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Combinatorial study of low-refractive Mg–F–Si–O nano-composites deposited by magnetron co-sputtering from compound targets

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ABSTRACT

Deposition of nano-composite Mg–F–Si–O films on optical grade silica glass was studied employing RF magnetron co-sputtering from magnesium fluoride (MgF_2) and fused silica (SiO_2) targets. The aim was to obtain a stable and reliable sputtering process for optical coatings exhibiting a refractive index lower than the one of quartz glass (1.46 at 550 nm) without adding gaseous fluorine to the deposition process. The two magnetrons were installed in a confocal way at 45° off-axis with respect to a static substrate, thus creating a lateral gradient in the thin-film composition. The deposited Mg–F–Si–O coatings were structurally analysed by electron dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The obtained films consist of MgF_2 nanocrystals embedded in a SiO_2-rich amorphous matrix. Spectroscopic ellipsometry and spectrophotometry measurements showed that they are highly transparent exhibiting a very-low extinction coefficient k and a refractive index n in the desired range between the one of MgF_2 (1.38) and SiO_2 (1.46). Films with $n = 1.424$ and 1.435 at 550 nm were accomplished with absorption below the detection threshold.

1. Introduction

Low-refractive-index materials are of special interest for optical coatings to reduce the reflection at dielectric interfaces [1,2]. Coatings with a refractive index n lower than the one of silica (SiO_2, $n = 1.46$ at 550 nm) are of particular interest as they allow for a larger spectral antireflection of optical coatings on silica glass. However, inorganic dense materials with a refractive index lower than silica are very limited. One of them is magnesium fluoride (MgF_2), well known for its outstanding optical properties: a refractive index of 1.38 at 550 nm, and non-absorbing in a large spectral range from 120 nm to 8 μm [3–5]. Several attempts were made to synthesise pure MgF_2 thin films by sputtering. When sputtering in pure Ar gas from a ceramic MgF_2 target, it is found that there is a fluorine deficiency leading to absorption in the film [6–9].

In principle, one could add fluorine gas to the process to suppress this fluorine deficiency. However, this is always a severe concern with regard to safety and corrosion. One possibility to overcome this problem was recently proposed by the authors [10], and consists of the use of a CF_4/O_2 gas mixture for reactive magnetron sputtering from an Mg target. With this method, fluorine is supplied to the growing film through the net gas reaction $CF_4 + O_2 \rightarrow CO_2 + 2F$ occurring on target and film surface, and enabling the overall reaction of $Mg(s) + CF_4(g) + O_2(g) \rightarrow MgF_2(s) + CO_2(g)$.

Another way to achieve a refractive index n below the one of SiO_2 is to mix the latter with MgF_2. Depositing composite films by mixing two materials (e.g., Si–Ti–O) can be performed by sol–gel [11], chemical vapour deposition [12] or magnetron co-sputtering [13,14]. The combination of SiO_2 with MgF_2 by sol–gel deposition was investigated by Hody-Le Caër et al. showing a tuneable n lower than the 1.46 of silica, and which becomes even lower than the one of MgF_2 at a mixing ratio of 50:50 [15]. Such a low value can only be explained by substantial porosity or low-density phases present in the nano-composite microstructure. Indeed, sol–gel deposited films tend to be porous [16], which is problematic for applications. In addition, one of the thin-film deposition techniques wide-spread in industry is magnetron sputtering. For large-area coating, e.g., on architectural glazing it is even the dominant technique [17].

This work deals with a study of magnetron co-sputtered nano-composite Mg–F–Si–O thin films from SiO_2 and MgF_2 targets using only O_2 as reactive gas. The goal was to find a stable and reliable sputter process for optical coatings with a lower refractive

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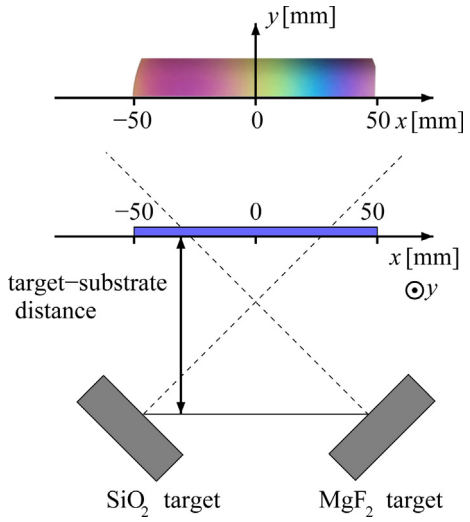

Fig. 1. Schematic drawing of the magnetron arrangement for co-sputter deposition. The film position on a 100-mm wafer is given by the x-coordinate whereas $x = 0$ corresponds to the substrate centre, $x = -50$ mm the edge close to the SiO_2, and $x = 50$ mm close to the MgF_2 target, leading to gradients of optical properties and thickness. The upper picture containing a photograph of a coated 100-mm wafer fragment illustrates the homogeneity of layer thickness and optical properties in y-direction.

index than $n = 1.46$ neither using the very corrosive F_2 gas, nor the moderate corrosive solution with CF_4 gas (the inert CF_4 itself is no problem, however, aggressive species are produced in the plasma). The planar magnetrons were operated with RF (radio frequency) power. A MgF_2 ceramic plate and a quartz glass plate were used as targets. The advantage of the co-sputter technique is that the film composition, and thus refractive index, can be tuned by varying the power ratio of the magnetrons. For the present work, an established RF magnetron sputter process for SiO_2 was applied, which included a small amount of oxygen gas to compensate oxygen loss during deposition [18]. However, neither pure fluorine nor fluorine-containing gas was added to compensate an eventual loss of F.

The produced films demonstrate that it is possible to deposit non-absorbing Mg–F–Si–O composite films by magnetron co-sputtering, which is – to the best knowledge of the authors – not yet reported in literature. In this work, optical films were synthesised on fused silica and Si wafers, exhibiting a refractive index down to $n = 1.424$ at 550 nm, which is well in between the refractive indices of sputtered SiO_2 and MgF_2, $n = 1.460$ [19] and $n = 1.382$ [10], respectively.

2. Experimental

2.1. Thin-film deposition

The films were deposited by co-sputtering from a ceramic MgF_2 (99.9% purity) and a glassy SiO_2 (99.995% purity) target, each having dimensions of $2 \times 5.26\,in^2$. They were installed at an angle of 90° to each other, facing the static substrate at 45° (see Fig. 1). This setup was chosen to deposit films with a spatial gradient in their composition and therefore a changing refractive index n in x-direction of the substrate, while along the y-direction concentrations and n remain constant. The targets were driven with RF power at 13.56 MHz; 350 W on the MgF_2 target and of 200 or 250 W on the SiO_2 target. The base pressure of the deposition chamber was in the range of 5×10^{-7} to 2×10^{-6} mbar. The same Ar mass flow of 100 sccm, corresponding to a pressure of 1.5×10^{-2} mbar, was used in all experiments. A small oxygen flow (0.5–1 sccm) was added to the process to compensate oxygen loss by particle–particle scattering. The process parameters for selected co-sputtered films are summarised in Table 1. The depositions were carried out simultaneously on half-disc 4-in silicon as well as fused silica wafers. The substrates were mounted on an electrically grounded sample plate. They were introduced into the chamber through a load-lock chamber by means of a linear manipulator to which the substrate holder was fixed at its end. The gate valve between main chamber and load-lock remained thus open during deposition. Main chamber and load-lock were pumped with turbomolecular pumps. The load-lock pumping stage was driven with reduced rotation speed during deposition to allow for a higher sputter gas pressure. The sample was simply transferred to its deposition position after a plasma stabilisation step of 10–15 min. The substrate holder was realised to adapt for different substrate positions (target–substrate distances combined with different deposition angles) and substrate sizes. For the described experiments the maximal possible target–substrate distance (17 cm) for the used chamber was set, since at shorter distances MgF_2 films became strongly absorbing, which is well known to be related to a fluorine deficiency in the films due to negative F^- bombardment from the target [6,9]. At the same time the relative large distance was beneficial reducing the sputter yield gradient across the substrate (see Fig. 1). The deposition rate was measured with a quartz microbalance, which was calibrated by scanning electron microscopy (SEM) cross sectional views, as well as with mechanical profilometry.

Table 1
Process parameters of coating depositions for absorption-free Mg–F–Si–O films in the spectral range 300–2500 nm. The target–substrate distance was set for all deposition to 17 cm and the process pressure to 0.015 mbar. The film thickness was measured with mechanical profilometry.

Film	Flow ratio	RF power [W]		Rate	Thickness	x pos.
	Ar:O_2	SiO_2	MgF_2	[nm/min]	d [nm]	[mm]
A	100:1	250	350	1.31	550	−40
B	100:1	250	350	1.21	510	−20
C	100:0.5	250	350	1.69	610	−40
D	100:0.5	250	350	1.52	550	−20
E	100:1	200	350	0.89	400	−40
F	100:0.5	200	350	0.95	430	−40

2.2. Chemical and structural characterisation

Film morphologies were assessed by SEM on a high-resolution Zeiss microscope of the type Merlin (1.5–2 kV and 40–50 pA) by cross sectional views. For chemical analysis the microscope is equipped with an Oxford X-Max 80 mm^2 EDX (energy-dispersive X-ray spectroscopy) detector. An electron acceleration voltage of 3 kV and probe current of 1.0 nA were used for the EDX measurements. The relative low acceleration voltage of 3 kV for EDX was used to avoid X-ray emissions from the substrate. For this voltage the electrons penetrate only 200 nm in SiO_2 and 150 nm in MgF_2 films [20], which is well below the used film thicknesses of 400–600 nm. The EDX measurements of the composite films were calibrated by measuring known MgF_2 and SiO_2 films at the same acceleration voltage.

Micro- and nanostructure of the films was examined in cross section by transmission electron microscopy (TEM) on an FEI Tecnai Osiris high-resolution microscope (200 kV accelerating voltage). The cross-section TEM specimens were prepared following the conventional method: mechanical cutting, gluing face-to-face, mechanical thinning and polishing. In a last step they were ion milled in a PIPS™ (precision ion polishing system) installation. Selected area electron diffraction (SAED) patterns were used to investigate the presence of nanocrystals in the films.