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Influence of water sorption on refractive index of fluorinated polyimide

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Abstract

The influence of water sorption on refractive index of a fluorinated polyimide was demonstrated by measuring water uptake and change in volume due to water sorption. The refractive index of the fluorinated polyimide increased with increasing the water uptake. The change as much as 10^{-3} in refractive index was observed at the temperature of 25 °C. These results reflected a one order smaller change in volume than that in weight due to water sorption. A loose intermolecular packing structure of the fluorinated polyimide mainly induced this small change in volume due to water sorption. We confirmed this dependence of refractive index on water uptake using a Mach-Zehnder Interferometer type switch fabricated using the fluorinated polyimide waveguide.

Keywords: Fluorinated polyimide; Water sorption; Refractive index

1. Introduction

A polymeric waveguide has attracted much attention for use as optical components and in optoelectronics devices due to their low cost and volume productivity. Recently, some researchers reported optical components such as an optical switch, a coupler, a splitter and a transceiver, using a fluorinated polyimide waveguide, because of its high thermal stability and high transparency [1,2]. Evaluating how environmental changes affect performances of a polymeric waveguide is important from the practical viewpoint. Especially, water sorption influences optical properties of a polymer, because water sorption induces changes of molar refraction and density of the polymer. Hida et al. [3] reported a drift phenomenon caused by water desorption–sorption in a thermo-optic (TO) Mach-Zehnder Interferometer (MZI) type switch using a PMMA waveguide. They revealed that the water desorption–sorption caused by the heating–cooling of the thin film heater of the switch resulted in the fluctuations of refractive index of the PMMA. Furthermore the humidity dependence of refractive index of the PMMA was calculated using a Lorentz–Lorenz formula. However, the data calculated using the dependence of refractive index of the PMMA on water uptake could not explain reasonably the experimental data, because of any assumptions for the calculation, such as a factor related to the density change due to water sorption [3]. Thus it is necessary to measure the humidity dependence of the density of the polymer. In addition, to the best of our knowledge, there have been no reports of the study of influence of water sorption on optical properties of a fluorinated polyimide.

In this paper, we demonstrated the influence of water sorption on refractive index of a fluorinated polyimide by measuring water sorption and change in volume due to water sorption. The change as much as 10^{-3} in refractive index was observed at the temperature of 25 °C. These results reflected a one order smaller change in volume than that in weight due to water sorption. This strong dependence of refractive index on water uptake was reasonably confirmed using a Mach-Zehnder Interferometer type switch fabricated using the fluorinated polyimide waveguide.

2. Experimental

A fluorinated polyimide derived from 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFDB) and a fluorinated copolyimide derived from 6FDA, TFDB and 4,4′-oxydianiline (ODA) were evaluated and used as a waveguide cladding and core, respectively, [4,5]. The

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chemical structure of the fluorinated polyimide studied is shown in Fig. 1. The fluorinated polyimide has loose intermolecular packing, amorphous structure and relatively low water uptake due to the bulky trifluoromethyl (CF_3) groups.

The fluorinated polyimide film of 10 μm thickness was obtained by spin-casting the fluorinated poly(amic acid) solution on a 3 in. silicon wafer and heating at 380 °C for 1 h. *N*,*N*-dimethylacetamide (DMAc) was used as a solvent for all poly(amic acid) solutions in this work. The solvent was completely eliminated by slow and enough heat treatment at the total time longer than 6 h during the imidization. More details of the polyimide preparations are given in some papers [4,5]. The fluorinated polyimide film was stripped from the wafer by dipping into a hydrofluoric acid aqueous solution. The film was cut out using a dicing machine for measurements. The thickness, sizes and weight of the film were measured using a Seiko Instruments Inc. Nanopics1000, an Olympus measuring microscope STM and a Yamato Labtop Balance LE180, respectively, at the atmospheric conditions of 25 °C and 50% RH. We could estimate a density of film with an accuracy of 0.002 g/cm^3. To investigate the influence of water sorption on refractive index of a fluorinated polyimide, it is necessary to measure the density of the film at the various humidity and temperatures. However, it is difficult to obtain humidity dependence of the density of a polymeric film at various temperatures, because the density of the film is generally measured by dipping into a solution, such as water. To the best of our knowledge, there are no reports of the suitable method for measurement of the humidity dependence of the density of a film. We tried to measure the changes in weight and volume of a fluorinated polyimide due to water sorption, instead of measuring directly the change in density. The changes in weight (water uptake) and elongation (corresponding to volume) due to water sorption were obtained by a thermogravimetric analysis (TGA) and thermomechanical analysis (TMA) using a Shimadzu TGA-51 and a MAC Science TMA4000S, respectively, equipped with a dew point controller. Controlling the dew point from 0 to 36 °C, the humidity in the tube of TGA and TMA equipment could be varied from about 0 to 100% RH at the various temperatures. We used the weight and the length of film at the humidity of 0% RH achieved using dry N_2 gas as the reference data for measurement of water uptake and elongation due to water sorption. The coefficient of thermal expansion (CTE) of the fluorinated polyimide without water sorption was measured between 20 and 100 °C by the TMA with dry N_2 gas. The refractive indices of the fluorinated polyimide were measured, as a reference for the calculation, by a prism coupling method at the atmospheric conditions of 25 °C and 50% RH.

3. Results and discussion

3.1. Dependence of refractive index on water sorption

Fig. 2 shows the water uptake *w* of the core and cladding fluorinated polyimide films at various temperatures as a function of humidity *H*. The relationship between the water uptake and humidity is independent of temperature. The water uptake obeys the equation of $w = SH$, where *S* is a coefficient that connected with water solubility in polymer [3]. The solid lines for water uptake are drawn by the least-square fitting method, which gives the *S* values of 0.010 and 0.008 wt%/%RH, respectively. Fig. 3 shows elongation of the fluorinated polyimide films at various temperatures as a function of humidity. No dependence of the water-induced elongation of the film on temperature is also observed. The water-induced elongation of the film at the humidity lower than about 50% RH increases linearly with increasing humidity. The slopes of the lines become 4.0 and 2.2 ppm/%RH for core and cladding, respectively. The change in volume is obtained approximately by 3 × (elongation due to water sorption), assuming that the elongation due to water

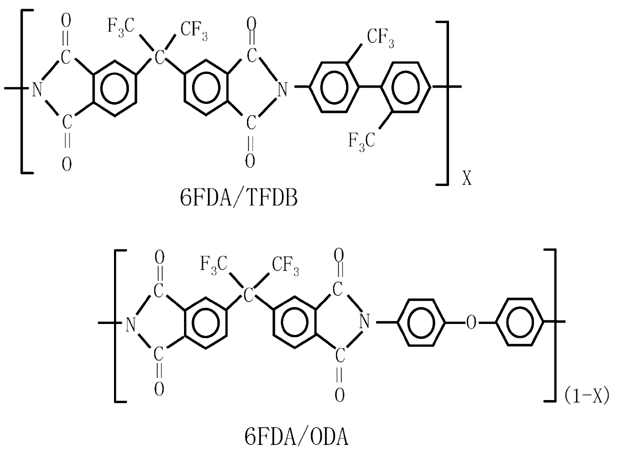

Fig. 1. Chemical structure of the fluorinated polyimide studied. The composition *x* is 1 and 0.6 for the cladding and core fluorinated polyimides, respectively.

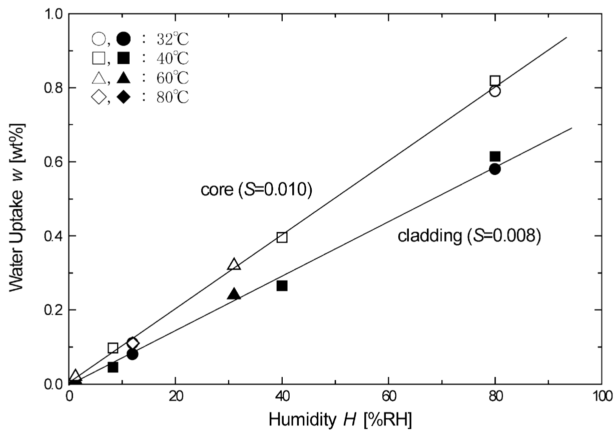

Fig. 2. The water uptake of the core and cladding fluorinated polyimides at various temperatures as a function of humidity. The open and closed symbols represent the data of the core and cladding, respectively.

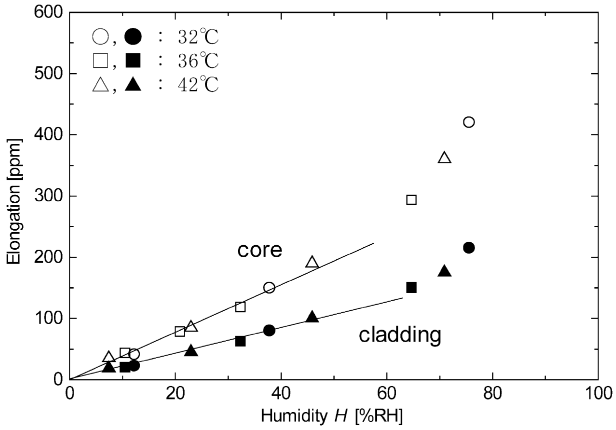

Fig. 3. The elongation of the core and cladding fluorinated polyimides at various temperatures as a function of humidity. The open and closed symbols represent the data of the core and cladding, respectively.

sorption is uniform in the film, because of the loose packing and amorphous structure of a fluorinated polyimide. It was found from Figs. 2 and 3 that the change in volume was one order smaller than that in weight due to water sorption, which results in the large change in refractive index, will be described later. The volume change for PMMA has been reported to be about a half of the change in weight due to water sorption [6]. According to Turner [6], microvoids contribute mainly to the reduction of volume change for PMMA. In general, morphological factors such as molecular order, chain orientation, intermolecular packing and microvoids affect mainly water sorption phenomenon in a polyimide, rather than water affinity [7–9]. For example, the poor ordering, amorphous structure and loose intermoleculer packing for a polyimide result in fast diffusion and high water uptake. While, high ordering, high crystallinity and tight intermoleculer packing for a polyimide result in slow diffusion and low water uptake. These morphological factors seem to affect the size and the number of the space in a polyimide for water sorption and diffusion, as similar to the effect of microvoids. We obtained the water uptake and the change in volume due to water sorption of the fluorinated polyimide films with the curing temperature of 340 °C having the looser packing structure than those for 380 °C [5,10]. Both the water uptake and the elongation due to water sorption for the curing temperature of 340 °C were 1.2 times larger than those for 380 °C at the whole humidity. The microvoids is formed by formation of water and degas of solvent during thermal imidization [6]. We consider that the number of microvoids does not change regardless of the decrease in curing temperature from 380 to 340 °C, because of the complete imidization and elimination of the solvent for both the curing temperature [4]. Thus the increase in water uptake is mainly due to the looser intermoleculer packing structure. Therefore we suggest that the loose intermolecular packing structure for the fluorinated polyimide induces mainly the small volume change due to water sorption.

Furthermore, the change of elongation due to water sorption becomes large at the humidity higher than 50% RH, as shown in Fig. 3, even though the water uptake increases linearly with increasing humidity. According to Han et al., [8] morphological factors also contribute to water diffusion and water sorption at the humidity higher than 50% RH. Some researchers reported that the cluster of water was formed at the high humidity in hydrophobic polymers and polyimides without hydrophobic groups [7,8,11]. The cluster formation at the intermoleculer and microvoids in polyimide perhaps results in the excessive elongation of the film, in terms of the volume change phenomenon due to water sorption we suggested. A detailed investigation is needed to clarify this phenomenon.

A refractive index n of a polymer with water sorption is given by the Lorentz–Lorenz formula [3]

$$(n^2 - 1)/(n^2 + 2) = \{k_w + k_p/(w/100)\} \times [\rho_0(w/100)/\{1 + f(w/100)(\rho_0/\rho_w)\}], \quad (1)$$

where k_w and k_p represent the molar refractions divided by the molecular weights of water and the polymer without water sorption, respectively, and ρ_w and ρ_0 represent the densities of water and the polymer without water sorption, respectively. The factor f is the fraction of sorbed water that contributes to an increase in polymer volume, and is estimated to be 0.08 and 0.06 for the core and cladding fluorinated polyimides, respectively, from Fig. 3. The small values of f reflected the small changes in volume, which are one order smaller than that (0.5) for PMMA [3,6]. We can obtain the value of k_p by using the value of k_w (0.2006 cm^3/g) estimated from the refractive index (1.324) [12] of water at the wavelength of 1300 nm, the densities of 1.466 and 1.458 g/cm^3 and the refractive indices of 1.537 and 1.521 at the wavelength of 1300 nm for the core and the cladding, respectively, at the atmospheric conditions of 25 °C and 50% RH. Fig. 4 shows the refractive indices of the core and cladding as a function of water uptake at the atmospheric temperature of 25 °C from Eq. (1) with determined k_p. The refractive indices increase with increasing water uptake. The change in refractive index (Δn) due to water sorption can be expressed by $\Delta n \sim 0.0053w$ for both the core and cladding fluorinated polyimides. The change as much as 10^{-3} in refractive index of the polyimide is observed from Fig. 4. In general, the increase in weight due to water sorption induces the increase in refractive index. On the other hand, the increase in polymer volume due to water sorption compensates for the increase in refractive index. Thus a one order smaller change in volume than that in weight due to water sorption induces this large change in refractive index. These results indicate that the refractive index of the fluorinated polyimide is highly sensitive with the water sorption, in comparison with that for PMMA ($\Delta n \sim 0.0014w$ [3]).

Furthermore, we try to obtain a dependence of water

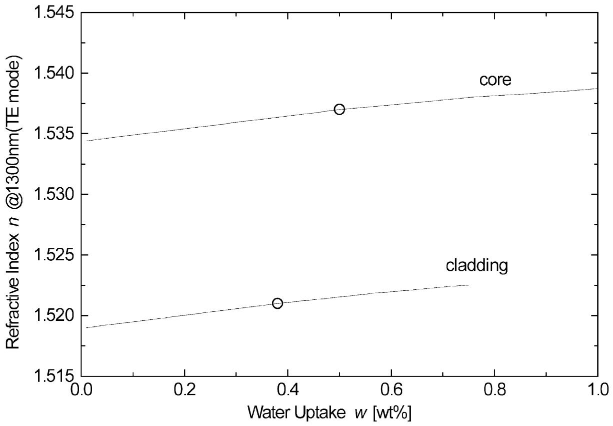

Fig. 4. The refractive indices of the core and cladding fluorinated polyimides at the atmospheric temperature of 25 °C as a function of water uptake. The open circles represent the experimental data at the atmospheric conditions of 25 °C and 50% RH. The solid curves represent the curves estimated by using Eq. (1) for the core and cladding.

uptakes of the core and cladding on the waveguide temperature at a constant surrounding atmosphere for understanding the temperature dependence of properties of the waveguide. The equation of $w = SH$ can be rewritten as follows [3]

$$w = SHp_s(T)/p_s(T) = SH_a p_s(T_a)/p_s(T_w), \quad (2)$$

where $p_s(T)$, T_a, T_w and H_a are a saturated vapor pressure at a temperature T, an atmospheric temperature, a waveguide temperature and an atmospheric humidity, respectively. The vapor pressure $Hp_s(T)$ in Eq. (2) can be replaced by that $H_a p_s(T_a)$ at a constant atmosphere, because the factor S is independent of temperature. For example, the water uptake obtained at 60 °C/8% RH corresponds to that at the waveguide temperature of 60 °C and the surrounding atmospheric conditions of 25 °C and 50% RH. Fig. 5 shows the water uptake of the core fluorinated polyimide film as a function of waveguide temperature. The solid curves represent curves obtained by using Eq. (2) fits well with the experimental data replotted from Fig. 2. As shown in Fig. 5, the water uptake decreases with increasing the waveguide temperature under a constant vapor pressure. This result indicates that the dependence of refractive index on water sorption becomes strong with lowering the waveguide temperature.

From Figs. 4 and 5 and differentiating Eq. (1) with respect to T, we can obtain the dependence of the refractive index on the waveguide temperature T_w. Fig. 6 shows the refractive indices as a function of the waveguide temperature at the atmospheric conditions of 25 °C and 50% RH. The solid curve represents the estimated curve taking water sorption into account, which shows the nonlinear dependence of refractive index on the waveguide temperature. The dashed curve represents the curve estimated for the fluorinated polyimides without water sorption (0% RH), which calculated approximately using CTE of the polymer. We estimated the temperature dependence of refractive index ($\partial n/\partial T$) of -8.3×10^{-5}/°C at 0% RH, using the CTE of 4.4×10^{-5}/°C obtained for both the core and cladding fluorinated polyimides between 20 and 100 °C. It is found from Fig. 6 that the $\partial n/\partial T$ of fluorinated polyimide strongly depends on the atmospheric humidity, especially for the waveguide temperature lower than 40 °C. We consider that the various values of $\partial n/\partial T$ for a fluorinated polyimide, reported by some researchers [1,2] can be explained reasonably by taking the effect of water sorption into account, will be described later. These results indicate that controlling not only the waveguide temperature but also the atmospheric condition is important for design of components using the fluorinated polyimide waveguide.

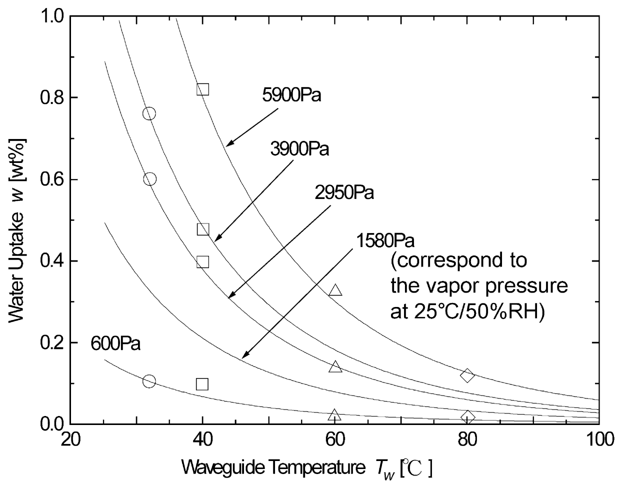

Fig. 5. The water uptake of the core fluorinated polyimide as a function of waveguide temperature at various constant vapor pressures. The symbols represent the data shown in Fig. 2.

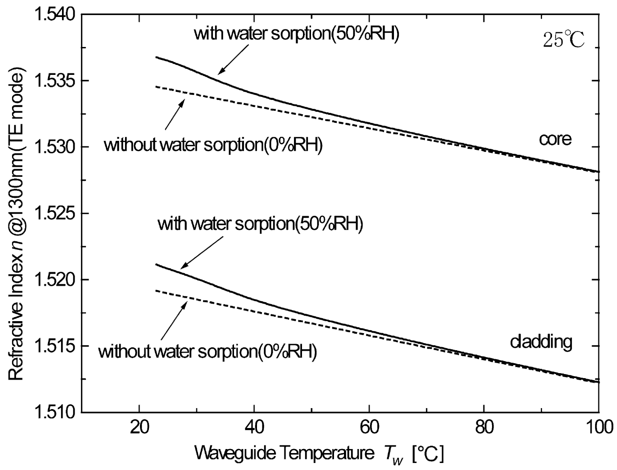

Fig. 6. The refractive indices of the core and cladding fluorinated polyimide at the atmospheric temperature of 25 °C as a function of the waveguide temperature. The solid and dashed curves represent the curves for fluorinated polyimide with (50% RH) and without (0% RH) water sorption, respectively.

3.2. Effect of water sorption on fluorinated polyimide waveguide

To confirm the influence of water sorption on refractive index of the fluorinated polyimide, we evaluated a MZI type switch using the fluorinated polyimide waveguide fabricated by conventional photolithography and reactive ion etching techniques. We used the circuit of a MZI type switch with two multimode interference (MMI) couplers, as shown in Fig. 7. Both the width and height of the core were 4 μm. The thickness of the upper cladding layer of the waveguide was 10 μm. A Cr thin film heater was formed on the upper side of the waveguide arms shown in Fig. 7 by a lift-off technique. The thickness, width and length of the heater on the arm waveguide were about 0.1, 40 μm and 2.0 mm, respectively. The output power at the cross port of the circuit is expressed by the following equation; $P_{cross} = P_{in}\cos^2(\Phi/2)$, where P_{cross} and P_{in} represent an output power at the cross port and an input power, respectively. The power-coupling ratio of the MMI is assumed to be 0.5. A phase shift Φ in MZI is proportion to difference between the products of the refractive index and the length for the two arms. We design the change of 3.5×10^{-4} in refractive index corresponding to the phase shift of π switches the output port at the wavelength of 1310 nm. Thus the change of an order of 10^{-4} in refractive index of the fluorinated polyimide can be observed as the change in output power or phase shift of this switch.

Fig. 8 shows the switching response of the MZI type switch at the atmospheric conditions of 25 °C and 35% RH and the waveguide temperature of 25 °C. The electric power of 10 mW is applied to the thin film heater. First, the output power is switched to the other port at the switching time of 4 ms, caused by the increase in temperature by the thin film heater, as shown in the inset in Fig. 8. Although the temperature is maintained at the switched state, the output power is spontaneously and slowly switched back, which results in the excessive phase shift of about 1.1π. The slow response time for the excessive phase shift is due to the water diffusion through the film [3,7–9]. The decrease of 3.5×10^{-4} in refractive index corresponds to the increase of 4.2 °C at the core by the thin film heater on the arm, estimated from $\partial n/\partial T = -8.3 \times 10^{-5}$/°C for dry fluorinated polyimide. This increase of 4.2 °C induces the decrease in water uptake of the core, which results in the excessive decrease in refractive index of the core and is observed as an excessive phase shift in MZI due to water desorption. Thus the excessive phase shift can be estimated from the data in Fig. 6 modified to the humidity of 35% RH. Fig. 9 shows the excessive shift as a function of the waveguide temperature at the atmospheric conditions of 25 °Cand 35% RH. The solid curve, which represents the calculated curve, fits well the experimental data. The excessive phase shift due to water sorption for the MZI switch can be explained reasonably by the dependence of refractive index of the core on the waveguide temperature. Therefore we confirmed

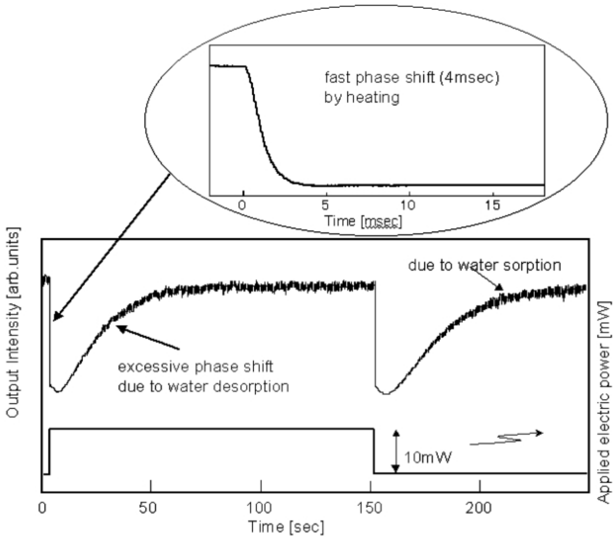

Fig. 8. The switching response of the MZI type switch at the waveguide temperature of 25 °C and the atmospheric conditions of 25 °C and 35% RH, when the applied electric power is 10 mW. The inset shows the switching response just after applying the electric power.

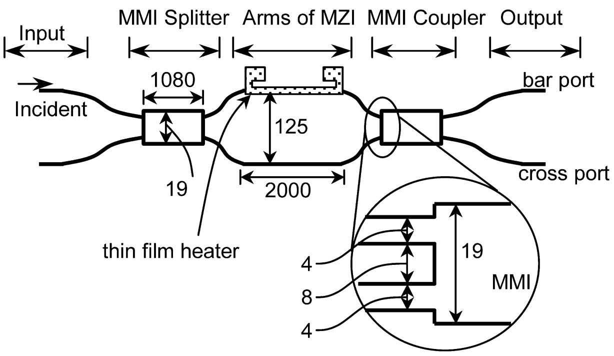

Fig. 7. The circuit of the MZI type switch. The unit is μm. The circuit consists of five parts: input port, MMI splitter, arms of MZI, MMI coupler and output port.

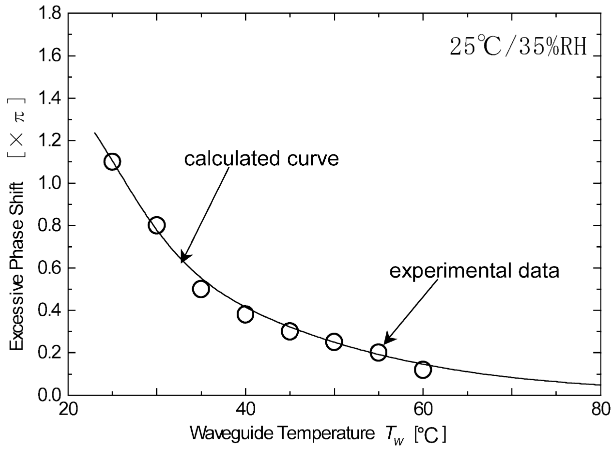

Fig. 9. The excessive phase shift of the switch as a function of the waveguide temperature at the atmospheric conditions of 25 °C and 35% RH. The open circles represent the experimental data.

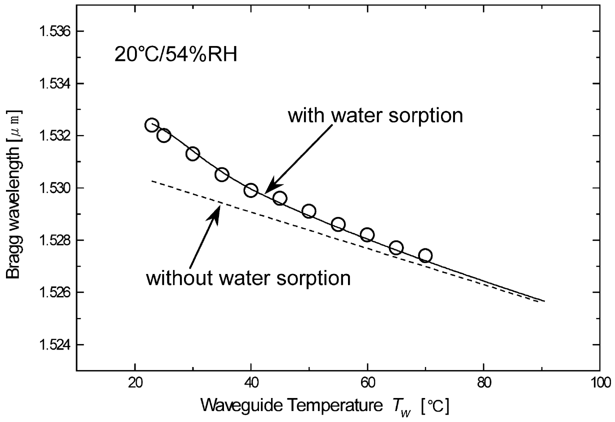

Fig. 10. The Bragg wavelength of the grating using a fluorinated polyimide waveguide as a function of the waveguide temperature at the atmospheric conditions of 20 °C and 54% RH. The solid and dashed curves are our estimated curves with and without the effect of water sorption, respectively, using the data shown in Fig. 6 modified to the atmospheric conditions of 20 °C and 54% RH. The open circles represent the data reported by Ojima et al. [2].

reasonably the strong dependence of the fluorinated polyimide waveguide on water uptake.

This analysis can be extended to any other wavelengths by simply replacing the refractive indices of water and fluorinated polyimide at 1300 nm with those at the desired wavelength. For example, we try to explain the nonlinear temperature dependence of the Bragg wavelength between 1525 and 1534 nm for the grating fabricated using a fluorinated polyimide waveguide, reported by Ojima et al. [2]. Thus the dependence of the Bragg wavelength λ_{Bragg} for the grating on the waveguide temperature can be estimated easily using the dependence of the refractive index of the core with water sorption on the waveguide temperature and the equation; $\lambda_{\mathrm{Bragg}} = 2n\Lambda$, where Λ represents the period of the grating, which is also a function of the CTE. Fig. 10 shows the Bragg wavelength of the grating as a function of the waveguide temperature. The period Λ of the grating was 0.5 μm and the measuring atmospheric conditions were 20 °C and 54% RH [13]. The open circles represent the experimental data reported by Ojima et al. [2]. The solid and dashed curves are our estimated curves with and without the effect of water sorption, respectively, using the data shown in Fig. 6 modified to the atmospheric conditions of 20 °C and 54% RH. The obtained Bragg wavelength is in excellent agreement with the calculated one, taking water sorption into account. Therefore we can estimate reasonably the influence of water sorption on performances of a fluorinated polyimide waveguide without fabricating the waveguide, using this simple analysis based on the experimental data of water uptake and change in volume due to water sorption.

4. Conclusion

The influence of water sorption on refractive index of a fluorinated polyimide was demonstrated by measuring the water uptake and change in volume due to water sorption. The refractive index of the fluorinated polyimide increased with increasing the water uptake. The change as much as 10^{-3} in refractive index was observed at the temperature of 25 °C. These results reflected a one order smaller change in volume than that in weight due to water sorption. A loose intermolecular packing structure of the fluorinated polyimide mainly induced the small change in volume due to water sorption. This dependence of refractive index on water uptake was reasonably confirmed using a Mach-Zehnder Interferometer type switch fabricated using the fluorinated polyimide waveguide. Therefore we can estimate reasonably the influence of water sorption on performances of a fluorinated polyimide waveguide without fabricating the waveguide, using this simple analysis based on the experimental data of water uptake and change in volume due to water sorption.

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