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Characterization of fluorinated silica thin films with ultra-low refractive index deposited at low temperature

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ABSTRACT

Structural and optical properties of low refractive index fluorinated silica ($SiO_xC_yF_z$) films were investigated. The films were deposited on p-type silicon and polycarbonate substrates by radio frequency plasma enhanced chemical vapor deposition method at low temperatures. A mixture of tetraethoxysilane vapor, oxygen, and CF_4 was used for deposition of the films. The influence of oxygen flow rate on the elemental compositions, chemical bonding states and surface roughness of the films was studied using energy dispersive X-ray analyzer, Fourier transform infrared spectroscopy in reflectance mode and atomic force microscopy, respectively. Effects of chemical bonds of the film matrix on optical properties and chemical stability were discussed. Energy dispersive spectroscopy showed high fluorine content in the $SiO_xC_yF_z$ film matrix which is in the range of 7.6–11.3%. It was concluded that in fluorine content lower than a certain limit, chemical stability of the film enhances, while higher contents of fluorine heighten moisture absorption followed by increasing refractive index. All of the deposited films were highly transparent. Finally, it was found that the refractive index of the $SiO_xC_yF_z$ film was continuously decreased with the increase of the O_2 flow rate down to the minimum value of 1.16 ± 0.01 (at 632.8 nm) having the most ordered and nano-void structure and the least organic impurities. This sample also had the most chemical stability against moisture absorption.

1. Introduction

Electrical insulator thin films with low refractive index (low-n) and low absorption are needed for various optical devices, such as low loss waveguides, resonators, photonic crystals, distributed Bragg reflectors, light-emitting diodes, passive splitters, biosensors, attenuators and filters [1–3]. Additionally, in multi-junction solar cells, an intermediate layer with a low refractive index and high transmittance can enhance the reflection of light, which can reduce the thickness of the middle absorption layer [4,5]. Lower refractive index thin films also reduce the number of high and low index multi-layers and widen the bandwidth of multilayer high reflectors [6,7]. These materials have also demonstrated low dielectric constants (low-k) being suitable for interconnecting layers in microelectronics to reduce the signal propagation delay, parasitic capacitance, cross-talk noise and power dissipation [7–9]. There are quite a few optical materials with refractive indices lower than silicon dioxide among which, MgF_2 has the lowest refractive index: n = 1.38, and is widely used as antireflection coatings. However, the mechanical properties of MgF_2 are less advantageous than those of silicon dioxide, which surpasses MgF_2 in hardness and abrasion resistance [10].

There are a wide variety of methods to synthesize silica based films among which, plasma enhanced chemical vapor deposition technique (PECVD) using tetraethoxysilane (TEOS) produces high quality and low defect films. Moreover, it has many advantages such as good step coverage, superior conformability, high thermal stability, good adhesion to silicon substrates, low temperature and safe processing and also having the ability to precisely control the thickness, composition and the microstructure of the films [11]. Several approaches have been investigated to lower the refractive index of silica films such as introducing porosity and doping fluorine into their structures [8,12–15]. High amount of porosity in the silica films leads to weak mechanical properties and chemical stability and also absorbs the ambient moisture which gives rise to increase the refractive index and the dielectric constant [15–18].

Moreover, in optical and microelectronic applications, the films' surface quality is also very important, because high surface roughness leads to increase light scattering and increment in the dissipation factor, meanwhile the films with high porosity often have high surface roughness [8,10]. For instance, Cheng et al. investigated the growth of high porous SiOCH film deposited by PECVD method with lowest refractive index of 1.39 [17]. Xi et al. also reported the deposition of very high porous SiO_2 nanorod layer with low refractive index of n = 1.08, grown by

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oblique-angle electron-beam deposition of SiO_2 [2,19]. On the other hand, fluorine doped silica films have attracted a lot of interest due to their excellent transparency and thermal stability with standard processes [6,7]. In addition, these films are required to be smooth and also have high chemical stability, which are also the prerequisite for reliable optical and microelectronic applications. Lu et al. [20], Barankin et al. [14] and Yoon et al. [6] prepared the fluorine-doped silicon oxide films in a PECVD system using gas mixture of $SiH_4/N_2O/CF_4$, tetraethoxyfluorosilane/tetramethylcyclotetrasiloxane, and $SiH_4/N_2O/CF_4$, respectively. They reported the minimum refractive index of 1.416, 1.411 and 1.38 at maximum values of fluorine content of 2.9 at.%, 2.6 at.%, and 5.5 at.%, respectively. Furthermore, Yu et al. [21] reported the deposition of the fluorine-doped silicon oxide film by liquid phase deposition using H_2SiF_6 precursor with very low amount of fluorine compared to other components (Si, O, and C). Many investigators have reported the deposition of fluorine doped silica films at high temperatures (from 300 °C to 500 °C). Films deposited at high temperatures have several problems, such as thermal stress, material interaction, and substrate warpage, resulting in film cracking and peeling issues [3,22,23].

In our previous work [8], it was shown that the refractive index and dielectric constant of silica films are highly influenced by the polarizability of chemical bonds in the silica film structure and are drastically decreased by incorporation of fluorine into the film matrix. In the present study, we investigate the structural and optical properties of fluorinated silica film deposited by low temperature PECVD. Effect of oxygen flow rate in the plasma gas mixture on the chemical bonding states, composition, structure and refractive index as well as optical absorption of the deposited films are investigated. Moreover, to ensure the silica film's performance and reliability in the optical applications their moisture absorptions and chemical stability are also studied.

2. Experimental details

The deposition of fluorinated silica films was performed in a PECVD system operating with radio frequency of 13.56 MHz in a parallel plate capacitively coupled configuration. Thin films were deposited on boron doped (p-type) silicon and polycarbonate (PC) substrates. Prior to the deposition, the substrates were ultrasonically cleaned in deionized water and ethanol bath for 15 min in sequence. Then, they were placed on the water cooled powered electrode without any external heating source.

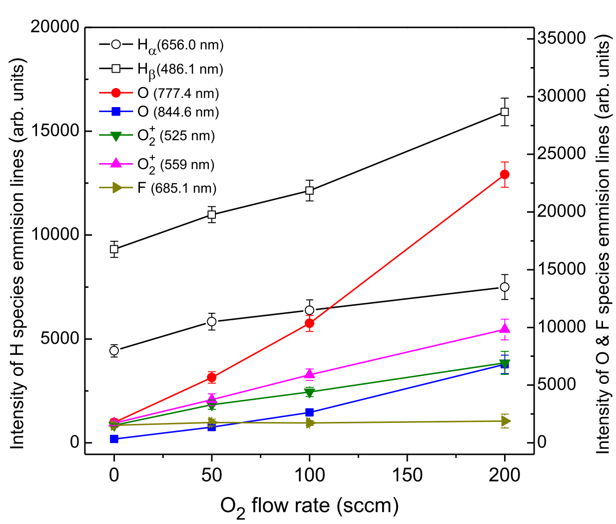

Fig. 1. Variation of emission line intensity of TEOS-O_2-CF_4 plasma as a function of O_2 flow.

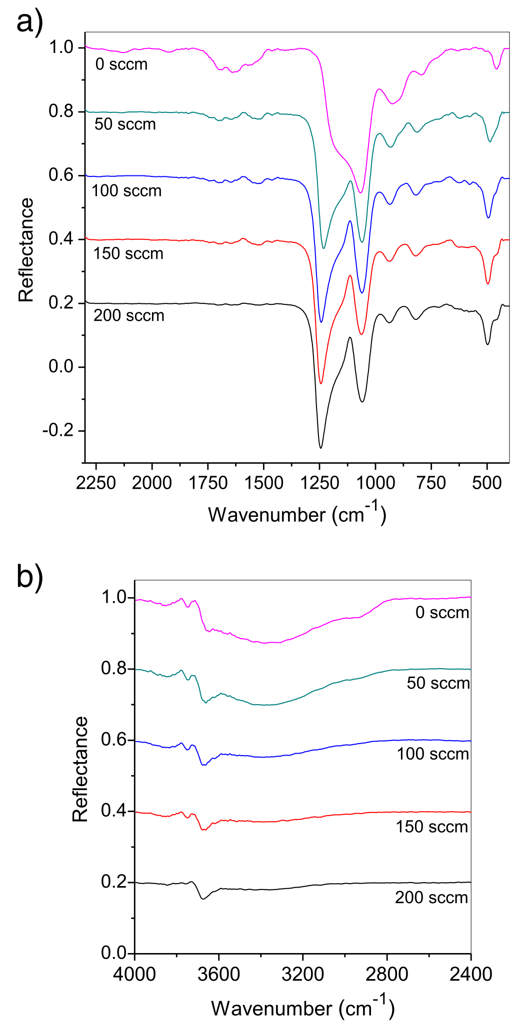

Fig. 2. FTIR spectra of the fluorinated silica films deposited in different O_2 flow rates which were taken right after the deposition in the range of (a) 400–2300 cm^{-1} and (b) 2400–4000 cm^{-1}.

In the deposition process, TEOS (Merck-99%) vapor was used as silicon precursor and was mixed with oxygen and CF_4. The oxygen flow rate was varied from 0 sccm to 200 sccm, while the working pressure, radio frequency power, TEOS and CF_4 flow rate were kept constant at 8.0 Pa, 150 W, 10 sccm and 150 sccm, respectively, throughout the

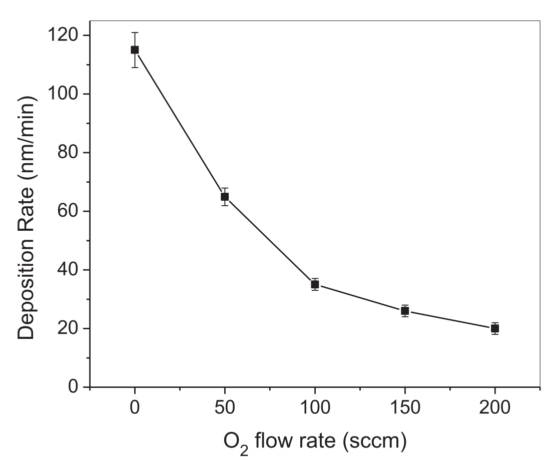

Fig. 3. Deposition rate of the $SiO_xC_yF_z$ films as a function of O_2 flow rate.