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White bright luminescence at room temperature from TEOS-based thin films via catalytic chemical vapor deposition

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ABSTRACT

Strong white luminescence, visible to naked eye at room temperature, was observed from as grown SiO_xC_y thin films without the need of annealing. SiO_xC_y thin films were prepared by using catalytic chemical vapor deposition method (Cat-CVD) employing TEOS solution as the precursor and bubbled with the argon gas to form vapors. TEOS vapors were catalytically decomposed in the deposition chamber with the help of a tungsten filament. Scanning electron microscope (SEM) and transmission electron microscope (TEM) confirmed the formation of nano-crystals in SiO_xC_y matrix. Inter-atomic spacing shows the transition of Si–SiC nano-crystals in matrix. The intense emission is believed to come up either from the carbon incorporation in the nanocrystalline-structured film and/or quantum confinement effect of the observed nano-crystals in SiO_xC_y matrix.

1. Introduction

Visible luminescence from porous Si was the foremost step related to optical investigation of this material [1]. Following that research, next phase was focused on fabricating nanocrystalline silicon (nc-Si) embedded in silicon oxide (SiO_x) or silicon nitride (SiN_x) matrix using various source gases by other deposition techniques [2–6]. In order to obtain an efficient photoluminescence (PL) response based on confinement effect from these Si based thin films, it is always necessary to anneal the samples [7,8]. This temperature range is quite high for device manufacturing in microelectronics industry. To overcome this restraint, it is desirable to find alternative and safe deposition process related to Si material at lower substrate temperature. Cat-CVD is one of the prospective techniques by offering advantages like efficient use of precursors and no plasma damage compared to other techniques. Basic film properties using TEOS (Si $(OC_2H_5)_4$) by means of Cat-CVD have been demonstrated previously by Nakayama et al. [9,10] and also there is report of Cat-CVD with TEOS as the precursor for dielectric applications [11]. Some other groups have reported defect induced PL in near infrared region [12,13] using TEOS with other deposition techniques. Also, some authors reported basic characterization and memory device application by means of same precursor [14,15]. In the present job, we fabricated for first time the nano-crystalline phased SiO_xC_y thin films by means of Cat-CVD at relatively low substrate temperature, which shows bright white emission without the need of any post-deposition heat-treatment.

2. Experimental

The Cat-CVD is also known as Hot wire CVD (HW-CVD) and the working operation have been described elsewhere [16]. In this study, TEOS (Sigma-Aldrich 131903- Purity 98%) related Si–O–C films were prepared using built in-house up-stream Cat-CVD equipment. TEOS was bubbled with a constant flow rate of 50 sccm using Ar gas. Both TEOS source and its vapors transportation tubing system to the deposition chamber were maintained at 30 °C using resistive heating element in order to avoid TEOS vapor condensation. Three different depositions by varying filament temperature (T_{fil}) were carried out. T_{fil} was maintained at 1700,

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1800 and 1900 °C for the depositions on the silicon substrate. Distance from the filament to substrate was kept 5 cm and temperature of substrate (T_{subs}) was maintained at 300 °C for all the three processes. Fourier Transform Infrared (FTIR) spectrum was recorded within the range of 400 to 4000 cm^{-1} by Thermo-Nicolet-nexus-470. Photoluminescence (PL) spectra were obtained using a Kimmon Koha He–Cd laser with excitation wavelength of 325 nm and output power of 20 mW, at room temperature. Compositional investigations of the samples were carried using Bruker energy dispersive analysis of X-ray (EDX) equipped in Carl Zeiss-AURIGA-FESEM. Bright field images and selected area electron diffraction (SAED) were obtained in a TEM JEOL-JEM-2010 at 200 kV.

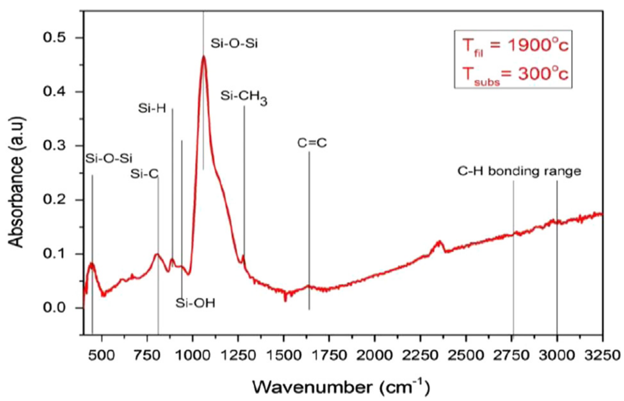

Fig. 1. Infrared absorption spectra of the thin film deposited at T_{sub}=300 °C and T_{fil}=1900 °C.

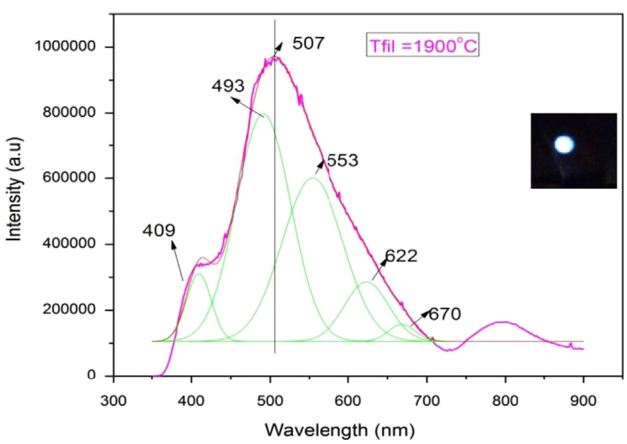

Fig. 2. Representative PL spectra of as-deposited film at T_{sub}=300 °C and T_{fil}=1900 °C, with the inset showing camera image of the white emission from sample.

3. Results and discussion

Intense white luminescence is observed for all the deposited samples. To demonstrate the structural analysis, results related to only one condition with T_{fil}=1900 °C have been illustrated. Fig. 1 shows the Infrared absorption spectra (FTIR spectra) of Si–O–C thin film at T_{subs}=300 °C and T_{fil}=1900 °C.

The spectra, in general, exhibited absorption peaks related to Si–O–Si rocking, Si–C stretching, Si–H bending, Si–OH, Si–O–Si antisymmetric stretching, Si–CH$_3$ bending T (≡O$_3$≡Si–CH$_3$), C=C and C–H modes [17–22] and confirms the presence of Si, O and C in the film. Fig. 2 shows a wide PL spectrum from 360 nm to around 710 nm for the same sample.

For more detailed investigation of the morphology and the possible PL mechanism, SEM studies have been carried out. Fig. 3(a) shows a SEM image of the film at T_{fil}=1900 °C and formation of some cluster structures can be observed.

For the compositional analysis of observed clusters and matrix surrounding them, EDX studies have been performed. Fig. 3(b) illustrates the elemental analysis of the thin film using EDX. Relative concentration of Si, O and C confirms the formation of SiO$_x$C$_y$ type of film.

To verify the type of clusters and to confirm the presence of crystalline phase, TEM study is also illustrated. Fig. 4(a) and (b) shows the bright-field TEM images for the deposited film.

For one of the selected portion in Fig. 4 electron diffraction (SAED) pattern is also shown in the inset. Inter-atomic spacing shows the presence of silicon and silicon carbide nanocrystalline-phase in the SiO$_x$C$_y$ matrix surrounded by amorphous material. Generally, in case of SiO$_x$C$_y$ or SiO$_x$:C films deposited by other methods, observed PL is normally attributed to bonding related to C, Carbon related defects (CODCs), neutral oxygen vacancy (NOV) defects or carbon rich silica [18,21,23,24]. In the present work, using low cost and safe precursor instead of gases like SiH4, we reported presence of nano-crystals related to Si and SiC obtained at low temperature without the requirement of annealing process. It should be stated that due to the structural complexity; it is a difficult situation to give any particular interpretation regarding PL mechanism. One of the possible explanation could be the presence of various C related bands at 800 cm^{-1} (Si–C stretching), 1638 cm^{-1} (C=C) and 2800–3000 cm^{-1} (C=H). It summarizes that the possible emission levels could be due to the element C or it may be due to the presence of Si–C bonding states [25]. At the same time, we cannot rule out the presence of nanocrystalline phases in the film and another probability is that the

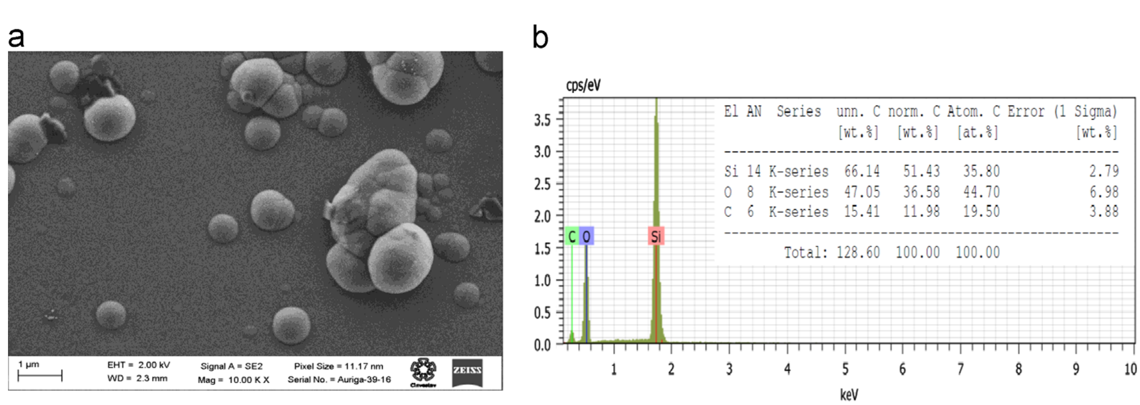

Fig. 3. (a) SEM image of sample deposited at T_{sub}=300 °C and T_{fil}=1900 °C, (b) Elemental analysis of the matrix involving Si, O and C using EDX

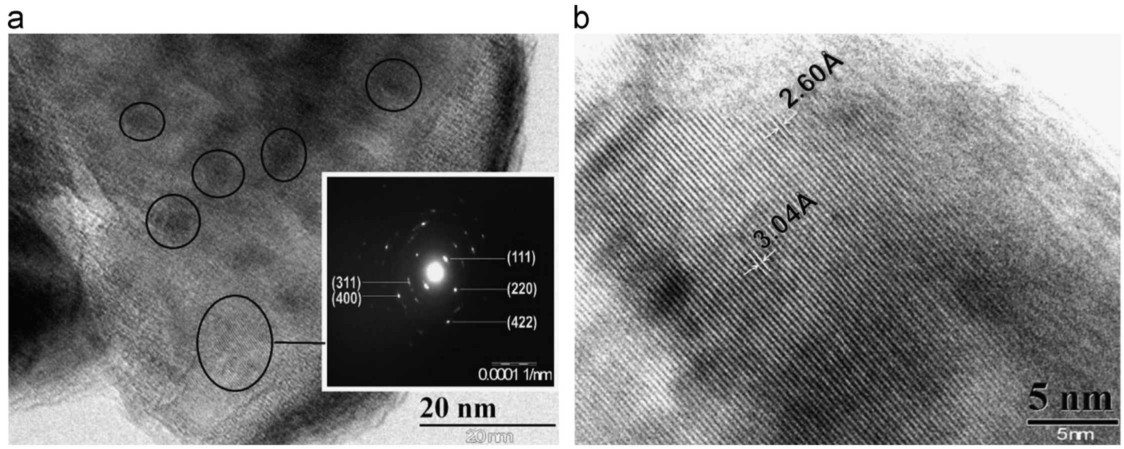

Fig. 4. (a) Cross sectional bright-field TEM image of the film deposited at $T_{sub}=300$ °C and $T_{fil}=1900$ °C with inset showing SAED pattern for the region highlighted, (b) Bright-field TEM image of one of the selected portion from Fig. 3(a).

nano-crystallites related to Si and SiC are well passivated by –CH3 (1270 cm^{-1}), –OH (960 cm^{-1}) or C groups which could lead to well defined quantum confinement effect. Passivation of nano-crystallites also plays an influential role for enhancing the recombination rate [26]. Further characterizations have to be carried out for understanding the role of carbon as well as nanocrystalline-clusters for this bright luminescence. This bright luminescence from TEOS based thin film could open many gateways for optical device fabrication.

4. Conclusions

In conclusion, we have demonstrated safe and low cost deposition technique to obtain bright white luminescence from as-deposited films using TEOS as the precursor without the requirement of any post-deposition temperature treatments. Comparative study of FTIR, SEM and TEM shows formation of silicon and silicon carbide based nano-crystals in a SiO_xC_y matrix. Further studies could help in understanding the PL mechanism. It could open a gateway for optical device related research based on this technology and make this TEOS related material comparable to direct band gap semiconductor materials.

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