

Spectral Detection of Metal Contaminants in Water Using an On-Chip Microglow Discharge

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Abstract—This paper reports on the detection of trace contaminants in water by spectroscopy of micro glow discharges that operate in air or at moderate vacuum using liquid electrodes. A liquid electrode spectral emission chip (LEd-SpEC) has been developed to perform this function. The device is fabricated by a four mask process, and provides a reservoir and channels in a glass substrate, along with electrodes that bias the water sample. Liquid from the cathode is sputtered into the discharge, for spectroscopic detection of impurities. Using a commercial spectrometer, Na concentrations < 10 ppm, and Pb concentrations of 5 ppm, and Al and Cr concentrations of 10 ppm have been measured. The ratio of Na spectral intensity to that of ambient N₂ is shown to be a suitable measure of Na impurity concentration over several orders of magnitude. The addition of HNO₃ to lower the pH of the liquid solution increases this ratio by almost an order of magnitude. By selectively doping the solution, the device can also be used as a customizable optical source for UV and visible wavelengths.

Index Terms—Chemical detection, microdischarge, microplasma, water spectroscopy.

I. INTRODUCTION

WITH threats to potable water sources from industrial and biochemical pollutants, diagnostic tools that can provide rapid on-site tests for contaminants are of significant interest. Presently, water quality assessment is a relatively elaborate process, requiring sample transportation and laboratory analysis at centralized locations. Analysis involves the use of a plasma spectrometer, which varies in size from a table top model to room size. The water sample is sprayed into a radio frequency (RF) inductively coupled plasma, and the optical emission is analyzed to determine the composition and quantity of the water impurities. This is similar to detection of gaseous species in plasmas.

A variety of methods are available for diagnosis of gas and water impurities and several of these are being explored for microsystems applications. For analyzing liquids, FET structures with ion-sensitive gate material are used [1]. Gas chromatographs separate different gases flowing through a heated tube together with a carrier gas, on the basis of their sticking coefficients to the heated wall. Recent efforts have been made

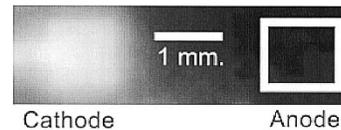


Fig. 1. Local confinement of a microplasma at 2 Torr and 410 V dc.

to miniaturize these [2]. Kelvin cell gas detectors have been micromachined [3]. These devices measure the change in the work function of a solid surface as it absorbs gas.

Devices that measure impurities by ionizing the sample and measuring the spectra have the potential for very sensitive measurements, and the advantages of a large database of spectral characteristics. Mass spectrometers, which measure the ratio of ion mass to charge are often used for detecting gases. In particular, quadrupole mass spectrometers have an ion source, an electrostatic lens with four poles to focus the ion flow, and an array of detectors to measure the spatial deflection of ions, which is proportional to their charge to mass ratios. Ions with smaller mass to charge ratios are deflected more. Using micromachining technology, a quadrupole mass spectrometer has been developed with 500- μm diameter electrodes [4]. Time of flight mass spectrometers ionize gas atoms in bursts, accelerate the ions electrostatically, and measure their time of flight, which is a function of ion mass. Ion mobility mass spectrometers, which have the capability of operating at atmospheric pressure, exploit differences in the mobilities of species in the presence of a background gas. An RF ion mobility spectrometer has recently been miniaturized [5].

Microplasmas have been the focus of increasing research in recent years. We have reported through-wafer etching of a silicon substrate using dc microplasmas which were ignited across a metal-polyimide-metal electrode stack patterned on the same substrate [6]. In contrast to the stacked electrode configuration, a configuration that uses two coplanar titanium electrodes is shown in Fig. 1. This particular microplasma was generated in air at 2 Torr, at 410 V. The glow in these coplanar electrode microplasmas is confined to the region over the cathode. Other efforts have been directed at miniaturizing inductively coupled plasmas to be utilized for gas spectroscopy [7], and to utilize dc microplasmas as an optical emission source for gas chromatography [8]. Atomic transitions of metallic impurities are typically best detected from spectroscopic analysis of dc plasma emissions [9]. Work has also been done employing the water sample as a cathode, with a metallic anode for spectroscopic use [10], [11], and detecting water impurities through spectral information. An effort to implement this system in a MEMS device has been reported very recently [12].

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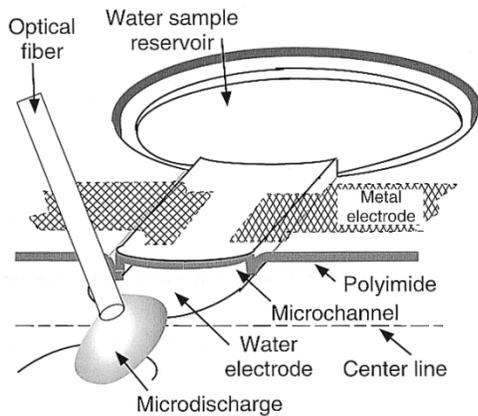


Fig. 2. Schematic of device concept showing half of the symmetrical structure.

This paper reports on the detection of trace contaminants in water by spectroscopy of micro glow discharges that operate in air using dual liquid electrodes (i.e., both the anode and cathode are liquid). A liquid electrode spectral emission chip (LED-SpEC) has been developed to perform this function.¹

Liquid from the cathode is sputtered into the discharge, and can be utilized for spectroscopic detection of impurities such as Pb, Cr, and others. This device can also be used as a customizable optical source for UV and visible wavelengths. The device structure and operation are described in Section II. Section III describes the fabrication of the device, and the experimental results are shown in Section IV.

II. DEVICE STRUCTURE

The LED-SpEC uses the water sample, inserted into microchannels on a glass substrate, as the electrode material for generating a glow discharge for spectroscopic analysis (see Fig. 2). This provides the following benefits:

- 1) the water sample and its impurities are effectively sputtered into the glow discharge, eliminating the need for spraying, which is otherwise necessary for detecting non-volatile contaminants;
- 2) concern for electrode wear is eliminated since it is replenished by liquid flow;
- 3) a continuous glow discharge can be sustained in air at atmospheric pressure, eliminating the need for a vacuum system.

Thin-film Pt features patterned within the channel provide lead transfers for the dc power supply. A 4.5-mm long channel covered by polyimide separates the exposed liquid in the $500\ \mu\text{m} \times 700\ \mu\text{m}$ electrode regions from reservoirs, which do not participate in the glow discharge. The two liquid electrodes in each device are separated by 2.5 mm. An optical fiber mounted above this region couples the device to a pager-sized spectrometer (see Fig. 3) (Ocean Optics USB-2000) connected to a data acquisition computer. (The LED-SpEC can accommodate a copackaged micro spectrometer as well.)

¹A portion of this work has been published in conference abstract form in [14].

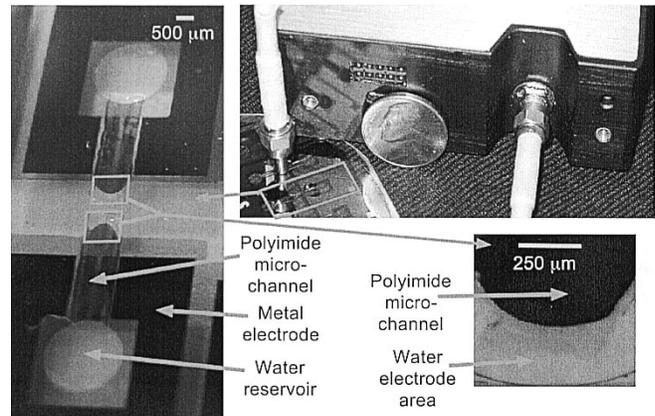


Fig. 3. Optical viewgraph of system and close-up view of the LED-SpEC.

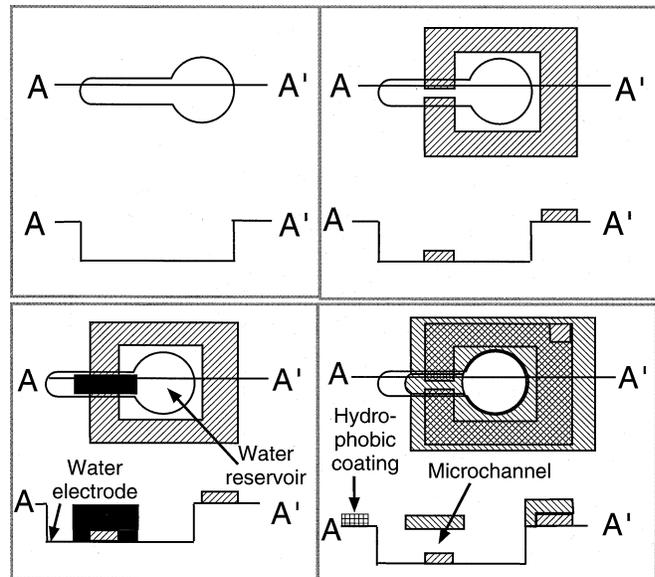


Fig. 4. Fabrication sequence: 1) recess glass substrate; 2) pattern Pt lead transfer; 3) electroplate Cu sacrificial layer for channel; and 4) pattern polyimide cover, etch sacrificial layer, and apply hydrophobic film between electrodes.

III. FABRICATION

The device is fabricated on a glass substrate using a 4-mask process (see Fig. 4). The first mask serves to pattern an etch in a glass wafer which serves to define the sample confinement region. In this step, a $300/800\ \text{\AA}$ Cr/Au layer is evaporated onto the glass substrate, and patterned by lift-off. The exposed glass substrate is wet-etched using a 3:5:7 HF/Nitric acid/DI water solution, following which the Cr/Au layer is removed. The second mask patterns thin-film Pt electrodes, which provide electrical contact for the liquid electrodes. These electrodes are formed by evaporating a $300/500\ \text{\AA}$ Cr/Pt layer which is also patterned by lift-off. Platinum was chosen as the electrode material, because it is unreactive with most acidic solutions. The third mask provides a photoresist mold for a $30\text{-}\mu\text{m}$ thick layer of electroplated Cu, which is used as a sacrificial layer. A $300\text{-}\text{\AA}$ Cu seed layer is first evaporated onto the sample. Photoresist is slow-spun onto the sample to $30\text{-}\mu\text{m}$ thickness, and the Cu sacrificial layer exposed. Copper is electroplated into the mold in a commercial

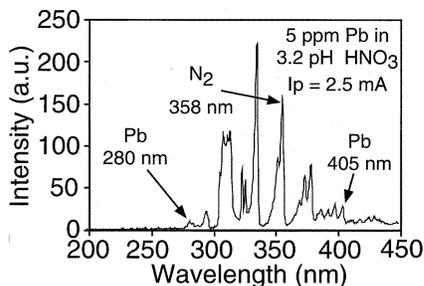


Fig. 5. Spectrum from sample containing 5 ppm Pb.

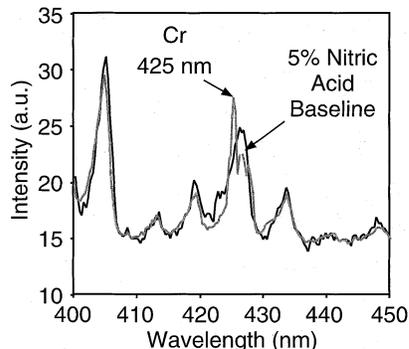


Fig. 6. Spectrum from sample containing 10 ppm chrome and 5% nitric acid, superimposed against a 5% nitric acid baseline.

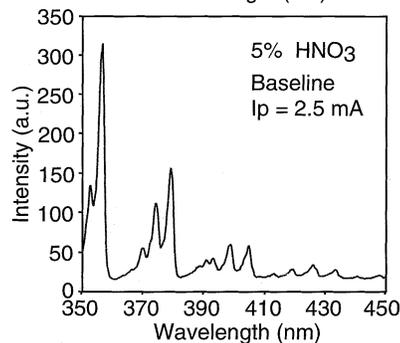
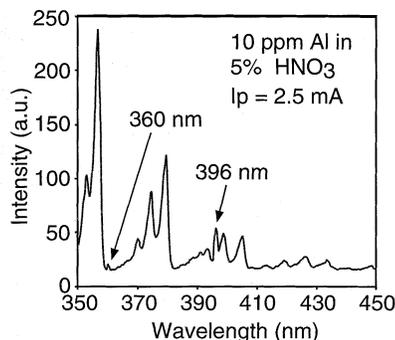


Fig. 7. (Top) Spectrum from sample containing 10 ppm Al in a 5% nitric acid solution and (bottom) 5% nitric acid baseline.

room temperature copper sulfate plating solution at 20 $\mu\text{m}/\text{h}$. After electroplating the photoresist is stripped and the Cu briefly etched to remove regions of the Cu seed layer that was not electroplated. A 9- μm thick polyimide is then spun on the sample, and is patterned with the fourth mask. This mask provides wet etched openings in a 200/500 \AA Al/Ti sputtered layer. The polyimide is then plasma etched with an 100 sccm O_2 /10 sccm CF_4 gas flow mixture, operated at 500 W power, and 200 mTorr operating pressure. This patterning exposes the openings in the microchannels, and provides polyimide walls for the sample reservoir. Finally, the sacrificial Cu is etched away with heated ferric chloride solution, and a hydrophobic film of petroleum jelly is applied to the inter-electrode surface to eliminate electrophoresis of water during prolonged operation [13].

IV. EXPERIMENTAL RESULTS

Fig. 5 shows the typical spectral output of a sample containing 5 ppm Pb dissolved in nitric acid with a pH of 3.2. Two dominant spectral lines characteristic to Pb are seen at 280 and at 405 nm. Fig. 6 shows the spectral output of a sample containing 10 ppm Cr, contained in a 5% nitric acid solution. The spectra is shown against a baseline spectra generated from 5% nitric acid only. The principal spectra due to Cr at 425 nm can be seen, as well as some lesser lines in the spectral region. Fig. 7(a) illustrates the spectra generated from 10 ppm Al in 5% nitric acid, whereas Fig. 7(b) illustrates the spectra generated from 5% nitric acid only. Fig. 7(a) shows the dominant spectral line at 396 nm due to Al, as well as a lesser line at 360 nm.

Although the intent of this effort is to permit detection of toxic metal impurities in water, a number of studies that provide basic device characterization were performed with Na, which is

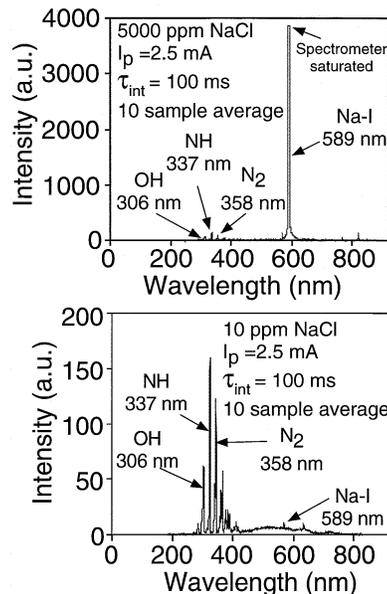


Fig. 8. Spectra for NaCl samples with concentrations of (top) 5000 ppm and (bottom) 10 ppm.

readily available, nontoxic, and provides a robust spectral intensity. Spectra of saline at 10 ppm to 5000 ppm concentrations are shown in Fig. 8. A discharge current of 2.5 mA was used. These show the primary Na contaminant line at 589 nm. The large spike at 358 nm is characteristic to N_2 . The Na spectra are a result of the impurities sputtered from the liquid electrode, while the N_2 spectra which are seen in all discharges in this effort, are due to the air ambient. The NH and OH ionic lines are also visible as a result of the sputtered water, and its reaction with the atmosphere. In Fig. 8(a), the case of 5000 ppm Na, the

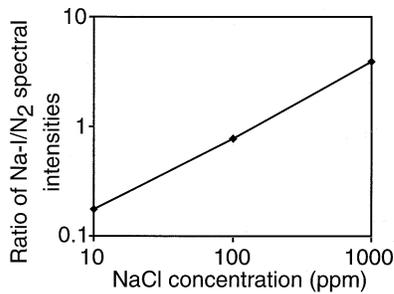


Fig. 9. Ratio of Na to N₂ spectral intensities as a function of NaCl concentration.

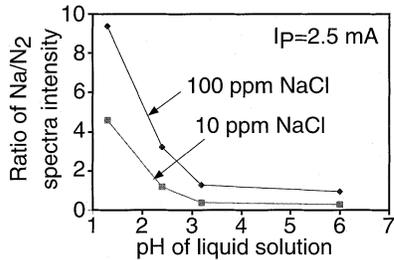


Fig. 10. Ratio of Na to N₂ spectral intensities as a function of pH of the tested solution.

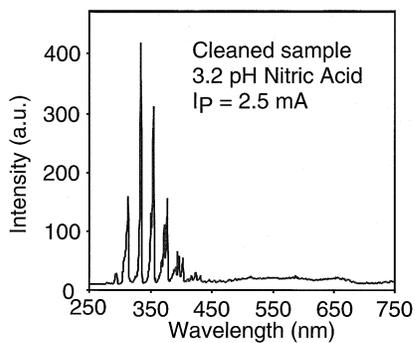


Fig. 11. Spectrum from device previously containing 5000 ppm NaCl, rinsed with DI water.

sodium spectral intensity is so strong the spectrometer is saturated at the Na wavelength, and the signal is much stronger than the N₂ lines. In Fig. 8(b), the case of 10 ppm Na, the N₂ lines dominate the Na lines.

By measuring the ratio of the spectral intensities of the primary contaminant to N₂, is it possible to determine the concentration of the impurity over a wide dynamic range. This is a valuable feature. Fig. 9 shows the averaged ratio of Na to N₂ spectra, for Na concentration ranging from 10 ppm to 1000 ppm. The ratio of spectral intensities varies by almost two orders of magnitude.

The intensity of the Na line can be increased by modifying the pH of the sample under test with nitric acid, while the intensity of the nitrogen line remains relatively unchanged. This results in the ratio of the Na to N₂ spectral intensity lines to increase as the pH is decreased, which can be useful for extending the impurity detection limits (see Fig. 10).

LED-SpEC is designed to be a disposable device, but it can also be reused. Fig. 11 shows deionized water spectra from the same device that was previously used for 5000 ppm NaCl in

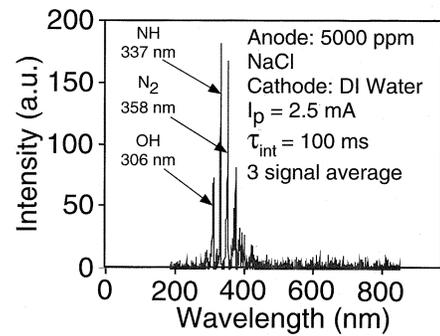


Fig. 12. Spectrum from experiment showing that all contamination measured is from cathode cell.

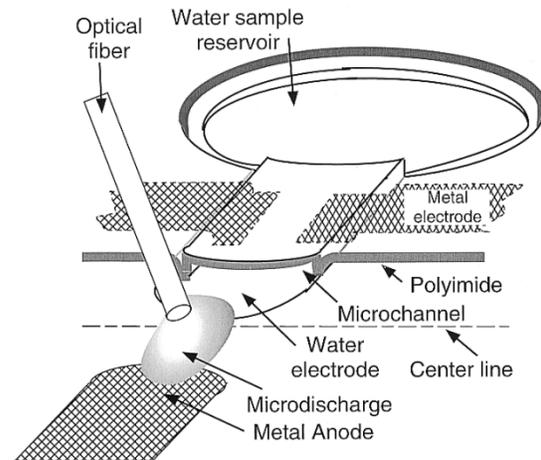


Fig. 13. Schematic of device concept using metal anode.

Fig. 8(a), and was then rinsed in DI water. No sodium spectra can be detected after cleaning.

To determine the source of the impurity ions in the glow discharge, the cathode of one device was filled with a 5000 ppm NaCl solution and the anode with DI water. This provided a spectrum similar to Fig. 8(a), indicating that positive gas ions from the discharge sputtered the cathode. The spectrum obtained under the reverse polarity did not show the Na line (Fig. 12). This indicates that the dominant impurity delivery mechanism is sputtering from the cathode as opposed to fluid heating and vaporization. This is an important feature of the LED-SpEC because it permits inorganic impurities which are nonvolatile to be introduced into the plasma. It eliminates the need for spraying the water into the plasma, which is the approach used in conventional devices.

Since it has been verified that the impurity delivery is due to sputtering from the cathode, the device can be constructed with a metal anode, as opposed to a liquid one (see Fig. 13). The dual water electrode configuration allows one reservoir to be filled with the solution under test, and the other reservoir to be filled with a baseline solution, while the metal anode configuration provides a simpler device. The metal anode configuration also provides a lower breakdown voltage. The device is able to detect impurities with sensitivities comparable to the liquid anode device. The spectra created from a solution with 100 ppm NaCl are shown in Fig. 14. The impact of varying the inter-electrode gap was tested using 5000 ppm NaCl on device variants (see

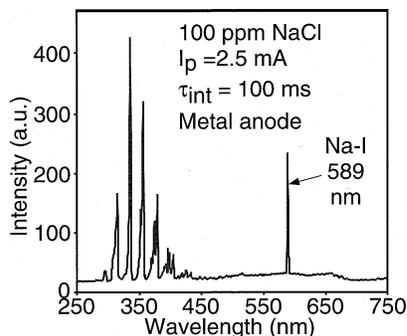


Fig. 14. Spectra generated from device with metal anode, and cathode filled with 100 ppm NaCl.

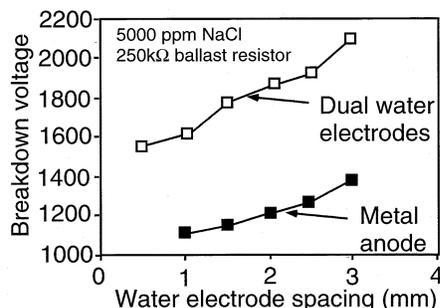


Fig. 15. Breakdown voltage dependence on inter-electrode gap for 5000 ppm NaCl for dual liquid electrode device, and metal anode device.

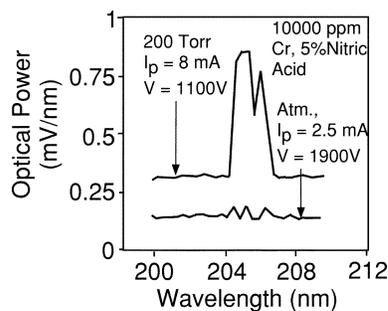


Fig. 16. Spectral intensity characteristics of LED-SpEC with cathode filled with 10000 ppm chrome, at atmosphere and 200 Torr.

Results showed a linear relationship between this dimension and the breakdown voltage, with the metal anode configuration providing a lower breakdown voltage.

In addition to use in the detection of water impurities, the LED-SpEC shows promise as a light source with a customizable spectrum. The device was tested with a 10 000 ppm Cr solution in 5% nitric acid. Cr provides multiple dominant spectral lines in the 200–207 nm range. It was found that the emission spectral power of the UV range increases if the device is operated in vacuum. Fig. 16 illustrates the spectral optical intensity both at atmosphere, and at 200 Torr in air. The intensity is found to increase at lower operating pressures. This is believed to be due to the increased electron energy in discharges at lower operating pressures.

V. CONCLUSIONS

The LED-SpEC device was shown to detect sodium impurities of concentration less than 10 ppm, lead impurities at 5 ppm, and aluminum and chrome impurities of 10 ppm. The device operates by sputtering the cathode, which is the liquid sample under test. The relative concentration of sodium is a function of the ratio of the Na/N₂ spectral intensities, and varies over orders of magnitude. The addition of acid to lower the pH of the sample increases the intensity of the impurity line. The device can be operated with a metal or liquid anode, and is reusable. The device shows promise as a possible on chip UV as well as optical source.

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