Low refraction properties of F-doped SiOC:H thin films prepared by PECVD

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Abstract

Low refractive index materials which F-doped SiOC:H films were deposited on Si wafer and glass substrate by low temperature plasma enhanced chemical vapor deposition (PECVD) method as a function of rf powers, substrate temperatures, gas flow ratios (SiH₄, CF₄ and N₂O). The refractive index of the F-doped SiOC:H film continuously decreased with increasing deposition temperature and rf power. As the N₂O gas flow rate decreases, the refractive index of the deposited films decreased down to 1.378, reaching a minimum value at an rf power of 180 W and 100 °C without flowing N₂O gas. The fluorine content of F-doped SiOC:H film increased from 1.9 at.% to 2.4 at.% as the rf power was increased from 60 W to 180 W, which is consistent with the decreasing trend of refractive index. The rms (root-mean-square) surface roughness significantly decreased to 0.6 nm with the optimized process condition without flowing N₂O gas.

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1. Introduction

F-doped SiOC:H film having low refractive index and dielectric constant has attracted a lot of interests for the applications of antireflection coatings and ultra-large scale integrated (ULSI) devices due to its excellent transparency, and chemical and thermal stability with standard microelectronic fabrication processes [1]. Low refractive index materials can decrease the number of the optical coating layer and increase the emission efficiency by matching the refractive indices between ambient air and emitting layer of the optical device. Antireflection coatings for the visible and near infrared regions play an important role in the development of flat panel displays (FPDs) and solar cell systems, in which efficient optical properties, such as low reflection loss, wider bandwidth, high transmission efficiency, and high durability against adverse terrestrial and space conditions are required [2,3]. Therefore, the substrate has to have a refractive index which is sufficiently higher than that of the available thin film material for it to be possible to design high performance antireflection coatings consisting entirely, or almost entirely, of layers having lower refractive indices than that of the substrate. Color displays based on organic light emitting devices (OLED) deposited on flexible substrates are being developed as a promising alternative to liquid crystal displays (LCD). The substrate for flexible OLED is a multilayer composite structure having a couple of functional coatings on a polymer-based substrate. For the fabrication of light emitting diodes (LEDs) and organic LEDs, semiconducting materials, such as Ge and Si are commonly used as substrates. Typically, germanium having a refractive index of 3.9 gives a reflection loss of around 36% and silicon having a refractive index of 3.5 gives a reflection loss of 31% [4,5]. Among many possible deposition techniques in obtaining refractive index materials, plasma enhanced chemical vapor deposition (PECVD) is considered to be an outstanding method because it provides an easy controllability of the film stoichiometry and refractive index, and excellent surface roughness [6–10].

In this study, the deposition characteristics of F-doped SiOC:H films grown by PECVD were investigated as a function of process parameters, such as flow ratio of mixing gases, rf power, and the adding amount of N₂O gas. In addition, the relationship between the fluorine contents in the F-doped SiOC:H thin film and the refractive indices in the visible range (632.8 nm) was discussed.

2. Experimental procedure

F:SiOC:H films were deposited by PECVD technique [11] using appropriate gaseous mixtures of silane (H₂ 90% dilution,
SiH₄), nitrous oxide (99.999% N₂O) and tetrafluoromethane (99.999% CF₄). The reactor is a parallel planar discharge type having a rectangular rf (13.56 MHz) electrode (lower). The upper electrode supporting the substrate is connected to a 13.56 MHz rf bias power supply. The substrate is placed on a tray with the surface to be coated facing downward, so that the possible depositions of dust particles and flakes can be minimized. Si and glass were used as substrates and, prior to the F:SiOC:H film deposition, a short in-situ pre-cleaning and plasma pre-treatment of the substrate was performed in order to improve the adhesion of the film to the substrate using H₂ discharge at an rf power of 60 W. Because the refractive index of thin film strongly depends on the deposition conditions, the influence of the main deposition parameters, such as mixing gas flow ratio, rf power, and N₂O/(SiH₄ + CF₄) ratio, on the qualities of F-doped SiOC:H thin films was systematically studied. The pressure for all the deposition conditions was held at a constant value of 1.3 × 10² Pa throughout the experiment. After the deposition of F-doped SiOC:H films under various process conditions, the refractive index was measured using a prism coupler operating at a wavelength of 632.8 nm. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were used to characterize the chemical binding state and the surface morphology of the films, respectively.

3. Results and discussion

F-doped SiOC:H films were deposited by low temperature PECVD using an SiH₄, CF₄ and N₂O gas mixture on glass substrates pre-treated with H₂ plasma. Fig. 1 shows the variation of the refractive indices of F-doped SiOC:H films as a function of rf power and deposition temperature. With the increase of deposition temperature from 100 °C to 300 °C, the refractive indices of all the samples increased. The lowest refractive index of F-doped SiOC:H film (1.385) was obtained at the deposition temperature of 100 °C and the rf power of 180 W. The variations of refractive indices with different rf power levels exhibited a similar trend with different deposition temperatures. For all of
the different rf power levels, the increasing rates of the refractive indices were approximately 0.03/°C at deposition temperatures between 100 °C and 300 °C, and the refractive indices continuously decreased with the increase of rf power. At the deposition temperature of 100 °C, the initial refractive index of the F-doped SiOC:H film was 1.424 and decreased down to the lowest value, 1.385 with the increase of an rf power from 60 W to 180 W. Because it is well known that F atoms incorporated in SiOC:H films reduce the refractive index, it is believed that the increase of rf power density dissociates CF4 molecules more effectively during the deposition and, subsequently, decreases the resulting refractive index values.

Fig. 2 shows the refractive indices of F-doped SiOC:H films as a function of rf power and CF4 gas flow ratio. With the increase of rf power from 60 W to 180 W, the refractive index of deposited film continuously decreased down to 1.398. When the CF4 gas flow ratio was 10 sccm, the refractive index of as-deposited film further decreased down to 1.378, reaching a minimum value at an rf power of 180 W without N2O gas. With the constant rf power and deposition temperature, the refractive index of continuously increased with the addition of N2O gas. According to the relative chemical composition of F-doped SiOC:H film as a function of N2O/(SiH4 + CF4) gas flow ratio as shown in Fig. 4, the concentrations of incorporated F atoms were continuously decreased due to reduction of the partial pressure of CF4 and the densification effect of N2O gas and decreased to concentration of oxygen in the deposited films which are believed to be the main reasons for the variation of the measured refractive index.

The XPS spectra of F-doped SiOC:H films with various rf powers at a constant deposition temperature (100 °C) and K=0 are shown in Fig. 5(A) and (B). As the rf power increases from 60 W to 180 W, the peak intensities of C 1s and F 1s signal were increased. But, that of Si 2p signal was decreased. The fluorine content of the as-deposited film was 5.5 at.% when it was deposited at 180 W and K=0. Fluorine incorporation leads to a less dense, more porous film by creating voids in the SiO2 matrix. And incorporation of Si–F of SiOF in place Si–O bonds reduces ionic character of remaining Si–O bonds and thus ionic contribution to the dielectric constant and refractive index. As shown in Fig. 5(B), the binding energy of the as-deposited film did not vary when the rf power was increased, however the peak intensity of the F 1s signal was increased. As a result, the higher rf power incorporates with fluorine contents of as-deposited film and refractive indices were decreased.

Surface roughness of optical coating layer is an important cause of optical scattering and plays an important role in reducing the optical loss at the surface of FPDs. Fig. 6 shows the AFM images of the F-doped SiOC:H films at a variety of rf powers. The rms surface roughness of the deposited film at an rf power of 60 W was 5.3 nm, which represents poor surface roughness. As the rf power was increased, the rms roughness decreased to 1.0 nm, with the optimum conditions being observed for the film deposited at an rf power of 140 W.

4. Conclusion

F-doped SiOC:H films were synthesized on Si wafer and glass substrate by low temperature PECVD, and systematically characterized with various deposition parameters. The lowest refractive index of F-doped SiOC:H film (1.385) was obtained
at the deposition temperature of 100 °C and the rf power of 180 W. The refractive index of as-grown film decreased with the increase of CF₄ gas flow and saturated after 30 sccm. As the deposition temperature decreases and the rf power increases, the refractive indices of the F-doped films decreased down to 1.378. Addition of N₂O gas resulted in a detrimental effect on the refractive index due to the reduction of F incorporation in the deposited films according to XPS measurements. The maximum fluorine content of the deposited F-doped SiOC:H was 5.5 at.% when it was deposited at 180 W. The higher rf power incorporates with fluorine contents of as-deposited film and refractive indices were decreased. As the rf power was increased, the rms roughness decreased to 1.0 nm, with the optimum conditions being observed for the film deposited at an rf power of 140 W.

**References**