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矽碳氮三元寬能隙半導體之光導電度及傳導特性研究

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矽碳氮三元寬能隙半導體之光導電度及傳導特性研究

計畫類別：■ 個別型計畫　　□ 整合型計畫

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台灣大學材料科學與工程學系　陳俊維

1. 中文摘要

本計劃主要是探討矽碳氮薄膜之光導電特性。主要是探討隨著碳成份之改變，矽碳氮薄膜之光學性質之變化。我們並成功的作出一個高光電流/暗電流比之紫外光偵測器。

。此研究即將於 Diamond and Related materials(2005)發表，並且有一篇正在預計投稿至 Applied Physics Letters。

2. 英文摘要

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.

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[3,4] 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 systematically study on the optical and photoconductive properties of a-SiCN thin films as a function of carbon content and the potential applications for UV light detection.

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 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 xxx, xxx, xxx nm respectively. It is clearly shown that the transmittance of a-SiCN thin films decreases with the increasing carbon content. 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.

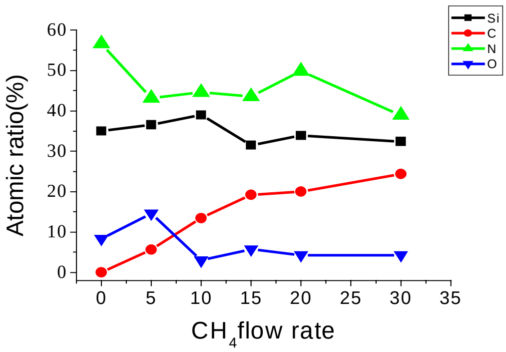


Fig.1. The composition of a-SiCN thin films deposited with different CH_4 flow rates determined by XPS measurement.

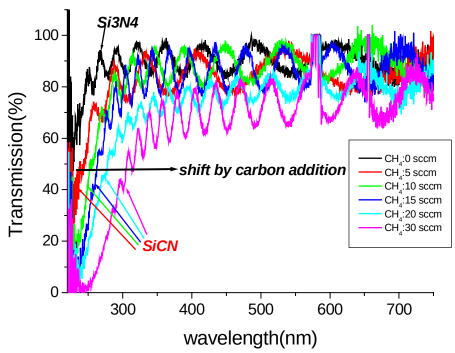


Fig.2. The transmission spectra of a-SiCN thin

films with various carbon content.

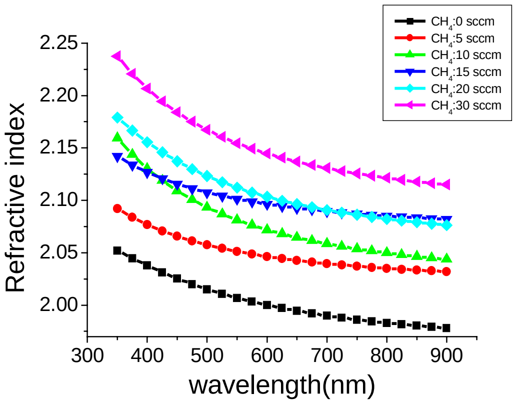


Fig.3. The dispersion of refractive index of a-SiCN thin films with various carbon content.

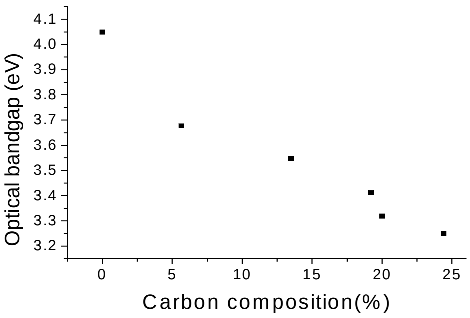
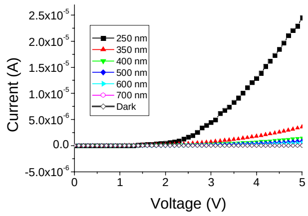


Fig.4 Variations of the optical band gap E_{opt} (Tauc gap) of a-SiCN thin films with various carbon content.

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], $(\alpha h\nu)^{1/2} = B^{Tauc}(h\nu - E_{opt})$ 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 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.



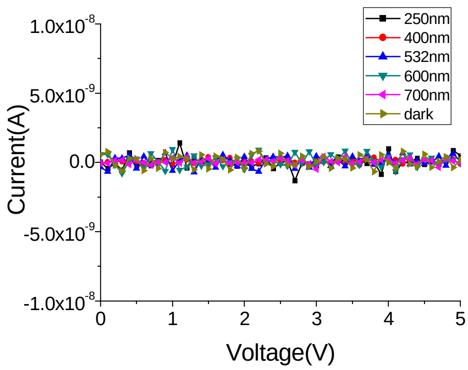


Fig.5.(a) Characteristics of photocurrent-voltage response of the Au/a-SiCN/Si MSM photodetector device under the irradiation of light sources with various wavelengths. The composition of the a-SiCN thin film in the device is Si(35%): C(24%): N(39%): O(2%) with a thickness of 800 nm. The photocurrent 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.

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 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 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.

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.

Acknowledgement

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本計劃發表之論文:

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2. C.W. Chen[a,*], C.C.Huang[a], Y.Y.Lin[a], L.C. Chen[b], K.H. Chen[c], 'Photoconductive and transport properties of a-SiCN thin films., (to be submitted)