdischarges between one or more planar thin-film titanium anode-cathode pairs that are patterned on a glass substrate, and separated by discharge gaps. The microdischarges are created by applying voltage across the electrode pairs [Fig. 1(a)], and result in sputtering of the titanium cathodes. This titanium selectively bonds to gas molecules and removes them from the environment. Titanium is attractive because it reacts with nitrogen and oxygen without interacting with helium, carbon, sulfur, and other gases of interest.[15]

In this effort, we use an electrode pattern with circular discharge gaps of 50 μm for uniform sputtering, with large cathodes (1.52 mm^2) to increase the available titanium. Three anode/cathode pairs are included on a single substrate and an entire device has an area of 25 mm^2, as shown in Fig. 1(b). The sputtered ions do not affect surrounding devices
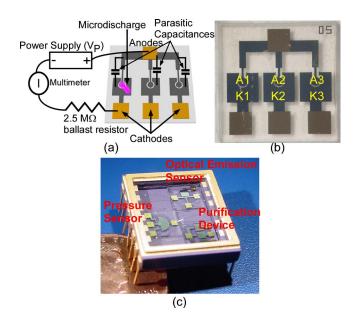

FIG. 1. (Color online) Gas purification device. (a) A dc voltage is applied to selectively remove nitrogen and oxygen. (b) Photograph of a single device. (c) Photograph of a device in a hybrid package that includes the optical emission sensor as well as a pressure sensor Ref. 18.

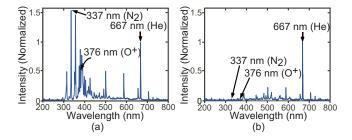a)Electronic mail: scottwri@umich.edu.

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FIG. 2. (Color online) Spectra of the pump discharge (normalized to helium at 667.8 nm) in 99.25% helium with air contamination at 27 kPa (a) before purification and (b) after purification. Small amounts of nitrogen cause intense emission lines compared to helium at time=0, demonstrating the necessity of nitrogen removal.
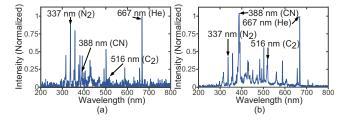

FIG. 3. (Color online) Spectra of acetone sample (normalized to helium at 667.8 nm) backfilled with helium during gas purification at 200 °C. (a) Spectrum recorded before purification, showing strong nitrogen emissions and low C_2 emissions. (b) Spectrum recorded after purification, showing diminished nitrogen and increased CN and C_2 emissions.

due to their short mean free path, which is on the order of 250 nm at 27 kPa.

The optical emission sensor in this effort also utilizes pulsed microdischarges. The emitted spectra, characteristic of the energy transitions of the ions and neutral species, are recorded by a spectrometer. The sensor is based on a previously reported three-electrode flashFET sensor configuration.[16,17] A 100 μm discharge gap separates the electrodes and the device has an area of 25 mm^2. This sensor is able to detect carbon in acetone vapor at concentrations as low as 17 ppm in an air ambient without any preconcentration. Figure 1(c) shows this sensor copackaged with the purification device.

Power for the microdischarge is applied through cavity leads (or, alternatively, by copackaged circuits). Depending on the gas mixture, the pressure, and the rate of purification desired, voltage pulses as high as 1000 V may be necessary. An external ballast resistor of 2.5 MΩ is used in series with the electrodes to limit the current and provide control over discharge energy. The optical emission sensor utilizes the same voltage and a 20 MΩ ballast resistor.

The microdischarge electrodes are fabricated with two masks. Titanium (1 μm) and gold (500 nm) films are thermally evaporated onto a #7740 Pyrex™ wafer (500 μm thick). Contact pads are patterned in the gold layer using the first mask and a selective wet etchant, while the electrodes are patterned in the titanium layer using the second mask. In this effort, the optical emission sensor is fabricated concurrently on the same wafer.

Microdischarges were used to purify both inorganic and organic gases for spectral detection. The gas purification was evaluated by examining the spectra produced by an optical emission sensor that was enclosed within the same test-volume. In each case, a known gas mixture was introduced into the test volume and an initial reading was obtained from the optical emission sensor prior to initiating the purification process. Variations in emission line intensity were used to monitor the changing concentrations of gases. The spectra were normalized to the emission line intensity of helium (667.8 nm) to account for possible variations in discharge intensity. The sensors were operated for 50 ms and the emissions were integrated for 300 ms to capture the afterglow.

As helium is the inert carrier gas most commonly used in gas chromatography, the ability of Ti-electrode microdischarges to remove nitrogen and oxygen contamination was evaluated in an environment containing 99.25% helium (99.995% pure) and 0.75% air. These experiments were conducted at a pressure of 27 kPa. A purification device and an

optical emission sensor were enclosed in a resealable package, 4 cm^3, during purification. Using a dc microdischarge, reduction factors of 56.5 in nitrogen and 16.2 in oxygen were typically achieved. The final concentrations of these contaminant gases were 90 and 70 ppm, respectively. The nitrogen concentration typically fell by 75% within 30 min. Figure 2 shows spectra produced before and after purification. In Fig. 2(a), nitrogen (N_2, 337.1 nm) and oxygen (O^+, 376.0 nm) produce strong background emission lines despite their relatively low concentrations. (This is the reason that these gases interfere with spectroscopic chemical sensing.) In Fig. 2(b), it is evident that the contaminating gases have been largely suppressed.

The ability of Ti-electrode microdischarges to purify environments for the detection of organic gases was also examined. An acetone sample was used to provide a carbon source with background nitrogen and oxygen contamination. The sample was introduced into a hermetically sealed commercial package, 0.33 cm^3, with an initial pressure of 27 kPa. In this set of experiments, discharges were operated at 200 °C in anticipation of use with chemical sensors operating in harsh environments. The strongest carbon emission line (C_2, 516.4 nm) increased in intensity relative to the strongest nitrogen emission line (N_2, 337.1 nm). Figure 3 illustrates the recorded spectra before and after purification, indicating the increased emission line intensities of carbon and CN relative to the contaminant nitrogen. Over the course of several minutes, the carbon emission line intensity increased by a factor of eight relative to the strongest nitrogen emission, as shown in Fig. 4. This purification increased the ability to detect carbon with respect to the contaminant gases by increasing the relative sensitivity.

One question that arises is whether the microdischarges cause the formation of ozone. Ozone is typically formed in corona discharges that occur at high fields, exceeding those
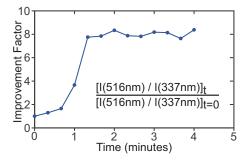

FIG. 4. (Color online) Ratio of carbon to nitrogen emission line intensity during gas purification at 200 °C, based on their strongest emission lines.

observed in this work. Ozone is difficult to detect because the characteristic glow discharge spectra are not within the optical range that is typically used for detection.[19] Whereas absorption spectra provide direct measurements,[20] ozone also can be detected indirectly by an enhanced signature of CO_2. The measured spectra did not show evidence of enhanced CO_2 production, indicating little or no ozone.

A method for gas purification in hermetically sealed microscale packages has been developed to improve the detection of microdischarge-based optical emission sensors and to provide a method of maintaining inert gas environments. These environments are essential for a variety of micromachined sensors and microelectronics as they reduce corrosion and oxidation. The method is useful over a wide range of temperatures, and has been tested from 23 to 200 °C. The method provides control over the extent of purification.

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