



Ar/H₂ Sputtering deposition of 350 μm thick Si:H/SiO_{2-x}:H multilayers having flat interfaces for optical applications

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Abstract

Thick Si/SiO₂ multilayered films with flat interfaces are needed to achieve optical devices with low optical propagation losses, such as a laminated polarization splitter operating at a 1550 nm wavelength. Such films can be realized by a sputtering method using an Ar/H₂ gas mixture because of the successful reduction of internal stress and surface roughness of films compared with those of conventional ones. We fabricate 350 μm thick Si:H/SiO_{2-x}:H multilayered films having flat interfaces by such a hydrogenation technique. The absorption losses at 1550 nm wavelengths of both films measured separately are negligibly small.

Keywords: Amorphous materials; Interfaces; Optical coatings; Stress

1. Introduction

Multilayered structures containing dielectric films are used in numerous film-based optical devices such as laminated polarizers [1], laminated polarization splitters [2] and interference filters [3]. The refractive indices and thicknesses of the films play an important role in the design of such devices. These parameters can be monitored in situ during the deposition through the feed-back control of the process. The fabricated devices, however, frequently do not exhibit satisfactorily good characteristics due to unexpected distortions in the multilayers. This is because the scattering conditions of the incident light beam differs from the designed ones, where ideally flat interfaces of the films are assumed.

Two kinds of distortions are commonly known for the multilayers. The first one is nodular defects which grow across the multilayers. Nodules are caused by large particles and/or contamination which come from films piled on the deposition chamber wall, and then settling on to the growing film surface [4,5]. The shadowing effects of the substrate surface are also related to the growth of the nodules, as reported by Patten [6]. Guenther reported that such nodules can be significantly reduced by prevention of formation of large particles and promotion of diffusion rates of the deposited particles on the substrates [7]. The other distortion is undulation of film surfaces due to rough film interfaces. The amplitude of undulation becomes large as the layers are piled up. However, in the fabrication of multilayered optical devices, it is

desirable to increase the total thicknesses of the multilayers for effective coupling with fibers. For instance, Si/SiO₂ multilayers are used to fabricate a laminated polarization splitter (LPS) device, as proposed by Shiraishi and Kawakami [2]. In this regard, they reported the reduction of interfacial roughnesses by a biased r.f.-sputtering technique [8]. Here, we demonstrated that the reduction of interfacial roughnesses and film stresses of thick Si/SiO₂ multilayers can be easily achieved by a sputtering process with an Ar/H₂ gas mixture. The Ar/H₂ sputtering also promises stable operating conditions for the equipment and is preferred in mass production processes because this process needs no additional bias.

2. Concepts in maintaining flat interfaces

The 1 μm order undulations of the lateral periodicity result in light scattering. As origins of the undulation of the growing film surface, the following two factors were mainly considered here, and experiments were carried out in order to eliminate them. The first factor is the possible ripples on the surface due to internal strains (stresses) of the films. It is experimentally known that the large undulations are observed near the surface of the multilayer, while the interfaces near the substrate are flat. Such phenomena seem to be ascribed to the internal strains (stresses) of films, which are magnified by succeeding film depositions. The strain-induced fluctuations of the surface morphology are very small, but they expand

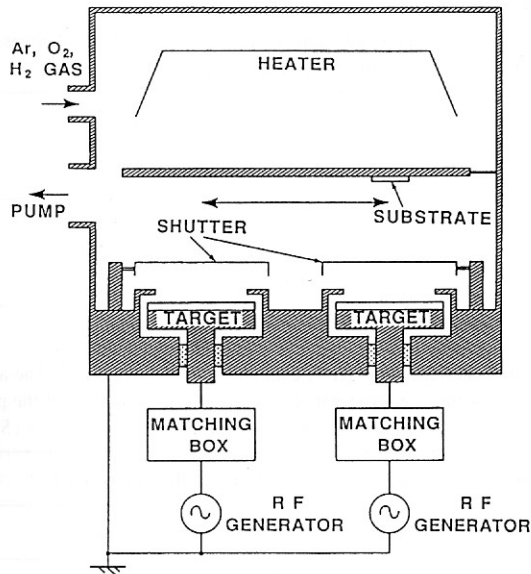


Fig. 1. configuration of the magnetron r.f.-sputtering system.

into large undulations by further film depositions. The second factor is the surface migration of sputtered species on the growing film. This factor is well investigated in chemical vapor deposition processes, and it is known that hydrogenation of the surface and/or the species is effective in achieving the flat surfaces of the films [9].

In order to overcome these two problems, the hydrogenation of Si and SiO₂ films carried out by addition of H₂ to the sputtering gas. The films of Si:H and SiO_{2-x}:H were deposited in a conventional oil diffusion pumped magnetron sputtering chamber using two targets of non-doped Si (99.99%, 20 Ω cm) and fused SiO₂ (99.99%) , as shown in Fig.1 . The Si:H/SiO_{2-x}:H multilayers were prepared without exposing them to air by switching the target alternately in the deposition chamber. The Ar/H₂ mixture at a flow rate of 120 sccm was used as the sputtering gas for both films. The distance between the target and the substrate was 120 mm. The sputtering pressures, r.f. powers, H₂ gas flow ratios and substrate temperatures were varied to find the suitable conditions for our attempts.

3. Results and discussion

3.1. Deposition parameters for Si:H films

Fig. 2 shows the relation between the internal stresses of the Si:H films and the r.f. powers of sputtering. The internal stresses of the films were measured for 1 μm thick films, according to the method reported by Mack and Reisman [10] . These films were deposited on Si {100} substrates at ambient temperature with a H₂ flow ratio of 5%. Although the substrate was not intentionally heated during film deposition, the substrate temperature increased up to about 80°C due to exposure to the plasma. The internal film stresses were compressive for both depositions at 0.20 Pa (Fig. 2, triangles)

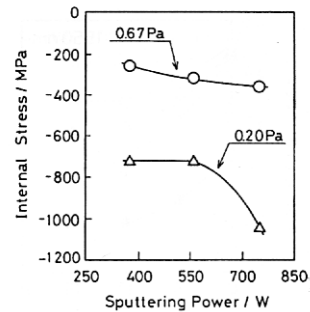


Fig. 2. Relation between the r.f. powers of sputtering and the internal stresses of the Si:H2 films deposited at ambient temperatures. The H2 flow ratio in the sputtering gas (Ar/H2: total 120 sccm) was kept at 5%. Negative sign of the stress values indicates that the measured internal stress is compressive.

and 0.67 Pa (Fig. 2, circles) . It was clearly observed that the internal stresses of the Si:H films decreased with the increase in the sputtering pressure, as pointed out by other stress studies of sputtered films [1 1 J , Further, it was found that the low sputtering power was preferable to obtain Si:H films with small internal stresses. The deposition rates, however, decreased under low-power sputtering. The sputtering rates of the films deposited under 0.67 Pa (H₂ = 5%) and ambient temperature with r.f. 375 W, 560 and 750 W were 0.309 nm s⁻¹, 0.426 nm s⁻¹ and 0.760 nm s⁻¹. Films deposited with a high deposition rate are generally required because they lead to shorter fabrication times in multilayer structures. Hence the sputtering gas pressure and the r.f. power were fixed at 0.67 Pa and r.f.-750 W to achieve small internal stresses at high deposition rates. Fig. 3 shows the influences of the H₂ gas flow ratios and the substrate temperatures on the film stress reduction, The film stresses were reduced together with the increase of H₂ gas flow ratios in the sputtering gas. We noted that the stresses of the films deposited at 200°C were changed from compression to tension at a H₂ flow ratio of 15 %. This deposition condition was tested twice, and similar results were obtained. We measured the densities and compositions of the present Si:H films. It was found that the film stresses were affected by the amounts of included Ar in the films and by Si densities of the films, which was in good agreement with previous papers [1 1 , 1 2 J . We also found that the film stresses were related to the distribution of Si-H bonds in the films.

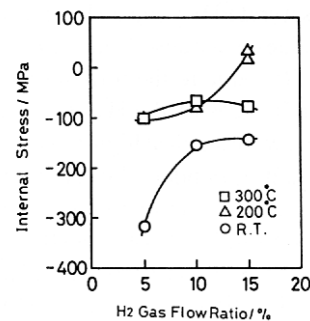


Fig. 3. Influences of the H₂ gas flow ratios and the substrate temperatures on stress reduction of the Si:H films deposited at 0.67 Pa. The flow rate of the sputtering gas (Ar/H₂) was 120 sccm in total.

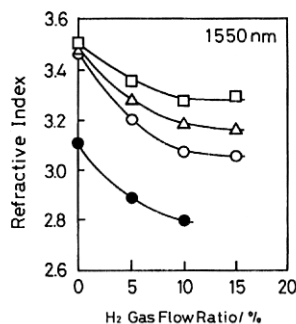


Fig. 4. Dependence of the refractive indices n (at 1550 nm) of the Si:H films deposited at 0.67 Pa on the H_2 gas flow ratios; ○, r.f.-750 W and ambient temperature; △, r.f.-750 W and 200 °C; □, r.f.-750 W and 300 °C; and ●, r.f.-375 W and ambient temperature.

The details of the results will be reported elsewhere.

In order to apply these Si:H films in the fabrication of LPS devices, a high refractive index (n) and a low absorption coefficient (α) of the films must be maintained, in addition to the low internal stresses [2]. Therefore, it is necessary to understand the influences of hydrogenation on the optical characteristics of the Si:H films, Fig. 4 shows the refractive indices (n) at 1550 nm for the Si:H films deposited under 0.67 Pa versus the H_2 gas flow ratios in the sputtering gas; the sputtering powers and the substrate temperatures were changed from r.f.-375 to r.f.-750 W and from ambient to 300 °C. The n values of the films were determined using reflection spectra of the 1 μ m thick samples deposited on fused SiO_2 substrates [13]. The n values of the films deposited at ambient temperature without H_2 , increased with the increase in the r.f. powers; $n = 3.177$ at r.f.-375 W and $n = 3.429$ at r.f.-750 W. The deposition with the high r.f. power resulted in a film with a high refractive index as well as a high deposition rate. This originated from the differences in the film density, as confirmed by Rutherford backscattering measurements. The densities of these films were 2.16 g cm^{-3} at r.f.-375 W and 2.25 g cm^{-3} at r.f.-750 W. The dependence of the substrate temperatures on the n values of the films was small; $n = 3.465$ at ambient temperature and $n = 3.508$ at 300 °C (both films were deposited under 0.67 Pa with r.f.-750 W). On the other hand, the n values of the films deposited using an Ar/ H_2 gas mixture decreased with the increase in H_2 gas contents and became almost saturated beyond a H_2 flow ratio of 10%. The reduction in n values was caused mainly by the decreasing Si densities of the films due to the formation of Si-H bonds in the films. The influences of the H_2 gas flow ratios on the n values of the films were small at high-temperature depositions because the amount of bonded H in the films was decreased due to increased substrate temperatures (see Table 1).

Si:H films absorb light of wavelength 1550 nm because of the dangling bonds in the films [14]. The presence of a large number of dangling bonds indicated that the $(SiH_2)_n$ structures were formed in the Si:H film network [15]. It is also reported that the amount of hydrogen homogeneously distributed in the Si network is about 10 at.%; bonded H contributes to form (SiH_2) structures if hydrogen contents exceed that

Table 1

The amounts of bonded hydrogen calculated from the IR peak areas at 630 cm^{-1} , in Si:H films of Fig. 2 (units in at.%)

Substrate temperature (°C)	H_2 gas flow ratios (%)		
	5	10	15
Ambient	16.6	22.7	23.6
200	13.3	15.4	15.6
300	10.0	11.5	12.3

Table 2

The relative amounts of $(SiH_2)_n$ chain in Si:H films of Fig. 2. The amount of $(SiH_2)_n$ chains are represented as the IR peak area ratios of the peak at 845 cm^{-1} for $(SiH_2)_n$ to the peak at around 890 cm^{-1} for $SiH_2 + (SiH_2)_n$.

Substrate temperature (°C)	H_2 gas flow ratios (%)		
	5	10	15
Ambient	0.70	0.66	0.62
200	0.50	0.39	0.29
300	0.18	0.18	0.16

value [16]. Table 1 shows the amount of bonded H in the films indicated in Fig. 3 (units in at.%). The relative amounts of $(SiH_2)_n$ in the films of Fig. 3 are also listed in Table 2. The amount of bonded H were calculated from the IR peak areas at 630 cm^{-1} ($Si-H$ wagging mode). The relative $(SiH_2)_n$ amounts were represented as the IR peak area ratios of the peak at 845 cm^{-1} for $(SiH_2)_n$ to the peak at 890 cm^{-1} for $SiH_2 + (SiH_2)_n$. The present films deposited at lower substrate temperatures included much hydrogen, and the amounts of $(SiH_2)_n$ structures also increased, which were in good agreement with other previous papers [17]. The constant photocurrent method (CPM) was carried out for the Si:H films with coplanar aluminum electrodes on the top surface to obtain the exact density of the dangling bonds (N_d) and the optical absorption at 1550 nm in wavelength (α_{1550}). The value of the calibration constant of the CPM was taken to be $1 \times 10^{16} cm^{-2}$ [18]. The N_d values of the films deposited at ambient temperature were too large and could not be measured by CPM. This result suggested that the Si:H films deposited at ambient temperature exhibit large optical absorption loss at a wavelength of 1550 nm due to large N_d values. The N_d values of the films deposited at 200 °C are listed in Table 3. As expected, the N_d values tended to increase with increasing amounts of $(SiH_2)_n$ in the films. However, the α_{1550} values were negligibly small.

From these results, the deposition parameters for the Si:H layers of the LPS were chosen as condition No. 4 in Table 3, mainly because of the small internal stress of the obtained film.

3.2. Deposition parameters for SiO_{2-x} :H films

The substrate temperature in the present study was fixed at 200 °C for the purpose of successive multilayer depositions with

Table 3

The deposition parameters and film characteristics for the Si:H films deposited at 200°C in the Ar/H₂ gas mixture (120 sccm). The AFM samples are 5 μm thick films deposited on Si wafers and the measured area was 10 x 10μm². The dangling bond densities (N_d) and absorption coefficients at 1 550 nm (α_{1550}) of the films were evaluated by the constant photocurrent method

No.	Deposition parameters			Deposition rate (nm s ⁻¹)	Internal stress (MPa)	Refractive index at 1550 nm	AFM measurements RMS value (nm)	CPM measurements	
	Power (W)	Pressure (Pa)	H ₂ ratio (%)					N_d (10 ¹⁶ cm ⁻³)	α (dB μm ⁻¹)
1	400	0.53	5	0.250	-156	3.180	17.88	1.7	2.4 × 10 ⁻⁵
2	750	0.67	5	0.729	-100	3.281	-	7.7	24.9 × 10 ⁻⁵
3	750	0.67	10	0.739	-81	3.186	6.86	6.4	11.0 × 10 ⁻⁵
4	750	0.67	15	0.752	17/33	3.163	8.33	6.2	9.0 × 10 ⁻⁵

Table 4

The deposition parameters and film characteristics for the silicon oxide films deposited at 200°C in the various gas (120 sccm) environments. The AFM samples are 5 μm thick films on Si wafers and the measured area was 10 x 10μm²

No.	Deposition parameters			Deposition rate (nm s ⁻¹)	Internal stress (MPa)	Refractive index at 1 550 nm	AFM measurements RMS value (nm)
	Power (W)	Pressure (Pa)	Gas				
1	560	0.20	20% H ₂	0.305	-104	1.485	0.32
2	560	0.20	30% H ₂	0.284	-101	1.590	-
3	560	0.20	40% H ₂	0.242	-109	1.693	-
4	750	0.20	10% O ₂	0.238	-160	1.450	5.96

the Si:H layers. In our previous paper, it was found that the sputtering conditions of r.f.-560 W, 0.2 Pa (Ar/H₂ = 120 (4:1) sccm) and ambient temperature resulted in a hydro-genated silicon oxide (SiO_{2-x}:H) film with a low compressive internal stress of - 88.5 MPa and a moderately high deposition rate of 0.375 nm s⁻¹ [19]. Here, the proper H₂ gas flow ratios for the depositions at 200°C were studied. The H₂ gas flow ratios were changed from 20% to 40%, while the r.f. power and gas pressure were kept at r.f.-560 W and 0.20 Pa. The internal film stresses were compressive and almost equal; - 104, - 101 and - 109 MPa for the depositions with 20, 30 and 40 H₂ gas flow ratios. On the other hand, the deposition rates decreased with the increase in the H₂ gas flow ratios (see Table 4). The magnitudes of stresses of the films deposited at 200°C were slightly increased due to the thermal stresses compared with - 88.5 MPa of the film deposited at the ambient temperature. However, the SiO_{2-x}:H film stresses were smaller than - 160 MPa of the SiO₂ film deposited by a conventional Ar/O₂ (10%)

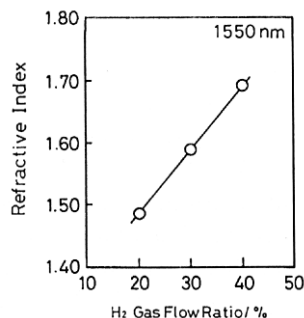


Fig. 5. Relation between the H₂ gas flow ratios and the refractive indices n (at 1 550 nm) of the SiO_{2-x}:H films deposited at r.f.-560 W, 0.20 Pa and 200°C, using an Ar/H₂ gas mixture of 120 sccm.

sput-tering (condition No. 4 in Table 4) .

The refractive indices (n) at the 1 550 nm wavelength of the SiO_{2-x}:H films mentioned above, were determined based on the four-terminal circuit model [20], using the measured optical spectra data and are shown in Fig. 5. The n values increased with the increasing of the H₂ gas flow ratios, which was due to the generation of Si-H bonds in the films as confirmed by IR measurements. Fig. 6 exhibits the optical spectra of transmission plus reflection (T+R) of the 1 μm thick SiO_{2-x}:H films deposited on fused SiO₂ Substrates indicated in Fig. 5. The films deposited with (a) 20% H₂ and (b) 30% H₂ exhibited similar results. All films were almost transparent at light wavelengths beyond 800 nm, suggesting that these films can be applied to the LPS devices operating at 1 550 nm wavelength. For the LPS applications, large n differences from Si:H films, i.e. a smaller n will be required for SiO_{2-x}:H films. Therefore, deposition parameters for the SiO_{2-x}:H films were determined as condition No. 1 in Table 4, mainly because of the small refractive index of the obtained film.

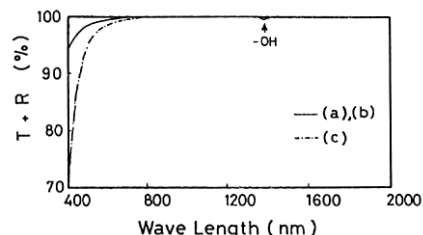


Fig. 6. Optical spectra of transmission + reflection of the SiO_{2-x}:H films indicated in Fig. 5. The films were sputtered using an Ar/H₂ gas mixture of 120 sccm; (a) 20% H₂, (b) 30% H₂ and (c) 40% H₂.

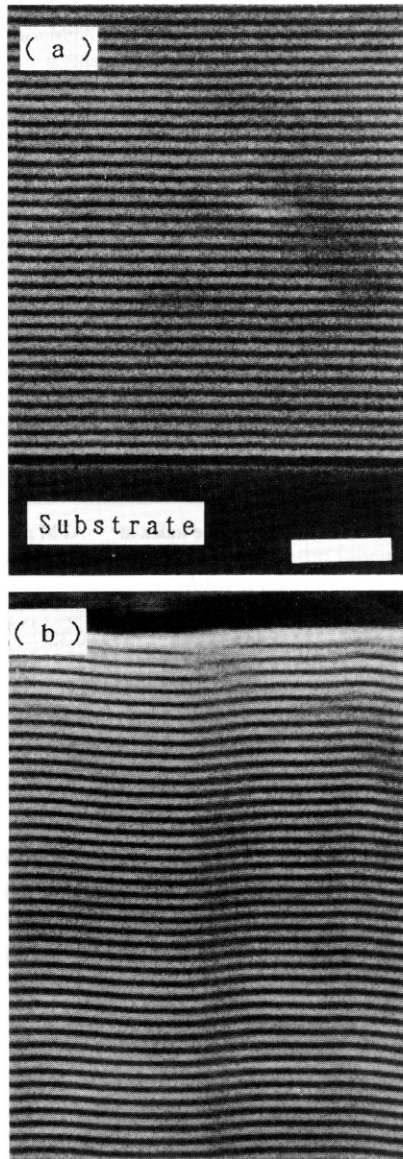


Fig. 7. Scanning electron microscopic (SEM) images of the cross-section of the 200 μm thick Si:H/SiO₂ multilayer structure fabricated by conventional sputtering conditions; (a) r.f.-400 W, 0.53 Pa, Ar/H₂ (5%) and 200°C for the Si:H layers (stress; - 156 MPa), and (b) r.f.-750 W, 0.20 Pa Ar/H₂ (10%) and 200°C for the SiO₂ layers (- 160 MPa). The bar in the photograph is 1 μm long.

3.3. Fabrication of the Si:H/SiO_{2-x}:H multilayer

The 350 μm thick Si:H/SiO_{2-x}:H multilayer with a film thickness period of 70 nm was fabricated, the sputtering conditions were No. 4 in Table 3 for the Si:H layer, and No. 1 in Table 4 for the SiO_{2-x}:H layer. This multilayer structure was sliced normal to the layers and polished for the observation of its cross-section. No break of the multilayer occurred during the machining processes, indicating that the film stresses were successfully reduced. Such a 200 μm thick multilayer comprising other Si:H films (stress of - 156 MPa, No. 1 in Table 3) and conventional SiO₂ films (stress of - 160 MPa, No. 4 in Table 4) was broken during the polishing process; both stresses were significantly larger than those of the present one.

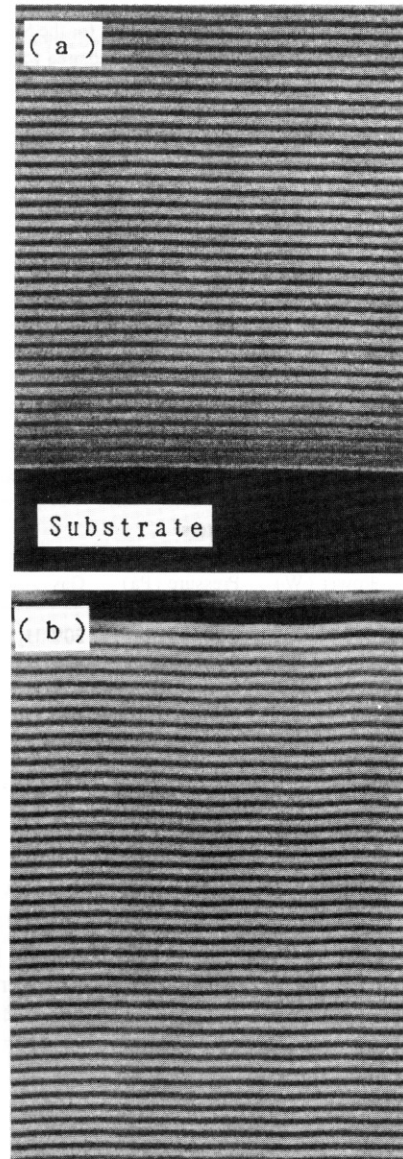


Fig. 8. SEM images of the cross-section of the 350 μm thick Si:H/SiO_{2-x}:H multilayer structure fabricated by the present conditions; (a) r.f.-750 W, 0.67 Pa, Ar/H₂ (15%) and 200°C for the Si:H layers (almost stress-free films), and (b) r.f.-560 W, 0.20 Pa, Ar/H₂ (20%) and 200°C for the SiO_{2-x}:H layers (- 104 MPa).

The surface roughnesses (σ) of the 5 μm thick films were measured by atomic force microscopy (AFM), as listed in Tables 3 and 4. The σ values of the Si:H films tended to become smaller as the deposition power was increased. As expected, sputtering for silicon oxide film deposited in the Ar/H₂ environment improved the surface roughnesses compared with that of conventional SiO₂ film deposited in the Ar/O₂ environment. Such improved surface morphology would be effective in achieving the flat interfaces of multilayers. Fig. 7 and Fig. 8 show the scanning microscopic (SEM) images of cross-sections of the multilayers fabricated by sputtering with the conventional and the present conditions. Photographs (a) represent the positions near the sub-strates, and (b) show the positions near the top layers. These cross-sections were chemi-

cally etched in HF solution for the convenience of the observation; the bright stripes in the photo corresponded to the Si:H layer. Evidently, the interfaces of the present multilayer were flat through increased accumulation (total thickness of $350\mu\text{m}$) by a factor of 1.75, compared with those of the conventional ones (total thickness of $200\mu\text{m}$).

4. Conclusion

We concluded that the Ar/H₂ Sputtering method achieved the fabrication of the Si:H/SiO_{2-x}:H multilayers up to $350\mu\text{m}$ thickness without any μm -order undulations in their interface flatness. The effect of stress reduction of the films on the interface flatness was also experimentally confirmed. Judging from our previous and the present results, we propose a model that the formation of Si-H bonds in both Si:H and SiO_{2-x}:H films will relax the structural network and lead to the stress reduction. Further investigations are necessary to unveil the flattening mechanism. We are sure that such multilayers can be applicable to film-based optical devices such as the LPS devices.

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