

# Effect of Ultraviolet Irradiation on the Defect States and the Charge Transport Properties of Low- $k$ SiOC(-H) Dielectric Films Deposited by Using UV-assisted PECVD

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Low- $k$  SiOC(-H) films with different structural orders were fabricated by using UV-assisted PECVD, and the influence of the replacement of Si-O bonds by (Si-C) bonds on the structural and the electro-physical properties was investigated. FT-IR spectrum shows that the SiOC(-H) films deposited at a RF power of 400 W have a cross-linking structure with nano-pores due to the combined Si-CH<sub>n</sub>-Si bond and Si-O-Si network, and their relative ratio changed with increasing RF power. From current transients, as well as the  $C$ - $V$  characteristics, we estimated the trap and the positive charge densities in the low- $k$  films. They were found to be on the order of  $10^{16}$  traps/cm<sup>3</sup> and  $10^{11}$  cm<sup>-2</sup>eV<sup>-1</sup>, having a tendency to increase with increasing UV irradiation. We also found that the barrier heights for electrons at the interfaces of low- $k$  insulators with metals were almost insensitive to the metal's Fermi energy, suggesting that the current injection was determined by some localized state in the insulator gap. The results were substantiated and directly correlated with the changes in transport properties and with the bond structure characteristics of SiOC(-H) films.

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## I. INTRODUCTION

The hybrid type SiOC(-H) films formed from organic and inorganic materials are very promising as low- $k$  materials because the spatial hindrance of the alkyl groups may produce abundant nano-pores in the film and decrease the dielectric constant. One of promising methods of low- $k$  SiOC(-H) film deposition is plasma enhanced chemical vapor deposition (PECVD) using organosilane molecules as source materials. The precursor and oxygen can be dissociated by the plasma and converted into the radicals, such as Si, O, C, and CH<sub>n</sub> that form the film on the substrate [1,2]. The intrinsic properties of carbon-doped barrier films (SiCN and SiCO) have been extensively investigated by many researchers [3,4]. Recently, the concept of ultraviolet (UV)-assisted plasma processing with a high-density plasma and low electron

temperature at low pressure has received much attention. The concept was to control the dielectric constant and the SiOC(-H) films structure dependently, as shown in Refs. 5 - 7. Although much work has been reported regarding the structural change, the dielectric constant and the reaction mechanism of SiOC(-H) films deposited by using UV source-assisted PECVD, no work has been reported regarding electron trap states and the conduction mechanism within these low- $k$  dielectric films. It is well known that the structural change often produces defect states embedded within the dielectrics, which can lead to dielectric damage. Electron trap states within low- $k$  dielectric films play a significant role in electrical leakage and time-dependent dielectric breakdown in these materials. Thus, the properties of the trap states are closely related to the overall reliability of low- $k$  dielectrics, a central problem for many industrial applications of these insulating films [8].

The trapped charges due to the structural changes

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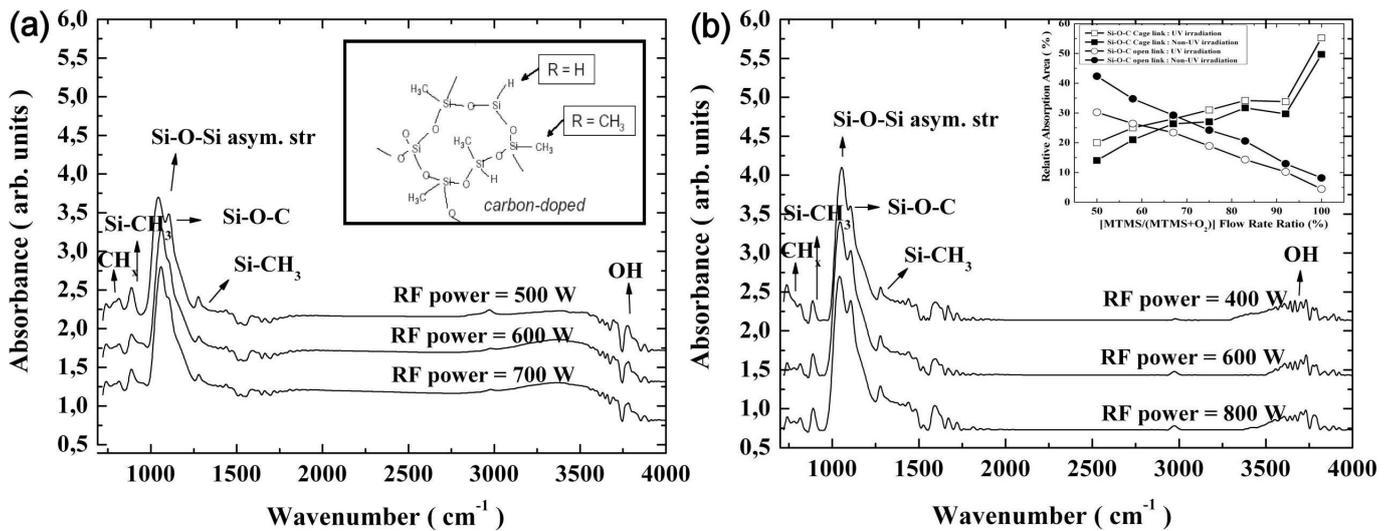


Fig. 1. FTIR spectra of as-deposited SiOC(-H) films (a) without UV and (b) with UV irradiation for different RF powers from 400 to 800 W. Inset: (a) possible structure of the SiOC(-H) films, and (b) relative absorption area of the components of the Si-O-C bond: open, and cage linked modes.

within the dielectric can be ideally monitored by examining the  $C$ - $V$  characteristics. This technique has been extensively used for high-purity  $\text{SiO}_2$  films, as well as for other insulating and semiconducting films [9]. Studies of the  $C$ - $V$  characteristics have also recently been reported on low- $k$  dielectric systems by Sinha *et al.* [10]. Those authors found that vacuum UV irradiation depopulate defect states whereas UV irradiation repopulated these defect states within a carbon-doped oxide system.

In the present investigation, we apply  $C$ - $V$  characteristic measurements to examine several important properties of low- $k$  SiOC(-H) films with different structural orders, which were fabricated by using an UV-assisted PECVD approach. As a complementary method of examining the role of the trapped charge, we also present measurements of the current-voltage ( $I$ - $V$ ) and the bond structure characteristics of SiOC(-H) films. Significant alterations of the  $I$ - $V$  and the  $C$ - $V$  curves with respect to the deposition conditions of the SiOCH films demonstrate that the variations in the properties of the SiOC(-H) material studied are the main reasons for the observed changes.

## II. EXPERIMENT AND DISCUSSION

SiOC(-H) composite films were deposited on p-type Si(100) wafers by using a mixture of methyltrimethoxysilane (MTMS) and oxygen gases with UV-source-assisted PECVD. The films were deposited at room temperature. The plasma was generated using a radio frequency (RF) power supply with a frequency of 13.56 MHz at power from 400 to 800 W. The flow rate ratio,  $R$  (%) =  $[\text{MTMS}/(\text{MTMS} + \text{O}_2)] \times 100$ , was kept at a constant 80%, and the total gas flow rate was 50 sccm. An UV

light source (Hg lamp;  $225 \text{ nm} < \lambda < 500 \text{ nm}$ , illumination density =  $0.6 \text{ mW}/\text{cm}^2$ ) with a wavelength peak near 265 nm and a power consumption of 400 W was installed to illuminate the plasma in the reaction chamber. To investigate the chemical bonding structure of SiOC(-H) composite films, we used Fourier transform infrared (FTIR) spectroscopy (Bruker, IFS-120HR/FRA-106S) in the absorbance mode. The film's thickness was measured using a field emission scanning electron microscope (FESEM: JSM-6700F). The  $C$ - $V$  characteristics at 1 MHz were investigated with a metal/insulator/semiconductor (Al/SiOC film/p-Si) structure by using a semiconductor parameter analyzer (HP4280A). An HP4155B semiconductor parameter analyzer was used to measure the  $I$ - $V$  behavior. Al, Cu, and CuTaN electrodes were deposited on the top and Al on the back sides of the SiOC(-H)/p-Si structures.

### 1. Structural Characterization

Figures 1(a) and 1(b) shows the typical FTIR spectra of as-deposited SiOC(-H) films with and without UV irradiation for different RF powers from 400 to 800 W, respectively. There were Si-CH<sub>3</sub> (889 and 1276  $\text{cm}^{-1}$ ), Si-O-Si(C) (1000 - 1250  $\text{cm}^{-1}$ ), CH<sub>*n*</sub> ( $n = 1, 2, 3$ ) (740 and 2970  $\text{cm}^{-1}$ ) and OH-related bonds in the film [11]. As the RF power was increased, the intensity of the Si-CH<sub>3</sub> band decreased, demonstrating that more C atoms were incorporated in the Si-O-Si network. When compared with the relative intensities of the related bonding modes, the peak intensities of the Si-O-C asymmetric stretching and the Si-CH<sub>3</sub> group of the SiOC(-H) films were greater with UV irradiation than without UV irradiation. This result indicates that the SiOC(-H) film

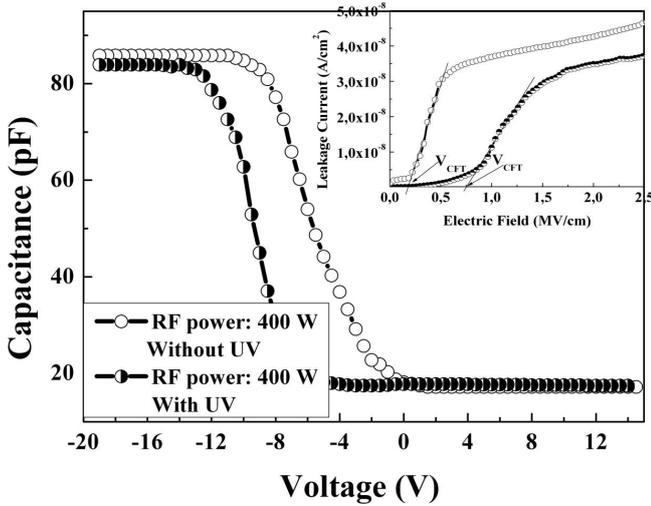


Fig. 2.  $C$ - $V$  ( $I$ - $V$ , inset) characteristics of SiOC(-H) films prepared with and without UV illumination using the MTSM+O<sub>2</sub> mixture at a RF power of 400 W.

with UV irradiation had a more cross-linked structure with chained Si-O-Si and -O-Si-CH<sub>3</sub> bonds, in which the incorporation of CH<sub>3</sub> groups broke the continuity of the -Si-O-Si- network (see Fig. 1(a), inset). We found that the relative area of the Si-O-C cage-link bond in the SiOC(-H) films with UV irradiation was higher than that in the films without UV irradiation but the relative area of the Si-O-C open link of the SiOC(-H) films with and without UV illumination decreased (Fig. 1(b), inset). Consequently, when the bulk plasma is irradiated with UV light, the related CH<sub>*n*</sub> or Si-C ions and the radicals are increased and the increase in the CH<sub>*n*</sub> groups on the SiOC(-H) film produces structural changes as a result of the bonding of -Si-CH<sub>2</sub>-Si- and -O-Si-CH<sub>3</sub> bonds in -Si-O-Si- chain structure. Our results for the SiOC(-H) film agreed with previous measurements reported in the literature [6,7].

## 2. Electrical Characterization

Figure 2 shows the high-frequency  $C$ - $V$  characteristics of Al-SiOC(-H)/Si-Al structures deposited at a 400-W RF power with and without UV irradiation. As shown the flat-band voltage ( $V_{fb}$ ) was shifted to the negative side because the SiOC(-H) film has effective positive charges coming from excessive (-CH<sub>3</sub>)<sup>+</sup> or (Si-CH<sub>*n*</sub>)<sup>+</sup> and (Si-H)<sup>+</sup> interstitial defects. The  $V_{fb}$  shifts of SiOC(-H)/Si capacitors deposited with UV illumination are larger than those deposited without UV illumination. From the  $C$ - $V$  curves, the  $V_{fb}$  shifts were found to decrease from -5 V to -9.8 V. This implies that UV illumination caused depopulation of the defect states and increased the charge density in the dielectric from  $6.45 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  to  $1.24 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ .

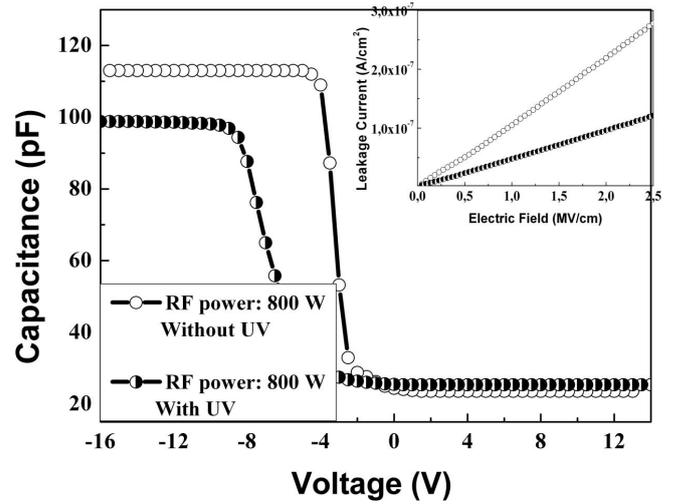


Fig. 3.  $C$ - $V$  ( $I$ - $V$ , inset) characteristics of SiOC(-H) films prepared with and without UV illumination using the MTSM + O<sub>2</sub> mixture at a RF power of 800 W.

We determined the insulating properties of the films by measuring the leakage current density with different applied fields. These results are shown in Fig. 2 (inset) for both UV- and no UV- deposited samples. We plot the data as a function of the applied electric field (rather than the applied voltage) to normalize for the different thicknesses of the films. The rectifying character of the  $I$ - $V$  curves together with the  $p$ -type silicon conductivity suggests  $n$ -type carrier transport in the SiOC(-H) films. The leakage currents on the electric field for SiOC(-H) films show that there is an decreasing trend with increasing the deposited UV irradiation. In addition, the “turn on” voltage of the  $I$ - $V$  curves occurs when all the traps that have been filled are shifted to higher bias fields. This means that the increased charge trapping induces greater screening of the applied field. As can be seen, on a log-log scale, the  $I$ - $V$  curve is comprised of several clearly defined straight portions with different slopes.  $I$ - $V$  curves of this kind are typical of space-charge-limited currents (SCLC) in insulators with traps for carriers [12]. According to the SCLC theory, the voltage  $V_{CFT}$  (arrays in Fig. 2, inset) at which the portion of completely filled traps with energy  $E_t$  begins is related to the concentration of initially empty traps ( $N_t$ ) by  $N_t = \epsilon\epsilon_0 V_{CFT}/eL^2$ . For  $V_{CFT} = 3.0$  V without UV and 10.5 V at UV illumination (see Fig. 2), we have  $N_t = 1.62 \times 10^{16} \text{ trap/cm}^3$  and  $N_t = 5.26 \times 10^{16} \text{ trap/cm}^3$ , respectively. The low- $k$  dielectric material is seen to exhibit a much higher density of traps than the SiO<sub>2</sub> films. This difference can be attributed to the combined effect of the porosity of the films and the more complex chemical composition of the films [13].

Figure 3 shows that there is a corresponding change in the  $V_{fb}$  at higher RF power. We observed a positive +4 V shift in the  $V_{fb}$  of the  $C$ - $V$  characteristics without UV illumination, indicating that the total positive

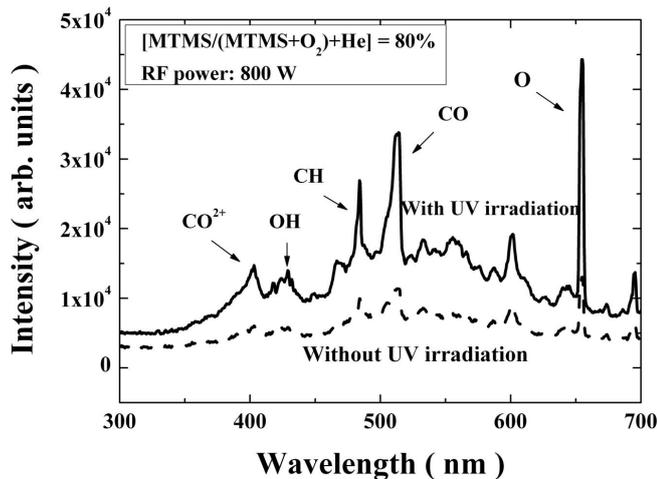


Fig. 4. Optical emission spectra of the plasma with and without UV irradiation.

charge was also decreased. Thus, in addition to reversing the effects of RF power, we observed an approximate 40% increase in the capacitance. As a result, the dielectric constants increased with increasing RF power. When the bulk plasma is irradiated with UV light at 800 W, we observed the expected decrease in the capacitance and an additional -3.5 V shift in the  $V_{fb}$ . This means that the measured capacitance is really determined by the properties of the SiOC(-H). The increasing dielectric constants can be explained by the increased density of the thin film. We infer that increasing RF power contributes more  $O^-$  ions and that a higher proportion of plasma-generated species having sufficient bonding energy has been incorporated into the film. As shown in Fig. 4, the intensities of  $CO^{2+}$ ,  $CH_n$ , and  $O$  species in the optical emission spectra are found to increase more rapidly for UV irradiation than for non-UV irradiation. A clear enhancement of the species is seen when UV irradiation is used, indicating that  $[Si(CH_3)_3]^+$  or  $[CH_3Si]^+$  ions are generated more than that they are without UV irradiation. In this case, the effective positive charges due to  $-CH_3$  or  $Si-CH_3$  and  $Si-H$  bonds were compensated for by the effective negative charges due to the  $Si-O-Si$  bond bonding modes, which increased with UV illumination. As a consequence, the positive charge density is reduced from  $6.45 \times 10^{11} \text{ cm}^{-2}eV^{-1}$  to  $3.05 \times 10^{11} \text{ cm}^{-2}eV^{-1}$  and the effect of oxygen is enhanced. In addition, there is a strong UV illumination effect on the surface states (interfacial traps) at the SiOC(-H)/Si interface. The calculated interfacial trap densities  $N_{ss}$  for samples deposited at 400 and 800 W with and without UV illumination were found to be  $3.06 \times 10^{11} \text{ cm}^{-2}eV^{-1}$  and  $0.81 \times 10^{11} \text{ cm}^{-2}eV^{-1}$ , respectively. In Si/SiO<sub>2</sub> systems, the interfacial traps are known to arise principally from dangling bonds at the interface [14]. These traps can be altered by UV illumination, which lowers the density of interfacial states by saturating the dangling bonds.

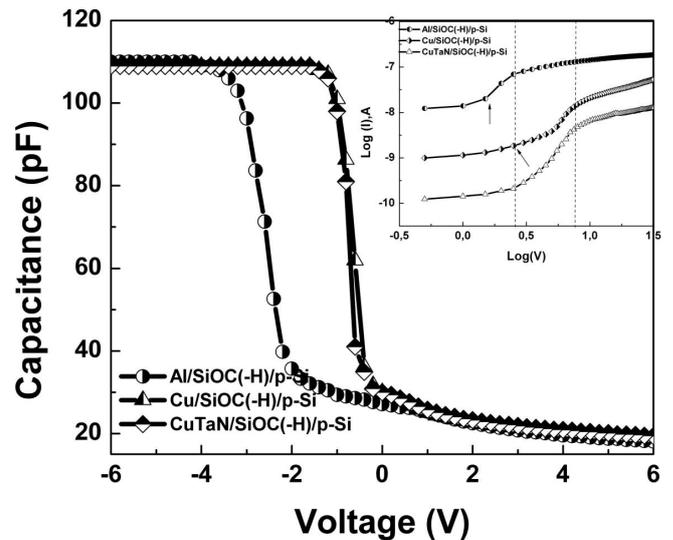


Fig. 5.  $C$ - $V$  curves for SiOC(-H) films with different Al, Cu and CuTaN electrodes. Inset: Plot of  $\log I$  vs.  $\log V$  for SiOC(-H) films. The “turn on” thresholds of voltage from these metals are indicated by arrows for comparison.

Interestingly, the  $J$ - $E$  plots of the SiOC(-H) films deposited at 800 W both with UV and without UV do not exhibit a plateau, and the leakage current increases linearly with electric field. The result in the inset of Fig. 3 shows that the leakage current density of the sample with UV illumination is lower than that without UV illumination. This may be due to changes in the bonding configurations and the number of effective defects. The data for the electrical characterization of the SiOC(-H) films show that electrons are the dominant carrier type. To identify the conduction mechanisms in the SiOC(-H) film deposited at an 800 W RF power, we modeled the  $J$ - $E$  curves in accordance with known conduction mechanisms. This is found that  $I$ - $E$  curves were linearized into  $\log(J/E) - E^{1/2}$  plots in order fit the Poole-Frenkel emission model at high electric field. Moreover, a higher value of the slope at lower voltages was observed and could be explained on the basis of space-charge buildup at the electrode from the charge carriers normally present in the dielectric, which enhanced the field at the electrode and led to a high slope of the  $\log I - \log V$  curve. Therefore, to further probe the charge-carrier-generation mechanism in the dielectric, we also carried out conductivity measurements with Cu and CuTaN electrodes, and the typical  $\log I - \log V$  plot with these electrodes is shown in Fig. 5. It is very clear from this figure that the conductivity of the SiOC(-H) film depends to a great extent on the electrode material, which is indicative of the Schottky-Richardson mechanism. This type of mechanism has also been observed in a polyblend of poly (methyl methacrylate) and poly (vinyl acetate) [15]. This suggests that the charge carrier generation is basically from the electrodes. Another possible explanation for the charge-carrier generation in the di-

electric may be the trapping of injected charge-carriers and their subsequent release following the Poole-Frenkel mechanism. It is well known that for the Poole-Frenkel mechanism to occur, the insulator must have a wide band gap and must contain donor levels [16] and its existence in the SiOC(-H) film deposited with a RF power of 800 W indicates the presence of donors and electron traps. As shown in Fig. 1 the intensity of the Si-C cage link and the Si-O-C open link increased with UV illumination due to the abundance of radicals produced, such as Si\* and CH<sub>n</sub>\*. This means that UV irradiation produces Si-C\* or Si-O\* as electron trap and donor radicals selectively [7]. Another interesting result that is evident from the curves of Fig. 5 is that the current value and the  $V_{fb}$  shifts of the  $C$ - $V$  characteristics decreases with decreasing metal-electrode work function. Moreover, a difference in the Fermi energies between Al and Cu [13] is seen to hardly have an effect on the threshold of the “turn on” voltage (arrows in Fig. 5, inset). This is possible if the effective electrode-dielectric potential barrier increases with decreasing metal-electrode work function. This observation suggests the formation of an additional barrier layer caused by negative charges located in the insulator above the metal surface (the so-called polarization layer) [17].

### III. CONCLUSION

By analyzing the changes in the  $C$ - $V$  characteristics, we found that UV irradiation repopulates defect states whereas increasing RF power can depopulate those defect states. From current transients, as well as the  $C$ - $V$  characteristics, we estimated the trap and the positive charge densities in the low- $k$  films to be on the order of  $10^{16}$  traps/cm<sup>3</sup> and  $10^{11}$  cm<sup>-2</sup>eV<sup>-1</sup>, respectively, having tendency to increase with increasing UV irradiation. We also found that the barrier heights for electrons at the interfaces of low- $k$  insulators with metals were almost insensitive to the metal Fermi energy, suggesting that the current injection could be determined by some localized state in the insulator gap. Some of these states are attributed to defects associated with excess silicon radicals or excess oxygen at or near the SiOC(-H)/Si interface. Some of the injected charge carriers seen to be getting trapped in the shallow traps present in the SiOC(-H) film, and their release is controlled by a Poole-Frenkel mechanism. This assignment is supported by the observed reduction in the density of traps in samples with increasing RF power because such defects react with oxygen to become electrically neutral. The

results were substantiated and directly correlated with the changes in the transport properties and with the bond structure characteristics of the SiOC(-H) films.

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