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Optical properties and photoconductivity of amorphous silicon carbon nitride thin film and its application for UV detection

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Abstract

Optical properties of amorphous silicon carbon nitride thin films as a function of carbon content have been studied by the spectral micro-reflectometry. The compositions of a-SiCN thin films deposited with different CH_4 flow rates were analyzed by X-ray photoemission spectroscopy (XPS). It was found that the transmittance of a-SiCN thin films decreases with the increasing carbon content; the index of refraction n varies from ~2.0 to ~2.2 and the optical gap (Tauc gap) E_{opt} value progressively decreases from 4.1 to 3.3 eV while the carbon content changes from 0 to 25% in the films. In addition, a MSM (metal-semiconductor-metal) photodetector device based on the a-SiCN thin film demonstrates excellent selective sensing features with a large photo-to-dark current ratio about 1800 under illumination of the 250 nm UV light source, providing potential applications for low-cost UV detection.
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Keywords: Amorphous silicon carbon nitride; Optical band gap; MSM; UV detector

1. Introduction

Silicon carbide (Si-C) and silicon nitride (Si-N) have wide applications in mechanical, optical and electronic devices [1]. Carbon nitride, a highly promising hard material, has also received increasing attention recently [2]. More recently, a new class of ternary silicon carbon nitride (SiCN) materials with large (several tens of microns) and well-facet crystals have been grown successfully by microwave plasma-enhanced chemical vapor deposition (MW-CVD) by Chen et al. [3,4] and Badzian and Badzian [5]. These newly discovered SiCN crystals have been found to demonstrate a great potential for applications in semiconductor technology as well as a structural material. They show excellent mechanical properties with hardness and bulk modulus around 30 and 322 GPa, respectively. The optical investigation of polycrystalline SiCN films shows a direct band gap of about 3.8 eV and a strong optical emission around 2.8 eV [4]. The ternary SiCN compound constitutes an important wide band gap material with a gap energy within the blue-UV spectral region. It is believed that the chemical bonding and atomic local order can be quite complex in the ternary SiCN system. The atomic structure of SiCN crystals can be described as the pseudo α-Si_3N_4 phase, which shows some deviation from the pure α-Si_3N_4 pattern in the X-ray diffraction experiment. The similarity of local atomic structures between SiCN and α-Si_3N_4 is also evident from the experiment by the X-ray-absorption spectroscopy [6]. Composition and bonding analyses strongly suggest the structure of SiCN to be a solid solution and SiNx and CNx, in that C atoms substitute only for the Si sites and vice versa [7]. It is expected that carbon content plays an important role in determining physical properties of a-SiCN thin films. Indeed, it has been reported that the thermal diffusivity, density and hardness of a-SiCN thin films decreased with increasing carbon content [8]. In this article, we would like to present a systematical study on the optical and photoconductive properties of a-SiCN thin films

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as a function of carbon content and the potential applications for UV light detection.

2. Experiment method

Microwave plasma enhanced chemical vapor deposition (MW-CVD, AsTex, 5 kW) systems were employed to grow the SiCN films on the Si(100) and fused silica substrates, respectively. Details of the MW-CVD systems have been described elsewhere [7]. In brief, a 1.5 kW microwave source was employed to generate plasma as a mixture of semiconductor grade SiH_4, NH_3,CH_4 and H_2 gases in various proportions was used to deposit a-SiCN thin films. By adjusting the flow rate ratio of different gases, films with various compositions were obtained. A microwave power of 1000 W was set and the chamber pressure was kept at about 3.73 kPa during deposition. In order to systematically investigate the bonding configurations of a-SiCN films, we varied the CH_4 flow rate from 0 to 30 sccm and kept the flow rates of SiH_4 3 sccm, NH_3 30 sccm and H_2 100 sccm unchanged during deposition. Incorporation of hydrogen in the film is inevitable in most CVD process. It has been reported that the a-SiCN films with and without hydrogen incorporation prepared by CVD and IBSD (ion-beam sputtering deposition), respectively, exhibit similar compositions and bonding states of C, N, and Si [9]. Incorporation of hydrogen assists the formation of C–H, N–H and Si–H bonds in the films, resulting in the termination of dangling bonds of the a-SiCN network. The chemical composition and bonding states of the a-SiCN films were determined by a Perkin-Elmer Phi 1600 XPS system with a $(800\text{-}\mu m)^2$ sampling area and 11.75 eV pass energy. MgK_α radiation of 1253.6 eV was used as the X-ray source, with a line width of 0.7 eV. The optical properties of refractive index (n and k) and transmittance and film thickness were determined by the spectral micro-reflectometry (Mission peaks optics, MP100-M), by measuring the interference between incident and reflected light with wavelengths ranging from UV to visible range (250–1000 nm). All the samples for optical properties measurements were deposited on the quartz substrates. From the phase shift, the film thickness and refractive index (n and k) can be determined. The photovoltaic device with a MSM structure was fabricated by depositing the 800 nm thick a-SiCN film on the silicon substrate and evaporating the Au on top to form the electrode. Photocurrent measurements were completed using a 300 W Xenon lamp (Oriel) coupled to a monochromator as an illumination source and a Keithley 6487 source measurement unit to obtain the current and voltage.

3. Result and discussion

The composition of a-SiCN thin films deposited with different CH_4 flow rates determined by XPS measurement is shown in Fig. 1. It is shown that the C content in the SiCN

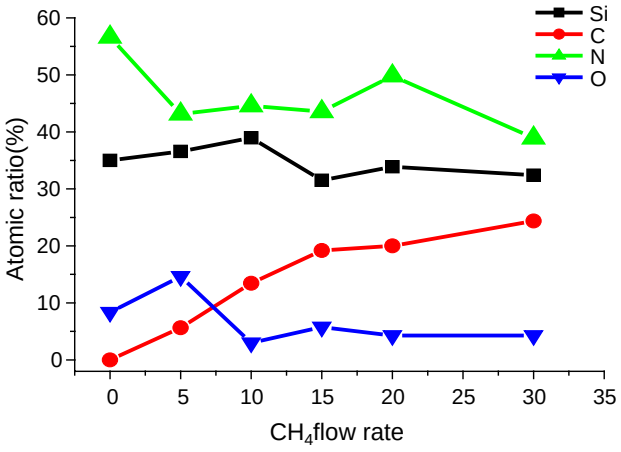

Fig. 1. The composition of a-SiCN thin films deposited with different CH_4 flow rates determined by XPS measurement.

films gradually increases with the increasing CH_4 flow rate up to 15 sccm and reaches to a value around 25% for the 30 sccm CH_4 flow rate. No significant variation of carbon content has been found in the a-SiCN thin films with further increasing the CH_4 flow rate under current experimental conditions. Oxygen as impurity was found in all the deposited samples and the percentage of the oxygen content was kept below 5% for the films deposited with the CH_4 flow rates higher than 10 sccm. Fig. 2 shows the transmission spectra of a-SiCN thin films with various carbon content. The film thicknesses for these films are 900(0 sccm), 950(5 sccm), 1040(10 sccm), 1060(15 sccm), 1095(20 sccm), 1020(30 sccm) nm, respectively. The average transmittance for these films in the visible light range is between 70%-90%. In addition, the optical absorption band edge shifts toward the lower energy position as the carbon content increases. The dispersion of refractive index for a-SiCN thin films with various carbon content is shown in Fig. 3. The refractive index values $n(\lambda)$ of the a-SiCN thin films increase as the carbon content increases. The refractive index of the a-SiCN thin films varies from ~2.0 to ~2.2 while the carbon content changes from 0 to 25%. These values are relatively closer to that of Si_3N_4 (~2.0) compared to that of SiC (~2.6) due to the similarities of local bonding configurations between SiCN and Si_3N_4 as mentioned above. The absorption coefficient $\alpha(\lambda)$ were deduced from the extinction coefficient $k(\lambda)$ measured by the spectral reflectometry and, subsequently, the optical band gap of the a-SiCN thin film E_{opt}, is obtained from the Tauc plot [10], $(\alpha h\nu)^{1/2}=B^{Tauc}(h\nu\text{-}E_{opt})$ where B^{Tauc} is a constant factor and $h\nu$ is the photon energy. Fig. 4 shows the variation of the optical band gap (E_{opt})obtained as a function of carbon content. It is clearly observed that the E_{opt} values progressively decrease with increasing carbon content in the films. This result is consistent with the theoretical calculations [11], which indicates that the addition of C atoms in the α-Si_3N_4 network will lower the value of conduction band minimum (CBM) due to the high

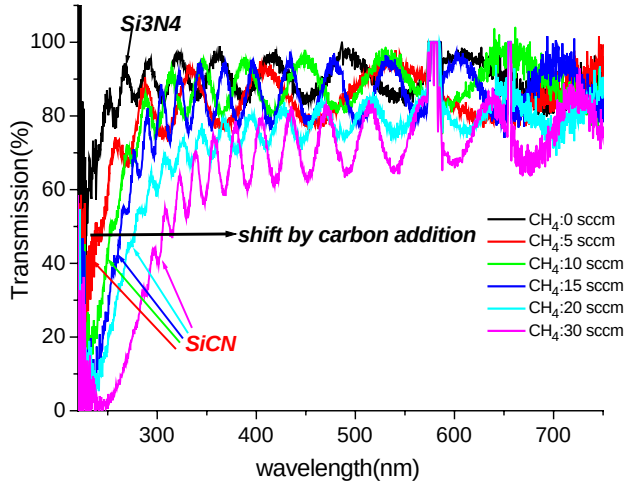

Fig. 2. The transmission spectra of a-SiCN thin films with various carbon content. The film thicknesses for these films are 900(0 sccm), 950(5 sccm), 1040(10 sccm), 1060(15 sccm), 1095(20 sccm), and 1020(30 sccm) nm, respectively.

localization of C compared to Si. From the above results, it is shown that optical properties of a-SiCN thin films can be tuned by varying the carbon content, providing the ability of band gap engineering.

Fig. 5(a) shows the characteristics of photocurrent-voltage response of the Au/a-SiCN/Si MSM photodetector device under the irradiation of light sources with various wavelengths. The composition of the a-SiCN thin film in the device is Si(35%):C(24%):N(39%):O(2%) with a thickness of 800 nm. It is clearly shown that the photoconductive current of the Au/a-SiCN/Si device increases dramatically for the illuminating light with a wavelength shorter than 350 nm, indicating that the device possesses a selective sensing feature of good solar-blind ability. The photocurrent I_p to dark current I_d ratio (PDCR) defined as $\frac{I_p}{I_d}$ reaches a value of 1800 for the incident light with a wavelength of 250 nm under an applied voltage of 5 V, which is the highest value

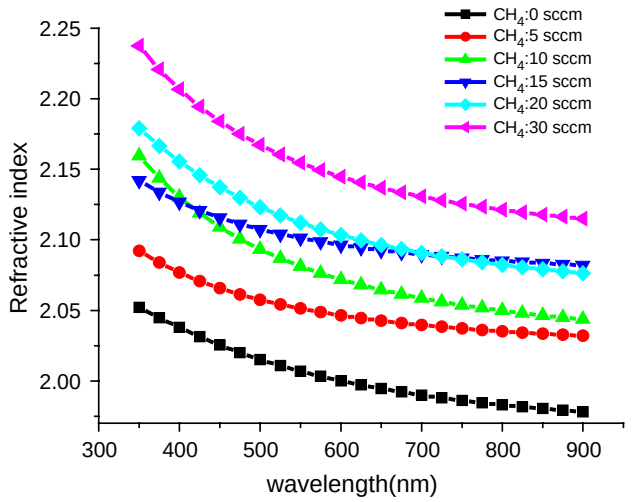

Fig. 3. The dispersion of refractive index of a-SiCN thin films with various carbon content.

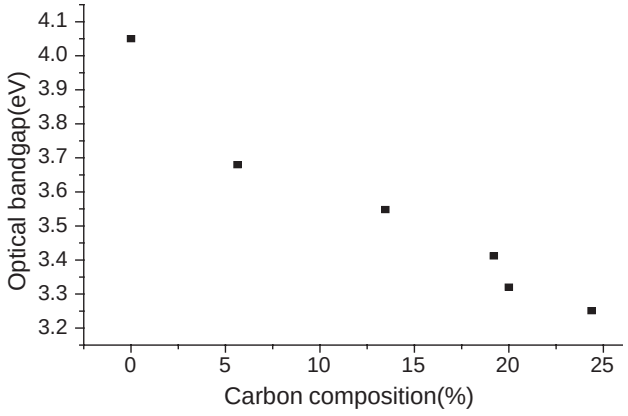

Fig. 4. Variations of the optical band gap E_{opt} (Tauc gap) of a-SiCN thin films with various carbon content.

so far reported for amorphous SiCN-based materials [12]. The small leakage current for the incident light with a wavelength longer than 350 nm is mainly due to the midgap states of the SiCN thin film in amorphous phase. For

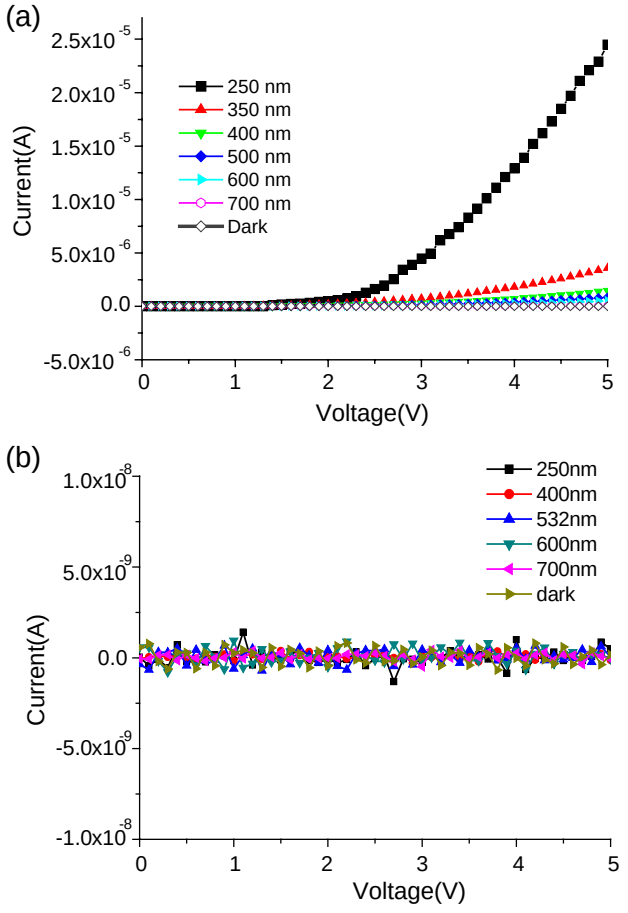

Fig. 5. (a) Characteristics of photocurrent-voltage response of the Au/a-SiCN/Si MSM photodetector device under the irradiation of light sources with various wavelengths. The composition of the a-SiCN thin film in the device is Si(35%): C(24%): N(39%): O(2%) with a thickness of 800 nm. The photocurrent I_p to dark current I_d ratio (PDCR) is 1800 for the incident light with a wavelength of 250 nm under an applied voltage of 5 V. (b) the I-V characteristics of the Au/a-Si3N4/Si device.

comparison, the I-V characteristics of the Au/a-Si3N4/Si device as shown in Fig.5(b) are measured under the same conditions as mentioned above. In contrast, there is no enhancement of current for the incident light with wavelength from 250 to 700 nm, indicating the highly insulating properties of a-Si_3N_4. The carbon content therefore plays an important role in determining the photoconductive response of the a-SiCN thin film. The reason for high photosensitivity of the a-SiCN thin film in the UV region is intriguing. It is believed that the significant enlargement of photoconductivity in the a-SiCN thin films may mainly result from the increase of absorption of light and from the enhancement of the conduction of photo-generated carriers as the carbon content increases. The increasing population of sp^2-bonded C═N or C═C sites with increasing carbon content may also contribute to the increase of photoconductivity due to the delocalization of π orbital characters. The detailed investigation of the transport mechanism depending on the carbon content in the a-SiCN thin film is on the way [13]. Combined with the excellent thermal stability and with the ability for band gap engineering by varying the carbon content, the a-SiCN based MSM device exhibiting high sensitivity to UV illumination can be further developed into the potential applications of UV photodetectors.

4. Conclusion

Optical properties of the a-SiCN thin films have been investigated as a function of carbon content. It was found that the refractive index *n* increases as the carbon content increases. On the other hand, the transmittances and the optical band gaps of a-SiCN thin films progressively decrease with the increasing carbon content, providing the ability for band gap engineering. In addition, the simple Au/a-SiCN/Si MSM device demonstrates excellent selective UV sensing feature, which can be further developed into the potential applications of UV photodetectors.

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