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Modified POF sensor for gaseous Hydrogen Fluoride monitoring in the presence of ionizing radiations

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Abstract — *This paper describes the development of a sensor designed to detect low concentrations of hydrogen fluoride (HF) in gas mixtures. The sensor employs a plastic optic fiber (POF) covered with a thin layer of a glass-like* material. The HF attacks the glass and alters the fiber transmission capability so that the detection simply requires a LED and a photodiode. The coated POF is obtained by means of a low pressure plasma enhanced chemical vapor deposition (PECVD) that allows the glass-*like* film to be deposited at low temperature without damaging the fiber core. The developed sensor will be installed in the recirculation gas system of the Resistive Plate Counter (RPC) muon detector of the Compact Muon Solenoid (CMS) experiment at the Large Hadron Collider (LHC) accelerator of the European Center for Nuclear Research (CERN).

Index Terms — *Optical fibers, Gas detectors, Radiation effects, Plasma materials processing, chemical sensors*

I. Introduction

Resistive Plate Chambers (RPC) are gas detectors extensively used in High Energy Physics and in Astroparticle experiments for particle detection [1].

In particular, the Compact Muon Solenoid (CMS) experiment [2] at the Large Hadron Collider (LHC) in the European Center for Nuclear Research (CERN) laboratory in Geneva (Switzerland) employs RPCs [3], [4] to detect muon particles, a primary tool for studying the basic components of matter, and for trying and observe the last fundamental brick postulated by the Standard Model and not detected yet - the Higgs boson, as well as the supersymmetric particles postulated to explain the dark matter enigma [5] [6].

The RPCs employed at CMS are composed of two bakelite plates, maintained at a voltage difference of about 9 kV and kept 2 mm away by spacers, so that an electric field of about 4.5 kV/mm is present between the plates.

The RPC are sealed and filled with a gas mixture whose ionization upon the passage of a charged particle will provide the output signal. The gas mixture is composed of 96.0% of $C_2H_2F_4$, 3.5% of C_4H_{10} and 0.5% SF_6, with 45% relative humidity. This mixture is quite expensive and the involved volume is of about 18 m^3, therefore a closed loop recirculation gas system is employed to maintain the gas composition constant and uniform within the RPCs.

The absence of contaminants is important in all gas detectors, but is critical in the case of RPC since their presence is responsible for an increase of the dark current until the RPC become not usable. For this reason a sets of three purifiers is installed in the system. One of the identified contaminants, which has been seen to be critical due to its reactivity, is the hydrogen fluoride (HF); the average HF production in the gas flow has been estimated to be about 25 μmol/h before the purifiers and 0.1 μmol/h after the purifiers, which corresponds to concentrations before the filters of some part per million [7], [8]. Unfortunately, the filters get intoxicated after few months of use and need to be regenerated so that it is important to monitor the contaminant concentration during the experiment run that extends over several months.

Actually, the contaminant concentration is controlled thanks to the presence of few gas sampling points, before and after each filter in the closed loop, which allow gas sampling for chemical (ICP-MS, INAA, etc.) and gaschromatographic analysis. A continuous monitoring of the gas mixture is, however, of outstanding importance in order to optimize the RPC detecting capability.

Several types of sensors are commercially available to detect the HF presence usually with measuring range of 20 ppm. Examples are galvanic-type sensors which are based on MnO_2 gas-diffusion electrodes which are used for hydrohalogens (HCl, HBr, HF) concentration measurement in the air [9]. Other examples are tin dioxide-based gas sensors, which can detect hydrogen fluoride traces at part-per-billion concentration [10], [11]. Moreover, Al-doped graphene sheets have been proposed to develop high sensitive HF sensors [12]. Most of these sensors, however, have a high cost so that the monitoring of more than 1000 RPCs can be difficult to be obtained, moreover sensor capable of working in the presence of high intensity electric fields and of high-energy radiations would be greatly simplifying the design of the monitoring system allowing the sensor to be installed close to the RPC.

The characteristics of fiber optics sensors (FOS), such as immunity to electrostatic discharge and the intrinsic small sensor dimension, make them particularly suitable for this application. Typically FOS sensors employ glass fibers which enable the use of powerful interferometric detection techniques, but the aggressiveness of HF, which attacks the glass, prevents their use in this application.

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Plastic Optical Fibers (POF) made of polymethylmethacrylate (PMMA) [13], [14] can be an interesting alternative as their use for sensing applications is rapidly growing [15], [16], [17]. Typical telecommunication [18] POFs have a large diameter in the range of 0.25 mm to 1 mm that permits to use simple and cheap plastic connectors still maintaining a good optical coupling. Optical fibers can be used to develop intrinsic sensors thanks to several different principles such as fiber grating, scintillation, light attenuation change due to pollutant absorbtion into the core, light losses due to fiber bending, etc.. [19], [20]. From this point of view, POF fibers have a remarkable evanescent field, which extend outside the core and can be used to develop intrinsic sensors based on the changes in the propagation losses connected to the interaction of the evanescent field with the surrounding media. A sensor therefore can be easily arranged by removing the cladding and coating the fiber with a substance capable of reacting with the pollutant to be measured.

One of the problems connected with POF sensor coating is the sensitivity of the PMMA to the temperature, which can be tackled by employing low pressure plasma treatments for the deposition process. Plasma Enhanced Chemical Vapor Deposition (PECVD) and plasma sputtering can be successfully employed for the development of sensors able to detect gases and chemicals with a very high sensitivity [21]. The PECVD processes versatility permits to modify the fiber surface chemical properties either by grafting different functional groups, or by depositing of thin films, whose properties can be changed simply by a proper selection of the experimental parameters. Moreover, plasma processes allow one to optimize the etching of the fiber cladding in order to deposit the sensitive film directly onto the fiber core without modifying its properties; this approach can lead to more sensitive and highly selective sensors.

II. Sensor preparation

A. Fiber selection and uncladding

A commercial step-index, highly multi-mode POF was used to set up the sensor prototypes. The fiber has a PMMA core of 0.98 mm in diameter, which is surrounded by a 0.01 mm thick fluoropolymeric cladding. The sensor preparation involves two steps:

1. etching of the cladding in an organic solvent (such as ethylacetate);
2. deposition of the sensitive film by plasma sputtering and/or PECVD.

All PECVD depositions were performed in a reactor consisting of a vacuum chamber made of stainless steel equipped with a turbomolecular pump backed by a rotary pump. A powered electrode connected to a 13.56 MHz RF power supply through an impedance matching unit and a grounded electrode. The RF electrode can be equipped with a metallic target and a magnetron which allows the plasma sputtering process to be obtained. A throttle valve, and a pressure gauge permit to keep the pressure fixed at the selected value. Reaction gas and film precursor vapor can be injected into the chamber with their flow rates controlled by mass-flow and vapor source controllers.

The fibers were processed onto the ground electrode at the floating temperature reached by the plasma, which was below 70°C, so that avoiding to damage the PMMA core.

B. Coating selection and deposition

The extremely high electronegativity of the F^- ions makes it difficult to find materials for which a reversible reaction can be found; once the fluoride ions react with a material it is almost impossible to break the bond at room temperature. For this reason the authors decided to try the development of a non-reversible or cumulative sensor. This type of sensor is sensitive not to the actual pollutant value, but to the total exposition to it. This behavior makes it difficult to obtain a fast response sensor, but is particularly suited for this application where the filter intoxication is related to the total exposure to the contaminants.

Initially the authors investigated the performance of metallic layers and specifically of a nanostructured silver layer. Silver reacts with hydrogen fluoride to form silver fluoride (AgF), changing its color from bright metallic to pale yellow so that the fiber transmission decreases due to decreasing reflectance of the silver fluoride as the reaction proceeds. Unfortunately such a change is minimal and in addition, silver reacts also with many other compounds such as hydrogen sulphide so that the sensor selectivity would be a problem.

Then the authors decided to take advantage of the capability of the fluoride ions to attack the glass. Glass is a very stable material that practically does not react with anything but the hydrofluoric acid so that a quite high selectivity should be obtained. HF reacts with glass leading to the formation of silicon tetrafluoride (SiF_4):

$$\mathrm{SiO_2 + 4HF \Rightarrow SiF_4 + 2H_2O} \tag{1}$$

Since the glass has a refractive index higher than the PMMA, covering the fiber with glass turns out in a dispersive fiber with very poor transmission ratio. When the glass is attacked by the hydrofluoric acid its dispersing capabilities greatly decrease so that an increase in the transmission ratio is expected.

The authors therefore decided to try covering the fiber with a thin SiO_2-*like* layer whose structure resembles the glass. A stoichiometric SiO_2 layer cannot be easily obtained at low temperature and in the form of films with thickness of few hundreds nanometers, however SiO_x thin films can easily be obtained by PECVD starting from organosilicon monomers.

The deposition was obtained by using a plasma fed with tetraethoxysilane (TEOS), O_2 and Ar in different ratio, at the pressure of 5 Pa and with an input power of 50 W. The film thickness, which can be controlled varying discharge power and deposition time, was set to about 200 nm. The thickness (Fig. 1) was measured by means of a Field Emission Scanning Electron Microscope (FESEM).

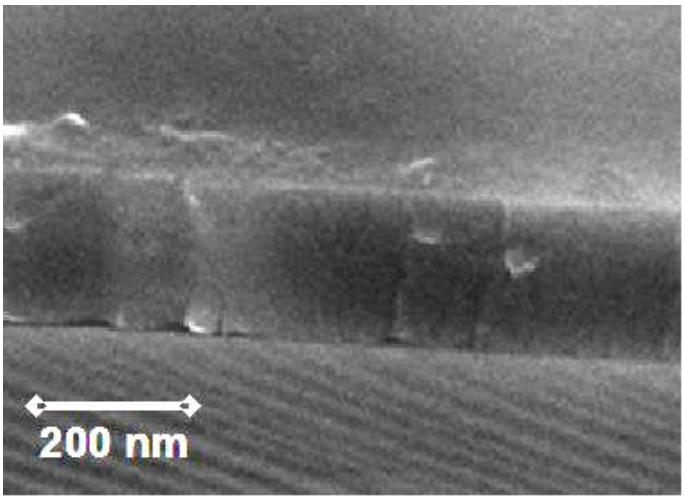

Fig. 1. FESEM image of the SiO_2-*like* film cross-section. The film thickness is about 200 nm.

C. Sensor assembly

The basic sensor structure is composed of the coated fiber with a length of about 10 cm, a LED for illuminating the fiber at one end and a photodiode that collects the light at fiber end and permits to estimate the light transmission capability. Typical POFs have good transmission capabilities in the red and green wavelengths; for this application the authors employed a red LED since the literature [22] reports a better behavior of the PMMA fiber exposed to radiations when employed with red wavelengths.

The sensor assembly is critical due to the aggressiveness of the HF vapors and the sensitivity of the fiber to the bending. For this reason no connectors are used: the LED and the photodiode cupolas are drilled with 1 mm holes, a liquid PMMA glue is then used to bond the already uncladded fiber which is inserted into the holes. The system is cured in oven at 60 °C for three days and then left to stabilize for other additional four days. At this point teflon insulated wires are connected to LED and photodiode. The connections and the diodes are then painted with an HF resistant black paint and the assembly bonded to a PVC support so that the fiber is in a fixed position. The complete fiber assembly is then inserted into the PECVD reactor for the deposition as described in previous section (Fig. 2). Since the reactor is not equipped with a rotating facility, the deposition is performed in two steps by reversing the fiber after half time to cover all the surface. This solution does not allows one to obtain a perfectly uniform coating, but insure all the fiber surface is coated with the glass-*like* material.

This assembling procedure, even though it proved to be suitable for the sensor arrangement, has two main drawbacks. Firstly, the sensitivity of the initial transmission ratio is strongly connected to the LED/photodiode hole position and to the fiber end polishing. This results in different couplings and, therefore, in different initial transmission ratio. Since this can be viewed as a scaling factor, the authors normalized all the traces to the initial value to present the results. The second problem is connected to the different expansion ratios of fiber and fiber support that turns out in minimal fiber stretching and/or bending. The effect of these mechanical alterations is a transmission change which turned out to be of the order of 5% for temperature changes of 5 °C. Even though this should not be a problem in the final installment, where the temperature is controlled, a new fix setup is being designed to solve this inconvenience.

Fig. 2. The fiber in the plasma reactor during the coating deposition.

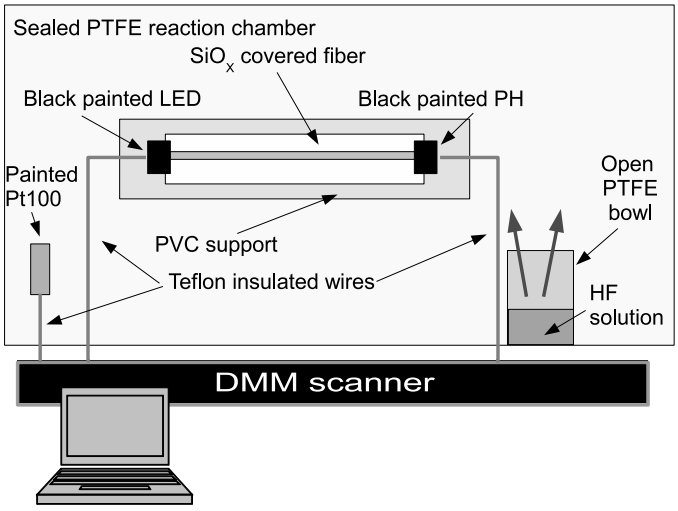

Fig. 3. Block diagram of the measurement setup. The sensor is composed of the coated fiber, a black painted LED and black painted photodiode. A painted $Pt100$ sensor is used for temperature measurement. All wires are teflon insulated and the connection painted to protect them from the HF vapors. The reaction chamber is made by polytetrafluoroethylene (PTFE) which is HF-resistant. The HF vapors are generated by inserting into the reaction chamber a small PTFE bowl containing a calibrated solution of HF.

III. Measuring setup

The measuring setup is sketched in Fig.3 and is designed to be suitable for working in the presence of the highly aggressive HF vapors. The setup is composed of a polyte-

trafluoroethylene (PTFE) reaction chamber which can be completely sealed to avoid dispersing the HF vapors in the environment. The sensor is arranged as described in the previous section and all the connections are painted to resist to the HF presence. A $Pt100$ sensor painted as well is used for monitoring the temperature. The LED is driven by a pulsed current generator; for each measurement session, a measure is taken with the LED off, to compensate for offsets and residual environmental light, then with the LED on. The led current is measured as well, so that its changes can be compensated.

The generation of a known concentration of HF vapors is obtained by using a small amount of HF solution let into an open PTFE bowl. Since the reaction chamber is completely sealed the air inside the reaction chamber reaches an equilibrium with the liquid HF solution and the partial pressure of the HF vapor can be computed by using the well known Antoine equation [23]:

$$log_{10}Pp = A - \frac{B}{C+T} \tag{2}$$

where A,B,C are constants connected to the concentration of the HF in the solution, T is the absolute temperature, and Pp is the partial pressure of the resulting vapor.

The value of the constants can be found in several places such as at NIST [24] and can be computed from partial pressure experimental measurements [25]. The authors employed a certified solution containing HF at a known concentration of 40% in volume which was diluted as requested. The temperature sensor was used to compute the actual partial pressure present in the reaction chamber.

IV. Experimental results

A. Radiation effect

Since the sensors are designed to be employed in an environment where a non-negligible amount of high-energy radiations may be present, it is important to verify the behaviors of both the plastic fiber and of LED and photodiode when exposed to such radiations. Different studies have been performed regarding the behavior of glass fibers in the presence of radiation [26], [27], [28], mainly from the point of view of their capability of transmitting data without errors. Few results are available regarding the plastic fibers [22]. In general, high energy radiations can induce fiber depolymerization and this in turns might reduce the fiber light transmission capability thus impairing the sensor performance. According to tests described in [22], the radiation induced attenuation should be of about 1 dB/m for a PMMA fiber excited with a red wavelength and subjected to a dose of 100 Gy. From these data one would expect an amplitude change of the order of 5% on a fiber with 10 cm length in the same condition. However since the production procedures have considerably changed since 1989, the authors performed some tests at the Gamma Irradiation Facility (GIF) at CERN to confirm the sensor feasibility. To this aim two sensor assemblies were prepared, one using a bare fiber and one using a fiber coated with a thin Ag film. The two assemblies were installed and left in place for about six months exposing them to a dose of about 2 Gy, corresponding to several months of typical CMS operation.

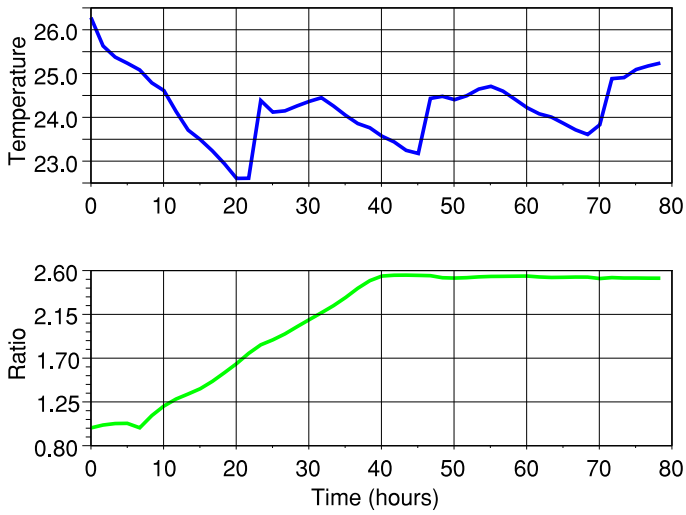

Fig. 4. Attenuation change due to the HF reaction on the SiO_x layer deposed on the fiber. The fluoride vapors are introduced at hour 7 and then let in place for about three days. It is clear how the degradation SiO_x layer due to the HF results in an increase of the transmission ratio. The trace is normalized to the initial transmission ratio. The transmission ratio changes of a factor 2.5 until the external coating reaches a stable degradation state after about 27 hours. The temperature during the test is not controlled and changes in the range of 22 °C to 27 °C with minimal effect on the result.

No changes in the transmission ratio were recorded on the bare fiber as expected, while a small transmission reduction, of the order of 5% was observed for the silver coated fiber, probably due to the chemical reaction between the Ag film and the gas mixture. Since the glass-*like* coating has negligible depolymerization problems, the radiation effect on a glass-*like* coated fiber should be almost the same as the one recorded on the bare fiber, so that the tests confirms the available data and confirms the feasibility of the proposed sensor.

B. Exposition to HF

The effect of HF on the plasma deposited sensitive layer was investigated by exposing the coated fibers to HF vapors obtained by the equilibrium of a 20% in volume solution (partial pressure of about 700 Pa), at a temperature of about 25°C. Chemical and morphological characterizations were performed on the fiber surface before and after the aggressive tests by employing a FESEM microscope equipped with a Energy Dispersive X-Ray Spectrometer (EDS).

All the tests were performed by leaving the fiber into the bowl for some hours in clean air and then inserting the PTFE bowl with the HF solution letting the measurement running until the fiber output remains stable.

Fig. 4 shows the result of an exposition of about three days to the vapors produced as described before. The hydrogen fluoride vapors are introduced at hour seven and then let in place for the remaining time. By exposing the

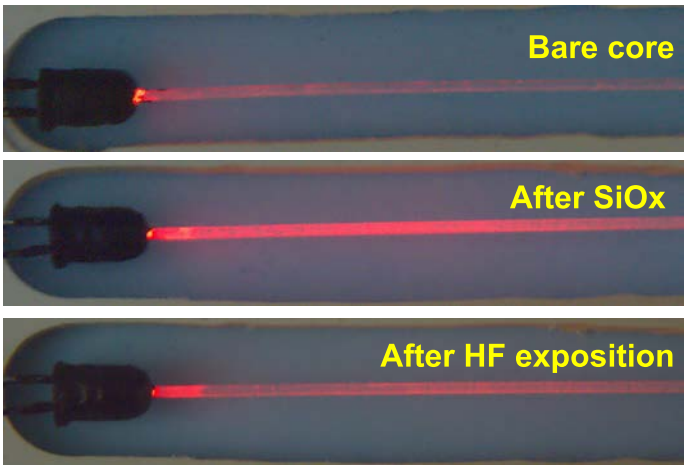

Fig. 5. Effect on the fiber light transmission capability of the SiO_x layer deposited on the fiber. The top image shows the fiber before deposition: the light is mostly confined inside the fiber as expected. The middle image shows the fiber after the deposition of a SiO_x layer with thickness of about 200 nm: the refractive index of the SiO_x, which is higher than the PMMA, makes the fiber dispersive. The bottom image shows the fiber after exposition to the HF vapors. The layer is attacked and the SiO_x mostly degraded, so that the fiber is much less dispersive even though more dispersive than the uncoated fiber.

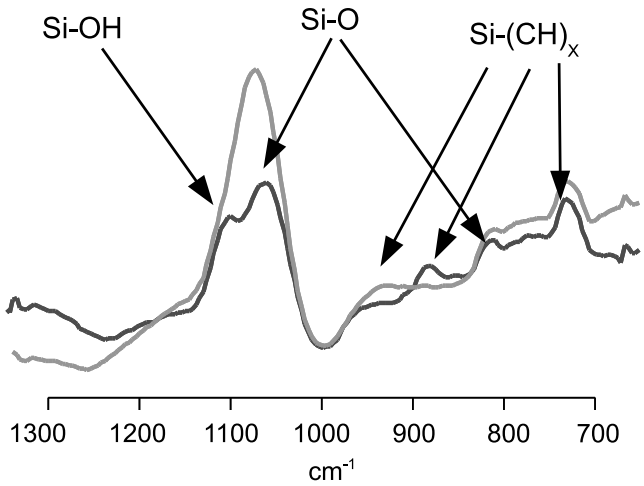

Fig. 6. FTIR spectra of the SiO_x film deposited at 50 W in plasma fed with two different gas mixtures: $TEOS : Ar = 1 : 30$ sccm (red line); $TEOS : O_2 : Ar = 1 : 20 : 10$ sccm (green line).

fiber to this concentration the light transmission increases of a factor about 2.5 in about 27 hours. The trace also shows a minimum effect of the temperature, with some minor irregularities due the fiber settling on its support.

Fig. 5 shows three fiber pictures taken with the LED on before and after the deposition of the SiO_x layer and after the exposure to the hydrogen fluoride vapors. It is clear how before the deposition (top image) the light is mostly confined inside the fiber, as expected, with a small dispersion due the fiber surface irregularities which are highlighted since the cladding has been removed. After the deposition of the 200 nm thick SiO_x layer (middle image) the fiber become dispersive as expected since the refractive index of the SiO_x film is higher than the PMMA. Eventually the bottom image has been taken after the exposition to the HF vapors. The SiO_x layer is almost completely corroded by the fluoride vapors so that the fiber becomes much less dispersive and this explains the received light increase.

V. Coating optimization

The described sensor relies on the glass nature of the coating i.e. on the higher refractive index of SiO_x with respect to the PMMA. Since the layer structure also depends on the discharge parameters, different sensors were prepared by changing the discharge recipe in order to optimize the sensor performance obtaining a SiO_2-*like* film, which should be particularly reactive in the presence of HF vapors [29]. A SiO_2-*like* film can be obtained by increasing the oxygen flow of the feeding gas mixture in order to obtain a glass-*like* film structure.

Fourier Transform Infrared Spectroscopy (FTIR) was used to assess the nature of the deposited SiO_x films. Fig. 6 shows two traces obtained by increasing the oxygen/monomer flow ratio. The FTIR shows that with high oxygen/monomer ratios ($TEOS : O_2 : Ar = 1 : 20 : 10$ sccm - green line) only the absorption bands of *Si-O* groups (stretching at 1070 cm^{-1}, bending at 820 cm^{-1}) and *Si-OH* groups (stretching at 1100 cm^{-1}) are detected, while the organic component, mainly present in the film deposited in an oxygen-free plasma ($TEOS : Ar = 1 : 30$ sccm - red line), is found in the minor peaks: the ethylsilyl group absorbs at 937 cm^{-1} and 737 cm^{-1}; the *Si-C* bond stretches at 887 cm^{-1}.

Fig. 7 shows the results obtained with two sensors coated with SiO_x films deposited in different conditions. The figure shows the normalized transmission change plotted *vs.* the computed HF exposition so that it is possible to directly compare the sensor sensitivities. The exposition is computed by integrating the partial pressure computed according to eqn. 2. It is clear how the sensor which produced the red line has not only an higher transmission rate change (about 3 instead of 2.5), but also a quicker transmission change that leads to sensor saturation after an exposition of about 13000 ppm · hour instead of 25000 ppm · hour. The ratio change per unary exposition r:

$$r = \frac{\delta R}{\delta E} \tag{3}$$

therefore increases from about 0.01%/ (ppm · hour) to about 0.02%/ (ppm · hour).

The different fiber behavior can be explained by observing the coating surface at the FESEM before and after the exposition to the HF vapors. Fig. 8 shows a low magnification image of the glass-*like* coated fibers before and after the exposition and highlights the different aspect of the coating which gets corroded by the HF vapors.

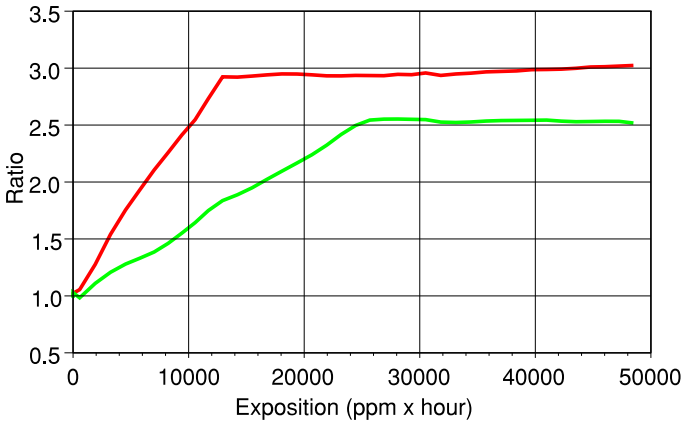

Fig. 7. Attenuation change as a function of the HF vapor exposition the two different fibers whose FTIR is shown in fig 6. The red line refers to the fiber obtained with an oxygen rich plasma and which has a SiO_2-*like* coating. The exposition is computed by integrating the partial pressure computed according to eqn. 2

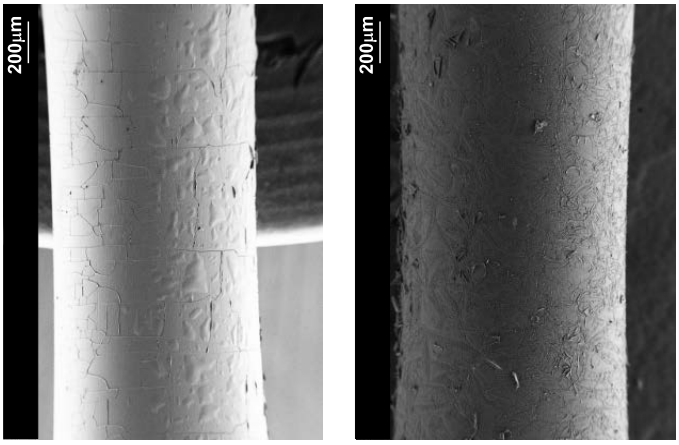

Fig. 8. FESEM images of coated fiber before (left) and after (right) the exposition to the HF vapors.

The behavior difference of the two coating types can be understood by observing the surface at a higher magnification as shown in Fig.9. The figure shows from the left an example of coating immediately after deposition coating. The image refers to the SiO_2-*like* coating, but the aspect does not change even for the coating deposed with low oxygen concentration. From the second row, which is a high resolution image of the first row, one can see how the coating appears as flat, uniform and compact. The center and right images show the aspect of the coating after the exposition to the HF vapors. Now the coating appears damaged and broken and this explains its reduced capability of dispersing the light. In particular, the detailed images of the second row highlight the different behavior of the coating that, in the case of the SiO_x film with an high organic fraction, tends to generate small clusters, which probably slow down the attack process thus reducing the sensor sensitivity.

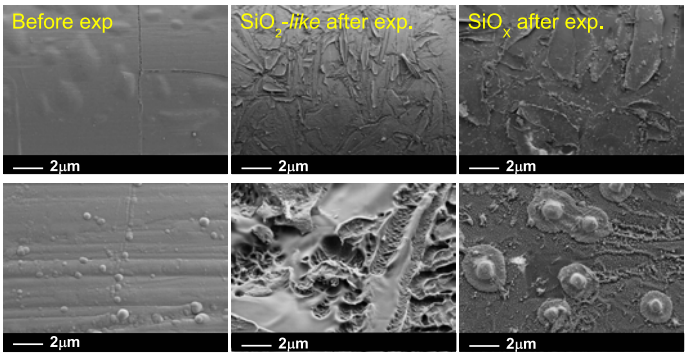

Fig. 9. Details of the fiber surface. On the left the surface before the exposition. In center the surface of the SiO_2-*like* fiber after the exposition to the HF vapors. On the right the surface of the SiO_x coating after the exposition to the HF. The bottom row contains images at higher magnification. These detailed images highlight the different behavior of the coating that, in the case of the SiO_x film with high organic fraction, tends to generate small clusters, which probably slow down the attack process thus reducing the sensor sensitivity

VI. Conclusions

The tests performed with sensors arranged by depositing a thin SiO_2-*like* layer on an uncladded POF demonstrate the feasibility of a sensor based on this principle. The sensor has a high selectivity to the fluoride ions that are able to attack the glass-*like* coating determining an increase of the transmitted light. The transmittance change is important with an increase of up to 3 times.

The cumulative response of the sensor that prevents its reuse after the exposition makes it complex the calibration procedure. However, since the attainable transmittance change mainly depends on the chemical-physical properties of the film and since these properties are determined by the discharge parameters employed during the deposition, the authors are working on a characterization procedure on a per-batch basis, where part of the sensors realized in a single session are employed for the characterization of the entire batch and then disposed. The sensor linearity for extremely low concentrations has not been assessed yet since the measurements require several months per test, however all the results obtained for HF vapor pressure in the range of 70 Pa to 7000 Pa did not highlighted linearity deviations.

The great light transmission change coupled with a cumulative behavior permits a quite good sensitivity to be obtained and makes the proposed sensor suitable for monitoring the presence of contaminants in the gas employed in the resistive plate chamber detectors (RPC) of the CMS experiment. With the expected gas concentration the sensor should be able to follow the entire experiment reaching its end of life after about one year in case of normal filtering actions.

The authors are now working on the characterization and on the two still open problems connected to the sensor development i.e. the optimization of the coating deposition, to enhance the sensitivity, and the mechanical

sensor mounting, which can affect the light transmission. However, the extremely low sensor cost coupled with its resistance to high energy radiation and high electric fields make them suitable for a massive installation on all the RPCs and for a continuous gas monitoring.

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