# A Highly Selective HF Sensor Based on A Potassium Ion-Exchanged Waveguide Polarimetric Interferometer

Zhi-mei Qi,[#] Naoki Matsuda,* Kiminori Itoh,[†] and Masayuki Murabayashi[†]
*Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8565*
[†]*Institute of Environmental Science and Technology, Yokohama National University, Yokohama 240-8501*

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A simple polarimetric interferometer constructed with a single-mode potassium ion-exchanged (PIE) glass waveguide was used as a disposable HF sensor with an excellent selectivity. By examining the interference between the transverse electric ($TE_0$) and transverse magnetic ($TM_0$) modes during the HF etching of PIE waveguides, the average rate of change in the phase difference was demonstrated to depend linearly on the HF concentration. The compressive stress-induced birefringence in the PIE layer was found to be responsible for the HF-sensing feature of the PIE waveguide polarimetric interferometer.

PIE waveguide is often used as a passive optical waveguide (OWG) because of an extremely weak evanescent field resulting from a graded-index PIE layer. In our research on OWG chemical/biological sensors, the evanescent field of the PIE waveguide was enhanced significantly by sputtering a tapered film of high-index materials on its surface.[1,2] Such a structure termed the composite OWG has been used to develop a highly sensitive polarimetric interferometer based on adiabatic taper-induced separation and recombination of the $TE_0$ and $TM_0$ modes.[3–5] Like an integrated optical Mach–Zehnder interferometer, the composite OWG polarimetric interferometer is a basic optical transducer and can form a variety of chemical/biological sensors by coating different sensitive materials on the tapered film.

A bare single-mode PIE waveguide can also be used to construct a polarimetric interferometer,[6] which is almost insensitive to changes in refractive index and/or adsorbed layer thickness on the waveguide surface because the $TE_0$ and $TM_0$ modes have approximately equal effective-refractive-index responses to these changes. However, we show here that the PIE waveguide polarimetric interferometer is sensitive to HF etching of the PIE layer. Thus, a PIE waveguide polarimetric interferometer can serve as a disposable HF sensor with an excellent selectivity. It should be noted that HF as an important industrial material and a conventional silicon etchant is highly poisonous and HF leakage will cause the air and water pollutions. The HF monitoring is, therefore, necessary in specific environment. As a matter of fact, disposable HF gas detectors made by Japanese Gastec Company based on chromometry are commercially available now. This kind of HF sensor is not immune from interfering gases such as HCl and $NO_2$ as noted in its instruction manual. This letter describes a quantitative measurement of HF concentration in liquids by using a PIE waveguide polarimetric interferometer based on the specific reaction of HF acid with glass. The experimental setup is schematically shown in Figure 1. Single-mode PIE waveguides were fabricated by immersing soda-lime slide glass substrates into molten $KNO_3$ at 400 °C for 30 min. With the prism coupling method a linearly polarized He–Ne laser beam was coupled into the PIE waveguide to simultaneously excite the $TE_0$ and $TM_0$ modes with equal intensities. A single beam coupled out of the PIE waveguide was passed through a 45° analyzer for causing interference between the TE- and TM-polarized components. A pen recorder was connected to a photomultiplier detector to record the output signal. A 3-cm-long Teflon cell was attached to the PIE waveguide and then a given concentration of HF acid was pumped into the cell at a constant rate to etch the PIE waveguiding layer at room temperature. Figure 2 presents a polarimetric interference pattern obtained from 460 ppm HF etching. The output signal oscillated 13.5 times during the etching time of 108.5 min and the average rate of change in the phase difference ($d\Delta\phi/dt$) was 0.887/min in the range from the second to the fifth fringe. Under the same experimental conditions such as the same HF flowrate and the same temperature, $d\Delta\phi/dt$ was measured to be equal to 0.353, 1.716 and 2.182/min, corresponding to 276, 690 and 920 ppm HF solu-

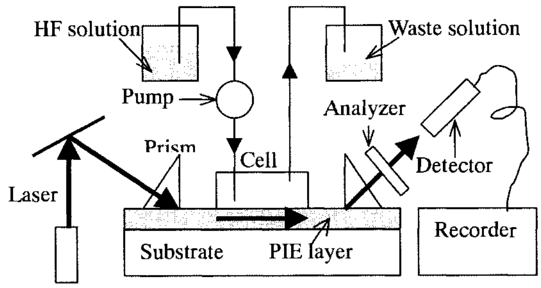


**Figure 1.** Schematic diagram of a PIE waveguide polarimetric interferometer for measuring the concentration of HF solution.

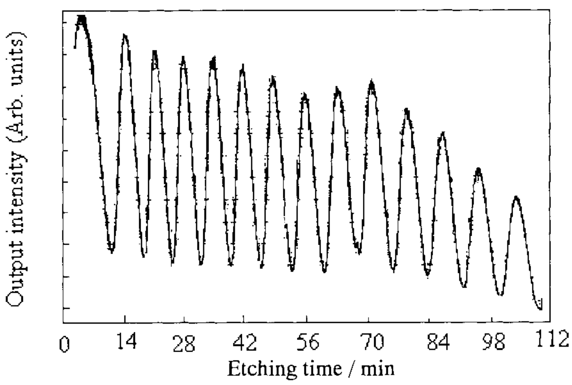


**Figure 2.** Polarimetric interference pattern obtained from 470 ppm HF etching of a single-mode PIE waveguide

tions, respectively. Figure 3 shows that $d\Delta\phi/dt$ depends linearly on the HF concentration. From the regression line, the HF concentration is derived to be 150 ppm for $d\Delta\phi/dt = 0$. It may represent a detection limit of the HF sensor under the present condition. In fact, the response of the sensor was too weak to detect for etching with less than 200 ppm HF. This limit can, however, be improved by optimizing the PIE waveguides.

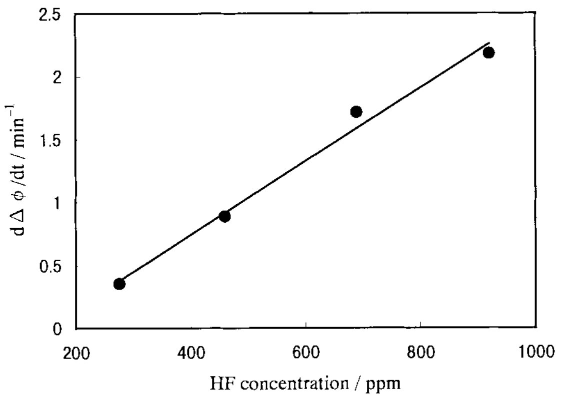


**Figure 3.** HF concentration dependence of the average rate of change in phase difference between the $TE_0$ and $TM_0$ modes in a single-mode PIE waveguide.

The mechanism for the PIE waveguide polarimetric interferometer being sensitive to HF etching is the compressive stress-induced birefringence that is a function of the PIE depth.[6] At the temperature of 400 °C, which is below the glass transition point, the $K^+$–$Na^+$ ion exchange results in the compressive stress in the PIE layer owing to a larger size of $K^+$ ions than $Na^+$ ions. On the basis of elastooptical effect, the compressive stress causes the birefringence of the PIE layer, that is, the refractive index for the TM-polarized light beam ($n_{TM}$) becomes larger than that for the TE-polarized one ($n_{TE}$). Because the compressive stress has a profile similar to that of $K^+$ ion concentration, the birefringence varies with the PIE depth. As a result, the modal birefringence defined as the difference between the effective index of the $TM_0$ mode ($N_{TM0}$) and that of the $TE_0$ mode ($N_{TE0}$) is also a function of the PIE depth. When the PIE waveguide is etched with HF acid, the phase difference, $\Delta\phi$, between the TE- and TM-polarized components of the output beam changes according to Equation 1 and the detected intensity, I, varies cosinuosoidally with $\Delta\phi$ following Equation 2,

$$\Delta\phi = (2\pi/\lambda)L[N_{TM0}(d) - N_{TE0}(d)] \quad (1)$$

$$I = I_0(1 + \cos \Delta\phi) \quad (2)$$

where $\lambda$ is wavelength in free space, L is the etching length and d is the etching depth, and $I_0$ is the TE- or TM-polarized output intensity. The average change in $\Delta\phi$ per minute (namely, $d\Delta\phi/dt$), representing sensitivity of the HF sensor, depends on the etching rate that is determined by the HF concentration in the case of a given HF flowrate. The value of $d\Delta\phi/dt$ can be increased easily by increasing L because the single-mode PIE waveguide is a low-loss OWG. It should be emphasized that $d\Delta\phi/dt$ can also be increased significantly by enhancing the birefringence of single-mode PIE waveguides. We have reported that the birefringence of PIE waveguides can be modified in a wide range by changing the exchange temperature and time duration.[6]

Another kind of single-mode glass waveguide containing in-diffused tin atoms because of the floating method was also used to measure the HF concentration with polarimetric interferometry. However, the interference pattern was not observed during HF etching. It indicates that the polarimetric interferometer constructed with an Sn-diffused glass waveguide is insensitive to HF etching. The reason for the insensitivity is that the diffusion of tin atoms into the slide glass took place at high temperatures above the glass transition point so that the stress in the diffused layer was relaxed before solidification of the slide glass. Therefore, the stress-induced birefringence vanished and the Sn-diffused layer became isotropic. For an isotropic glass waveguide, the modal birefringence, $N_{TM0} - N_{TE0}$, resulting from different contributions of the waveguide-cladding interface to $N_{TM0}$ and $N_{TE0}$ is so small that the interferometer cannot respond to HF etching. This finding further supports the HF-sensing mechanism for the PIE waveguide polarimetric interferometer proposed above.

In addition to the insensitivity to the cladding material change, the PIE waveguide polarimetric interferometer as a disposable HF sensor has the following advantages: (1) Glass substrate is very cheap. (2) Precise controlling of exchange temperature and time duration provides reproducible fabrication of single-mode PIE waveguides with the equal birefringence. (3) The $TE_0$ and $TM_0$ modes in a single-mode PIE waveguide have almost identical traveling paths so that the PIE waveguide polarimetric interferometer is immune to temperature interference. (4) The PIE waveguide is resistant to various acids and alkalis except HF acid. (5) The PIE waveguide polarimetric interferometer is convenient to operate. These features give the PIE waveguide polarimetric interferometer a large potential of practical application as a disposable HF sensor.

**References and Notes**


# Zhi-mei Qi is on leave the State Key Laboratory of Transducer Technology, Institute of Electronics, Chinese Academy of Sciences, Beijing 10080, P. R. China.

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