Photoluminescence properties of SiO_xC_y-films deposited under argon atmosphere and Si-based organometallic precursor by O-Cat-CVD

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***Abstract*— We report the deposition of silicon-based photoluminescent thin-films i.e. silicon oxycarbide (SiO_xC_y), with the help of organic catalytic chemical vapor deposition (O-Cat CVD) technique. Tetra-ethyl orthosilicate (TEOS) material was used as the single source organometallic precursor while tungsten (W) filament was exploited as catalyst during deposition. The deposition chamber worked under an atmosphere of argon (Ar) gas while the deposition time was 30 minutes. In this work, the influence of the argon flow was evaluated on the photoluminescence (PL) properties of the thin films which was varied from 20-60 sccm. Different bonding states and chemical states of the deposited films were analyezed by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) techniques, respectively. Through FTIR and XPS measurements, the formation of SiO_xC_y thin films has been confirmed. The thickness of the films and the refractive index were investigated from an ellipsometer at constant wavelength (632.8 nm) with variable angle measurements. The intense PL emissions were observed in a wide spectra of visible region for as-deposited films. The possible origin of PL emissions can be either from the incorporation of different luminescence-related defect centers and/or quantum confinement effect in the SiO_xC_y matrix.**

Keywords*— SiO_xC_y, Photoluminescence, Tetraethyl orthosilicate, O-Cat CVD

I. INTRODUCTION

Nowadays, silicon-based photoluminescent materials are attracting a lot of attention due to their wide use in optoelectronic devices such as flat panel display, solar cell and LEDs technologies, etc. [1–3]. Although silicon-based nitride, oxide, carbide, and oxynitride matrixes have also shown the PL properties but the hybrid nature of silicon oxycarbide (SiO_xC_y) due to organic and inorganic functional groups makes it a more versatile material in comparison to others [3–7]. Different applications such as piezoresistive sensors [8], anode material for storage batteries [9], radiation-tolerant material [10], biomedical application [11,12], gas barrier coating for PET bottles [13], etc. have been explored with SiO_xC_y matrix until now. Although SiO_xC_y thin films have been deposited by different techniques and precursors but currently, O-Cat CVD based SiO_xC_y thin films have attracted attention due to the use of safer and cheaper organometallic precursors such as TEOS ($Si(OC_2H_5)_4$) rather than silane (SiH_4) gas [14–17]. Besides, less damage of plasma and a high deposition rate are other advantageous properties of O-Cat CVD over plasma-enhanced CVD (PECVD) [18].

Some previous authors have investigated the role of argon gas to identify the structural and crystalline properties of different materials such as hydrogenated nanocrystalline silicon thin films, Micro-crystalline diamond and nano-carbon structures etc. [19–22]. Although the importance of the presence of argon gas has been proved for several thin films properties but no-one has investigated the effect of Ar gas on the photoluminescent properties of SiO_xC_y thin films. In this work, the effect of the argon atmosphere has been studied on the PL properties of O-Cat CVD deposited SiO_xC_y thin films by using TEOS precursor.

II. EXPERIMENT

A. Sample preparation

The O-Cat CVD system was used to deposit the SiO_xC_y thin films on the polished p-type crystalline silicon (100) substrate. An organometallic compound TEOS (Sigma-Aldrich, reagent grade, 98%) was used as a single source liquid precursor in the presence of argon (Ar) atmosphere. Tungsten (W) wire (0.75 mm diameter) was situated at a distance of 5 cm with substrate and used as catalyst material.

The flow of argon was variable from 20-60 sccm for the constant deposition duration of 30 minutes while the filament temperature (T_f) and substrate temperature (T_s) were 1800ºC and 200ºC, respectively. At the same time, the filament temperature (T_f) was monitored with an IR detector (Chino model IR-AHS). The initial pressure of the chamber was 0.08 torr and the deposition pressure was 0.30 torr.

B. Characterization

The chemical bonding structures of thin films were analysed by Fourier Transform Infrared (FTIR) spectroscopy (Nicolet 560) to study the different absorption bands, while the chemical

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composition was investigated by X-ray Photoelectron Spectroscopy (XPS) (PHI 5000 VersaProbe II) spectrometer using a monochromatic Al Kα X-ray source. Spectral Data Processor (SDP) v4.1 (32-bit version) software was used to analyze the XPS data where Shirley-type baseline was used for the peak-fit of the data. The refractive index (RI) and thickness were measured by using an ellipsometer (Gaertner) with a constant wavelength (632.8 nm) and variable angle mode (45-80 degrees). A photoluminescence (PL) spectroscopy (Kimmon Koha-Co. Ltd., Centennial, CO, USA) were used for the optical studies where a He-Cd laser (325 nm) was used with the output power of 20 mW at room temperature.

III. Results and Discussion

Fig. 1 shows the FTIR spectra where the effect of different argon flow is observable on the various absorption bands. The silicon-oxygen (Si-O) bending and stretching vibrational modes appear at 800 and 1080 cm^{-1}, respectively, where Si-O related stretching bonds shown a shift from its stoichiometry position [23]. This shifting in Si-O stretching bond is a result of the deficiency in oxygen atoms which generates a luminescent defect center due to having bonding with one or more silicon and/or carbon neighboring atoms [5,23]. Hence, the PL properties such as intensity and spectral composition can also be controlled by using this shifting phenomenon through optimized deposition [24]. Moreover, the intensity of the Si-O stretching bond shows anti-proportional behavior with the argon flow due to the Brownian motion of argon atoms, which change the kinetics of the CVD process [25]. The absorption bands of Si-H, Si-C, Si-H_n, Si-CH_n, and CO_2 bondings are also observable at 680, 800, 880, 1250, and 2300 cm^{-1}, respectively, where Si bound hydrogen and carbon bondings are decreasing with the increment of Ar flow. This phenomenon can be due to the presence of a higher flow of inert argon which initially, decomposes the ethyl radical associated with the outer part of the TEOS molecule [15,20,26]. Besides, the SiOC bonding-related absorption band is visible at 1100 cm^{-1}.

The chemical analysis of the deposited sample for 20 sccm

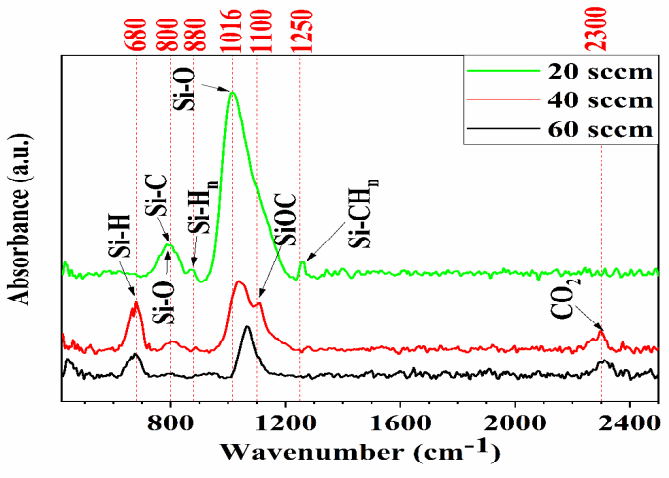

Fig. 1. FTIR spectra of the as-deposited samples at various argon flow.

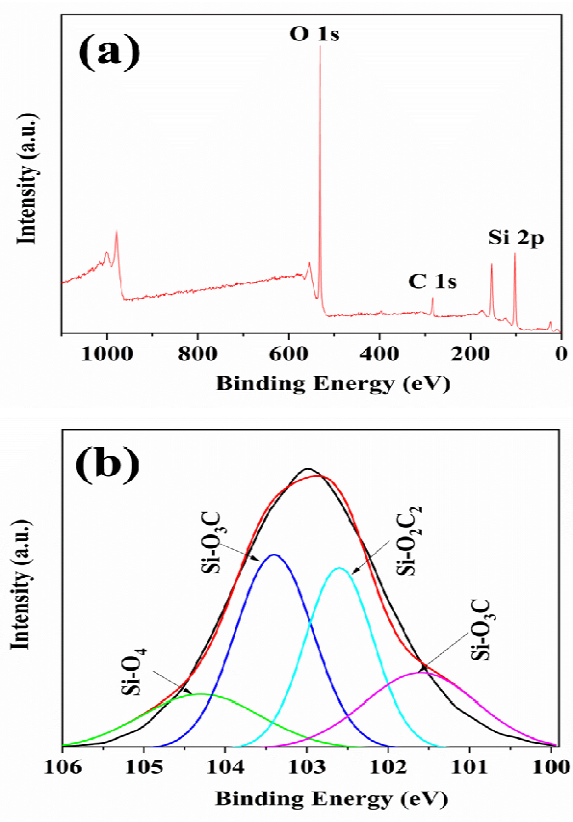

Fig. 2. a) XPS Spectrum b) Si 2p XPS fitted spectrum for the deposited sample at 20 sccm argon flow.

argon flow is performed and shown in Fig. 2 which may help to understand the high intensity and shifting of Si-O stretching bond through different SiO_xC_y phases for this thin film. Si 2p, C 1s, and O 1s peaks are observable in Fig. 2 (a), while different gaussian deconvoluted bonding phases of Si 2p Spectra are shown in Fig. 2 (b). At the same time, Table I shows the four types of bonding phases such as SiC_3O, SiC_2O_2, $SiCO_3$ and SiO_4 at 101.6 eV, 102.6 eV, 103.4 eV and 104.3 eV, respectively [27], where the full width at half maximum (FWHM) of these bonding phases were 1.62, 1, 1.12 and 1.71, respectively. The high presence of SiC_3O, SiC_2O_2 and $SiCO_3$ bonding phases confirm the SiO_xC_y content in the thin film. These XPS results also correlate with the description of FTIR results where the bonding of Si and/or C atoms were discussed with Si-O stretching bonds.

Fig. 3 shows the refractive index (RI) variation and the thickness of the deposited thin films with argon flow. The addition of argon gas affects the RI and the thickness of the thin film because it influences the structure and growth rate of

TABLE I. DIFFERENT BONDING PHASES OF Si 2P SPECTRA.

Bonding	BE (eV)	Atomic %
SiC_3O	101.60	20.1
SiC_2O_2	102.60	29.0
$SiCO_3$	103.40	35.6
SiO_4	104.30	15.2

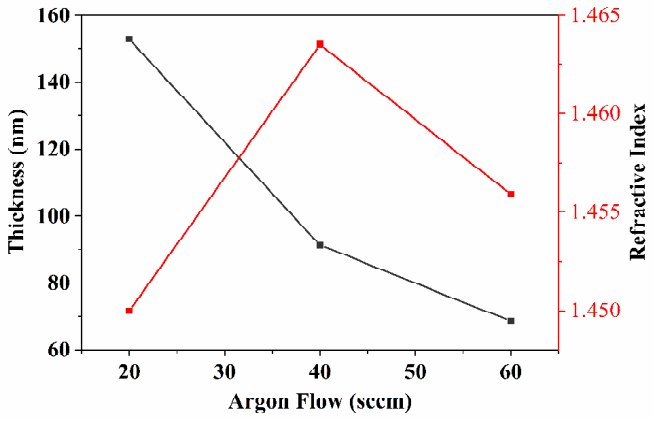

Fig. 3. Thickness and refractive index of as-deposited samples at various argon flow.

the thin film. It is noteworthy that argon gas cannot ionize in O-Cat CVD because the ionization energy of Ar is very high (15.8 eV) due to which inert Ar gas have a large electron collision cross-section. This phenomenon immediately cools down the emitted electrons by the hot tungsten filament which results in the abatement of the dissociation of molecules at the filament and this is the reason for the decrease in the thickness of thin film with the increment of Ar gas [19,21]. Moreover, Fig. 1 clearly illustrates the formation of different bonding and their intensity at different argon flows which also subsequently justify the variation of RI and thickness of the films.

Fig. 4 represents the photoluminesce (PL) spectra of deposited films where the wide PL spectra are observable in the visible region (385-700 nm) and PL peak is positioned at 477 nm (2.7 eV). Moreover, a PL shoulder at 550 nm for 40 and 60 sccm deposited films is also noticeable due to the presence of carbon-related bonding in the samples [5]. The intensity of PL is directly proportional to the thickness of the deposited film, which increases with the diminution of argon flow. Hence, the high intensity of PL is obtained at the less presence of argon environment during deposition.

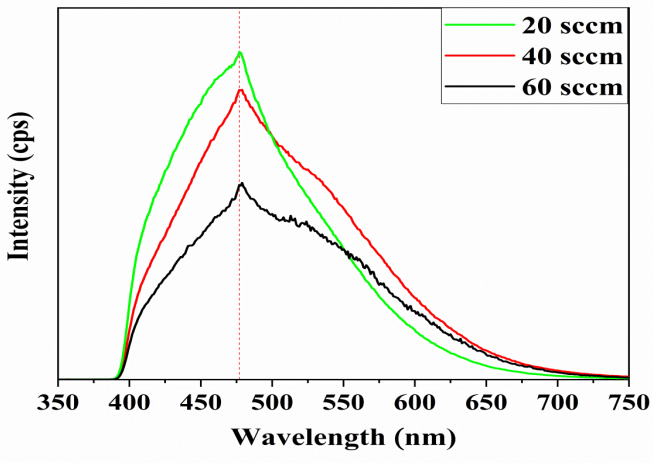

Fig. 4. PL spectra of samples obtained at different argon flows.

Although the mechanism of the PL emission is not clear so far, several reasons may be possible in which the presence of defects related to carbon or silicon due to non-stoichiometric composition [5,28,29], quantum confinement effect (QCE) [4] are possible. Moreover, hydrogen and oxygen-related defects such as oxygen deficiency centers, silicon-related neutral oxygen vacancy (NOV) defects, carbon-related NOV, or non-bridging oxygen hole center (NBOHC) can also be possible as the optical path for the PL emission in the visible region [1,30]. Here, It is worth mentioning that the NOV defect density and crystallinity of thin film are a function of argon gas [26] and hence the presence of argon environment during the deposition affect the photoluminescence properties as well.

IV. Conclusions

The effect of argon environment on the optical properties of SiO_xC_y thin films has been discussed where the O-Cat CVD technique was used to deposit the samples with a safe and low-cost organometallic precursor i.e. TEOS. The presence of argon environment alters the dissociation process of TEOS molecule which consequently changes the composition of thin films. This phenomenon was observed by using the FTIR spectra while the XPS spectrum confirms the formation of SiO_xC_y matrix in the thin film. Wide PL emission was observed in the visible region of the spectra where different mechanisms for the PL emissions were discussed. Although argon is an inert gas but it may help to modify the optical properties of devices. This work would draw attention to the role of argon flow in the deposition process, where SiO_xC_y thin film deposited at 20 sccm argon flow could be used for the development of opto-electronic devices.

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