The effect of defects on the optical nonlinearity of thermally poled SiO_x thin films

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Available online 13 July 2007

Abstract

Defects were deliberately induced in SiO_x thin films during their deposition using a helicon plasma activated reactive evaporation technique. The films were thermally poled and the poling induced second-order optical nonlinearity was investigated by measuring the second harmonic generation of the samples. It was found that oxygen-rich SiO_x thin films containing mainly peroxy radicals enabled a much larger optical nonlinearity than stoichiometric SiO_2 films after poling, and their optical nonlinearity was long-time stable; while silicon-rich SiO_x thin films containing mainly oxygen vacancy defects presented a smaller and unstable optical nonlinearity after poling.

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Keywords: Defect; Silica; Optical nonlinearity; Thermal poling; Helicon plasma

1. Introduction

Silica-based thin films are important engineering materials utilized for passive or active optical devices in the field of optical communications, because of their low loss over a wide frequency range, thermal and mechanical stability, and ease of processing. Large second-order optical nonlinearity (SON) is expected but does not exist in the amorphous silica, because of its centro-symmetric or isotropic structure. Nevertheless, Myers et al. reported in 1991 that SON was produced in silica glass as a result of breaking its centro-symmetric structure by a thermal poling process [1]. The poling involves heating the sample to $\sim 300^\circ\text{C}$, then applying a dc bias of 3–5 kV across the sample (1.6-mm-thick). After ~ 15 min of poling the heater was turned off and the sample was cooled to room temperature while keeping the voltage constant, and then the applied dc voltage was removed. It is generally believed that poling under high temperature and high electric field leads to re-orientation of bonds and dipoles in the materials, and to re-distribution of various charges in the materials; thus a frozen-in electric field remains in the sample after poling, which breaks the centro-symmetric structure of the materials, and induces SON [1–3].

Silica thin films with a very large SON may have greater applications for, such as, fabricating cheap and efficient integrated electro-optic devices, or modulators to be used in optical telecommunication. Great efforts were thus spent since 1991 in generating and increasing the SON in silica materials using various poling techniques [1–6]. Besides improving the poling methods, we regard that inducing more charged defects in silica thin films before poling could be another way to enhance the generated SON in the silica films after poling. This ideal was tested and proved by our work as reported in this paper.

High-densities of nonimpurity defects in silica can be induced through Ar ion implantation [7], or γ -radiation [8]. In our work they are induced during the thin film growth using a helicon plasma activated reactive evaporation (HARE) technique. The Si/O atomic ratio in the film was varied by controlling the deposition parameters, especially argon/oxygen gas flow ratio, so that defects was induced in the films by making the films either silicon or oxygen rich.

2. Experiments

The applied thin film deposition device combines an evaporation source (electron beam) and a low-pressure high-density helicon plasma source in a configuration where the

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Fig. 1. The dependences of the optical refractive index (@630 nm) and O/Si atomic ratio of the SiO_x films on the applied O_2/Ar gas flow ratio during the deposition. The gas pressure was kept at ~ 1 mTorr, helicon plasma 500 W, and average substrate bias -60 V for all the depositions.

evaporant is transported through the plasma source region to condense on a substrate [9]. Substrate holder was water-cooled to keep the substrate temperature below 200°C during deposition, and it was biased using another rf power source that was independent to the helicon rf source.

1-millimeter thick silica glass plates were used as the substrates. A 30-nm-thick indium tin oxide (ITO) layer was sputter-coated on the substrate before SiO_x thin film deposition. The ITO is electrically conductive, and transparent in visible and infrared light region, so it can serve as one poling electrode, while causing no absorption of second harmonic signal in visible wavelength region. This makes it convenient for both poling process and second harmonic generation measurement to the SiO_x films.

In this study 4- μm thick SiO_x films with different O/Si atomic ratios were deposited for poling test. An O_2 and Ar gas mixture was used as reactive plasma for the SiO_x deposition. The gas flows were accurately controlled using two mass flow controllers. Small pieces of pure Si (99.99%) filled in a carbon crucible were used as the Si evaporation source material. The e-beam power directed to the crucible was around 4 kW. The evaporation rates of Si usually decrease as the material in the crucible is consumed during evaporation. To keep constant evaporation, it is necessary to monitor the evaporation rate and adjust the e-beam power during deposition. A rate crystal sensor was employed to monitor the evaporation rate based on the change in the oscillation frequency of the crystal as material accumulates on its surface. In addition, an optical emission spectrometer named *Monolite 6602 OSA* was also used to monitor the evaporation rates by displaying the optical emission intensity of the evaporated and excited Si atoms at the wavelength of 302 nm.

The O/Si atomic ratios of the films were measured with Rutherford backscattering spectrometry (RBS) with a 2 MeV 4He^+ beam at a backscattering angle of 169° . The RBS spectra were analyzed using RUMP software [10]. The refractive index and thickness of the thin films were determined by using a 44-wavelength ellipsometer and a prism coupler. Optical absorption of the SiO_x films coated on bare silica plates was measured using a Cary 5000 UV–Vis–NIR spectrometer.

During the thermal poling process of the samples, a small piece ($4 \times 4 \text{ mm}^2$) of p-type silicon wafer (0.5 mm thick) was put on the surface of the SiO_x film as the top electrode; the bottom ITO electrode under the SiO_x film was connected through areas which was not coated by the SiO_x ; a 300 V DC voltage was applied to the electrodes; the sample was heated to $\sim 300^\circ\text{C}$ by a hot plate during poling; and the poling time was ~ 15 min.

The SON of the poled sample was investigated and the second-order optical nonlinear coefficients d_{eff} of the samples were determined using Make-fringe method [11–13]. In this experiment, the applied fundamental laser light had a wavelength of $\lambda = 1053 \text{ nm}$, and was obtained from an Nd:YLF laser running at a 20 Hz repetition rate. The laser beam was unfocused (spot size $\sim 2 \text{ mm}$ in diameter) before entering the sample. The second harmonic signal ($\lambda = 526.5 \text{ nm}$) came out from the sample was collected with a photomultiplier tube. A Y-cut quartz crystal was used as a reference specimen.

3. Results and discussions

Fig. 1 depicts the dependences of the optical refractive index (@630 nm) and O/Si atomic ratio of the deposited SiO_x films on the applied O_2/Ar gas flow ratio during the deposition. The gas pressure was kept at ~ 1 mTorr, helicon plasma power 500 W, and average substrate bias -60 V. As seen in the figure, stoichiometric SiO_2 films (O/Si=2) was obtained at $\text{O}_2/\text{Ar}=3$; silicon-rich films (O/Si<2) were generated at $\text{O}_2/\text{Ar}<3$, and oxygen-rich films (O/Si>2) were produced at $\text{O}_2/\text{Ar}>3$; the optical refractive index drops dramatically as the film changes from silicon rich to stoichiometric SiO_2 films ($n=1.470$), but it does not vary much when the film become oxygen rich. All the films contained $\sim 1\%$ Ar as determined by the RBS measurement.

It is easy to understand that silicon-rich films grow when there is not enough reactive oxygen species (O atoms or ions) to meet the evaporated Si atoms. For the formation of oxygen-rich films, Ar^+ and O^+ bombardment to the growing film could be one major fact apart from the excess O reactive species in the plasma, since we found that such kind of films could not be

Fig. 2. Optical absorption* of the SiO_x films measured before and after thermal annealing at temperature of 400°C in atmosphere for 30 min. (*there is no unit for the absorption, since it equals to $\log(1/T)$, where T is the transmittance of the film).

Fig. 3. Schematics of the models of nonimpurity defects in silica: (a) oxygen vacancy E' center, (b) non-bridging oxygen hole (NBOH) center, (c) peroxy radical.

generated without sufficient ion bombardment. The density of the defects in a $\text{SiO}_{2.12}$ film is estimated to be in the order of 10^{19} cm^{-3} , which is higher than that of the γ -irradiated silica (10^{16} cm^{-3}) [14], and is in the same order with that of Ar-ion implanted silica [15].

Optical absorption of the SiO_x films in the wavelength range of λ : 200–3000 nm was measured before and after thermal annealing at temperature of 400 °C in atmosphere for 30 min. All the films showed nearly zero absorption in the infrared range of $\lambda > 900 \text{ nm}$, but they exhibit quite different absorption in UV and visible light ranges, which is illustrated in Fig. 2. As seen in the figure, a silicon-rich $\text{SiO}_{1.52}$ film presents a strong absorption between 200 and 800 nm, and the absorption decreases significantly after annealing; while a oxygen-rich $\text{SiO}_{2.12}$ film shows nearly zero absorption at $\lambda > 400 \text{ nm}$, and annealing causes only minor decrease of its absorption at $\lambda < 400 \text{ nm}$. These phenomenon and effects could be associated with the defects in the films.

The defects in silica have been well-studied using electron-paramagnetic-resonance or electron-spin resonance technique [14–17]. It is believed that there are 3 principle nonimpurity-related defects in amorphous SiO_2 : paramagnetic oxygen vacancy center (E') and its variants, nonbridging oxygen (NBO) hole center and peroxy radical with trapped hole. Model for these defects are shown schematically in Fig. 3 [3,16]. The E' center ($\equiv \text{Si}^+ - \text{Si} \equiv$) is an oxygen vacancy with a hole trapped primarily on one of the silicon atoms nearest the vacancy. The unpaired electron remaining on other silicon molecule is electro-paramagnetic-resonance active. The NBO center ($\equiv \text{Si}^+ - \text{O}^-$) is a trapped hole on a single coordinated O^- ion. The peroxy radical ($\equiv \text{Si}^+ - \text{O} - \text{O}^-$) is a trapped hole on a single coordinated O_2^- molecule ion. There are also various possible impurity charge carriers, such as Na^+ , Ca^+ , H^+ , Li^+ , and Al^+ , existing in the silica. These positive charge carriers may exist in the vicinities of the negative NBO and the peroxy radicals, so that the lowest energy configurations in the material are formed. Such configurations (i.e. polar structure unites) are electrical dipoles [3].

It has been observed by Griscom and co-workers that, for temperature below 400 °C, the concentration of peroxy radicals grows with annealing temperature, while in the same temperature range the concentration of E' and NBO centers decrease [16,17]. These indicate that the peroxy radical is stable, but the E' and NBO centers are unstable in that temperature range. This phenomenon can be applied to understand our experimental results. The E' center should be the dominated defect in the silicon-rich SiO_x films, and its concentration decreases during annealing due to the oxygen vacancies are filled through oxygen

diffusing from atmosphere. Therefore the optical absorption of the $\text{SiO}_{1.52}$ films decreased obviously after annealing as shown in Fig. 2. We observed physically that the original light brown color of the silicon-rich $\text{SiO}_{1.52}$ films became lighter brown and the film was more transparent after annealing.

In the oxygen-rich SiO_x films, the chance for the E' centers to occur is very small, so that its concentration in the films is low; while the peroxy radicals and NBO centers are very likely to form, and thus they should be the dominated defects in the films. This makes the optical absorption of the oxygen-rich films much lower than the silicon-rich films in the UV–visible light range. During the annealing process, neutral oxygen molecules may diffuse through the solid film and combine with E' centers to form new peroxy radicals; the existing bridging peroxy $\text{Si}-\text{O}-\text{O}-\text{Si}$ linkages may be broken into nonbridging $\text{Si}-\text{O}-\text{O}^-$ peroxy radicals [16,17]. The reduction of the absorption of the $\text{SiO}_{2.12}$ film at $\lambda < 400 \text{ nm}$ after annealing (shown in Fig. 2) could be the results of the decrease of the concentration of the E' centers and the structure relaxation of the film. The good stability of the existing peroxy radical and its regeneration with increasing temperature below 400 °C are favorable to the generation of large and stable SON in the oxygen-rich SiO_x films using thermal poling process, which usually require a heating temperature of 250–350 °C.

Table 1 exhibits the second-order optical nonlinear coefficients (d_{eff}) of the poled SiO_x films with different O/Si atomic ratios that were achieved by varying O_2/Ar gas ratio during the deposition. The coefficients were re-measured after 3 months of poling, and were marked as d_{eff}^* in the table. As seen from the table, the d_{eff} is nearly zero for sample A, which is a high-degree silicon-rich $\text{SiO}_{1.52}$ film. A d_{eff} of 0.08 pm/V was obtained for sample B, a low-degree silicon-rich $\text{SiO}_{1.93}$ film. This d_{eff} value is higher than $d_{\text{eff}} = 0.03 \text{ pm/V}$ of the stoichiometric SiO_2 film (sample C), but it dropped to $\sim 0.02 \text{ pm/V}$ after 3 months, indicating the poling induced SON of sample B was not long-time stable. Much larger

Table 1

Second-order optical nonlinear coefficients (d_{eff}) of the poled SiO_x films with different O/Si atomic ratio that was achieved by varying O_2/Ar gas ratio during the deposition

Sample	O_2/Ar	O/Si	d_{eff} (pm/V)	d_{eff}^* (pm/V)
A	0.3	1.52	0	0
B	1.6	1.93	0.08	0.02
C	2	2	0.03	0.03
D	3	2.07	0.13	0.13
E	4	2.12	0.15	0.14

The d_{eff}^* was re-measured value of the coefficients after 3 months of poling.

nonlinear coefficients ($d_{\text{eff}} \geq 0.13$ pm/V) were achieved for samples D and E that were oxygen-rich, and they did not show obvious decay after 3 months. The maximum d_{eff} (0.15 pm/V) achieved in the $\text{SiO}_{2.12}$ film is larger than the reported $d_{\text{eff}} \sim 0.1$ pm/V of thermally poled Ge–SiON thin films [18]. Further increase of the d_{eff} of the oxygen-rich films may be achieved by improving and optimizing the poling conditions, or by doping the films with germanium or other elements.

Above results can be understood by considering the poling mechanisms. During thermal poling, various mechanisms, such as re-orientation of dipoles, and re-distribution, re-combination, or re-generations of charged defects, may happen [1–6]. It is expected that the more charged defects present in the poled material, the more chance that a larger “frozen-in” electric field could be built in the material to induce its SON. Oxygen vacancy E' centers are the dominated defects in the silicon-rich SiO_x films. The E' centers are not stable since the oxygen vacancy can be filled by the oxygen diffusing from atmosphere. The oxygen diffusion happens slowly at room temperature, or quickly if the sample is heated. Thus the concentration of E' centers may decrease quickly or slowly during or after thermal poling process, respectively. Therefore the thermal-poling generated SON in the silicon-rich films is small and not long-time stable. The zero d_{eff} of the high-degree silicon-rich $\text{SiO}_{1.52}$ film (sample A) could be due to another reason: strong absorption of the film to the SH signal ($\lambda = 526.5$ nm), as indicated in Fig. 2. A high concentration of peroxy radicals may exist in the oxygen-rich SiO_x films, and the peroxy radical does not vanish, instead, its number grows with heating temperature below 400 °C. Therefore large and stable d_{eff} was achieved for the oxygen-rich SiO_x films. The concentration of defects in the stoichiometric SiO_2 film is very low; so that the poling produced SON in sample C is relatively small.

4. Summary

SiO_x thin films with different defect dominations were produced using a helicon plasma activated reactive evaporation technique. The films were made either silicon or oxygen rich by varying the O_2/Ar gas flow ratio during the film deposition. For the silicon-rich films, optical absorption in the visible light

range was not zero and it decreased after annealing at 400 °C, but for the oxygen-rich films the absorption in the visible light range was nearly zero and unchanged after the annealing. Investigation to the poling induced optical nonlinearity of the films revealed that the oxygen-rich SiO_x thin films always enabled a much larger optical nonlinearity than the stoichiometric SiO_2 films, and their optical nonlinearity was long-time stable; while silicon-rich SiO_x thin films presented smaller and unstable optical nonlinearity after poling.

Acknowledgment

Financial support from Australian Research Council (ARC) to this research work is acknowledged.

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