Optical nonlinearity of oxygen-rich SiO_x thin films

W.T. Li, R. Boswell, M. Samoc, A. Samoc and Q.H. Qin

Highly oxygen-rich SiO_x thin films were prepared using a helicon plasma activated reactive evaporation technique. A small second-order optical nonlinearity was observed in the as-grown films, and thermal poling induced nonlinearity in the films was found to be much larger than that in stoichiometric SiO_2 films. These phenomena were associated with the non-impurity defects in the oxygen-rich films.

Introduction: Second-order optical nonlinearity (SON) is highly desirable but does not exist in amorphous silica, because of its centro-symmetric structure. Great efforts were spent since 1991 in generating the SON in silica using various poling techniques [1, 2]. It is generally believed that poling under high temperature and high electric field leads to reorientation of bonds and dipoles in the silica, and to redistribution of various charges in it; thus a frozen-in electric field remains in it after poling, which breaks its centro-symmetric structure, and induces SON [1, 2]. Apart from improving the poling techniques and doping the silica, we regard that inducing more non-impurity charged defects in silica thin films before polling could be another way to enhance the SON in the silica films after poling, since the more charged defects existing in the poled material, the more chance that a larger 'frozen-in' electric field could be built in the material after poling. This ideal was tested and proved by our work reported in this Letter.

Experiments: In this study, 4 μm-thick SiO_x films were deposited on silica glass substrates using a helicon plasma activated reactive evaporation (HARE) technique [3]. The Si/O atomic ratio in the films was varied by controlling the deposition parameters, especially argon/oxygen gas flow ratio. The films were made either silicon or oxygen rich, so that non-impurity defects in the film were induced during their growth. Before the SiO_x deposition, a 30 nm-thick indium tin oxide (ITO) layer was sputter-coated on the silica substrates. The ITO is electrically conductive, and transparent in the visible and infrared light region. Thus it can serve as one polling electrode, but it does not absorb the second-harmonic signal in the visible light region. This makes it convenient for carrying our polling process and second-harmonic measurement to the SiO_x films. The O/Si atomic ratios of the films were measured with Rutherford backscattering spectrometry (RBS). Optical absorption of the SiO_x films was measured using a UV-Vis-NIR spectrophotometer. Birefringences of the films were measured at the wavelength of 630 nm with a prism coupler.

The poling of the SiO_x films was performed in air on a hot plate at temperature of ~300°C. A poling voltage of 300 V was applied to the SiO_x film through its underlying ITO layer and a top p-type silicon electrode. The poling time was ~15 min. Second-order optical nonlinear coefficients (d_{eff}) of the samples were determined using the Maker-fringe method [4]. The applied fundamental laser light had a wavelength of $\lambda = 1053$ nm, and was obtained from a Nd:YLF laser running at a 20 Hz repetition rate. The second-harmonic signal ($\lambda = 526.5$ nm) was detected with a photomultiplier tube.

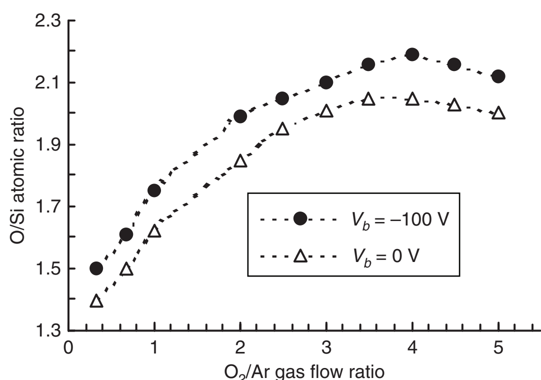

Fig. 1 *Dependences of O/Si atomic ratio of SiO_x films on applied O_2/Ar gas flow ratio*

Gas pressure kept at ~1 mTorr; helicon plasma 500 W; substrate bias V_b ~ 0 V or –100 V during deposition

Results: Fig. 1 depicts the dependence of the 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 substrate bias (V_b) 0 V or −100 V. As seen in Fig. 1, at low O_2/Ar ratio, Si-rich SiO_x films (O/Si < 2) were generated, since there were not enough reactive oxygen species to meet the evaporated Si atoms; stoichiometric SiO_2 and O-rich SiO_x films (O/Si > 2) were obtained when the O_2/Ar ratio was increased to a certain value. All the films were found to contain ~1% Ar as determined by the RBS measurement. Apart from the excess oxygen reactive species in the plasma, Ar^+ and O^+ ion bombardment to the growing film could be another factor causing the formation of the O-rich film, because high-degree O-rich films did not form at V_b = 0 V, but they did form at V_b = −100 V, as indicated in Fig. 1, and it has been found that O-rich related defects could be generated in silica by Ar^+ implantation [5, 6].

Optical absorption of the SiO_x films deposited on bare silica plates was measured before and after thermal annealing at temperature of 400°C for 30 min. All the films showed nearly zero absorption in the infrared range of λ > 900 nm, but they exhibit quite different absorption spectra in UV and visible light ranges, which are illustrated in Fig. 2. As seen in Fig. 2, a Si-rich $SiO_{1.4}$ film presents a much stronger absorption between 200–800 nm than a O-rich $SiO_{2.2}$ or a stoichiometric SiO_2 film; the $SiO_{2.2}$ film shows nearly zero absorption at λ > 400 nm; and the absorptions of both the Si- and O-rich films decrease obviously after annealing. These phenomena can be associated with the defects in the films.

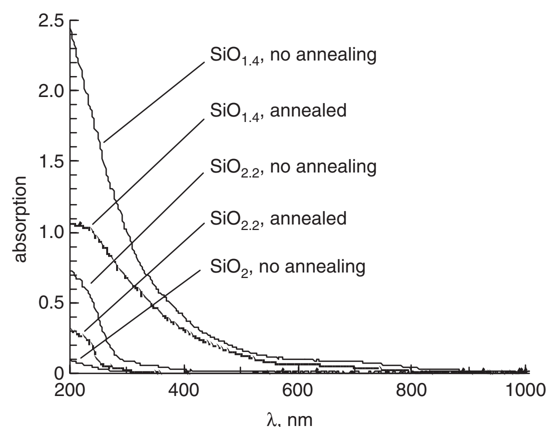

Fig. 2 *Optical absorption of SiO_x thin films measured before or after thermal annealing at temperature of 400°C in atmosphere for 30 min*

Absorption equals to log(1/T), where T is transmittance of film

The defects in silica have been well-studied using electron-spin resonance technique [5, 6]. It was found that there are three principal non-impurity-related defects in amorphous SiO_2: paramagnetic oxygen vacancy centre (E') and its variants, non-bridging oxygen (NBO) hole centre and peroxy radical with trapped hole. The E' centre ($\equiv Si^+$–$Si\equiv$) is an oxygen vacancy with a hole trapped primarily on one of the silicon atoms nearest the vacancy. The NBO centre ($\equiv Si^+$–O^-) is a trapped hole on a single co-ordinated O^- ion. The peroxy radical ($\equiv Si^+$–O–O^-) is a trapped hole on a single co-ordinated O_2^- molecule ion. There are also various possible impurity charge carriers, such as Na^+, Ca^+, H^+, Li^+, Al^+, existing in the silica. These positive charge carries may locate 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 [1]. It has been observed 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 centres decrease [5, 6]. During the annealing process, O_2 may diffuse through the silica and combine with E' centres to form new peroxy radicals; existing bridging peroxy Si–O–O–Si linkages may be broken into non-bridging Si–O–O^- peroxy radicals [5, 6]. The good stability of the existing peroxy radical and its regeneration at high temperature below 400°C are favourable to the production of large and stable SON in the SiO_x films using thermal poling process, which usually require a heating temperature of 250–350°C.

The E' centre should be the dominated defect in the Si-rich SiO_x films, since there is a greater chance for it than for other defects to form when O atoms are in a shortage; on the contrary, the peroxy radicals and NBO centres could be the dominated defects in the O-rich films. This may be one of the main reasons for the difference in the optical absorption spectra of the Si-rich and O-rich films, as illustrated in Fig. 2. The reduction of the optical absorptions of the films after annealing could be caused mainly by the decreases of their E' centre concentrations, besides the relaxation of their structures.

Table 1 exhibits the second-order optical nonlinear coefficients of the as-grown (d^0_{eff}), and poled (d^p_{eff}) SiO_x films with different O/Si atomic ratios. As seen in Table 1, both the d^0_{eff} and d^p_{eff} are zero for the $SiO_{1.8}$ film. This however does not mean that there is no optical nonlinearity for the as-grown and poled $SiO_{1.8}$ film, because their second-harmonic signal could have been completely absorbed by the films. The as-grown stoichiometric SiO_2 film also presented no nonlinearity, but a d^0_{eff} of around 0.05 or 0.06 pm/V was measured for the as-grown $SiO_{2.1}$ or $SiO_{2.2}$ film, respectively. The reason for this phenomenon is still unclear. Ion bombardment during the film growth may cause an anisotropic distribution of the charges and dipoles in the film. Oxygen may diffuse from the air into an as-grown film at room temperature, causing reactions or changes of the defects in the film. All these facts may lead to the break of the centro-symmetric structures of the films, and to their optical nonlinearity. The anisotropies of the as-grown O-rich films were evidenced by the fact that they present much larger birefringence (Δn_{TE-TM}) than the stoichiometric SiO_2 film, as shown in Table 1. The ITO layer sandwiched between the silica glass and the SiO_x films may have some influences on the growth, morphology, and defect formation of the SiO_x films, but these influences should be nearly the same for all the tested samples. Therefore the observed difference in the optical properties of the samples should come mainly from the SiO_x films.

Table 1: Second-order optical nonlinear coefficients of as-grown (d^0_{eff}) and poled (d^p_{eff}) SiO_x films with different O/Si atomic ratios

Sample	Δn_{TE-TM} ($\times 10^{-3}$)	d^0_{eff} (pm/V)	d^p_{eff} (pm/V)
$SiO_{1.8}$	—	0	0
$SiO_{2.0}$	0.5	0	0.03
$SiO_{2.1}$	1.6	0.05	0.15
$SiO_{2.2}$	2.1	0.06	0.17

The nonlinear coefficients of the as-grown $SiO_{2.1}$ and $SiO_{2.2}$ films were increased to 0.15 and 0.17 pm/V, respectively, after thermal poling, as shown in Table 1. These values are obviously much larger than that (0.03 pm/V) of the SiO_2 film poled using the same poling conditions. Further increase of the d^p_{eff} of the O-rich films may be achieved by improving and optimising the poling conditions, or by doping the films with germanium or other elements.

Conclusion: SiO_x thin films with different O/Si atomic ratios were produced using a helicon plasma activated reactive evaporation technique. A small optical nonlinearity was observed in the as-grown highly O-rich SiO_x films, and the nonlinearity was increased significantly after thermal poling. The poling induced nonlinearity in the O-rich SiO_x films was much larger than that in the stoichiometric SiO_2 films.

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