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Short communication

Novel transparent Mg–Si–O–N thin films with high hardness and refractive index

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ABSTRACT

There is an increasing demand for glass materials with better mechanical and optical properties for display and electronic applications. This paper describes the deposition of novel thin films of Mg–Si–O–N onto float glass substrates. Amorphous thin films in the Mg–Si–O–N system with high nitrogen and magnesium contents were deposited by reactive RF magnetron co-sputtering from Mg and Si targets in $Ar/N_2/O_2$ gas mixtures. The thin films studied span an unprecedented range of compositions up to 45 at% Mg and 80 at% N out of cations and anions respectively. Thin films in the Mg–Si–O–N system were found to be homogeneous and transparent in the visible region. Mechanical properties like hardness (H) and reduced elastic modulus (E_r) show high values, up to 21 GPa and 166 GPa respectively. The refractive index (1.87–2.00) increases with increasing magnesium and nitrogen contents.

In a wide variety of glass products, the strength, toughness and surface hardness are very important. Generally, there are inevitably many defects on a glass surface, as micro cracks, break-down of chemical bonds and brittle fractures generated from surface defects under loading [1–4]. Consequently, surface coating becomes important to improve mechanical, optical and chemical properties of glass products.

The technology of thin films coatings on glass was developed in the early 1970s in order to reduce sunlight transmission in buildings [4–6]. Thin films of metal oxides and metal nitrides have been used in many applications including solar energy devices, catalytic and photo catalytic processes, light emitting devices, fuel cells, etc [7–12]. In recent years, silicon oxynitride thin films have attracted much attention, because of their versatile properties. Silicon oxynitride is a promising material system for the development of optics, photonics and microelectronics applications, including waveguide devices, anti-reflection coating, nonvolatile memories and gate dielectrics [13–17]. One of the benefits of silicon oxynitride (SiO_xN_y) thin films is the possibility to tailor the chemical and physical properties by altering the amounts of oxygen and nitrogen in the material. SiO_xN_y thin films with varying oxygen and nitrogen ratios, can be grown by using various techniques, e.g. chemical vapor deposition (CVD) [18,19], plasma nitridation [20,21], and physical vapor deposition (PVD) by laser ablation [22], and specially magnetron sputtering [23,24]. Compared with CVD, the major advantage of magnetron sputtering of SiO_xN_y is the elimination of the hydrogen incorporation as there are no hydrogen-containing precursors involved. Additionally, magnetron sputtering can flexibly yet reliably control the microstructure and stoichiometry of SiO_xN_y films to tune the mechanical and optical properties of the films [16].

Studies of bulk oxynitride glasses in the M–Si–O–N (Where M = Mg, Ca, Sr, Ba) have shown that many physical properties (hardness, elastic moduli, glass transition and crystallization temperatures, refractive index, corrosion resistance etc) improve markedly with increasing incorporation of nitrogen [25–29]. The property changes are due to an increased connectivity of the glass network, caused by the presence of three-coordinated N atoms in the matrix. It is, however, clear that the properties not only depend on the N concentration but also depend on the type of modifier element and its concentration. We anticipated that the above properties can be achieved by the deposition of thin film of Mg–Si–O–N onto the float glass surfaces.

This paper presents the first results on thin films in the Mg–Si–O–N system deposited on the float glass surface by RF magnetron sputtering.

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The substrates used were commercial soda-lime silicate float glass, silica wafers and sapphire. The thickness of float-glass substrate is 4 mm, while silica wafers and sapphire have thickness of 1 mm and 0.5 mm, respectively. For experiments, individual pieces of 10 mm × 10 mm were prepared. Prior to deposition the substrates were ultrasonically cleaned for successive five minute treatments in trichloroethylene, acetone, and ethanol, then blow dried in N_2 prior to introducing them in the growth chamber through a load-lock system.

Reactive sputter deposition from silicon (purity 99.99%) and magnesium (purity 99.95%) targets having 50 mm diameter and 6.5 mm thickness (from Plasmaterials, Inc.) was performed in a ultra-high vacuum (UHV) deposition system described elsewhere [30,31] with a base pressure below $1\cdot10^{-7}$ Torr ($\approx 1.3\cdot10^{-5}$ Pa). The substrates were mounted at positions equidistant from the rotation axis with a substrate holder rotation of 20 rpm to ensure uniformity. The target to substrate distance was 130 mm. The substrate temperature was kept to 510 °C, just below the float glass transition temperature. The Mg and Si targets were clean-sputtered in Ar for 5 min before starting the deposition. Mg–Si–O–N thin films were deposited on float-glass surface, silicon wafers and sapphire for 2 h.

X-ray diffraction (XRD), was performed using a Panalytical X'pert PRO MPD diffractometer. A light microscope (Olympus PMG3, Japan) equipped with a digital camera was used to observe the surface morphology of the samples. Some of the samples were examined by energy dispersive X-ray (EDX) point analysis to determine the qualitative concentration of cations (Mg, and Si) and anions (O_2 and N_2), using LINK AN10000 and LINK INCA systems. The SEMs were operated at acceleration voltages of 15 and 7 kV.

The surface chemical composition of the thin films was analyzed with X-ray photoelectron spectroscopy (XPS) technique. XPS analyses were performed with Axis Ultra DLD instrument from Kratos Analytical (UK) using monochromatic A1 Kα radiation ($h\nu = 1486.6$ eV) following sample sputter-cleaning with 0.5 keV Ar^+ ions incident at an angle of 70° with respect to the surface normal. Mg 2p, Si 2p, C 1s, O 1s and N 1s core-level XPS spectra were obtained from a 0.3 × 0.7 mm^2 area at the center of the sputter-cleaned region. Elemental concentrations were derived using CasaXPS software employing Shirley-type background [32] and manufacturer's sensitivity factors.

Mechanical properties, i.e., hardness H and reduced elastic modulus E_r, of the thin films were measured by nano-indentation using a Triboindenter Ti 950 instrument from Hysitron. A standard Berkovich diamond tip at 1 mN load was used, with penetration depth in all cases lower than 10% of the film thickness. The Berkovich diamond tip was calibrated on a fused-silica sample and each sample was measured twelve times to get a statistically valid average value. Hardness (H) and elastic modulus (E_r) were calculated by the method of Oliver and Pharr using the unloading elastic part of the load-displacement curve [33].

Mueller matrix spectroscopic ellipsometry (MMSE) was used to study the refractive index n_r of the films. The measurements were performed by using a Mueller matrix ellipsometer, the RC2®, from J.A. Woollam Co., Inc. The samples were measured at four incident angles 45°, 55°, 65° and 70° and the full Mueller matrix was recorded in the wavelength range of 210–1690 nm. The data were analyzed with the software CompleteEASE, version 4.72, also from J.A. Woollam Co., Inc. and fitted with a Tauc-Lorentz model [34] for amorphous films to assess their optical properties.

Table 1 summarizes the XPS-determined elemental compositions of Mg–Si–O–N films on float glass, silica wafers and sapphire substrates, with Mg target power from 40 W to 140 W the Si target power was 100 W and the N_2 and O_2 concentrations were 20% and 1.5% respectively. X-ray diffraction confirmed that all films were X-ray amorphous. The deposited films were inspected visually and by optical microscopy at 200× magnification, on each film, to evaluate their homogeneity. The surface morphology and homogeneity were confirmed by back scattered electron SEM images. No evidence of metallic inclusions, phase separation, or other heterogeneities was found on examining several areas, and it was concluded that the films were homogeneous on this length scale. The thin film-forming region in the Mg–Si–O–N system, extends to Mg/(Mg + Si) content up to 45 at% and N/(N + O) content up to 80 at%. The Mg concentration increases linearly with increasing power of the Mg target, as shown in Fig. 1. The increase in Mg content is approximately accompanied by a corresponding increase in N content. The thicknesses and roughness of the thin films deposited on the float glass substrate in Mg–Si–O–N system are given in Table 1. The thickness in Mg–Si–O–N system varies between 372 nm and 463 nm, and increase with the increasing Mg target power. The roughness of the Mg–Si–O–N films varies between 4.63 nm and 9.35 nm and approximately increases with increasing power of the Mg target and N contents.

The hardness and reduced elastic modulus values for the Mg–Si–O–N thin films are plotted vs Mg/(Mg + Si) content in Fig. 2. The hardness values vary between 17 GPa and 21 GPa. A linear regression fit on both Mg and N content yielded $H = 18.5(1) + 0.43(0.05)\cdot[Mg] - 0.18(0.04)\cdot[N]$, with $R^2 = 0.90$. It can thus be concluded that hardness increase with Mg content. However, the separate effects of the Mg and N contents on hardness are difficult to ascertain because of the strong correlation of the Mg and N content, i.e. increase in N with increasing Mg content. The reduced elastic modulus values for the Mg–Si–O–N films vary between 130 GPa and 166 GPa. A high hardness of a material is generally accompanied by a high elastic modulus [35]. A linear regression fit on both Mg and N content yielded $Er = 170(25) + 3.26(1)\cdot[Mg] - 2.08(0.7)\cdot[N]$, with $R^2 = 0.60$, indicating a positive dependence on Mg content.

Fig. 3 shows a plot of the refractive index vs. Mg/(Mg + Si) content and Fig. 4 shows refractive index as a function of wavelength. The refractive indexes n_r of the films were obtained from the Tauc-Lorentz model fitted to the ellipsometric data collected for each sample. The refractive index in the Mg–Si–O–N system varies between 1.87 and 2. Regression analysis yielded $n_r = 1.67(0.06) + 0.018(0.003)\cdot[Mg] + 0.002(0.001)\cdot[N]$, with $R^2 = 90$. The refractive index is thus found to increase with both Mg, predominantly, and N content.

Our results, demonstrate that magnesium silicon oxynitride thin films can be prepared with a wide variety of compositions. Thin films in Mg–Si–O–N system are transparent in the visible region as compared to bulk oxynitride glasses in the same system, which are translucent in the visible region [27]. The Mg-containing thin films have high nitrogen content of N/(N + O) = 80 at%. Generally, Mg has high affinity towards nitrogen, and an increase in N content in the present work is accompanied approximately by a corresponding increase in Mg content with the exception of sample having composition $Mg_{19}Si_{23}O_{27}N_{31}$, (Table 1).

The mechanical properties of the glasses are improved as a result of the deposition of magnesium silicon oxynitride thin films. The float glass surfaces coated with Mg–Si–O–N thin films have higher hardness than the uncoated float glass. A high value of hardness of 21 GPa was obtained for float glass surface coated with Mg–Si–O–N film, which is up to three times higher than the parent float glass having hardness value of 7 GPa. Furthermore, float glass surface coated with Mg–Si–O–N films have higher hardness than pure Si_3N_4 (17 GPa) and SiON (14 GPa) [16] and comparable with the crystalline α-Al_2O_3 (22 GPa) [36,37]. The hardness of the amorphous materials is not only affected by the network former but also by the type and concentration of the modifier element (i.e., here Mg). For the present films, the hardness increases with