# Characterization of low refractive index SiOCF:H films designed to enhance the efficiency of light emission

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**Abstract** An anti-reflection (AR) coating was deposited on the surface of flat panel displays to increase the efficiency of the light emission. The use of low reflective index material can decrease the thickness of the optical coating layer. In this work, low refractive index SiOCF:H films were deposited on $P$-type (100) Si and glass substrates by the plasma enhanced chemical vapor deposition (PECVD) method using an $SiH_4$, $CF_4$ and $N_2O$ gas mixture. The refractive index of the SiOCF:H film continuously decreased with increasing deposition temperature and rf power, exhibiting a minimum value of 1.3854. As the rf power was increased, the fluorine content of the film increased linearly to 5.41% at an rf power of 180 W. The rms surface roughness decreased to 1.0 nm with increasing rf power, with the optimum conditions being observed for the film deposited at an rf power of 140 W.

**Keywords** SiOCF:H · Low refractive index · PECVD · Anti-reflection (AR) coating · OLED

## 1 Introduction

With their low refractive index and dielectric constant, SiOCF:H films have attracted a great deal of interest for applications involving antireflection coatings and ultra-large scale integrated (ULSI) devices, due to their excellent transparency, and chemical and thermal stability with standard microelectronic processes [1]. Low refractive index materials can decrease the thickness of the optical coating layer. Fluorine incorporation leads to a less dense, more porous film by creating voids in the $SiO_2$ matrix. The combination of voids and $SiO_2$ dielectric properties determines the refractive index of the resulting thin film, which is less than that of dense $SiO_2$ films. Antireflection coatings in the visible and near infrared regions play an important role in the development of flat panel displays (FPDs) and solar cell systems, in which the coatings are required to have efficient optical properties, such as low reflection loss, wider bandwidth and a high efficiency of transmission, in addition to high durability against adverse terrestrial and space conditions [2, 3]. The substrate has to have a refractive index which is sufficiently higher than that of the available thin film materials for it to be possible to design high performance antireflection coatings consisting entirely, or almost entirely, of layers with refractive indices lower than that of the substrate. Semiconductors, light emitting diodes (LEDs) and OLEDs, fabricated using materials such as germanium, with a refractive index of around 4.0, giving a reflection loss of around 36% per surface, and silicon, with a refractive index around 3.5 and a reflection loss of 31%, are commonly used [4, 5]. To increase the efficiency of the light emission, an antireflection coating is required in order to match the optical element with the surrounding air. PECVD technology is considered to be a suitable method for the fabrication of low refractive index materials, because it provides for easy controllability of the film stoichiometry and refractive index, and excellent surface roughness [6–10].

In this study, the variation in the quality of SiOCF:H films was examined as a function of the deposition temperature and rf power. In addition, we discuss the relationships between the

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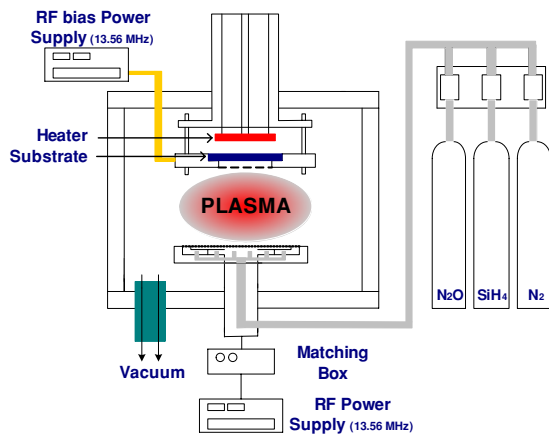
Fig. 1 A schematic diagram of the RF PECVD equipment



Fig. 2 The refractive index of the SiOCF:H films as a function of the rf power and deposition temperature

fluorine contents in the SiOCF:H thin film and the refractive index in the visible range.

## 2 Experimental procedure

F:SiOC:H films were deposited by the PECVD technique using appropriate gaseous mixtures of silane ($H_2$ 90% dilution, $SiH_4$), nitrous oxide (99.999% $N_2O$), methane (99.999% $CH_4$) and tetrafluoromethane (99.999% $CF_4$). A schematic diagram of the rf PECVD equipment used in this experiment is shown in Fig. 1. The reactor is of the parallel planar discharge type, using 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. *P*-type Si wafers with a (100) orientation were used as the substrates. Before the deposition, a short *in-situ* pre-cleaning of the wafers was performed in order to improve the adhesion of the film to the substrate, using $H_2$ discharge at an rf power of 60 W. Because the refractive indices of thin films strongly depend on the deposition conditions, the influence of the main deposition parameters on the qualities of these films was systematically studied as a function of the deposition temperature (100–400°C) for the S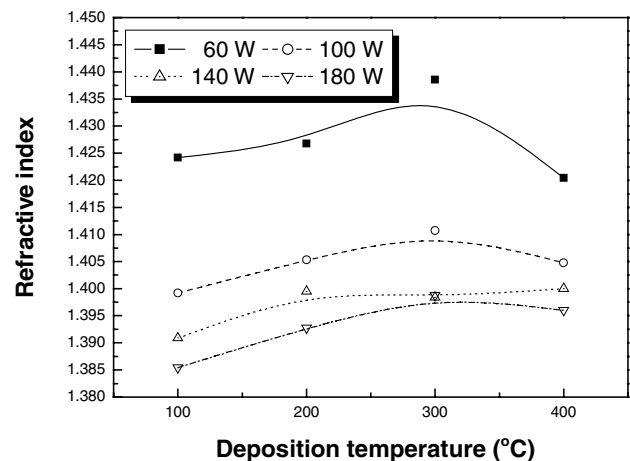iOCF:H thin films. The pressure for all the deposition conditions was held at a constant value of 1.0 Torr. In this study, we mainly focused on investigating the influence of rf power and substrate temperature during the deposition of the SiOCF:H films based on the process conditions given in Table 1.

The refractive index was measured using a prism coupler operating at a wavelength of 632.8 nm. Fourier Transform Infrared Spectrometry (FT-IR) and X-ray photoelectron spectroscopy (XPS) were used to characterize the chemical binding state and atomic force microscopy (AFM) was used to characterize the surface morphology of the SiOCF:H films.

## 3 Results and discussion

Figure 2 shows the variations in the refractive indexes of the SiOCF:H films as a function of the rf power and deposition temperature. The refractive index was measured at a wavelength of 632.8 nm using a prism coupler. The refractive indices of all of the samples at first increased as the deposition temperature was increased from 100°C to 300°C, and then decreased as the temperature was increased further. As the deposition temperature decreased, the refractive indices of the SiOCF:H films decreased down to 1.3854, reaching a minimum value at an rf power of 180 W. Similar results

**Table 1** The process conditions and XPS data used for the deposition of the SiOCF:H films

| Sample | Gas flow ratio (sccm) | rf power (W) | Chemical composition (%) | | | | Deposition Temp. (°C) |
| | | | F | O | C | Si | |
|---|---|---|---|---|---|---|---|
| SiOCF:H | $SiH_4 = 20$ | 60 | 2.87 | 59.43 | 15.67 | 21.74 | 100–400 |
| | $N_2O = 100$ | 100 | 3.22 | 58.24 | 17.54 | 21.00 | |
| | $CF_4 = 30$ | 140 | 4.32 | 57.67 | 15.32 | 22.69 | |
| | | 180 | 5.41 | 58.45 | 16.31 | 25.53 | |
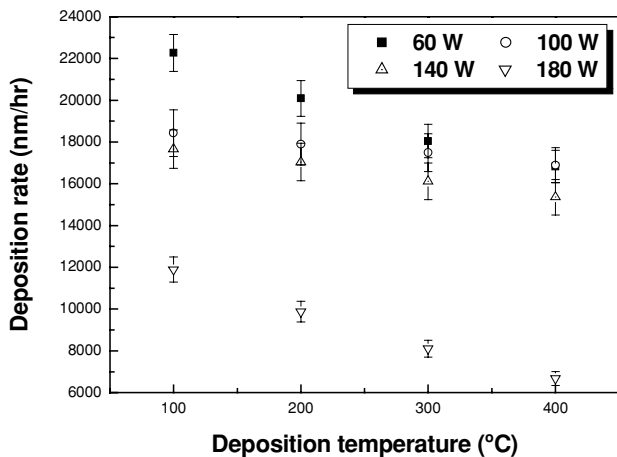
**Fig. 3** The deposition rate of the SiOCF:H films as a function of the rf power and deposition temperature



**Fig. 4** C 1s XPS spectra for the SiOCF:H film deposited at an rf power of 180 W and a temperature of 100°C

were observed for the other samples using different rf power levels, in that the refractive index was reduced at low deposition temperature. The rates of increase of the refractive indices were approximately 0.03/°C for all of the samples at deposition temperatures between 100°C and 300°C. The refractive indices of the SiOCF:H films of all of the samples decreased with increasing rf power. The initial refractive index of the SiOCF:H film was 1.4242 for the film deposited at 100°C. As the rf power was increased, the refractive indices of the films decreased continuously to a final value of 1.3854. It is well known that silane and carbon radicals react preferentially with fluorine radicals rather than with oxygen radicals, because the electronegativity of fluorine is greater than those of other gases. Therefore, Si-F, C-F and C-C-F bonds are formed in the solid phase only when all of the tetrafluoromethane radicals have been consumed in the reaction.

Figure 3 shows the deposition rate of the SiOCF:H film as a function of the deposition temperature and rf power. The deposition rate decreased as the deposition temperature and rf power increased. This behavior is contrary to the thermally activated process which usually occurs during the formation of thin films. The apparently high deposition rate at low temperature may be associated with the presence of voids within the films, due to the creation of Si-CH, C-F, and Si-C-H bonds [11].

Figure 4 shows the C 1s XPS spectra of SiOCF:H film deposited at 100°C with an rf power of 180 W. The C 1s spectrum of this film was fitted into two peaks using a Gaussian distribution function. The peaks at about 288.0 and 288.8eV can be attributed to C–CF and C–F [12] bonds, which account for about 42.15 at% and 47.85 at%, respectively. The change in the chemical composition of the deposited films was calculated as a function of the rf power using measured XPS spectra and shown in Table 1. The fluorine content
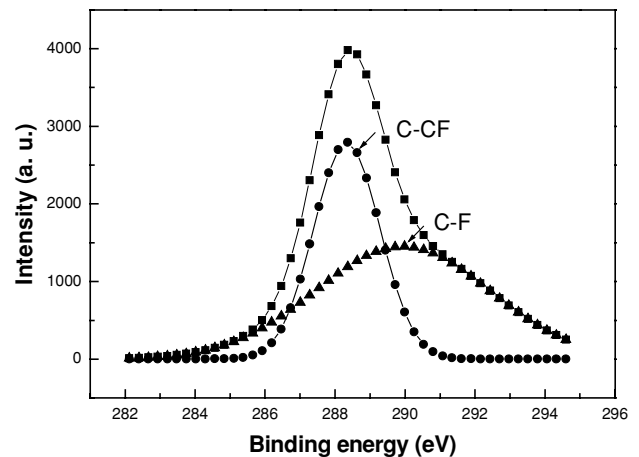


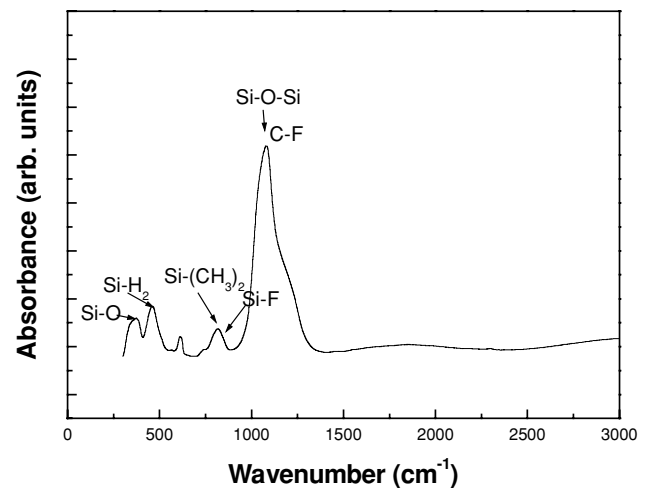**Fig. 5** The variations in the FTIR absorption spectra over the range of 400–4000 cm$^{-1}$ for the SiOCF:H film deposited at an rf power of 140 W and a temperature of 300°C

of the deposited SiOCF:H film was 2.87% when it was deposited at 60 W and 100°C. As the rf power was increased, the fluorine content of the film increased linearly to 5.41 % at 180 W. It is known that the use of high rf power may increase the amount of C-C-F, C-F and F-Si-F bonds, thereby increasing the fluorine content. These results were used to plot the graphs shown in Fig. 2.

Figure 5 shows the variation in the FTIR absorption spectra over the wavelength range of 400–4000 cm$^{-1}$ for the SiOCF:H film deposited at 300°C with an rf power of 140 W. The intense absorption peak at about 1062 cm$^{-1}$ results from the asymmetric stretching of the oxygen atoms along the direction parallel to the Si–O–Si bonds, the peak at about 809 cm$^{-1}$ corresponds to symmetric Si–O–Si stretching, while the peak at about 938 cm$^{-1}$ is due to the Si–F vibration [12]. The absorption band of CH$_3$ in Si-(CH$_3$)$_2$ is also observed among the bands centered at about 840

**Fig. 6** AFM images of the SiOCF:H films at a variety of rf powers



60 W

100 W

140 W

180 W
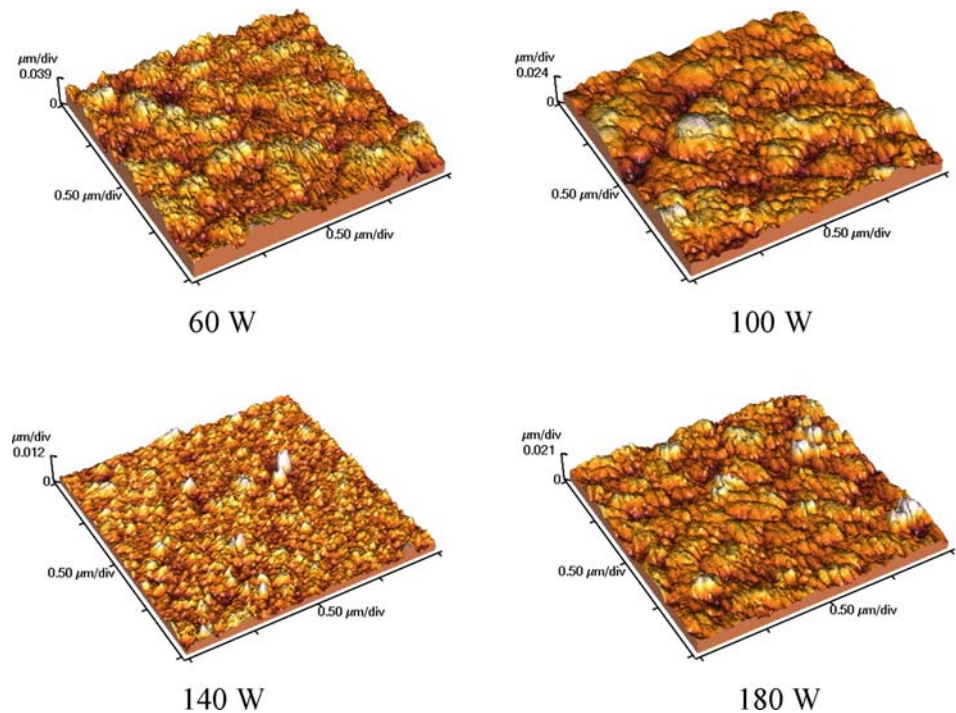
cm$^{-1}$ [13]. The C–F vibration is located in the range 1000–1400 cm$^{-1}$, while the absorption band between 1000 and 1300 cm$^{-1}$ can be attributed to the superposition between the Si–O and C–F vibrations. Because O and H radicals exist in the plasma, Si–OH bonds can be formed in the deposited films [14].

Surface roughness is an important cause of optical scattering and plays an important role in reducing the optical loss at the surface. Figure 6 shows the AFM images of the SiOCF: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 deposition temperature was increased, the rms roughness decreased to 1.0nm, with the optimum conditions being observed for the film deposited at an rf power of 140 W.

## 4 Conclusion

SiOCF:H films were synthesized by plasma enhanced chemical vapor deposition (PECVD). These films had excellent characteristics which allowed a low temperature deposition and the amount of light emitted by OLED and solar cells to be increased because the refractive index was lower. As the deposition temperature decreased, the refractive indices of the SiOCF:H films decreased down to 1.3854, reaching a minimum value at an rf power of 180 W. The rate of increase of the refractive indices was approximately 0.03/°C for all of the samples at deposition temperatures of between 100°C and 300°C. As the rf power was increased, the refractive indices of the films continuously decreased, reaching

a value of 1.3854 at an rf power of 180 W. The fluorine content of the deposited SiOCF:H film was 2.87% when it was deposited at an rf power of 60 W and a temperature of 100°C. As the rf power was increased, the fluorine content of the film increased linearly up to 5.41% at an rf power of 180 W. The rms surface roughness decreased to 1.0 nm with the optimum condition being observed for the film deposited at an rf power of 140 W.

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