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The influence of carbon on the structure and photoluminescence of amorphous silicon carbonitride thin films

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ABSTRACT

Silicon carbonitride (SiCN), an intermediate structure between silicon carbide and silicon nitride, has emerged as a material of interest to increase the performance of silicon-based visible luminescence. In this work, thin films of SiCN were deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition using silane, nitrogen, and methane as the gas precursors. The microstructure, composition, and optical properties of the SiCN layers were determined by elastic recoil detection, Rutherford backscattering spectrometry, ultraviolet–visible spectroscopy, variable angle spectroscopic ellipsometry, photoluminescence, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, high-resolution transmission electron microscopy, and X-ray diffraction spectroscopy techniques. The optical and electrical characteristics were linked with the structural properties to investigate the effect of carbon incorporation on the nature of SiCN thin films. Successive increases in the carbon content from 0 to 41.6 at.% resulted in an increase in refractive index and growth rate of the films, while band gap narrowing occurred. Structural studies showed that carbon preferred to form bonds with silicon rather than nitrogen in SiCN thin layers. The produced films contained mainly amorphous silicon nitride and silicon carbide structures and small amounts of an amorphous SiCN network. Photoluminescence emission showed two peaks centred at 475 and 550 nm. The observed link between the photoluminescence behavior and the composition and structure of SiCN layers revealed the details of the most luminescent SiCN thin film. Silicon nitride (carbon-free) thin films exhibited lower emission intensities indicating that the presence of carbon in the silicon nitride matrix enhanced the visible light emission.

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1. Introduction

Silicon (Si)-based light sources are low cost and compatible with integrated photonics in multiple areas such as lighting, panel displays, and other optical devices [1]. Intensive research has been conducted in the introduction of new materials as the luminescent active layers in Si-based light sources. Silicon carbide (SiC) [2] and silicon nitride (SiN) [3] are two well-studied candidates to enhance the light emission from Si-based devices. The combination of superior properties of binary compounds (SiC and SiN) leads to a less-studied and multifunctional material, silicon carbonitride (SiCN) thin film. SiCN film has appeared to be a material of interest in light element-based technologies due to some optical properties benefiting integrated photonics and solid-state lighting. One of the important features of SiCN matrices is the broad range of stoichiometries that can be adjusted to tailor optical and structural properties [4]. SiCN has an intermediate band gap between that of SiC (2.4–3.2 eV) [5] and that of stoichiometric SiN (5.0 eV) [6] providing the potential for band gap engineering. Chen et al. [7] reported a direct band gap of about 3.8 eV and an intense visible emission around 2.8 eV demonstrating the possibility of SiCN thin films as a low cost UV detector operated at high temperatures [8,9]. Another application is the use of SiCN films in the next generation of luminescent materials with wide band gaps [10,11]. In addition, the presence of carbon (C) in the SiN matrix decreases the dielectric constant of SiN films which makes SiCN layer as a significant barrier against copper diffusion in low k materials [12]. These potential applications necessitate the understanding of the relationship between the luminescent properties and film structures. Although extensive results have been reported on the properties of SiCN thin layers, only a few publications focused on the photoluminescence (PL) properties of SiCN films [13–17].

SiCN films have been produced using several methods including pulsed laser deposition [11,18], ion beam and reactive magnetron sputtering [15,19], and various chemical vapor deposition (CVD) techniques [8,20]. However, the growth of SiCN films is not very easy due to the possibility of the formation of SiC and SiN phases in the SiCN network. The method and condition of the growth affect the phases formed in the deposited layer. Among the above techniques, plasma-assisted deposition allows formation of amorphous nitrides and carbides at

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much lower temperatures than those deposited by conventional CVD [14,21]. High-temperature growth is one of the drawbacks in the production of commercialized devices. Plasma-assisted techniques also provide higher homogeneity of films over the substrate surface, which enhances the formation of the SiCN phase.

In this paper, thin films of SiCN are grown using electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR PECVD). Our approach is towards the enhancement of luminescence properties of SiN films by addition of C. The effect of C incorporation on the optical, compositional, and structural properties of the thin films grown at various methane (CH_4) flow rates are investigated. Then, the optimal conditions with respect to the most luminescent sample are reported in detail, using various optical characterization techniques.

2. Experimental methodology

2.1. Film deposition

A series of hydrogenated amorphous SiCN (a-SiCN:H) thin films were deposited on n-type (0.01–0.03 Ω-cm resistivity) and un-doped (100) silicon, Corning glass 7059, as well as on glassy carbon plate substrates by ECR PECVD. Further details of the system were previously described [22]. Prior to the deposition, the silicon wafers were cleaned with buffered hydrofluoric acid (HF) for 60 s to remove the native oxide layer while the carbon plates were cleaned using acetone followed by methanol, both using sonication for 10 min. Silane (SiH_4), CH_4, and nitrogen (N_2) gases were used as precursors for Si, C, and nitrogen (N), respectively, and were fed into the chamber in the form of 30% SiH_4 in Ar, 10% N_2 in Ar, and pure CH_4. Before the growth, the chamber was evacuated to a base vacuum better than 10^{-6} Pa using a load lock chamber and a high-speed turbomolecular pump. Setting the microwave power to 500 W, several deposition runs were performed where the total process gas flow rate was varied in the range of 15 to 35 (±5%) cubic centimeters per minute at standard temperature and pressure (sccm). Deposition times of 30 min resulted in films with thicknesses varying from 180 to 440 nm. The deposition process was conducted using a stage heater temperature of 350 °C, corresponding to the substrate temperature of approximately 120 °C. To achieve more uniform and homogeneous samples, stage rotation was used at a rate of 20 rotations per minutes. A systematic study of the influence of C on the SiCN network was performed by using the parameters for stoichiometric Si_3N_4 and then adjusting the CH_4 flow rate from 0 (pure Si_3N_4) to 20 sccm, while the flow rates of SiH_4 and N_2 were held constant at 5 and 10 sccm, respectively.

2.2. Characterization techniques

The compositions of SiCN thin films, deposited with different CH_4 flow rates, were determined using Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) analysis carried out on samples deposited on glassy carbon substrates. The RBS and ERD data sets were collected using 1.8 MeV and 1.6 MeV $4He^+$ ions, respectively. The experimental data was then fit through computer simulation using the SIMNRA 6.0 software package to determine atomic concentrations as a function of film thickness [23]. The band gap energy of films at room temperature was determined by optical transmission measurements. The transmission spectra of the films were recorded over the region 200 to 1100 nm using an Agilent Technologies Carry 300 ultraviolet–visible (UV–VIS) spectrophotometer. A J.A. Woollam M-2000U UV–VIS variable angle spectroscopic ellipsometer (VASE) was employed to investigate the thicknesses and optical constants of the films. The ellipsometric parameters Δ and Ψ data were obtained at five angles of incidence (55°, 60°, 65°, 70°, and 75°) over the UV–VIS–NIR (300–1600 nm) range. The VASE spectra were analyzed using J. A. Woollam's CompleteEASE software package [24]. PL spectra were measured at room temperature using a 17 mW, 325 nm HeCd laser excitation source. More details regarding the spectrometer and system response used for the correction can be found in reference [25]. X-ray photoelectron spectroscopy (XPS) measurements were also conducted to characterize the chemical bonds. The C 1s, N 1s, Si 2p, and O 1s core level spectra were recorded using a Kratos AXIS Ultra with Al K_α X-ray excitation (15 mA, 14 keV) and the obtained spectra were analyzed using CasaXPS software version 2.3.14. Survey scans were carried out with an analysis area of 300 × 700 μm and a pass energy of 160 eV. High-resolution scans were then performed with an analysis area of 300 × 700 μm and a pass energy of 20 eV. Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Bruker Vertex 80v vacuum infrared spectrometer to facilitate electronic structural analysis. The spectra were recorded in the 400 to 4000 cm^{-1} wavenumber range (mid-IR), with a resolution of 4 cm^{-1}. Baseline subtraction and normalization was performed using a Bruker OPUS 6.5 software package. The crystal structure of the films was examined by 2D Powder X-ray diffraction (XRD) technique using a Bruker Smart6000 CCD area detector, Bruker 3-circle D8 goniometer, Rigaku RU200 Cu-$K\overline{\alpha}$ rotating anode, Göebel cross-coupled parallel focusing mirrors, and Fixed Chi at 54.8°. The scans were at a fixed incident angle of 2° with a frame exposure of 300 s in a distance of 16.74 cm from the detector (power setting of 90 mA, 50 kV). High-resolution transmission electron microscopy (HR-TEM) images of film cross-sections were captured using the FEI Titan 80-300 Cryo-in situ and JEOL 2010F microscopes at the Canadian Centre for Electron Microscopy (CCEM) at McMaster University. The procedure of HR-TEM sample preparation started with bonding two SiCN slices in the centre of silicon bars with a fast-curing epoxy. After polishing and ultrasonic cutting, two circular samples were produced to which Moly ring was attached, followed by dimple grinding and ion milling.

3. Results and discussions

All luminescent samples studied in this work were as-deposited samples with amorphous structure. XRD and HR-TEM revealed no crystalline phases in the as-deposited layer. The amorphous matrix may form due to no post thermal treatment and/or different composition and structure reported in other crystalline Si-C-N network [7]. In the next three subsections the composition, optical properties, and structure of a-SiCN:H films were investigated. The corresponding link of the chemical and structural properties with the PL properties was discussed.

3.1. Film composition

The samples grown on the C substrate were used in RBS measurements as opposed to the common used substrate, Si, in most of the similar studies. The concentration of the constituent elements was reported by the atomic percentage.

3.1.1. Films grown on C substrate

A representative RBS spectrum for a sample containing atomic concentrations of 25.4 ± 0.3 at.% Si, 17.5 ± 1.1 at.% N, 32.2 ± 1.0 at.% C, and 22.8 ± 0.9 at.% H grown on two different substrates, C and Si, is shown in Fig. 1(a) and (b), respectively. The experimental data (red dots) and the fitted data (solid black line) are plotted and the spectral contribution from each element is depicted and labelled. To avoid differences in the process parameters, both samples were prepared simultaneously under the same experimental conditions. Results of RBS and ERD measurements of SiCN sample deposited on two different substrates are provided in Table 1. Table 1 also shows that the use of a Si substrate resulted in relatively larger uncertainties for C and N in comparison with using a C substrate.

The RBS spectra of samples deposited on glassy carbon substrates gave well separated C and N peaks. The C and N peaks cannot, however, be accurately distinguished in the SiCN matrix deposited on the Si

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