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**Synthesis and characterization of the mechanical and optical properties of
Ca-Si-O-N thin films deposited by RF Magnetron sputtering**

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Abstract

Ca-Si-O-N thin films were deposited on commercial soda-lime silicate float glass, silica wafers and sapphire substrates by RF magnetron co-sputtering from Ca and Si targets in an Ar/N₂/O₂ gas mixture. Chemical composition, surface morphology, hardness, reduced elastic modulus and optical properties of the films were investigated using X-ray photoelectron spectroscopy, scanning electron microscopy, nanoindentation, and spectroscopic ellipsometry. It was found that the composition of the films can be controlled by the Ca target power, predominantly, and by the reactive gas flow. Thin films in the Ca-Si-O-N system are composed of N and Ca contents up to 31 eq. % and 60 eq. %, respectively. The films thickness ranges from 600 to 3000 nm and increases with increasing Ca target power. The films surface roughness varied between 2 and 12 nm, and approximately decreases with increasing power of Ca target. The hardness (4-12 GPa) and reduced elastic modulus (65-145 GPa) of the films increase and decrease with the N and Ca contents respectively. The refractive index (1.56-1.82) is primarily dictated by the N content. The properties are compared with findings for bulk glasses in the Ca-Si-(Al)-O-N systems, and it is concluded that Ca-Si-O-N thin films have higher values of hardness, elastic modulus and refractive index than bulk glasses of similar composition.

Keywords: Ca-Si-O-N thin films; magnetron sputtering; high calcium content; hardness; elastic modulus; refractive index.

1. Introduction

Due to combined metallic, covalent and ionic bonding character, oxynitride glasses offer a wide range of structural design concepts in optimizing material properties. Bulk silicon oxynitride glasses have received considerable attention since their initial development during the 1970s. Silicon oxynitride glasses were first discovered as grain boundary phases in silicon nitride based ceramics. Since, the results show that the presence of these glassy phases in the Si_3N_4 based ceramics greatly impair their high temperature properties, studies of the glasses became quite important [1-3]. Considering the experimental difficulties to solely analyse the properties of grain boundary phases, research on these phases in bulk form was initiated. The mechanical, chemical, thermal and optical properties of oxynitride materials are related to their chemical composition, in particular the O/N ratio. Even at a doping level, the incorporation of nitrogen into an oxidic network will alter the properties. Oxynitride glasses in M-Si-O-N systems (*M* is a modifying cation such as Na [4, 5], Li [6], Mg [7, 8], Ca [7, 9-12], Sr [13], Ba [14], Y [15, 16], Al [17], La [18-22], Ce [23]) have been prepared with a wide variety of compositions. Although M-Si-O-N bulk materials exhibit outstanding mechanical, thermal and optical properties, M-Si-O-N thin films have received much less attention.

In recent years, silicon oxynitride (SiO_xN_y) thin films without modifying cations have attracted much interest, because of their chemical, optical and mechanical characteristics. These properties are tunable with the elemental composition in most cases, and enable silicon oxynitrides to find a wide range of applications such as optics, photonics, microelectronics, waveguide devices, anti-reflection coating, nonvolatile memories and dielectrics [24-28]. In comparison with Si_3N_4 , SiO_xN_y materials are transparent in the visible range and their refractive index can be varied between SiO_2 (1.46) and Si_3N_4 (2.02) by altering the N/O ratio [29]. Their optical band gap could also be controlled by tuning the N/O ratio [30] and the residual stress can be transformed from compressive (SiO_2) to tensile (Si_3N_4) mode [31, 32]. SiO_xN_y thin films of varying oxygen and nitrogen ratios can be grown by using, e.g. chemical vapor deposition (CVD) [33, 34], laser ablation [35], plasma nitridation [36, 37], ion-assisted deposition [38] and sputtering [27, 39-44].

In the magnetron sputtering process, silicon oxynitride thin films are usually deposited using a mixture of argon, nitrogen and oxygen [39, 41, 42, 44]. Recently, Hänninen et al [24] reported the preparation of SiO_xN_y thin films by magnetron sputtering using nitrous oxide as a single-source precursor. Compared to other techniques, magnetrons sputtering

have high degree of flexibility and reliability to control the microstructure and stoichiometry of SiO_xN_y films to alter the mechanical, chemical and optical properties of the films [27].

Previous studies have shown that the incorporation of nitrogen into the bulk Ca-Si-(Al)-O-N glasses [7, 9-12] increase their glass transition and crystallization temperatures, hardness, elastic moduli, refractive index, etc. The property changes are due to structural changes and the presence of three-coordinated N atoms leads to increased connectivity of the glass network. However, the properties not solely depend on the N concentration but also on the Ca element concentration. The structures of the silicon oxynitride glasses contain frameworks of corner-linked $\text{Si}(\text{O},\text{N})_4$ tetrahedral that are depolymerized depending on the amount of modifier cations. The N atoms can take the form of either $\text{N}^{[3]}$, $\text{N}^{[2]}$ and $\text{N}^{[1]}$. The species $\text{N}^{[0]}$ and $\text{N}^{[4]}$ are in general disregarded, since $\text{N}^{[0]}$ has never been observed in crystalline phases, and $\text{N}^{[4]}$ only very rarely [45]. The O atoms may be present as $\text{O}^{[0]}$, $\text{O}^{[1]}$ and $\text{O}^{[2]}$, although $\text{O}^{[0]}$ usually unlikely.

The motivation for this study comes from the results of our recent studies in Mg-Si-O-N thin films system [46] which shows that the float glass coated with Mg-Si-O-N thin films have superior mechanical (Hardness and reduced elastic modulus) and optical (refractive index) properties as compared to the uncoated float glass. Furthermore, the coated surfaces have higher hardness than pure Si_3N_4 (17 GPa) and SiON (14 GPa) [27] and comparable with the crystalline $\alpha\text{-Al}_2\text{O}_3$ (22 GPa) [47]. We anticipate that the glass surface properties can also be enhanced by the deposition of thin film of Ca-Si-O-N onto the flat/float glass surfaces.

Reports on magnetron sputtered Ca-Si-O-N thin films and their properties; are very limited. De Jong *et al.* [48] studied the luminescent properties of $\text{Ca}_3\text{Si}_2\text{N}_2\text{O}_4\text{:Eu}^{2+}$ thin films. In the present paper, results on Ca-Si-O-N thin films deposited by RF magnetron sputtering are presented. Values of hardness, reduced elastic modulus and refractive index of the thin films in the Ca-Si-O-N system are reported. The measured properties are compared with those of previously reported bulk glasses in the Ca-Si-(Al)-O-N systems and thin films in the Mg-Si-O-N system. In addition, property variations are discussed with respect to the effect of nitrogen and calcium contents in the thin films.

2. Experimental details

Ca-Si-O-N thin films were prepared in three different sample series. The first series (N10) has Ca target power 60, 100 and 140 W and N₂ flow of 10 % of the total gas flow [Ar+N₂+O₂] and having Ar=35.4 sccm, N₂=4 sccm, O₂=0.6 sccm. The second series (N20) has Ca target power 40, 60, 80, 100, 120 and 140 W and N₂ flow of 20 %. The third series (N30) has Ca target power 60, 100 and 140 W and N₂ flow of 30 %. The Si target of power 100 W and O₂ flow of 1.5% were kept constant in all three series. The films were prepared in a RF magnetron sputtering apparatus. The films were deposited on commercial soda-lime silicate float glass, silica wafers and sapphire substrates. The thicknesses of the float glass substrates, the silica wafers and the sapphire substrates are 4 mm, 1 mm and 0.5 mm, respectively. For the 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 N₂ prior to introducing them in the growth chamber through a load-lock system. Reactive sputter deposition was made from the sources silicon (purity 99.99 %), and calcium (purity 99.95 %) targets having the dimensions 50 mm in diameter and 6.5 mm thickness. These target materials were acquired from Plasmaterials, Inc. The sputtering was performed in an ultra-high vacuum (UHV) deposition system described elsewhere [49, 50] with a base pressure $<1 \cdot 10^{-7}$ Torr ($\approx 1.3 \cdot 10^{-5}$ Pa). The substrates were mounted at positions equidistant from the rotation axis with a substrate holder rotating at a speed of 20 rpm to ensure uniformity of the coating. The target to substrate distance was set to 130 mm. The substrate temperature was kept at 510 °C. i.e. just below the float glass transition temperature. The substrate temperature was chosen to be just below the glass transition temperature of the float glass, in order to achieve good adhesion. Ca and Si targets were clean-sputtered in Ar environment for 5 minutes before starting the deposition. The Ca-Si-O-N thin films were prepared by changing the Ca target power between 40 W to 140 W and the N₂ concentration between 10 and 30 %. The deposition time was 2 hours.

The amorphous nature of the thin films was varified by X- ray diffraction, using a Panalytical X'pert PRO MPD diffractometer. The surface morphology of the thin films were studied by a light optical microscope (Olympus PMG3, Japan) equipped with a digital camera. The microstructures of some of the samples were probed by back-scattered electron images using a JSM 7000F scanning electron microscope. The SEMs were operated at acceleration voltages of 7 and 15 kV.

The chemical composition of the samples deposited on Si wafers was monitored by X-ray photoelectron spectroscopy (XPS). XPS analyses were performed with an Axis Ultra DLD instrument from Kratos Analytical (UK) using monochromatic Al K α 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. Ca 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 [51] and the manufacturer's sensitivity factors.

The mechanical properties, i.e., hardness H and reduced elastic modulus E_r , of the thin films deposited on float glass substrate were measured by nano-indentation using a Triboindenter TI 950 instrument from Hysitron. A standard Berkovich diamond tip at 1 mN maximum load was used. In the indentation experiments, the penetration depth of the indenter was kept lower than 10% of the film thickness to avoid influence from the substrate. 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. The 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 [52].

Mueller matrix spectroscopic ellipsometry (MMSE) was used to study the refractive index of the obtained thin 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 [53] for amorphous films to assess their optical properties. The UV pole and IR Pole in the model are equivalent to Lorentz oscillations with zero-broadening, and are positioned well outside the considered spectral range. They describe dispersion created by absorption that occurring outside the measured spectral range and are defined by the equation:

$$\varepsilon_{pole} = \frac{Amp}{En^2 - E^2}$$

where En (eV) & Amp (eV 2) are fit parameters. For the IR Pole $En=0$ eV. The glass substrate was modeled with a Cauchy dispersion model with parameters $A=1.498$, $B=0.00509$ and $C=-9.536 \times 10^{-6}$.

3. Results

3.1. Thin film growth and characterization

The elemental compositions of Ca-Si-O-N thin films determined by XPS are summarized in Table I. Fig. 1 represents the thin-film-forming region obtained by changing the Ca target power between 40 W to 140 W, and N₂ flow between 10, 20 and 30 %, respectively. The sample with composition Ca_{3.4}Si_{33.4}O_{63.1}N_{0.1}, prepared with a Ca target power of 40 W and nitrogen flow of 20 %, has very low amount of Ca and N and is therefore not included in the further discussion. The thin-film-forming region in the Ca-Si-O-N is 30-60 eq. % Ca, and 4-31 eq. % N, respectively, where eq. % N = (3[N] / (3[N]+2[O])), where [N] and [O] are the atomic concentrations of N and O respectively. The eq. % Ca is defined as eq. % Ca = (2[Ca] / (2[Ca]+4[Si])), where [Ca] and [Si] are the atomic concentrations of Ca and Si respectively. The equivalent content is thus on the basis of the ratio of charges for a given species with respect to the total atomic concentration of species with charge of the same sign. X-ray diffractograms acquired from all films exhibited featureless characteristics, indicating that the films were amorphous.

The surface structure of the films was imaged at several positions on the selected area of the film using optical microscopy, SEM and AFM. A flat featureless surface was observed, typical for the films with extremely fine grains. Detectable phase separation or evidence of crystallization was not observed in the surface images of Ca-Si-O-N films, on all different length scales observed. Typical examples of SEM and AFM, image is shown in Fig. 2a and 2b, respectively. Thin films in the Ca-Si-O-N system are homogeneous and transparent as shown in Fig. 3. The Ca and N concentrations increase and decrease linearly with increasing Ca target power for all three series, as shown in Fig. 4a and 4b respectively. A high content of N was obtained for Ca target power of 60 W and high content of Ca was obtained with Ca target power of 140 W in all three series.

3.2 Film properties

The thicknesses of the thin films deposited on the float glass substrate in Ca-Si-O-N system were determined by using MMSE. It should be noted that the model used in this study is very simple and does not replicate the experimental data perfectly in all parts of the spectra. However, considering the relatively high thickness and surface roughness of the samples the model is regarded as fairly accurate, albeit with large error bars. The thickness in Ca-Si-O-N system varies between 600 nm and 3000 nm, and increases with the increasing Ca content in

the films. The highest thickness is obtained for sample $\text{Ca}_{27.5}\text{Si}_{9.6}\text{O}_{60.3}\text{N}_{2.6}$. The surface roughness of the Ca-Si-O-N films varies between 2 nm to 12 nm and approximately decreases with increasing power of the Ca target as can be seen in Table II.

The hardness values of the Ca-Si-O-N thin films are given in Table III and plotted vs the Ca and the N contents in Fig. 5a, 5b respectively. The hardness values vary between 4 GPa and 12 GPa. The hardness increases with N content and decreases with the Ca content. Similar trend was also observed in nitrogen rich glasses in the Ca-Si-O-N system [54]. High value of hardness, 12 GPa, was obtained for composition $\text{Ca}_{17.0}\text{Si}_{20.7}\text{O}_{50.8}\text{N}_{10.7}$. In general, series N20 has higher values of hardness as compared to series N10 and N30. The reduced elastic modulus values for the Ca-Si-O-N films vary between 62 GPa and 145 GPa as shown in Fig. 6a and 6b as a function of the N and the Ca contents, respectively. A similar trend observed for hardness was also observed for the E_r . The reduced elastic modulus increases linearly with the N content and decreases with the Ca content for all three series. For reference, the hardness and the reduced elastic modulus values were measured on all three coated substrates, (float glass, silica wafers and sapphire) being coated with Ca target power of 60 W and nitrogen flow of 10, 20 and 30%. The results show that all the three substrate have approximately similar values of hardness and reduced elastic modulus and furthermore a similar trend is observed in all three series.

The refractive indices n_r , extinction coefficients k , and band gap E of the films show a strong correlation to the amount of both Ca and N in the films. The refractive indices and extinction coefficients in the Ca-Si-O-N system as a function of wavelength is shown in Fig. 7a and 7b respectively. The refractive index at wavelength 633 nm varies between 1.56 and 1.82 and increases linearly with the N content. Series N20 have high value of refractive index as compared to series N30 for the same target power. The extinction coefficient at wavelength 233 nm varies between 0.001 and 0.033. The band gap values vary between 3.82 and 4.85 eV and increases roughly with the Ca content and decrease linearly with the N content.

4. Discussion

The results of the present study demonstrate that calcium-containing silicon oxynitride thin films can be prepared with a wide variety of compositions by changing the Ca target power and N_2 gas flow. Most of the obtained films have high Ca content and thus fall in the category of invert amorphous film, i.e. the modifier (Ca) content is higher than the former (Si) in the network ($\text{Ca/Si} > 1$). The overall Ca and N content is not significantly influenced

by the N₂ flow, while the film composition is tuned with the Ca target power. For a Ca target power of 60 W, compositions containing high amount of nitrogen were obtained for all three series. Increasing Ca target power above 60 W lead to a Ca/Si ratio above 2, which is very rare in amorphous materials. No systemic relation was observed between the N content and the Ca content. This is different from the Mg-Si-O-N system [46], where an increase of the N content was accompanied roughly by a corresponding increase of the Mg content. The low nitrogen content in the Ca-Si-O-N system as compared to the Mg-Si-O-N system [46] is probably due to the fact that Ca metal has higher affinity to oxygen and low affinity towards nitrogen as compared with Mg. Similar trends were observed in the bulk Mg/Ca-Si-O-N glasses [55].

The mechanical properties of the glass surfaces are improved as a result of the surface coating by the deposition of calcium silicon oxynitride thin films. Hardness value of 12 GPa was obtained for float glass surface coated with Ca_{17.64}Si_{20.68}O_{50.79}N_{10.65} film, which is almost twice that of the uncoated float glass having hardness value of approximately 7 GPa. Furthermore, thin films having N content above 15 eq.% show high hardness as compared to bulk glasses of similar composition in the Ca-Si-O-N system [54]. The observed hardness change for Ca-Si-O-N thin films with an increased N content is consistent with the structural model for bulk oxynitride glasses in which the introduction of nitrogen in the oxide glass network, case differences in bonding and anion coordination, produces a more compact linked network. Generally, the hardness of a silicate-based oxide glass is controlled by, the bond strength, atomic packing density, and the polymerization of the network tetrahedra [56-59]. The M⁺ and M²⁺ (M⁺ = alkali metals M²⁺ = alkaline earth metals) ions depolymerize the network by creating more non-bridging oxygen (NBO) species. Thus, the hardness generally diminishes when the alkali/alkaline-earth ion content increase in both oxide [60], and oxynitride bulk glasses [55]. The hardness of the amorphous materials is also strongly influenced by the type and concentration of the modifier element (i.e., here Ca). For the present films, the hardness decreases with increasing Ca content. The cation field strength *CFS*, given by their valences and ionic radii of the element (M), also effect on hardness values by increasing the strength of the M-O bonds in the glass network. Ca has a low *CFS* value (1.780 Å⁻²) as compared to Mg (3.858 Å⁻²). That is likely Mg-Si-O-N thin films [46] have higher hardness than the present Ca-Si-O-N containing thin films. The present results are in overall agreement with those of the previous studies in bulk Ca-Si-O-N system, that the hardness of glasses is increasing with N content and decreasing with Ca content [54, 55, 61, 62].

The elastic moduli of a non-crystalline material depend on the inter-atomic forces and the packing density of the atoms. In the case of oxide and oxynitride glasses, high elastic moduli are often desirable, e.g., for the manufacturing of thin and light-weight windows for cars and buildings, portable computing devices such as mobile phones and tables, computer hard drives, and substrates for high-speed magnetic memory disks [58, 63]. The float glass surface coated with Ca-Si-O-N thin film has up to two times higher value of reduced elastic modulus (145 GPa) as compared to the parent float glass having value of approximately 62 GPa. The variation in reduced elastic moduli with Ca and N contents indicates an alteration of the film structure that take place with the variation of Ca and N contents over the compositional range. For all films in the Ca-Si-O-N system, an increase of the N content increases the cross-linking in the film network via three-coordinated nitrogen, resulting in an increase of hardness and reduced elastic modulus properties. An increase of the Ca content of these films likely induces weaker bonds and disrupts the network, resulting in a decrease in hardness and reduced elastic modulus. The present results agree with those of previous studies in the bulk oxynitride glasses in the Ca-Si-(Al)-O-N systems [55, 61, 62]. Thin films in Ca-Si-O-N system have higher elastic moduli as compared to bulk glasses in the Ca-Si-O-N system, of similar compositions. [55, 61] Furthermore, Ca-Si-O-N thin films show lower reduced elastic moduli as compared to the Mg-Si-O-N system [46].

The refractive indices (n_r) of Ca-Si-O-N thin films correlate with the elemental compositions, and are found to increase predominantly with the N content. Similar trend was also observed in bulk Ca-Si-O-N glasses [54]. Generally, refractive index increases with either electron density or polarizability of the elements. Low indices are found for glasses with only low atomic number ions, which have both few electrons and low polarizabilities for example, Bulk glasses in the M-Si-(Al)-O-N systems (M=Mg, Ca, Sr, Ba) show that the Mg containing glasses exhibits lower values of refractive index than the Ca, Sr and Ba [55, 64]. In contrast Ca-Si-O-N thin films have lower value of n_r than the Mg-Si-O-N thin films. All the measured samples in Ca-Si-O-N system have band gap values above 3.50 eV. Mainly the deposited films on float glass substrate are transparent in the visible region. Our future investigation will aim to study these thin films by UV-lithography.

5. Conclusions

We have reported the thin-film-forming region in the Ca-Si-O-N system. Several physical properties were compared with the bulk oxynitride glasses in the Ca-Si-(Al)-O-N systems and

thin films in Mg-Si-O-N system. As evidenced by XPS analysis, a large range of composition in the Ca-Si-O-N system can be achieved by RF magnetron co-sputtering from Ca and Si targets. High percentage of nitrogen in the as-deposited films was obtained for the films prepared with the Ca target power of 60 W in all three series. The composition of the thin film is mainly controlled by the Ca target power. Variation of the N₂ gas flow rate (10%, 20% and 30%) has only minor effects on the composition. The as-deposited films are amorphous and transparent in the visible region.

Thin films in Ca-Si-O-N system, with N content between 5 and 31 eq. %, coated onto float glass surfaces, show hardness values up to 12 GPa and reduced elastic modulus values up to 145 GPa, which are significantly higher than those for uncoated float glass having hardness 7 GPa and reduced elastic modulus 62 GPa. Both hardness and reduced elastic modulus increase linearly with the N content, and linearly decrease with Ca content. The increase in hardness and reduced elastic modulus with the N content implies that the incorporation of nitrogen into the thin films strengthens the network due to the presence of three-coordinated nitrogen. The decrease of mechanical properties with Ca content confirms that high cation modifier content induces a depolymerization and a fragmented network. The refractive indexes of the films have higher values up to 1.82 as compared to uncoated float glass having refractive index 1.50. The refractive indices are found to increase predominantly with the N content. In general, the addition of Ca to SiON thin films often reduces the hardness and refractive index, but for the compositions, Ca_{21.0}Si_{20.6}O_{51.1}N_{7.4}, Ca_{17.0}Si_{20.7}O_{50.8}N_{10.7} and Ca_{19.5}Si_{22.0}O_{45.4}N_{13.7}, higher values of reduced elastic modulus and refractive index are obtained as compared to SiON thin films. The method and compositions (prepared with Ca target power of 60 W) presented here could also be used for improving the surface properties of other materials e.g. metals, ceramics and polymers.

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Figure Captions:

Fig.1: thin films obtained in the Ca-Si-O-N system. The black circles show N10 series, the red rectangles show N20 series and the blue triangles show N30 series

Fig. 2a: SEM image of $\text{Ca}_{17.0}\text{Si}_{20.7}\text{O}_{50.8}\text{N}_{10.7}$ film

Fig. 2b: 3-D AFM image of $\text{Ca}_{17.0}\text{Si}_{20.7}\text{O}_{50.8}\text{N}_{10.7}$ film

Fig. 3: Deposition of $\text{Ca}_{17.0}\text{Si}_{20.7}\text{O}_{50.8}\text{N}_{10.7}$ film on silicon wafer, float glass and sapphire substrates, prepared with Ca target power 60 W and N_2 flow of 20%

Fig. 4a: Ca content as a function of Ca target power for Ca-Si-O-N films

Fig. 4b: N content as a function of Ca target power for Ca-Si-O-N films

Fig. 5a: Variation of hardness vs N content for Ca-Si-O-N films

Fig. 5b: Variation of hardness vs Ca content for Ca-Si-O-N films

Fig. 6a: Variation of reduced elastic modulus vs N content for Ca-Si-O-N films

Fig. 6b: Variation of reduced elastic modulus vs Ca content for Ca-Si-O-N films

Fig. 7a: Variation of refractive index as a function of wavelength for Ca-Si-O-N films

Fig. 7b: Variation of extinction coefficient as a function of wavelength for Ca-Si-O-N films

Fig.1:

Fig.2a:

Fig.2b:

Fig. 3:

Fig. 4a:

Fig. 4b:

Fig. 5a:

Fig. 5b: *Fig. 6a:*

Fig. 6b:

Fig. 7a:

Fig. 7b:

Table I. Film designation, Determined films composition (atomic %), Ca target power, Nitrogen gas flow (N_2), Ca/Si and O/N ratio, Ca and N equivalent % (eq. %).

ID	Thin film composition (atomic %)	Ca target power (W)	N_2 flow (%)	Ca/Si ratio	O/N ratio	Ca (eq. %)	N (eq. %)
Series-N10, Ar=35.4 sccm, N_2 =4 sccm, O_2 =0.6 sccm							
C06-1	$Ca_{21.0}Si_{20.6}O_{51.1}N_{7.4}$	60	10	1.0	6.9	33.8	17.8
C10-1	$Ca_{25.5}Si_{11.0}O_{61.3}N_{2.4}$	100	10	2.3	25.5	53.7	5.5
C14-1	$Ca_{26.0}Si_{10.0}O_{63.4}N_{1.9}$	140	10	2.6	33.4	56.5	4.3
Series-N20 Ar=31.4 sccm, N_2 =8 sccm, O_2 =0.6 sccm							
C04-2	$Ca_{3.4}Si_{33.4}O_{63.1}N_{0.1}$	40	20	0.1	63.1	04.9	0.2
C06-2	$Ca_{17.0}Si_{20.7}O_{50.8}N_{10.7}$	60	20	0.8	04.7	29.1	24.1
C08-2	$Ca_{30.4}Si_{13.4}O_{53.9}N_{2.2}$	80	20	2.3	24.5	53.1	5.8
C10-2	$Ca_{23.8}Si_{9.1}O_{63.5}N_{2.7}$	100	20	2.6	23.5	56.7	6.0
C12-2	$Ca_{24.4}Si_{10.4}O_{61.6}N_{2.6}$	120	20	2.3	23.7	54.0	5.9
C14-2	$Ca_{27.5}Si_{9.6}O_{60.3}N_{2.6}$	140	20	2.9	23.2	58.9	6.1
Series-N30 Ar=27.4 sccm, N_2 =12 sccm, O_2 =0.6 sccm							
C06-3	$Ca_{19.5}Si_{22.0}O_{45.4}N_{13.7}$	60	30	0.9	03.3	30.8	31.1
C10-3	$Ca_{25.1}Si_{11.1}O_{60.4}N_{3.4}$	100	30	2.3	17.8	53.0	7.8
C14-3	$Ca_{28.3}Si_{9.7}O_{60.1}N_{2.0}$	120	30	2.9	30.1	59.3	4.8

Table II. Film designation, Mean squared error (MSE), Roughness, Thickness, UV pole amp, UV pole en, IR pole amp, A, Br, E₀, E_g (E), Intermix thickness, n of substrate float glass (FG) and Einf.

ID	C06-1	C06-2	Ca10-2	Ca14-2	Ca60-3	Ca14-3
MSE	2.443	2.719	7.795	5.927	4.312	4.180
Roughness (nm)	7.94	11.84	3.13	3.13	8.62	2.33
Thickness # 1 (nm)	970.61	709.86	2149.73	2939.15	585.61	2601.54
UV Pole Amp. (eV ²)	432.856	415.179	353.335	242.554	391.550	264.369
UV Pole En. (eV)	12.338	11.798	14.176	14.905	11.699	15.000
IR Pole Amp. (eV ²)	0.0180	0.0119	0.008368	0.008735	0.0142	0.0364
A (eV)	12.4534	7.2828	9.2351	15.3196	8.8872	14.1537
C (eV)	1.343	0.916	15.015	1.856	1.065	0.468
E ₀ (eV)	6.151	5.913	10.145	8.233	5.901	7.428
E _g (eV)	4.341	3.816	4.155	4.618	4.505	4.847
Intermix Thickness (nm)	15.96	11.34	0.00	0.00	25.19	0.05
n of Substrate_FG at 632.8 nm	1.51100	1.51100	1.51100	1.51100	1.51100	1.51100
Einf			0.519			

Table III. Film designation, Hardness (H), Reduced elastic modulus (E_r), Refractive index (n_r) and Extinction coefficient (k) for films deposited on float glass.

ID	H (GPa)	E_r (GPa)	n_r at 633 nm	k at 233 nm
SiN	10.1	91	2.07	0.017
SiON	15.5	120	1.650	0.019
C06-1	10.3	130	1.67	0.033
C10-1*	3.7	62	-	-
C14-1*	3.1	59	-	-
C06-2	12.0	145	1.82	0.061
C10-2	3.2	63	1.58	0.012
C14-2	3.3	67	1.56	0.004
C06-3	11.0	133	1.73	0.034
C10-3*	2.9	58	-	-
C14-3	3.2	65	1.56	0.001
Experimental error	± 0.5	± 3		

*Were not possible to analyze by ellipsometry, might be due to high surface roughness.

Highlights:

1. Ca-Si-O-N thin films were deposited by reactive RF magnetron sputtering.
2. The thin films composition can be tuned by Ca target power.
3. Most of the Ca-Si-O-N films have atomic concentration $[Ca]/[Si] > 1$.
4. XRD and SEM indicate that films are amorphous with smooth surface morphology.
5. Hardness, reduced elastic modulus, and refractive index increases linearly with the N content.