Processing, Characterization, and Impact of Nafion Thin Film on Photonic Nanowaveguides for Humidity Sensing

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Herein, the impact and spin-coating process of Nafion thin films on photonic nanowaveguide structures fabricated via a complementary metal–oxide–semiconductor compatible process for the first time is investigated. Particularly, the effect of Nafion thin films (~23–776 nm) on microring resonators (MRRs) with compact waveguide sizes (480 nm by 220 nm and 380 nm by 220 nm) is focused on, where the microring provides enhanced interactions between the Nafion and light, which is related to Nafion thin-film properties such as the refractive index, water uptake, and swelling. The results demonstrate small, compact, and cost-effective MRR devices to characterize Nafion thin film and high-resolution on-chip humidity sensing for real-time and continuous measurements.

1. Introduction

Microring resonators (MRRs), as a waveguide-based, monolithically integrated resonant interferometer having a small size, have attracted great interest in a wide range of applications including optical communications, signal processing, and sensing.\cite{1,2,3} A generic integrated optical MRR consists of a ring waveguide as the resonant cavity and at least one bus waveguide that can couple light into the ring. When light propagates via the ring waveguide, the evanescent field extends outside of the waveguide and interacts with materials on the waveguide surface. This light–matter interaction is enhanced via the ring cavity. A change in the cladding material on MRR waveguides varies the effective refractive index of the propagating mode of the light within the MRR, resulting in an instantaneous optical spectrum change such as shifts in the resonant wavelength of the MRR and alterations to the free spectral range (FSR).\cite{6,7,13} This enables characterization of thin films deposited on MRR waveguides via an optical spectrum measurement.

Nafion, as a perfluorosulfonic acid polymer wherein sulfonic acid-terminated perfluorovinyl ether chains are grafted onto a Teflon-like backbone, has spurred substantial attention in recent years for its wide range of applications,\cite{14,15,16,17,18,19} particularly in fuel cells and similar electrochemical energy conversion devices. Nafion thin films, the properties of which could differ significantly from those of the bulk film, are finding increasing research interest, driven by the need to reduce overall resistances with its high proton conductivity and growing applications in sensors.\cite{20,21,22,23} Due to the presence of electrostatic interactions, hydrogen bonding, and a less well-defined chain structure, water solubility and water transport in Nafion thin films are complex problems.\cite{33,34,35,36,37,38,39,40,41} Currently, the characterization of Nafion thin films relies on large equipment such as ellipsometry,\cite{28,29} infrared spectroscopy,\cite{30,31} grazing incidence small-angle X-ray scattering,\cite{25,32} neutron reflectometry,\cite{38,39} and positron annihilation lifetime spectroscopy,\cite{40} which are bulky and expensive and have restrictions in real time and continuous measurement. The use of on-chip MRRs provides great potential to achieve a compact, lightweight, cost-effective solution to investigate Nafion thin film, via characterizing the continuous light–Nafion interactions.

In this article, for the first time, Nafion thin films with various thicknesses are deposited onto a silicon MRR waveguide device via spin coating, and their impact on MRR devices with nanoscale-dimension waveguides is investigated both theoretically and experimentally, which provides a new way to investigate Nafion’s properties in real time on a lightweight and portable platform. Moreover, utilizing the impact of Nafion thin films on the optical waveguides, and Nafion’s advantages, particularly high hydrophilicity, we propose and demonstrate a highly sensitive and ultracompact humidity sensor based on the MRRs with a Nafion thin-film coating. The MRR based on silicon-on-insulator (SOI) nanowaveguides has a small footprint of 76 μm² and complementary metal–oxide–semiconductor (CMOS) compatibility for mass production. We use focused ion beam (FIB) micromachining and scanning electron microscopy (SEM) to measure the waveguide dimension, X-ray photoelectron spectroscopy (XPS) to examine the chemical composition of the Nafion coating, ellipsometry, and quartz crystal microbalance (QCM) to investigate properties of the Nafion film on the silicon wafer, and atomic
force microscopy (AFM) to conduct surface topographical analysis on Nafion-coated waveguides. To characterize the interactions between the light and the Nafion thin film, which are related to the film thickness, refractive index, and water uptake, we analyze the fraction of light intensities in Nafion cladding, simulate the group index and effective refractive index of the propagation mode within the Nafion-coated waveguide, and measure the FSR change of the optical spectrum, as well as the resonant wavelength shift. The optical properties (group index and effective refractive index) obtained by the MRR devices show good agreement with the results based on ellipsometry evaluated refractive index. Moreover, the trend of the optical resonant wavelength shift of the MRRs with a Nafion thin-film coating at different humidity agrees with the water sorption isotherm of Nafion thin film measured by ellipsometry and QCM. These results demonstrate that the small, compact, and cost-effective MRR devices provide great promise for characterizing Nafion. Using a silicon MRR with a Nafion thin film of 23 nm thickness as a sensor probe, we demonstrate humidity sensing in real time. The proposed sensor detects the relative humidity (RH) via measuring the shift in the optical resonant wavelength caused by the swelling of Nafion film at different humidity levels. Experimental results show a unidirectional resonant wavelength shift as a function of RH level, a higher sensitivity provided by the MRR with 380 nm waveguide width, and low hysteresis under humidity cycling.

2. Results and Discussion
2.1. Operating Principle, Device Characterization, and Surface Chemical Composition

This study focuses on processing, characterization, and impact of Nafion thin films ranging from about 23 to 776 nm on photonic nanowaveguide MRRs and their application in humidity sensing. A generic MRR cladded with a Nafion thin film is shown in Figure 1a. The operation of the MRR is based on codirectional evanescent coupling between a ring and an adjacent bus waveguide, where a π-phase difference can occur at resonant wavelengths between the coupled and transmitted light waves. This phase difference introduces destructive interferences, thus resulting in sharp notches on-resonance and pass-through responses off-resonance in the resonant optical transmission spectrum. By engineering the waveguide geometry, strong evanescent waves on the sides and the top of the silicon waveguide core evidently penetrate into Nafion coating. This creates continuous light–matter interactions during light propagation, which are then further enhanced by the MRR structure. As the environmental RH changes, the porous Nafion film exhibits different degrees of water uptake. This leads to a change in both the thickness and the optical properties of the film, affecting light transmission via the evanescent fields and thereby altering the optical resonances. In this way, the impact of Nafion on the

Figure 1. a) Illustration and operating principle of Nafion thin film-coated MRRs, showing a strong light–matter interaction in response to humidity variation. Changes in Nafion film due to vapor-induced hydration impact the evanescent wave propagation within the ring waveguide, thus producing FSR variations in the output spectrum. Orange wave packets represent "on-resonance" wavelengths, whereas the green represents "off-resonance" wavelengths. b) Overview of the fabricated MRRs with 380 and 480 nm waveguide widths and their VGC pairs. SEM micrograph of c) a fabricated MRR with a circumference of 216 μm and d) its VGC region. Cross-sectional SEM micrograph of waveguides with top widths of e) 480 nm and f) 380 nm. Simulated mode profile at 1550 nm of the waveguide with top widths of g) 480 nm and h) 380 nm. i) Measured optical transmission spectra of the MRRs with 480 nm- (solid) and 380 nm (dashed)-wide waveguides and their measured FSR values at room temperature.
photonic nanowaveguides is manifested by the shift of the optical resonant wavelength of the MRR, which can be monitored in real time via continuously measuring the optical transmission spectrum. The resonance $\lambda_{\text{res}}$ of the MRR occurs at the wavelength that fits an integer number of times inside the optical length of the ring waveguide and is given by\(^{(1)}\)

$$\lambda_{\text{res}} = (n_{\text{eff}} \cdot L)/m$$

where $m$ is an integer, $L$ is the circumference of the MRR, and $n_{\text{eff}}$ is effective refractive index, which reflects the phase velocity of single-wavelength light and depends on the geometry and optical properties of both waveguide core and claddings. The FSR defined as the wavelength spacing between two adjacent resonances is expressed as

$$\text{FSR} = \lambda_{\text{res}}/(n_g \cdot L)$$

where $n_g$ is the group index which reflects the group velocity of narrow-band light in the waveguide and varies with the effective refractive index $n_{\text{eff}}$ via a relation given by

$$n_g = n_{\text{eff}} - \lambda_{\text{res}} \cdot \frac{dn_{\text{eff}}}{d\lambda}$$

To demonstrate and verify the proposed concept, MRRs based on an SOI platform were chosen due to their lightweight, compactness, and CMOS compatible fabrication capability suitable for high yield production.\(^{(42,43)}\) The devices were fabricated on an SOI wafer consisting of a 220 nm monocrystalline silicon layer on top of a 2 μm-buried silicon dioxide layer that sits on a 725 μm silicon substrate. The MRR structures were patterned using electron beam lithography with a high-resolution positive electron-beam resist (ZEP520A). Next, a fluorine-based inductively coupled plasma reactive ion etcher (Oxford Plasmalab 100) was used to fully etch the silicon layer to form the strip waveguides utilizing the combination of SF$_6$ and Cl$_2$F$_8$. After atmospheric exposure, a thin native oxide (SiO$_2$) layer was formed on the waveguide surface.\(^{(44)}\) Figure 1b shows an optical micrograph of two fabricated MRRs with 380 and 480 nm waveguide widths, which were chosen as they feature single-mode operation. An SEM micrograph of one fully etched MRR with a circumference of 216 μm is shown in Figure 1c. A close-up SEM image of one vertical grating coupler (VGC) shown in Figure 1d exhibits the partially etched gratings with a depth of 70 nm on top of the adiabatic taper waveguide region. This VGC provides a high coupling efficiency at an 8° light coupling angle and guides the transverse electric (TE) modes of any light waves into and out of a device. To examine the cross section of the waveguides, FIB micromachining was used to section the waveguides. The SEM images of the two waveguides are shown in Figure 1e,f, demonstrating that the waveguide geometries agree well with the desired 480 and 380 nm widths. These waveguides have steep sidewalls with an inner etching sidewall angle of around 84°. A triangle-like silicon residual on both sides of the waveguides was observed, which can be eliminated by improving the efficiency of the dry etching process to fully remove the silicon. Based on the FIB-SEM results, the cross-section geometry of the fabricated waveguides was abstracted and modeled with the numerically calculated optical field distribution of the fundamental mode at 1550 nm (Figure 1g,h). By narrowing the waveguide width to 380 nm, a stronger evanescent field in the air cladding surrounding the waveguide core was achieved as compared with the 480 nm-wide structure, which enlarges the light–Nafion interaction. An optical setup, including a tunable laser, an optical coupler, and a multichannel optical power meter (see Figure S1, Supporting Information), was used in the optical spectrum measurement. The optical transmission spectra of the two MRRs were measured at room temperature (see Optical Spectrum Measurement, Experimental Section), which exhibit clear differences in the notch depth and width, indicating a different coupling coefficient and transmission loss caused by the waveguide width difference (Figure 1i). The FSRs near 1550 nm for the fabricated MRRs with 480 and 380 nm wide waveguides were measured to be around 2.555 and 2.319 nm, respectively.

Then, a 1 wt% Nafion dispersion prepared by diluting a 20 wt% Nafion solution in lower-aliphatic alcohols and water mixer (34% water) purchased from Sigma Aldrich with isopropyl alcohol (IPA) was spin coated on three samples. Coatings were applied on an SOI wafer with the fabricated 380 and 480 nm waveguide structures, a plain SOI wafer, and a plain silicon <100> wafer (see Film Preparation, Experimental Section). To examine the chemical composition on these three samples with about 20 nm thickness of Nafion coating, XPS analysis was conducted on the surfaces (see XPS Surface Analysis, Experimental Section). The survey spectra were scanned at desired regions to a depth of around 10 nm,\(^{(45)}\) where the large fluorine signal, oxygen, carbon, and sulfur signals show the presence of peaks at a comparable binding energy, thus indicating the successful coating of Nafion thin films onto the surface (Figure 2a).\(^{(46,47)}\) High-resolution spectra of C1s, O1s, and S2p peaks were measured. Deconvolution of the C1s spectra gives at least five peaks at 286.8, 289.6, 291, 292.2, and 293.7 eV, which correspond to C−O−C, C−SO$_3$, C−F, CF$_2$, and CF$_3$ groups in the Nafion chains, respectively (Figure 2b). The two dominant peaks in the O1s spectra at 533 and 535.5 eV correspond to C−O−C and C−SO$_3$ oxygen bonding in Nafion (Figure 2c). The dominant peak in the S2p spectra at 169.8 eV is attributed to the C−SO$_3$ bond (Figure 2d). The relative intensities and locations of these peaks reveal that the types of functional groups and their chemical environment of Nafion coatings on all three samples remain unchanged (see Figure S2, Supporting Information) and consistent with previous XPS studies.\(^{(47,48)}\)

\[2.2.\] Ellipsometry and QCM Measurement of Nafion Thin Films on Silicon Wafers

Before placing spin-coated Nafion thin films on MRR structures, ellipsometry, and QCM were undertaken on plain silicon wafers, respectively. To extract the film thickness and optical properties of the Nafion films, a variable-angle spectroscopic ellipsometry (VASE) study was conducted using J. A. Woollam M-2000VI at three incident angles of 55°, 65°, and 75° over a wavelength range from 400 to 1700 nm. Nafion thin films spin coated onto a Si<100> substrate with a native oxide layer (SiO$_2$/Si<100>) (see Film Preparation, Experimental Section) were measured in a room-temperature environment, where the humidity was
monitored to be stable at 50% RH. To achieve the best fitting, a structural model composed of air, Nafton thin film (modeled as a Cauchy layer), \(\text{SiO}_2\) and a silicon substrate with 1.5 nm native oxide layer was made, where the native oxide layer thickness was determined by measuring multiple bare silicon reference wafers. The squares in Figure 3a are the measured refractive index at 1550 nm of Nafton thin films with different film thicknesses. These thin films were obtained by spin coating Nafton concentrations diluted from 20 wt% Nafton dispersion in IPA at different spin rates (see Film Preparation, Experimental Section). The refractive index of the films with thickness greater than 27 nm remains comparable, whereas the thinner films show deviations in refractive index values, which likely arise from difficulties in precisely determining the film thickness and refractive index simultaneously as the thickness approaches the ellipsometric measurement threshold.\(^{29,50}\) The measured VASE response of amplitude ratio (\(\Psi\)) and phase difference (\(\Delta\)) spectra at an incident angle of 65\(^\circ\) of the Nafton thin films, whose refractive indexes are highlighted as red squares in Figure 3a, are shown in Figure S3 in Supporting Information. The Cauchy model provided an excellent fit to the experimental data for various film thicknesses at all three angles (see Figure S4, Supporting Information).

Next, ellipsometry and QCM measurements were carried out on Nafton thin films by spin coating various concentrations of solutions diluted from 20% Nafton with IPA on a Si\(<100>\) substrate with a native oxide layer and a platinum electrode quartz crystal coated with a 5 nm layer of e-beam-evaporated amorphous SiO\(_2\), respectively, in a controlled RH environment at room temperature (see Film Preparation and Ellipsometry and QCM measurement, Experimental Section). The ellipsometry and QCM measurements were taken at different humidity levels from less than 5% RH to 90% RH, where the time interval between adjacent measurements was set to 5 min to ensure that the humidity level was stable in the environment cell before each measurement. SiO\(_2\) on the surface of quartz crystal provides comparable substrate conditions with the amorphous native oxide layer on the silicon substrates. In addition, the mass of surface water uptake without coating the Nafton due to the hygroscopic properties of SiO\(_2\) needs to be subtracted from the QCM-measured mass uptake.
total uptake values.\[^{[52]}\] Figure 3b,c shows the hydration numbers \(\lambda_{\text{hydration}} = \frac{\text{M}_2\text{H}_2\text{O}}{\text{MS}_3\text{O}}\)[26] obtained via ellipsometry and QCM measurement. The results follow the same trend of increasing water content as humidity increases for all Naﬁon film thicknesses, which validate the humidity dependency of the Naﬁon thin ﬁlms spin coated on substrates with an oxide layer and agree well with previous studies regarding the swelling kinetics for Naﬁon thin ﬁlms.\[^{[26,52]}\]

### 2.3. Impact of Naﬁon Films on MRR Waveguides and Optical Humidity Sensing

The devices with Naﬁon thin ﬁlms of different thicknesses were produced through spin coating 1, 2, 3, and 5 wt% solutions on MRR structures. Coatings were fabricated by dropping 15 \(\mu\)L of the Naﬁon solution on a substrate at rest to fully cover it, and then the substrate was spun at 6000 rpm with a ramp rate up to 3000 rpm \(\text{s}^{-1}\) to achieve uniform ﬁlms. AFM (Bruker Icon) was implemented to extract the surface topography of the MRR with Naﬁon coatings in room-temperature conditions. Figure 4 shows the waveguide surface topographical analysis for Naﬁon thin ﬁlms on MRRs with 480 and 380 nm waveguide widths, respectively. The corresponding ﬁlm thicknesses of 23, 52, 110, and 273 nm were obtained by measuring the depth difference between the ﬁlm surface and the bottom of a region where the Naﬁon ﬁlm was manually removed.\[^{[29,53]}\] Each waveguide image displays a measurement area with a dimension of 2 \(\times\) 2 \(\mu\)m and the spin-coated Naﬁon ﬁlm surface on the device is found to be uniform and smooth over this area. Fine AFM scans were conducted on the top surface of the coated waveguides within an area of 250 \(\times\) 250 nm. The measured root-mean-square (RMS) roughness is between 0.55 and 0.65 nm for all the thicknesses. The sidewall proﬁles for waveguides with spin-coated Naﬁon thin ﬁlms of 23 and 52 nm thicknesses are similar, due to the geometry limitations of AFM tip used in the measurement.\[^{[54,55]}\]

Next, we calculated characteristic values to determine the optical ﬁeld conﬁnement and the interaction of light with its surrounding materials. A ﬁnite-difference eigennode (FDE) solver was adopted to numerically calculate the TE mode optical electric ﬁeld distribution of the Naﬁon-clad waveguide cross section by incorporating the measured AFM proﬁle (Figure 4) with the geometry of the fabricated waveguides. Mesh cells with a minimum step of 0.5 nm were adopted within an overall simulation area of 9 \(\mu\)m \(^2\). The optical refractive index of the Naﬁon layer was set to the ellipsometry measured values obtained at room temperature and 50% RH shown in Figure 3a, whereas the refractive indexes of silicon \((n = 3.476)\) and silicon dioxide \((n = 1.444)\) were obtained from Sellmeier’s equation\[^{[56,57]}\] at 1550 nm wavelength. Figure 5a shows the light intensity distributions in silicon core, Naﬁon ﬁlms, and air of the 480 and 380 nm waveguides at various Naﬁon ﬁlm thicknesses, along with the calculated 2D and 3D optical electric ﬁeld distributions in the cross sections of the waveguides after being clad with 23 nm Naﬁon ﬁlm. It can be seen that the optical electric ﬁelds center in the silicon core and gradually distribute in the transverse direction. There are strong optical evanescent waves distributing around the silicon.

![Figure 4](image-url) - 3D AFM micrograph images and RMS values of waveguide surface roughness for Naﬁon-coated MRR devices with a) 480 nm and b) 380 nm waveguide width.
waveguide surface and penetrating in the claddings and air. When the Nafton film thickness increases, the fractions of light intensity in silicon core ($P_{\text{Core}}$) and air ($P_{\text{Air}}$) are both reduced, whereas the fraction of light intensity in Nafton ($P_{\text{Nafton}}$) increases. The impact of the Nafton coating on the optical electric field distribution is significant. Over 7% of the light intensity is distributed into the Nafton films for both 380 and 480 nm waveguide widths, despite the film thickness becoming ultrathin ($\leq 20$ nm). Although there is a slight difference in light intensity between these two waveguides with ultrathin Nafton coating, the usage of MRR structure enhances the light–matter interaction via circulating the light in the ring cavity, which results in a notable optical spectrum change.

The optical transmission spectra near 1550 nm of the Nafton-clad MRRs were measured at room temperature and 50% RH using a scanning laser approach (see Optical Transmission Spectrum at Different Humidity Levels, Experimental Section). The results are shown in Figure 5c,d, where the optical transmission spectra of the MRR without Nafton coating, that is, air cladding, are also shown to make a comparison. Increases in Nafton film thickness enlarge the average refractive index of the cladding, which changes the optical spectrum of the MRR. As the evanescent waves on the waveguide surface propagate through Nafton films of different thicknesses, where the optical refractive index is different from that of the air ($n = 1.0003$ at 1550 nm) and related to the Nafton characteristics, clear spectral shifts or detuning of the optical notch positions are observed, showing the impact of Nafton on the optical spectrum. The change of the notch depth is mainly caused by the variation of light coupling to the MRR. Optical notches with a minimum depth of 4 dB are obtained across all the measured optical transmission spectra, which are sufficient to measure the resonant wavelength and FSR. For both 380 nm MRR and 480 nm MRR, it can be seen that the FSR changes along with the thickness of Nafton films, showing the general trend that the FSR reduces as the film thickness decreases.

To further study the impact of Nafton thin films on MRR waveguides, we compared the group indices obtained from the measured FSRs via Equation (2) with the simulation results obtained from the calculated optical electric fields. The results are shown in Figure 6a, which are in good agreement. The group indices of MRRs exhibit a decreasing tendency along with the thickness increase in Nafton thin film, as shown in Figure 6a, due to the distribution of more light intensity in

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**Figure 5.** a) Simulated cross-sectional light intensity distributions in silicon core (black), Nafton films (blue), and air (green) of the 480 (solid lines) and 380 nm (dashed lines) waveguides for various Nafton film thicknesses. b) 2D and 3D optical electric field distributions in the cross section of the waveguides after being clad with 23 nm Nafton film, where the Nafton cladding profiles are shown as dashed lines in the cross section. Measured optical transmission spectra and their FSRs near 1550 nm of c) 480 nm MRR and d) 380 nm MRR before coating (0 nm) and after being clad with different thicknesses of Nafton thin film (23 nm, 52 nm, 110 nm, 273 nm, and 776 nm), respectively.
the thicker Nafion films. Moreover, the existence of the Nafion film increases the refractive index of the cladding, leading to an increasing tendency of the effective refractive index of the MRR, as shown in Figure 6b, where the results were calculated via the FDE solver. This leads to a shift in the resonances to longer wavelengths that is consistent with the observed optical transmission spectra shown in Figure 5c,d. Moreover, the change of both group index and effective refractive index of 380 nm MRR clearly shows higher variation gradients than those of the 480 nm MRR, proving its higher sensitivity to the surroundings, due to the larger portion of optical electric fields that penetrated into the claddings. In addition, because of the low optical propagation loss of silicon waveguide and compact size of the ring resonator, multiple MRRs can be integrated on one chip or be cascaded to form an MRR array, which enable multiple measurements within 3 days. The amount of time interval between each RH step in each day is about 5 min, and the measurement results are shown in Figure 7. The unidirectional resonant wavelength shift with increasing or decreasing humidity is clearly seen, which shows that the proposed sensor is able to be used for humidity sensing, by measuring the changes in optical resonant wavelengths that is consistent with the observed optical transmission spectra shown in Figure 5c,d. Moreover, the change of both group index and effective refractive index of 380 nm MRR clearly shows higher variation gradients than those of the 480 nm MRR, proving its higher sensitivity to the surroundings, due to the larger portion of optical electric fields that penetrated into the claddings. In addition, because of the low optical propagation loss of silicon waveguide and compact size of the ring resonator, multiple MRRs can be integrated on one chip or be cascaded to form an MRR array, which enable multiple measurements on the same chip, thus providing great promise for characterization of Nafion and other materials in real time on a lightweight and portable platform.

Utilizing the impact of Nafion thin films on the optical waveguides, we propose and demonstrate a highly sensitive and ultracompact humidity sensor based on the MRRs with a Nafion thin-film coating. When the humidity goes up, the Nafion film absorbs water molecules, resulting in the swelling of the film and decrease in the optical refractive index at the same time. The increase in film thickness enlarges the effective refractive index of the clad waveguides, as more light propagates into the cladding, which shifts the resonance toward longer wavelengths. However, as the refractive index of water is 1.3167 at around 1550 nm, the refractive index of the Nafion film decreases after absorbing water from the vapor phase or from the liquid phase, which shifts the resonance toward shorter wavelengths. Therefore, these two opposite effects need to be considered in the total resonant wavelength shift in response to humidity variation. Figure 7a,b shows the simulated wavelength shifts at a certain order of resonance for the Nafion thin film-clad 480 nm MRR and 380 nm MRR, where the film thickness and refractive index range from 0 to 800 nm and from 1.3 to 1.45, respectively. It can be seen that the change of the resonant wavelength is almost linear when the film thickness is less than 150 nm and becomes flat after the thickness is greater than 300 nm. Moreover, when the Nafion film is ultrathin (<55 nm), the resonant wavelength shift induced by refractive index change becomes minor, showing the film thickness variation, for example, swelling or shrinking has the dominating effect on the optical resonance change. Therefore, the fabricated MRRs coated with 23 nm Nafion film were selected and implemented for humidity sensing demonstration, to minimize the ambiguity in the optical resonance shift in response to humidity change.

An on-chip humidity sensor probe was placed in a gas chamber, where the humidity level was controlled by adjusting the humid and dry airflow (see Figure S5, Supporting Information). A tunable laser and a multichannel optical power meter were connected to the optical input and output ports of the two MRRs respectively, to measure the optical transmission (see Optical Transmission Spectrum at Different Humidity Levels, Experimental Section). A polarization controller (PC) was added before the MRR chip to ensure the optimum transmission of the TE mode. A hygrometer was installed in the chamber and placed beside the chip as a reference sensor. A temperature controller module was used to keep the chip at room temperature (22 °C) to eliminate the temperature variation. The optical transmission spectra were captured at different humidity levels. Figure 7c,d shows the measured optical spectra at different humidity levels, showing an obvious resonance shift toward longer wavelengths due to the swelling of the Nafion film as the humidity increases. To evaluate the performance of the sensor, we measured the relationship between the resonant wavelength shifts versus the RH levels. Both 480 nm MRR and 380 nm MRR were cycled through a stepwise increase and decrease in humidity, from less than 5% RH to 90% RH and back to less than 5% RH, for nine times within 3 days. The amount of time interval between each RH step in each day is about 5 min, and the measurement results are shown in Figure 8. The unidirectional resonant wavelength shift with increasing or decreasing humidity is clearly seen, which shows that the proposed sensor is able to be used for humidity sensing, by measuring the changes in optical resonant
Figure 7. Simulated resonant wavelength shift versus thickness and refractive index of Nafton film coated on MRRs with a) 480 nm- and b) 380 nm-wide waveguides. Measured optical transmission spectra at different humidity levels for c) 480 nm MRR and d) 380 nm MRR.

Figure 8. Measured resonant wavelength shifts versus increasing and decreasing humidity for a–c) 480 nm MRR and d–f) 380 nm MRR.
wavelength. The total resonant wavelength shift of the 380 nm MRR is about two times larger than that of 480 nm MRR in the same humidity range, due to a stronger evanescent field in the Nafion thin film provided by a narrower waveguide. It is interesting to note that only the first hydration cycle of the Nafion thin film in Day 1 measurement shows a large degree of hysteresis (Figure 8a,d). This is likely attributed to the hydration-induced polymer chain reorganization, where the Nafion polymer chains relax from their initial spin-cast state into their hydrated equilibrium state during the first hydration cycle.\[^{[62\text{-}64]}\] Any effects from aging the Nafion thin films were not observed during the 3 day experiment, which is consistent with neither the structure of the Nafion nor the native oxide on the Si wafer changing significantly over the duration of the experiments.\[^{[65]}\] Figure 8 also shows that the optical resonant wavelength shift presents a monotonically increasing relationship with the humidity variation. This trend agrees with the water sorption isotherm of Nafion thin films obtained by ellipsometry and QCM measurement, as shown in Figure 3b,c. In contrast with the chemical modification of optical waveguide approaches which have limited reusability\[^{[66]}\] or a complex setup\[^{[63]}\] with restrictions to be scaled up as sensor arrays, the new humidity sensor provides a real-time and continuous sensing capability, and a high scalability for sensor arrays as the usage of an optical bus waveguide provides the convenience to evanescently couple the light into multiple MRRs.\[^{[66\text{-}68\text{,}69]}\] The usage of cascaded MRRs with different waveguide widths also enables sensing the temperature and humidity at the same time.\[^{[70]}\] The sensing performance can further benefit from Nafion’s features, such as chemical stability, fast response, and mechanical toughness.\[^{[32\text{-}41\text{,}71]}\] Moreover, MRRs can be fabricated on different materials, such as silicon carbide,\[^{[72]}\] which enables the sensor to operate at a broadband wavelength, ranging from visible light to the midinfrared.

3. Conclusion

In this article, the impact and spin-coating process of Nafion thin films on photonic nanowaveguide structures and the application in humidity sensing are investigated. Nafion films with various thicknesses were deposited onto silicon MRRs with small waveguide sizes (480 nm by 220 nm and 380 nm by 220 nm) via spin coating. Evanescent waves that penetrated into the Nafion coating of the waveguides lead to continuous light coupling in the MRR. The XPS surface analysis of spin-coated Nafion films on a wafer with 480 and 380 nm waveguides, a plain SOI wafer, and a plain silicon <100> wafer shows types of functional groups, and their chemical environment of Nafion coating on all three samples remains unchanged and consistent. Moreover, the spin-coated Nafion films on the waveguides are uniform and smooth with a surface roughness from 0.55 to 0.65 nm measured by AFM. The fraction of light intensities in Nafion films remains over 7% for both 380 nm and 480 nm waveguides, despite the film thickness becoming ultrathin (\(\approx\)20 nm). The measured FSR and the corresponding group index of the MRR exhibit a decreasing tendency along with the increase in spin-coating thickness of Nafion, whereas the effective refractive index of the propagation mode within the Nafion-coated waveguide shows an overall increasing trend, consistent with the observed shifting of the optical resonance. Finally, the silicon MRR with a Nafion thin-film coating of 23 nm thickness was used as the sensor probe in the humidity sensing demonstration. Results show a low hysteresis and a unidirectional resonance shift as a function of RH level, where the trend agrees with the water sorption isotherm of Nafion thin film determined by ellipsometry and QCM. The MRRs can form on many different optical materials using standard photonic circuit-fabrication techniques, providing a new way to study Nafion and other thin films and enabling new device architectures for on-chip sensing.

4. Experimental Section

**Optical Spectrum Measurement:** To examine the optical transmission spectrum of the MRRs, a tunable laser (Keysight 81960A) with a spectrum range between 1505 and 1630 nm and a maximum scan speed of 200 nm s\(^{-1}\) was used as a light source, followed by a PC to optimize the polarization state of the incident light, and a 50:50 optical coupler evenly split the light into the 380 nm MRR and 480 nm MRR, respectively (see Figure S1, Supporting Information). The output light of the two MRRs was launched into a multiport optical power meter (Keysight N7744A). By sweeping the tunable laser wavelength, and detecting the optical power at the two output ports, the optical transmission spectra of the two MRRs were obtained simultaneously.

**Film Preparation:** A 20 wt% Nafion solution in lower aliphatic alcohols and water mixer (34% water) purchased from Sigma Aldrich was diluted with IPA to concentrations of 1%, 2%, 3%, 5%, and 10% by weight. The diluted dispersions were equilibrated for at least 24 h before coating, to allow the Nafion polymer to aggregate to relax into its low aggregation state.\[^{[73]}\] The silicon<100> and SOI wafers were diced into 10 × 10 mm substrates, cleaned via ultrasonication by 5 min in acetone (ACS reagent, \(\geq\)99.5%), followed by IPA for 5 min respectively, and then dried under filtered compressed nitrogen flow. The Nafion–IPA dispersions were spin coated onto cleaned substrates using a spin coater (POLOS SPIN150i) at 4000–6000 rpm for 45 s to achieve uniform films and then dried under vacuum for 1 h before being stored under a nitrogen atmosphere.

**XPS Surface Analysis:** The XPS measurement was carried out using a Thermo ESCALAB250Xi system equipped with a microfocused monochromated aluminum K\(_{\alpha}\) X-ray source (1486.68 eV) operating at 14.5 kV voltage and an emission current of 11 mA at room temperature. The X-ray beam was incident to the sample surface at about 45°, and the emitted photoelectrons were collected at a take-off angle of 90°. To compensate for the charging effect, the F–C–F bonding at 292.2 eV from the C1s spectra was used for binding energy calibration. The curve fitting and peak deconvolution of the XPS spectra were conducted using Avantage software. After subtracting a Shirley-type background, all peaks were fit by pure Gaussian–Lorentzian lines to determine the binding energy of different element levels more accurately.

**Ellipsometry and QCM Measurement:** The swelling and water uptake were measured by ellipsometry and QCM for selected samples at room temperature. The thicknesses of films coated on silicon<100> wafers were measured using ellipsometry (J. A. Woollam M-2000) at an incident angle of 65° at various RH levels by incorporating a customized environment cell, where nonpolarized quartz windows were fit at a compatible angle on the cell to maximize the magnitude of light transmission. The mass water uptake studies of Nafion films were conducted using a QCM (QCM200 Stanford Research Instruments). The contact surface of the platinum electrode quartz crystal was coated with a 5 nm layer of e-beam-evaporated amorphous SiO\(_2\) and an ultrathin titanium adhesion layer to provide comparable substrate conditions, thus enabling multimeasurement comparison. The coated crystal was enclosed within a customized humidity cell. The humidity in the cell was controlled by adjusting the...
airflow of the dry air obtained by passing ambient air through desiccant (Drierite without indicator, B mesh, Sigma Aldrich) and wet air obtained by bubbling ambient air through a deionized water-filled vessel, whereas the in-cell humidity was monitored via a hygrometer (IC-humimeter RH1).

**Optical Transmission Spectrum at Different Humidity Levels:** To evaluate the humidity sensing performance, the Nafion-coated MRR chip was enclosed in a self-made humidity chamber (see Figure S5, Supporting Information), where the chip was stabilized at room temperature by a temperature controller, and the chamber humidity was controlled by the same system used for Ellipsometry and QCM Measurement. The optical transmission spectra of the MRRs were obtained at the output of the MRRs via synchronizing the input tunable laser with the multiport optical power meter as described in Optical Spectrum Measurement.

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**
The authors declare no conflict of interest.

**Data Availability Statement**
The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**
humidity sensors, Nafion films, nanophotonics, silicon-on-insulator microresonators, thin-film devices and applications

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