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Highly sensitive optical humidity probe

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Abstract

A highly sensitive optical humidity probe based on reflectance measurements has been developed using Nafion®-crystal violet (CV) films. This sensor can be used to calibrate relative humidity (RH) in the range 0–0.25% with a detection limit (blank signal + $3\sigma_b$, where σ_b = the standard deviation (S.D.) of the blank signal) of 0.018% RH (∼4.37 ppm) and exhibited low hysteresis. The sensor films were fully reversible in dry nitrogen and reversal times were shown to be dependent on exposure time and % RH. The response to 1% RH was highly reproducible (S.D. = 1.67%, number of samples (n) = 5). Hydrogen chloride gas did not interfere with the response of the sensor to RH but did reduce sensor reversal times. This sensor displayed sufficient sensitivity that it could be used to detect ppm levels of moisture in process gases such as nitrogen and HCl.

Keywords: Relative humidity sensor; Moisture detection; Reflectance probe; Optical fibre sensor

1. Introduction

The ability to monitor low levels of moisture has become even more critical in the semiconductor-manufacturing process since the demand for process gases with more stringent moisture specifications has continued to grow. Commonly used process gases include both nitrogen (N_2) and hydrogen chloride (HCl) [1]. Moisture is a particularly problematic contaminant in gas supplied from a cylinder as it can adsorb strongly onto metallic surfaces and cannot be easily removed by purging with dry inert gases. Humidity is often referred to as relative humidity (RH) and is defined as the ratio (%) of the concentration of water vapour in the gas to the saturated concentration at the same temperature and pressure. Humidity can also be expressed as volume concentration (ppm). In this paper, both units of concentration will be referred to intermittently.

Recent research in optical humidity sensing has been described in the literature [2–5]. Cobalt (II) chloride ($CoCl_2$) was one of the earlier reagent schemes investigated for this purpose [2]. Immobilised in gelatine it could be used to determine the RH of air between 40% and 80% [2] and, when immobilised on acetylated cellulose substrates, it could determine RH down to 4% [3]. Recently an evanescent wave sensor has been fabricated using PVA doped with $CoCl_2$ coated on the surface of a U-bend core of a plastic clad silica (PCS) fibre and this sensor responded to RH in the range 10–90% with a detection limit of 15% (∼3660 ppm) and it displayed fast response and reversal times <1 s [4]. Using the same U-bend sensing principle phenol red was incorporated into a polymethylmethacrylate (PMMA) film and the resulting sensor was shown to respond to RH in the range 20–80% with a response time of 5 s [5].

In the identification of a suitable reagent scheme for the determination of moisture in process gases crystal violet in Nafion® is of considerable interest. It is well known that the colour of CV is very sensitive to the acidity of protons [6] and this property has been exploited in the development of an optical humidity sensor. Nafion® is a perfluorosulfonate resin in which hydrophilic perfluorinated ether side chains terminate with sulfate groups, which are periodically attached to hydrophobic perfluoroethy-

Abbreviations: ANN, artificial neural networks; a.u., arbitrary units; CO_2, carbon dioxide; $CoCl_2$, cobalt (II) chloride; CV, crystal violet; H, hydrogen; HCl, hydrogen chloride; HPC, hydroxypropylcellulose; kHz, kilohertz; LiCl, lithium chloride; N_2, nitrogen; NH_3, ammonia; NIR, near-infrared; nm, nanometres; NO_2, nitrogen dioxide; PCS, plastic clad silica; PMMA, polymethylmethacrylate; ppm, parts per million (v/v); PVA, poly(vinyl alcohol); r, correlation coefficient; RH, relative humidity; S.D., standard deviation; s/n, signal/noise ratio; wt, weight

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lene backbone molecules. Nafion® is commercially available as a 5 wt.% solution in low aliphatic alcohols and 10% water. The fluorocarbon backbone provides exceptional chemical and thermal stability while the sulfonate groups are responsible for ion exchange [7]. The acidity of the proton bound to the sulfonate group depends on the water content in the film. When a solution of Nafion® and CV in a polar solvent is left to dry a phase inversion occurs with the Nafion® polymer and the dye remaining entrapped in an ionic cluster [8]. Nafion® is very strongly acidic and CV exists in the diprotonated form; dried Nafion®–CV films appear to be yellow in colour. In response to an increase in the water content within the film the sulfonate groups become less acidic and CV is converted to its mono - and non-protonated forms which is accompanied by a colour change from yellow to green [9,10]. The degree of deprotonation is accelerated with increasing water content. This colour change can be monitored using both absorbance [9,11] and reflectance measurements [9,12–15] at 630 nm. This allows the use of cheap plastic optical fibres in the development of an optical fibre sensor for humidity. This method exhibits low hysteresis and fast response times (1 min and 10 s, respectively) [9,10]. The response range using this system was extended from 40–55 to 40–82% using artificial neural networks (ANNs) [12] and a later paper written by the same authors described the detection limit for RH to be <2% [13], which shows promise for detection of low ppm levels of humidity. The linear response range was further extended to 30–70% RH by using an optimum Nafion®:CV molar ratio of 10:1 and the homogeneity was improved by treating the Nafion®–CV films with methanol [10]. Nafion®–CV films can also be used to simultaneously detect ammonia (NH_3) and RH [14,15] and although NH_3, HCl and nitrogen dioxide (NO_2) react with the films, only humidity caused a decrease in reflectance at 630 nm [14].

This paper describes investigations into the sensitivity and reversibility of an optical fibre sensor for the detection of humidity at low ppm levels in gases such as N_2 and HCl gases.

2. Experimental

2.1. Apparatus

Experiments were carried out using a commercially available miniature fibre-optic based spectrometer (Ocean Optics PC 1000) which utilises a small tungsten halogen lamp (Ocean Optics) as the light source and a CCD based detector for both absorbance and reflectance measurements. A combination of Ocean Optics PC 1000 data sampling rate of 25 kHz and averaging of 70 scans was used to obtain the highest signal/noise (s/n) ratio of the blank signal. A gas blender comprising of three mass flow controllers (Brooks 5850 TR) was used. Two controllers, with flow rates ranging from 0 to 1000 ml/min, were employed to deliver dry nitrogen or dry HCl gas. The third controller (flow rate 0–100 ml/min) was employed to deliver humid nitrogen. All measurements were made using an optimum total flow rate of 1000 ml/min [10,14,15]. One hundred percent RH nitrogen was obtained by bubbling dry air into a series of bubbling flasks filled with de-ionised water and mixing of dried gases with 100% RH produced samples of different RH. The accuracy of the gas blender was verified with a commercial humidity meter (Kane-May, KM8006). Initial studies used the spectrometer in conjunction with purpose built flow cells designed for absorbance [16] and reflectance measurements (Fig. 1). Temperature was maintained at 20 °C throughout the study by conducting experiments in a Thermotron environmental chamber. Films were stored in a desiccator until use.

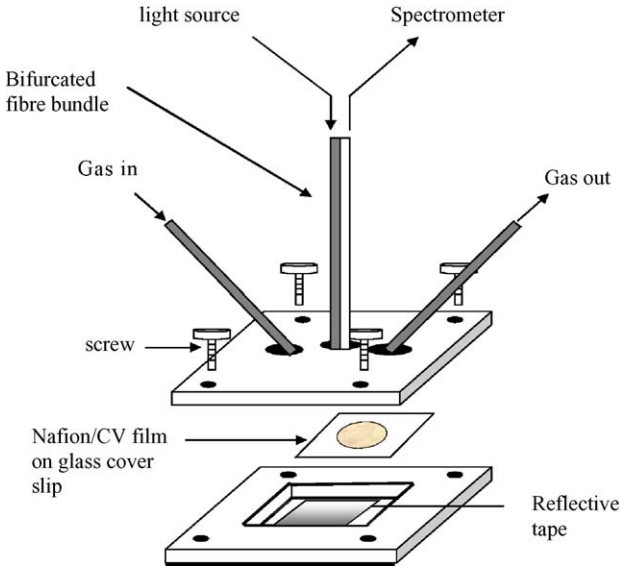

Fig. 1. Flow cell for reflectance measurements.

2.2. Probe design

The reflectance probe design employed in this work has been described elsewhere [10,15] and uses a randomized 32 bifurcated optical fibre bundle to transmit source and detected light.

2.3. Reagents and solutions

A 5 wt.% Nafion® solution (in low aliphatic alcohols and 10% water) and crystal violet were purchased from Aldrich and used without further purification. A 0.1 M crystal violet stock solution was prepared in methanol and was prepared on the day it was required for use. Nitrogen (100%) and HCl gas (1000 ppm) were supplied by BOC.

2.4. Procedure

2.4.1. Film preparation

Nafion®–CV films of ~5 μm thickness were either prepared by pipetting 5 μl of solution onto clean glass cover slips (22 mm^2, BDH) for use in the flow cells or onto a glass disc (1.0 mm high × 4.5 mm diameter, UQG Optics Ltd.) for use in conjunction with the reflectance probe. 5 μl of Nafion®–CV solution was pipetted onto the chosen glass substrate and allowed to dry for 30 min in the environmental chamber kept at 20 ± 1 °C.