Journal of the Korean Ceramic Society
Vol. 45, No. 9, pp. 524~530, 2008.

Influence of Deposition Method on Refractive Index of SiO_2 and TiO_2 Thin Films for Anti-reflective Multilayers

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(Received August 6, 2008; Accepted September 2, 2008)

ABSTRACT

Anti-Reflective (AR) thin film coatings of SiO_2 (n=1.48) and TiO_2 (n=2.17) were deposited by ion-beam assisted deposition (IBAD) with End-Hall ion source and conventional electron beam (e-beam) evaporation to investigate the effect of deposition method on the refractive indicies (n) of the films. Green-light generation using a GaAs laser diode was achieved via excitation of the second harmonic. The latter resulted from the transmission of the fundamental guided-mode wave of 1064 nm through periodically poled $LiNbO_3$. Large differences in the refractive indicies of each of the layers in the multilayer coating may improve AR performance. IBAD of SiO_2 reduced its refractive index from 1.45 to 1.34 at 1064 nm. Conversely, e-beam evaporation of TiO_2 increased its refractive index from 1.80 to 2.11. In addition, no fluctuations in absorption at the wavelength of 1064 nm were found. The results suggest that films prepared by different deposition methods can increase the effectiveness of multilayer AR coatings.

Key words*: *SiO_2, TiO_2, Anti-reflective (AR) coatings, Refractive index (n), electron-beam evaporation, IBAD (Ion Beam Assisted Deposition)

1. Introduction

Periodically poled ferroelectric crystals with domain inverted periods of QPM (Quasi-Phase-Matching)-SHG (Second Harmonic Generation), QPM-SFD (Self Frequency Doubling), QPM-DFG (Difference Frequency Generation), QPM-OPO (Optical Parametric Oscillator), and wavelength conversion for optical signal processing have attracted immediate attention due to their large nonlinear optical coefficients, d_{33}.[1-5] Periodically poled $LiNbO_3$ (PPLN) is known to be one of the most promising candidates for QPM-OPO devices for the development of efficient visible lasers by conversion of existing infrared beam sources in QPM-OPO devices.[2,3,5]

Non-doped LN in a Ti:LN waveguide with a 6.8 μm domain-inverted period was previously studied in the investigation of green-light generation using a GaAs laser diode. These studies[6-8] revealed that the SHG power increased in proportion to the square of the input pumping power. For PPLN in a Ti:LN waveguide with a 6.8 μm domain-inverted period, the fundamental guided-mode wave and radiated SHG wavelengths were 1068 nm and 534 nm, respectively. It was found that a coupling power of 29 mW (1.138% conversion efficiency) resulted in 330 μW of SHG power. The average duty cycle of the etched PPLN was determined to be 50.2%. The 2 nm difference in wavelength of the 532 nm green-light was due to experimental error.[8]

Non-doped PPLN is plagued by photorefractive damage at room temperature.[3] Utilization of MgO-doped $LiNbO_3$ (MgO : LN),[1] PPLN with a shorter domain-inverted period,[6-9] and anti-reflective (AR) coatings,[10-13] reportedly alleviate such optical damages. Wavelength conversion in the mid-infrared (MIR) frequency range was mainly attributed to the periodic domain reversal, and photorefractive damage was known to be relatively insignificant due to low beam power.[4] Neither periodic deterioration of the +Z surface nor domain damage were detected. This suggests that PPLN, having a shorter domain inverted period, can be applicable to green and/or blue-light sources as used in optical disk and laser printer applications.[8] The fundamental wave was transmitted into an infrared pass filter followed by PPLN.

In this work, AR coatings were studied as a possible means to minimize leakage of stray light from the incident fundamental wave on PPLN and to enhance adhesion of the coatings. Optical AR coatings are prepared by conventional physical vapor deposition (PVD) techniques in order to control refractive index, adsorption, stress, microstructure, and

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more.[10-12] However, these optical films thus produced can have a porous columnar microstructure, lower packing density, and a lower refractive index due to low mobility.[10-12] On the other hand, ion bombardment of thin films can influence their microstructure and optical properties significantly; ion energy transferred to the adatoms results in increased mobility of the latter.[11] One of the main advantages of IBAD is that better quality AR films can be obtained at lower substrate temperatures. This effectively lessens large scale interdiffusion typical of high temperature processing techniques. In addition, the lower energy ion impacts reduce localized mixing, thus improving film-substrate adherence. An improved refractive index (*n*) and layer stabilization (and significantly reduced damage) can be achieved by using low ion energy with high current.[10]

Multilayer systems operating on the basis of optical interference consist of thin film structures with alternating layers of contrasting refractive indices. A large difference in refractive indices is beneficial.[13] It has also been noted that the two thin film materials should have low optical absorption.[13] Before drawing any concrete conclusion regarding the structure of multilayer thin films, properties of single-layer thin films must first be studied. The goal of this work is to study the experimental conditions for single-layer AR coatings. TiO_2 (n=2.17) and SiO_2 (n=1.48) were selected as high- and low-refractive index materials in optical AR coatings, respectively.[13] In the present study, high quality AR films (TiO_2 and SiO_2) were deposited on glass and Si wafers by IBAD with End-Hall ion source as well as conventional electron beam (e-beam) evaporation to investigate the effect of deposition method on index of refraction of the films. The optical and structural properties of the AR coatings were investigated using atomic force microscopy (AFM, Seiko Instruments Inc., SAP 400, Japan, JPK Instruments, NanoWizard II, Germany), ellipsometry (Woolam Inc., V-VASE, USA), and UV/Vis/Nir spectrometer (Jasco Inc., V-550, Japan).

2. Experimental Procedure

Glass (50×24 mm², Corning Inc., USA) and Si (4 inch, Siltron Inc., Korea) wafers were used as substrates. The glass was surface cleaned by sonification in a solution of acetone (10 min), $NH_4OH:H_2O_2:H_2O$ (1:1:5, 30 min at 80°C), $HCl:H_2O:H_2O_2$ in (1:1:6, 30 min at 80°C), and finally by rinsing and drying. The Si wafers were surface cleaned for 15 min at 120°C in $H_2SO_4:H_2O_2$ (4:2), followed by rinsing and drying. The starting materials were 1 to 3 mm average diameter SiO_2 granules (99.99%) and 10 mm diameter by 2 mm thickness TiO_2 pellets (99.99%). The substrate was rotated at a speed of 20 rpm during the deposition.

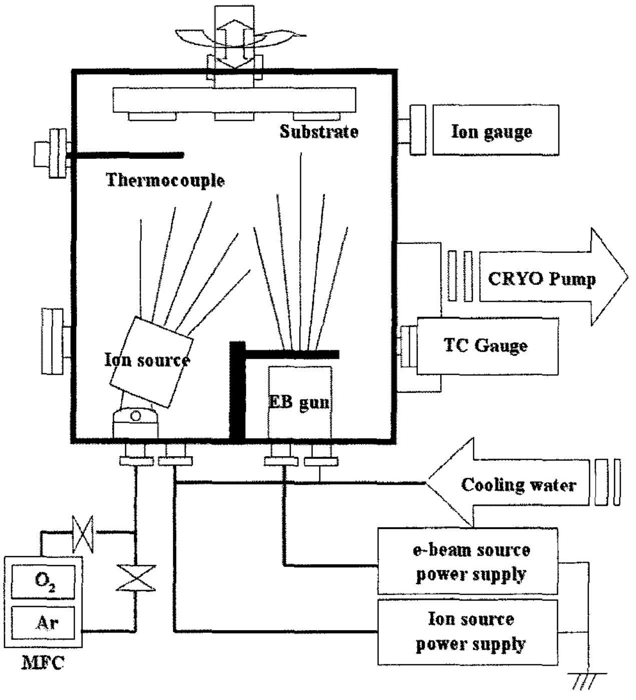

Fig. 1. Experimental setup for e-beam evaporation with and without the ion source.

TiO_2 and SiO_2 films were prepared in a coating system (Advanced Materials Science Corp.(AMS), Korea), as depicted in Fig. 1, consisting of an e-beam gun (AMS, AEC-650P, Korea) and a hot-cathode type End-Hall ion source (AMS, AIS-400E, Korea). The growing film on the substrate was bombarded with argon and oxygen atoms coming from the ion source. The base pressure was maintained to be 3.3×10^{-6} Torr. The deposition rate of both films was 0.5 Å/s, and the thickness of the films was kept at 100 nm. The ion gun voltages and currents were in the range of 30~82 V 0.1~0.3 A, respectively. The experimental conditions are summarized in Table 1. TiO_2 and SiO_2 thin films were

Table 1. Deposition Conditions of SiO_2 and TiO_2 Thin Films

Materials		Conditions				
IBAD	SiO_2	Ar /[Ar+O_2] ratio	1	1	1	0.9
		anode current (A)	0.1	0.2	0.3	0.1
		anode voltage (V)	30	50~44	54	75
	TiO_2	Ar /[Ar+O_2] ratio	1	1	1	0.9
		anode current (A)	0.1	0.2	0.3	0.1
		anode voltage (V)	50~65	82~65	70~140	77
e-beam	SiO_2 TiO_2	substrate Temperature	100°C	150°C	200°C	250°C

deposited on glass (UV spectrometer) and Si wafers (AFM, ellipsometer) by IBAD with End-Hall ion source as well as conventional e-beam evaporation.

3. Results and Discussion

The optical and mechanical properties of thin films prepared by conventional e-beam processes are known to be dependent on substrate temperature, gas pressure, and deposition rate.[10] The substrate temperatures were varied from room temperature to 250°C (Table 1). Surface morphology of SiO_2 thin films on Si wafer was analyzed by using an AFM, as shown in Fig. 2. The roughness of the SiO_2 surface, as quantified by the root mean square surface height (RMS) of 2.837 nm, was probably due to low mobility as previously mentioned. Surface microstructure (consisting of columns and voids) observed in the past has been attributed to arrival of low mobility particles on thermally unstable condensate particles.[12] In this work, it was found that surface roughness decreased with increasing substrate temperature, presumably due to increased mobility. The least rough surface of 0.162 nm resulted from deposition on a substrate of temperature of 200°C. The refractive indices of the SiO_2 films were measured by a variable-angle spectroscopic ellipsometer (V-VASE). For substrate surface deposition temperatures of room temperature and 150°C, they were found to be in the range of 1.4476 to 1.4853. At substrate temperatures from 200°C to 250°C, they were 1.4610 ~ 1.5065. It was found that the refractive index rose slightly when the substrate was heated above 150°C, as shown in Fig. 3. The highest refractive index of the SiO_2 films was obtained when the substrate temperature was 200°C, which is consistent with the lowest roughness results. The higher degree of smoothness on the films is likely to be related to higher refractive index and transmission,[13] suggesting that substrate temperature may be attributed to optical properties of the e-beam evaporated AR films.

RMS roughness of IBAD SiO_2 films on unheated Si wafer ranged between 1.874 nm and 1.843 nm where the Ar/($Ar+O_2$) ratio was unity and the anode currents were 0.1 A and 0.3 A, respectively (Fig. 4). RMS roughness dropped to 1.107 nm when the anode current and the Ar/($Ar+O_2$) ratio were 0.1 A and 0.9, respectively. Although the lowest RMS roughness of 1.060 nm was obtained for films prepared at an anode current of 0.2 A without oxygen gas, a lower refractive index was detected, which is contrary to previous results. The refractive indices of the films deposited without oxygen gas (Ar/($Ar+O_2$) = 1) decreased with increasing wavelength as shown in Fig. 5. In that figure, the refractive index ranged from 1.34 to 1.46. Films produced with oxygen gas present were found to have a minimum refractive index of 1.348 at 608 nm. Refractive indicies steadily increased from this value up to 1.368 at 1200 nm. These results suggest that different surface structure (morphology) may be due to the presence of oxygen gas. RMS roughness resulting from IBAD was approximately one order of magnitude

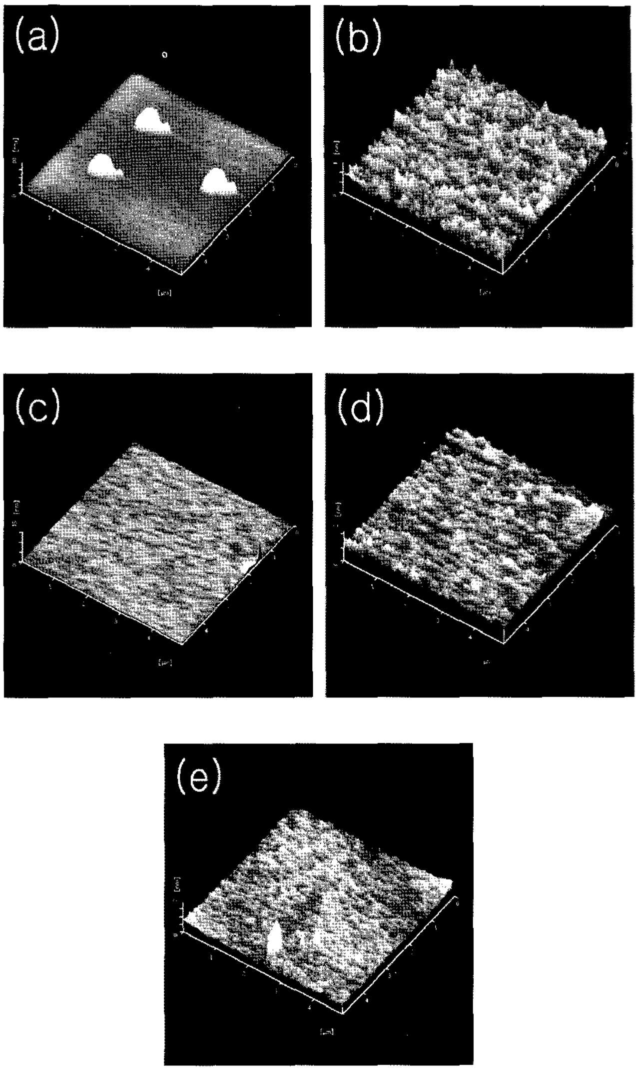

Fig. 2. AFM micrographs of SiO_2 thin films on Si wafer prepared by e-beam processes. The substrate temperatures were (a) room temperature, (b) 100°C, (c) 150°C, (d) 200°C, and (e) 250°C.

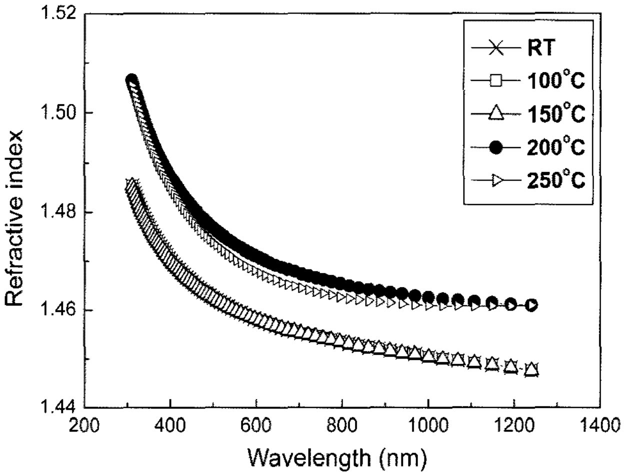

Fig. 3. Refractive index for the SiO_2 thin films deposited by e-beam evaporation under different substrate temperatures.

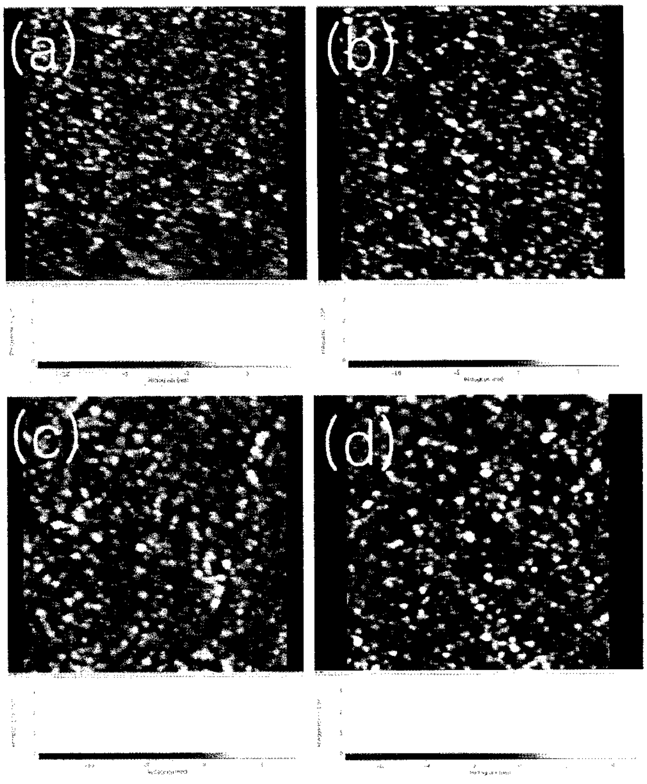

Fig. 4. AFM micrographs of SiO_2 thin films on Si wafer prepared by IBAD. The $Ar/(Ar+O_2)$ ratio and current were (a) 1, 0.1 A, (b) 1, 0.2 A, (c) 1, 0.3 A, and (d) 0.9, 0.1 A, respectively.

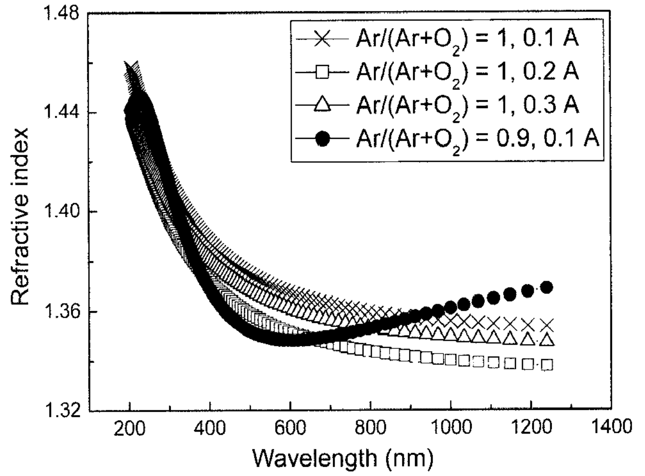

Fig. 5. Refractive index for the SiO_2 films prepared by IBAD under different currents and $Ar/(Ar+O_2)$ ratios.

larger than the RMS roughness resulting from e-beam evaporation. As expected, the refractive index of the SiO_2 films produced by IBAD was about 0.1 lower than that produced by the e-beam deposition. To date, SiO_2 is the material that shows the lowest absorption ($k=1\times10^{-5}$) and refractive index ($n=1.48$).[13] Experimental results suggested that the refractive index of SiO_2 can be substantially reduced via appropriate ion-assisted treatment.

Surface morphology of TiO_2 thin films prepared by e-beam is shown in Fig. 6. The AFM morphology of the TiO_2 films deposited at room temperature showed the lowest RMS roughness of 0.1318 nm. Unlike the SiO_2 films, the roughness worsened (0.1463 nm ~ 0.2054 nm) with increasing substrate temperature. It is clear from Fig. 7 that the refractive index of the TiO_2 film was largest for a substrate temperature of 250°C.[10] A dramatic rise of 1.75 to 2.9 in the refractive index was observed with increasing wavelength from 200 nm to 310 nm. Further increases in wavelength indicated a reduced refractive index. This reduction continued all the way up to 1200 nm where the refractive index was found to be 2.1.

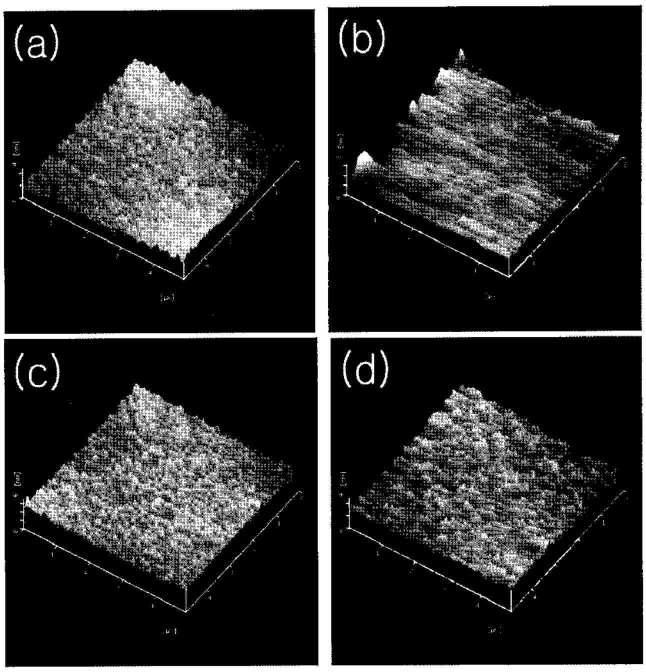

Fig. 6. AFM micrographs of TiO_2 thin films on Si wafer prepared by e-beam process. The substrate temperatures were (a) room temperature, (b) 100°C, (c) 150°C, (d) 200°C, and 250°C.

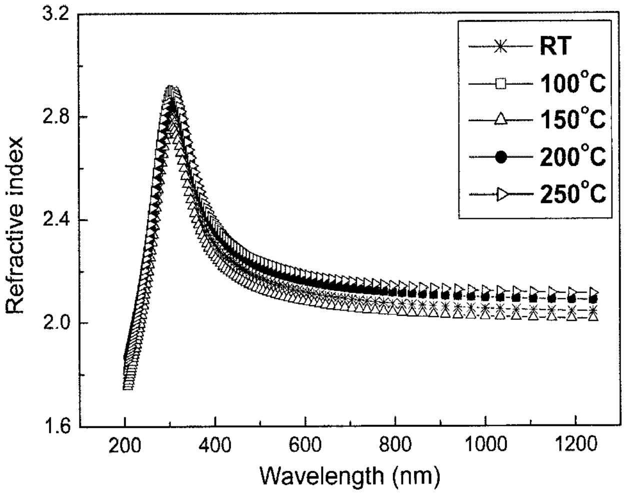

Fig. 7. Refractive index for the TiO_2 thin films deposited by e-beam evaporation under different substrate temperatures.

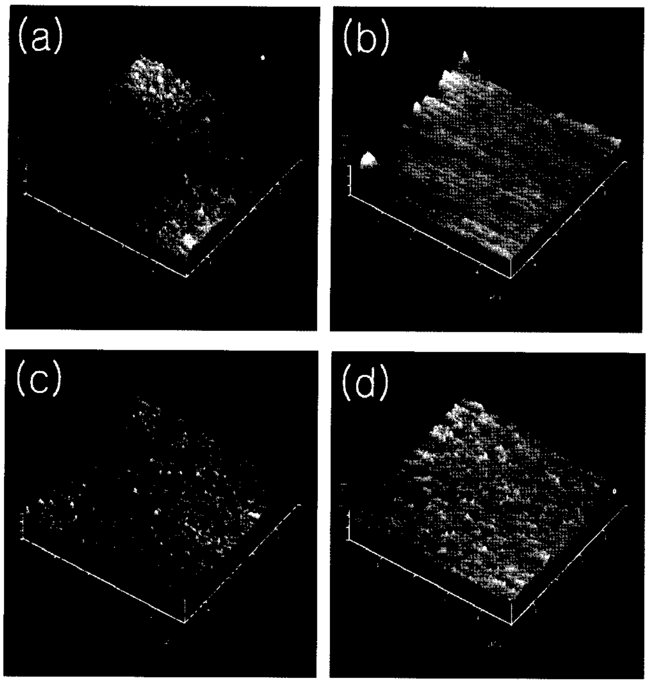

Fig. 8. AFM micrographs of TiO_2 thin films on Si wafer prepared by IBAD. The $Ar/(Ar+O_2)$ ratio and current were (a) 1, 0.1 A, (b) 1, 0.2 A, (c) 1, 0.3 A, and (d) 0.9, 0.1 A, respectively.

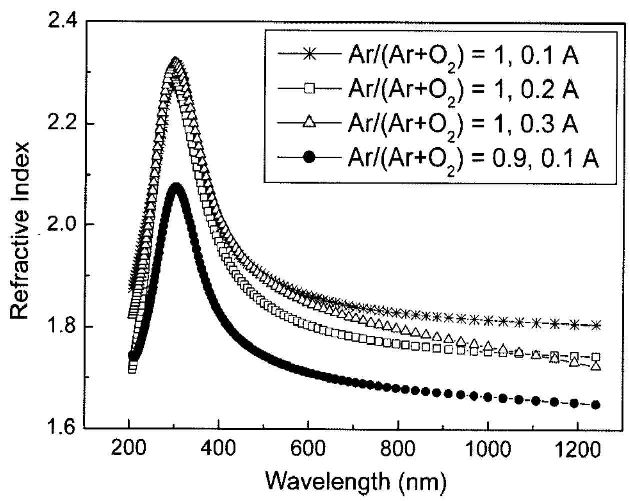

Fig. 9. Refractive index for the TiO_2 thin films deposited by IBAD under different currents and $Ar/(Ar+O_2)$ ratios.

RMS roughness of IBAD TiO_2 films on unheated Si wafer ranged between 0.2711 nm and 0.6118 nm where the $Ar/(Ar+O_2)$ ratio was unity and the anode currents were 0.2 A and 0.1 A, respectively (Fig. 8). Fig. 9 indicates that the highest index of 2.31 was observed at 300 nm wavelengths for the IBAD films prepared without oxygen gas; the lowest index of 1.81 (current=0.1 A) was observed at 1200 nm wavelengths. Interestingly, the highest RMS roughness of 0.6118 nm obtained for the films produced with an anode current of 0.1 A also produced the highest refractive index. The lowest refractive indices were found for the films deposited with oxygen. Experimental results suggest the e-beam process can produce TiO_2 films with a refractive index in excess of those produced through IBAD.

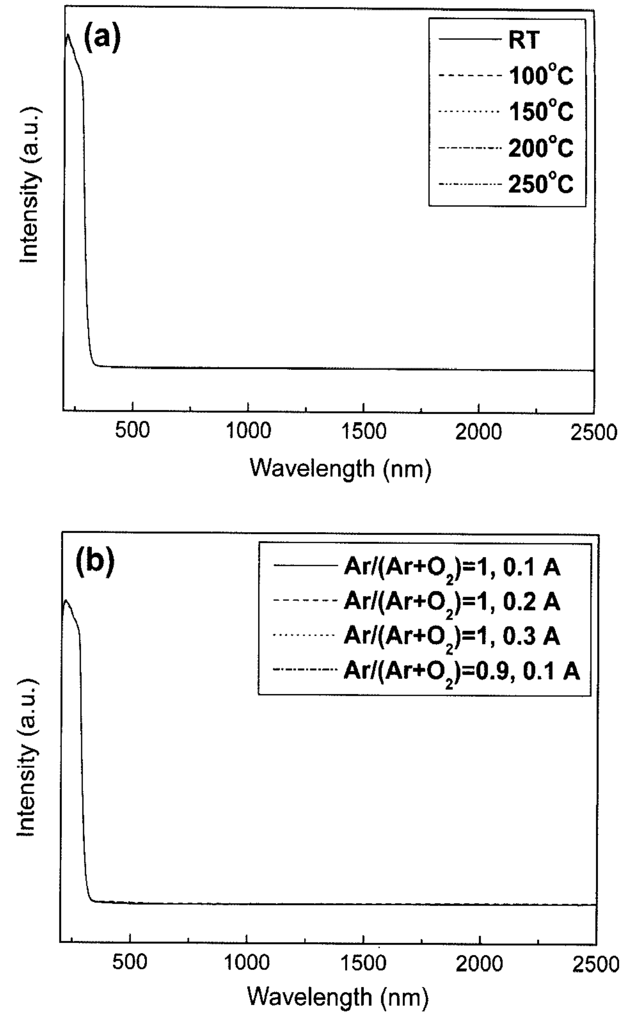

Fig. 10. Transmittance spectra of the SiO_2 films on glass substrate (a) without and (b) with ion beam source.

In the present study, SiO_2 and TiO_2 were selected as the low and high refractive index materials, respectively. AR coatings are optical coatings applied to the surface of PPLN in order to enhance adhesion and reduce reflection. This may improve the efficiency of QPM-OPO devices. To achieve green-light generation using a GaAs laser diode, the fundamental guided-mode wave of 1064 nm was transmitted into PPLN for the SHG green power.[8] It has been shown that large differences in the refractive indicies of multilayer coatings can increase AR performance.[13] As already stated, the SiO_2 and TiO_2 used in this work serve this difference.

The transmittance spectra of the SiO_2 films on glass substrate were measured by an UV/Vis/Nir spectrometer (Jasco Inc., V-550, Japan) in the wavelength range of 200 to 2500 nm as shown in Fig. 10. Transmittance intensity of the SiO_2 films prepared under various conditions was reduced dramatically in the ultraviolet (UV) region at 330 nm, indicating that the absorption edge for these films may be 330 nm. This was found to be independent of the ion-beam source. No variation in intensity for the SiO_2 films prepared under

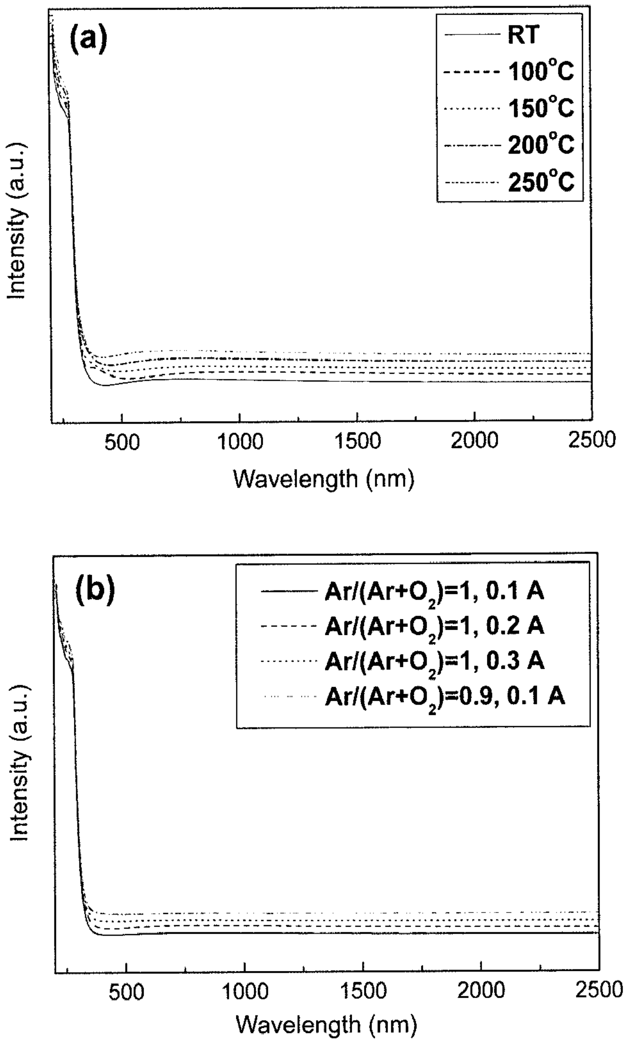

Fig. 11. Transmittance spectra of the TiO_2 films on glass substrate (a) without and (b) with ion beam source.

different deposition conditions, such as substrate temperature, Ar/(Ar+O_2) ratio, and (ion) current, was observed in the wavelength range of 330 to 2500 nm. The lack of fluctuations in transmittance intensity at 1064 nm evident in Fig. 10 suggests that SiO_2 films can be used as the PPLN AR coating.

The transmittance spectra of the TiO_2 films are depicted in Fig. 11. The absorption edge of the films was found to be 370 nm. Contrary to the SiO_2 films, the transmittance intensity of the e-beam evaporated TiO_2 films increased with increasing substrate temperature (Fig. 11(a)). This indicates reduced absorption at higher substrate temperatures. In addition, the highest transmittance intensity was observed for IBAD TiO_2 films produced with oxygen gas, as shown in Fig. 11(b). Similar to the SiO_2 films, there is a clear lack of fluctuations in transmittance intensity at 1064 nm.

To reiterate, large differences in the refractive indicies of the films in multilayer coatings are beneficial to multilayer AR coatings.[13] Although multilayer coatings were not synthesized in the present study, single layer deposition conditions (such as those thought to be present in the formation of multilayer films) were deduced. This study indicates that large differences in refractive indicies of TiO_2 and SiO_2 films can be achieved through IBAD and e-beam processes; IBAD and e-beam were found to be appropriate for the low-*n* SiO_2 and high-*n* TiO_2, respectively.

4. Conclusions

AR coatings of SiO_2 and TiO_2 thin films were deposited by IBAD and conventional e-beam evaporation, respectively, in order to investigate the effect of deposition method on thin film refractive index. Green-light generation using a GaAs laser diode was achieved via excitation of the second harmonic. The latter resulted from the transmission of the fundamental guided-mode wave of 1064 nm through periodically poled $LiNbO_3$. To improve the multilayer AR coating performance, a large difference in the refractive index may be beneficial, as such, our goal in this work was to produce thin films with large difference in refractive indicies. The refractive index of SiO_2 was reduced from 1.45 to 1.34 at the wavelength of 1064 nm by employing the IBAD. On the other hand, the index of TiO_2 rose from 1.80 to 2.11 with an aid of the e-beam process. No variation of absorption at the wavelength of 1064 nm was detected. The results suggest that the single films prepared by different deposition methods may be applicable to the AR multilayers.

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