Deposition and characterizations of GeCN thin films

Fuchun Xu and Junyong Kang*

Pen-Tung Sah MEMS Research Center, Photonics Research Center, and Department of Physics
Xiamen University, Xiamen 361005, China

ABSTRACT

Germanium-carbon-nitride (GeCN) thin films were deposited on different substrates by reactive magnetic co-sputtering. As-deposited films were characterized with respect to composition, microstructure, and optical reflection. The results show that quality of the film deposited on ZrN substrate is better and the band gaps is about 3.4 eV.

Keywords: GeCN, deposition, structure, optical property

1. INTRODUCTION

In group IV, carbon-based IV-IV compound GeC has very low stress density and small absorption coefficient, which is similar to that of SiC. It is thus easy to modulate its optical band gap in a large scale, making it a very promising semiconductor thin film material for the photo-voltaic and photo-thermic applications[1]. On the other hand, SiC and Si₃N₄ compounds are electronic materials with excellent performance. The miscible compound SiCN display rather peculiar behavior with potential applications in microelectronics and coating technologies. In recent years, SiCN compound has aroused great interest due to its wide band gap and good field emission characteristics[2]. In the literature, there are only a few reports on the research of SiCN and GeC, mainly on the manufacture of the thin films. Moreover, there is no report on ternary GeCN films. In this work, GeCN thin films were prepared by reactive magnetic co-sputtering. The films were investigated by SEM, EDS, XRD and ultraviolet-visible spectrometer.

2. EXPERIMENTAL

GeCN films were deposited using an ultra-high vacuum reactive magnetron sputtering system with a base pressure of 1.3X10⁻⁷ pa. The targets were pure germanium and pyrolytic graphite with 75 mm in diameter. The targets were located at the position of 80 mm from substrate and sputter-cleaned prior to each deposition. A gas mixture of Ar and N₂ were introduced into the growth chamber through a mass-flow controlling system. The total pressure was kept at 8 mTorr and the sputtering power was 350W. The substrates were TiN (100), TiN (111) and ZrN (111). Films were deposited at substrate temperature of 550 °C. The morphologies of the thin films were examined by a field emission scanning electron microscope (FE-SEM, LEO 1530). Meanwhile, their compositions were analyzed by an energy dispersive x-ray spectroscopy (EDS) with a primary electron beam voltage of 20 kV and a liquid N₂ cooled Ge-detector. X-ray

*Corresponding author, email: jykang@xmu.edu.cn, tel: +86-592-2185962, fax:+86-592-2187196
Diffraction (XRD, Rigaku D/Max-RC) was employed to investigate the structure using Cu $K\alpha$ radiation ($\lambda = 0.154178$ nm). Reflection spectra of these films were taken at room temperature with an ultraviolet-visible spectrometer (Varian Cary 300). The energy band gaps of these films were determined from the reflection spectra.

3. RESULTS AND DISCUSSION

XRD and SEM were used to characterize the crystallinity and homogeneity of the GeCN films. The diffraction spectra (Fig. 1) clearly show that all films have new lines, which are distinctly different from those of TiN (100), TiN (111) and ZrN (111). Since the corresponding diffraction data are not available, this makes it difficult to determine the GeCN structure. However, the intensity of the film deposited on ZrN substrate is much stronger than those on TiN. These indicate that the crystallinity the former film is better than later.

The surfaces of as-deposited films appear smooth. The SEM images show that they consist of a number of grains, as shown in Fig. 2. Detail examination exhibits that there are a lot of tiny hollow pits in the films deposited on TiN while the surface of the film deposited on ZrN shows no hollow pit and distinct grain boundaries. These observations agree to the XRD analysis that the quality of the film deposited on ZrN substrate is better.

In addition, the compositions of the films were analyzed by EDS. The atomic percentages of Ge, C, and N are listed in Tab. 1. The mole fraction of Ge is higher in the films deposited on TiN substrates. Moreover, Ge in the film deposited on TiN (100) is more than that of TiN (111). These suggest that Ge is likely to deposit on (100) than on (111). On the basis of the above results, it seems that the quality of GeCN film is better with lower mole fraction of Ge.
The optical properties of the films were investigated by measuring the reflectance spectra. Fig. 3 shows the energy-dependent reflectivity $R$ of the films. The signal noise ratio of the film deposited on ZrN substrate is higher than those on TiN. This makes clear that the film crystallinity also influences the optical properties.

The absorption coefficient $\alpha$ is related to the reflectance light intensity $I$ as bellow:\[^3\]:

$$I = I_1 + I_2 \exp(-2\alpha t), \quad (1)$$

$$2\alpha = \ln[(R_{\text{max}} - R_{\text{min}})/(I - I_{\text{min}})] = \ln[(R_{\text{max}} - R_{\text{min}})/(R - R_{\text{min}})], \quad (2)$$

where $I_1$ is the reflection from the upper surface and $I_2 \exp(-2\alpha t)$ from the inner surface of the film, respectively; $R_{\text{max}}$ and $R_{\text{min}}$ are the maximum and minimum reflectivity in reflection spectra and $R$ is the reflectivity for any intermediate energy photons; $t$ is the thickness of the films. The $\alpha$ due to electron transitions between valence and conduction bands has a power law behavior \[^4\],

$$\alpha h \nu = A(h \nu - E_g)^r, \quad (3)$$

where $A$ is the edge width parameter, $E_g$ is the band gap and $r$ is a number of 1/2 for direct allowed transition and 2 for indirect allowed transition. Suppose GeCN has direct band gap, plots of $\alpha^2$ vs. $h \nu$ can be obtained according to the Eq. (2), as shown in Fig.4. By fitting the data with Eq. (3), the value of $h \nu$ extrapolated to $\alpha = 0$, representing the energy band gap, is determined to be about 3.4 eV. This value shows the GeCN is wide band gap semiconductor that is potential for application to short wavelength optoelectronic devices.
This work was partly supported by “973” Projects (001CB610505), the National Nature Science Foundation (60376015, 90206030, 60336020, and 10134030), grants from the Ministry of Education, Fujian Province, and Xiamen of China.

ACKNOWLEDGMENT

Fig.4 Plots of $\alpha^2$ vs. $hv$ for determination of band gap of GeCN deposited on different substrates: (a) TiN (100); (b) TiN (111); (c) ZrN (111).

REFERENCES