Effect of oxygen flow rate on the properties of SiO_x films deposited by reactive magnetron sputtering

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SiO_x ($x = 0-2$) films were deposited on BK-7 substrates by a low frequency reactive magnetron sputtering system with the oxygen flow rate (OFR) changing from 0 to 30 sccm. The samples were characterized by atomic force microscopy, spectrophotometer, and X-ray photoelectron spectroscopy. The extinction coefficient and refractive index decrease, while the optical transmittance increases with the increase of OFR from 0 to 17 sccm. The root mean square surface roughness has a maximum at 10 sccm OFR. The highest deposition rate is at 15 sccm OFR. Our results show that the films deposited at 20 sccm OFR are stoichiometric silica with relatively high deposition rate, low extinction coefficient, and low surface roughness. Therefore, a precise control of OFR is very important to obtain high quality films for optical applications.

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Silicon oxide films have been investigated extensively due to their important applications in both micro-electronic and optical technologies because of their excellent electrical and optical properties[1−5]. SiO_2 films can be deposited by magnetron sputtering[4,5], ion beam sputtering (IBS)[6], chemical vapor deposition (CVD)[7−9], and so on. Magnetron sputtering technique is capable of making dense amorphous films with very good repeatability and is widely used in optical coating industry. However, during the deposition, the change of the oxygen flow rate (OFR) will cause a stoichiometry problem, and this, in turn, will influence the refractive index, extinction coefficient, deposition rate, and surface roughness[6−9]. The increase of surface roughness will increase the optical scattering[10], especially in multi-layer optical films. Therefore, preparing smooth SiO_2 films with relatively high deposition rate and appreciative optical properties is very important. In previous researches, the variations of deposition rate, refractive index, and surface roughness with different oxygen pressure in some metal oxide films by IBS were investigated by Lee *et al.*[6]. In addition, Song *et al.*[7] and Roschuk *et al.*[8] reported the influence of OFR on the optical and structural properties of the SiO_x films deposited by CVD. However, few investigations on the SiO_x films with the change of OFR by reactive magnetron sputtering have been reported.

In this letter, we study the influence of OFR on the surface roughness, stoichiometry, microstructure, and other optical properties of SiO_x films prepared by low frequency reactive magnetron sputtering technique. Our results show that SiO_2 films deposited at 20 sccm OFR are of high quality for optical application.

A low frequency reactive magnetron sputtering system (ASC-800, Shincron Co., Ltd.) was used to deposit the SiO_x films. The sputtering power was kept at 1 kW. The sputter targets were doped Si of 3N purity. The base vacuum level was 2.0×10^{-4} Pa. The O_2 and Ar flow rates were controlled by mass flow meters. The total flow rate was kept at 200 sccm and the total pressure was 0.17 Pa during the deposition. The films were deposited upon BK-7 substrates of 1.0-mm thickness and 3.0-cm diameter with 1000-s sputtering time.

The crystallinity and microstructure of the SiO_x films were examined by an X-ray diffractometer (XRD) (MXPAHF) and a field-emission scanning electron microscopy (FESEM) (JSM-6700F). The surface morphology was observed by an atomic force microscopy (AFM) (SPA300HV) under ambient conditions. The root mean square (RMS) surface roughness of the films was calculated from AFM images. The composition of the SiO_x films was determined by an X-ray photoelectron spectroscopy (XPS) system, which has a Mg $K\alpha$ source worked at 1256.3 eV energy.

The reflectance and transmittance of the films were measured in the $300 < \lambda < 2000$ nm wavelength range by a spectrophotometer (U-4100, Hitachi Co.) equipped with an integrating sphere. The thicknesses, refractive indices, and extinction coefficients were calculated from the optical spectra by an envelope method[11], and the refractive indices were fitted by Cauchy dispersion law.

The XRD results show that all our samples are amorphous. Figure 1 shows the cross-sectional microstructure of the SiO_x film deposited at 20 sccm OFR. No column structures, voids, or any other defects can be observed by FESEM. This indicates that dense and uniform films were obtained, which is important for optical applications.

Figure 2(a) illustrates the variation of the transmittance spectra with OFR for the SiO_x/BK-7 samples. The magnitudes of the transmittance increase as the OFR increases from 0 to 17 sccm and tend to be saturated when OFR is larger than 17 sccm. When the OFR is larger

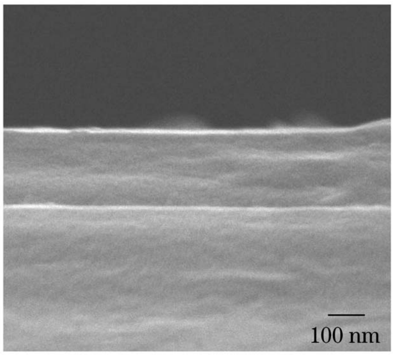

Fig. 1. The cross-sectional microstructure of SiO_x film deposited at 20 sccm OFR.

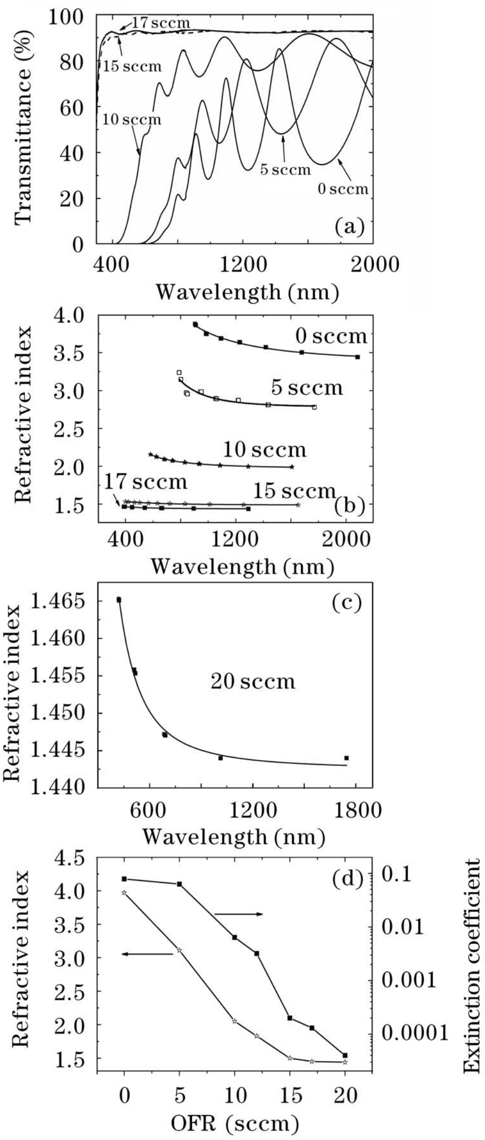

Fig. 2. The transmittances (a) and the refractive indices (b) of the SiO_x films as a function of OFR, the refractive indices (c) at 20 sccm OFR, and the refractive indices and extinction coefficients (d) at 830-nm wavelength.

than 17 sccm, the minima of SiO_x transmittance peaks coincide with the transmittance of the bare substrate, which indicates that a good optical film is formed. The refractive indices at different wavelengths of the films when the OFR changes from 0 to 20 sccm are shown in Figs. 2(b) and (c). The refractive indices decrease as the OFR increases. When the OFR is 20 sccm, the refractive index is about 1.452 at 550-nm wavelength. Figure 2(d) shows the changes of the refractive indices and extinction coefficients at 830-nm wavelength with OFR for the SiO_x films. As shown in Fig. 2(d), the refractive index at 830 nm wavelength is 3.97 at 0 sccm OFR, and decreases to 1.45 at 17 sccm. Further increase of OFR will not change the refractive index obviously, because the index is not sensitive to OFR as the silicon is almost fully oxidized[12]. On the other hand, the extinction coefficients at 830-nm wavelength also decrease monotonously from 10^{-2} to 10^{-3} and 10^{-4} order of magnitudes when OFR increase from 0 to 10 and 17 sccm, respectively. When OFR is larger than 20 sccm, the extinction coefficients are lower than 10^{-4}, which can not be calculated accurately by the envelope method[13]. The behaviors of transmittance, refractive indices, and the extinction coefficients all indicate that as the OFR increases from 0 to 15 sccm, the films become more and more oxidized. When the OFR is larger than 17 sccm, the films become fully oxidized, and transparent SiO_2 films are formed.

Figure 3(a) shows XPS spectra of a Si 2p core level with different OFRs. We can find in Fig. 3(a) that the Si 2p peaks move from Si to Si^{4+} oxidation state peaks[5] as OFR increases from 0 to 17 sccm. The stoichiometry of the films can be seen from the ratio x = [O]/[Si], where [O] and [Si] are the stoichiometry of oxygen and silicon in SiO_x film respectively, which were calculated from the peak area of O 1s and Si 2p combined with their sensitivity factors, and the results are shown in Fig. 3(b). As shown in Fig. 3(b), the ratio x increases from 0.10 to 1.0 and 1.9 when OFR increases from 0 to 10 and 17 sccm,

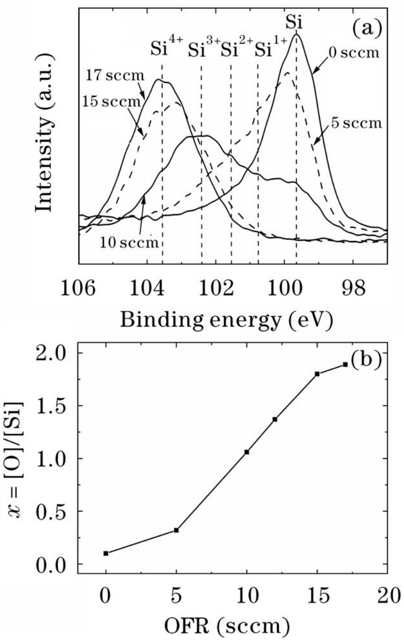

Fig. 3. XPS spectra of Si 2p core level for SiO_x films with different OFRs (a), the ratio x = [O]/[Si] derived from XPS measurements as a function of OFR (b).

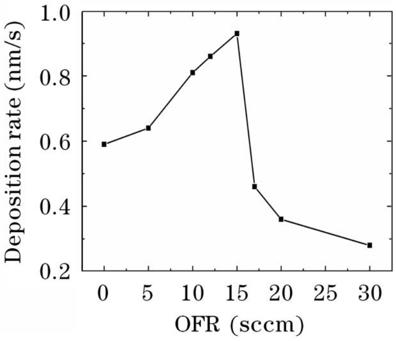

Fig. 4. The variation of deposition rate as the increase of OFR.

respectively. All these results indicate that our SiO_x film is Si at 0 sccm OFR and closes to SiO_2 at 17 sccm OFR.

The deposition rate equals the film thickness divided by the deposition time. Lee *et al.* reported in their previous work[6] that during the reactive sputtering deposition, the deposition rate should increase if the adhesion energy of the suboxide layer on the target surface is less than that of the corresponding full oxide layers, and also less than the adhesion energy of atoms in the target metals. Figure 4 shows the variation of deposition rate as the variation of OFR. The deposition rate increases initially as OFR increases from 0 to 15 sccm, drops dramatically at 17 sccm, and then decreases slowly with increasing OFR. The increase in deposition rate at the early stage could be due to suboxides loosely bonded on the surface of the target which can be sputtered off easily. The drop in the deposition rate as OFR continues to increase could be explained as due to the fact that the ratio of suboxide to oxide decreases while the full oxide increases, with the latter bonding more strongly to the target. As shown in Fig. 4, the highest deposition rate appears at 15 sccm OFR. The target surface changes from suboxide to full oxide at 17 sccm OFR, which causes the dramatic decrease of the deposition rate at this OFR.

Figures 5(a), (b), and (c) are the AFM images of the SiO_x films with 10, 15, and 20 sccm OFR respectively. As one can find in Fig. 5, the particle size on the film surface at 20 sccm is smaller than those at 10 and 15 sccm. Additionally, the height of the particles at 20 sccm OFR is also lower than those at 10 and 15 sccm OFR. The variation of RMS surface roughness with OFR is shown in Fig. 6. RMS surface roughness increases when OFR increases from 0 to 10 sccm, and then decreases as OFR is larger than 12 sccm. It is believed that the surface roughness is larger when the film was deposited with higher deposition rate[14]. In our experiments, the highest deposition rate of the SiO_x films is at 15 sccm (Fig. 4). However, the maximum roughness (about 2.2 nm) is at 10 sccm. This mismatch phenomenon may be explained as: the surface roughness is not only correlated to the deposition rate, but also dependent on the composition of the deposited species. When OFR is 10 sccm, the ratio of [O]/[Si] is close to 1.0. However, in this case, our SiO_x film is neither SiO nor only a simple mixture of α-Si and SiO_2, but a complex of Si, Si_2O, SiO, Si_2O_3, and SiO_2 as shown in Fig. 3(a). This complex deposition species contribute to the RMS surface roughness when OFR is about 10 sccm.

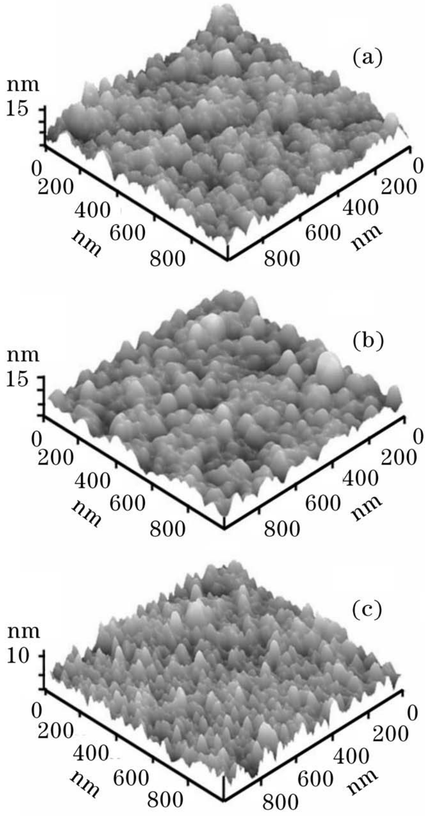

Fig. 5. AFM images of the SiO_x films when OFR is 10 (a), 15 (b), and 20 sccm (c).

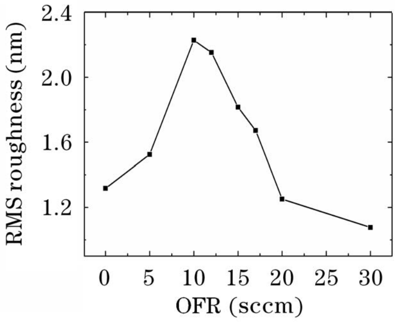

Fig. 6. RMS surface roughness of the SiO_x films as a function of OFR.

To fabricate a good optical SiO_2 film, one has to make a trade-off between the deposition rate and the surface smoothness. In our experiment, 20 sccm is an optimum OFR which yields a good optical film with relatively high deposition rate and low surface roughness.

In summary, we have studied the influence of OFR on the microstructure, morphology, stoichiometry, and optical properties of the SiO_x films on BK-7 deposited by a low frequency reactive magnetron sputtering system. The refractive indices and extinction coefficients decrease monotonously and the transmittance increases as OFR increases from 0 to 17 sccm. The highest deposition rate appears at 15 sccm OFR while the maximum RMS surface roughness occurs at 10 sccm OFR. This suggests that the surface roughness correlates not only to the deposition rate, but also to the composition of the deposited species. We find that the films deposited at 20 sccm OFR are stoichiometric silica with relatively high deposition rate, low extinction coefficient, and low surface roughness. Therefore, a precise control of OFR is very important to obtain high quality films for optical applications.

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