Vacuum 129 (2016) 23–30

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Structural evolution and optical properties of hydrogenated germanium carbonitride films

Chaoquan Hu [a], [b], *, Yuan Tian [a], Jianbo Wang [c], Sam Zhang [d], Diyi Cheng [a], You Chen [a], Kan Zhang [a], [b], Weitao Zheng [a], [e], **

[a] School of Materials Science and Engineering and Key Laboratory of Mobile Materials, MOE, Jilin University, Changchun 130012, China
[b] State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China
[c] School of Science, Changchun University of Science and Technology, Changchun 130022, China
[d] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[e] State Key Laboratory of Automotive Simulation and Control, Jilin University, Changchun 130025, China

ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form
5 April 2016
Accepted 6 April 2016
Available online 8 April 2016

Keywords:
Germanium carbonitride films
Composition
Structure
Optical properties

ABSTRACT

Although the control of bond structure and optical properties in hydrogenated amorphous germanium carbonitride films (a-GeC$_{1-x}$N$_x$:H) is important for technological applications, the composition dependence of chemical bonds, especially hydrogen-containing bonds, is not yet well explored. The evolution in refractive index (n) and Urbach tail width (E_0) remains unclear. Here, we show that nitrogen content (C_N) exerts a significant effect on bonding structure and optical properties of a-GeC$_{1-x}$N$_x$:H films. As C_N increases, the fraction of N—H increases, whereas that of C—H and Ge—H bonds reduces, and Ge—N bonds form at expense of Ge—C bonds. The replacement of carbon by nitrogen induces a substantial decrease in n from 3.0 to 2.3 because of decrease in electronic polarizability. With increasing C_N, a significant increase in E_0 from 198.8 to 327.9 meV takes place. This behavior arises from decrease in dielectric coefficient (ε), rather than the change in the degree of disorder previously believed. The change in E_0 is proportional to the variation in $1/\varepsilon^2$, which agrees well with hydrogen-like atom model. This study discovers that a-GeC$_{1-x}$N$_x$:H films have the apparent tunability of n and E_0 over a wide range, which is useful in controlling the optical transmission and absorption characteristics of these films.

1. Introduction

In recent years, researches on ternary semiconductor films including germanium carbonitride (GeC$_{1-x}$N$_x$) and silicon carbonitride (SiC$_{1-x}$N$_x$) attracted much attention [1–4] because of their wide optical gap [5], strong oxidation [6] and corrosion resistance [7,8], thermal stability (up to 1350 °C) [9,10], high hardness and low friction [11]. These properties make them promising candidates in applications of antireflective and protective coatings on infrared windows as well as using as antireflective coatings on solar cell panels [12–14]. In these applications, the structural and optical properties are of the utmost importance, as these properties of the coatings determine the ultimate performance of the devices. Therefore, it is crucial to understand how to control them.

Studies have revealed that in GeC$_{1-x}$N$_x$ and SiC$_{1-x}$N$_x$ films [15,16], there are Ge—C (Si—C), Ge—N (Si—N), C—C and C—N bonds. Carbon and nitrogen content dramatically affect the bonding structure and optical properties of the films. For instance, the number of Ge—N (Si—N) bonds increases, while that of Ge—C (Si—C) bonds decreases as nitrogen content increases in GeC$_{1-x}$N$_x$ and SiC$_{1-x}$N$_x$ films [17,18]. The Si—C bonds gradually form at the expense of Si—N and C—C bonds with increasing of carbon, and the fraction of C—N first increases and then decreases in SiC$_{1-x}$N$_x$ films [19]. Furthermore, researches have shown that GeC$_{1-x}$N$_x$ and SiC$_{1-x}$N$_x$ films are transparent in the region of visible to infrared wavelengths. By controlling the carbon and nitrogen content, the refractive index of SiC$_{1-x}$N$_x$ films can be modulated from 1.7 to 2.2, and the optical gap from 3.5 to 5.0 eV. These tailored optical properties are favored in applications in solar cell panels and low wavelength emitting diodes.

---

* Corresponding author. School of Materials Science and Engineering and Key Laboratory of Mobile Materials, MOE, Jilin University, Changchun 130012, China.
** Corresponding author. School of Materials Science and Engineering and Key Laboratory of Mobile Materials, MOE, Jilin University, Changchun 130012, China.
E-mail addresses: cqhu@jlu.edu.cn (C. Hu), wtzheng@jlu.edu.cn (W. Zheng).

http://dx.doi.org/10.1016/j.vacuum.2016.04.007
0042-207X/© 2016 Elsevier Ltd. All rights reserved.

Although studies on the bonding structures and optical properties of $GeC_{1-x}N_x$ and $SiC_{1-x}N_x$ films have been reported, the following three questions remain: (i) Hydrogen always appears in the films because of the introduction of hydrogen-containing gases such as methane and acetylene during film deposition. However, how hydrogen atoms are bonded to other atoms in $GeC_{1-x}N_x$ and $SiC_{1-x}N_x$ films remains unanswered. (ii) Although the refractive index of $SiC_{1-x}N_x$ films with different carbon and nitrogen content has been reported, the research on the refractive index of $GeC_{1-x}N_x$ films has not been attempted yet. How does the refractive index of $GeC_{1-x}N_x$ films evolve with composition? (iii) The Urbach tail width (E_0) is an important parameter in determining the optical transmission and optical absorption of amorphous semiconductor films. Although E_0 of unitary (a-Si, a-Ge) and binary (a-SiC, a-SiN, a-GeC) semiconductor films have been reported [20], the studies on E_0 of the ternary films are still lacking. How is the E_0 affected when the film becomes ternary?

With the above three questions in minds, we sputtered $GeC_{1-x}N_x$:H films with different nitrogen content (C_N) by controlling the nitrogen flow rate, and carried out studies of the following three aspects: (i) identifying the evolution of structure and chemical bonds, especially hydrogen-containing bonds; (ii) elucidating the variation in the refractive index with C_N; (iii) clarifying the main contributing factor to E_0 in the ternary $GeC_{1-x}N_x$ films.

2. Experimental details

The germanium carbon films were prepared using radio-frequency (RF) magnetron sputtering single crystal Ge (111) target (100 mm in diameter and 3 mm in thickness) in the mixed discharge gases of Ar (99.99%) and CH_4 (99.99%), wherein the flow rate of CH_4 and Ar were kept at 7.2 and 57.6 sccm at a ratio of 1/8. The incorporation of nitrogen into the germanium carbon films was realized through addition of nitrogen gas in the sputtering atmosphere, where the flow rate of N_2 increased from 0 to 24 sccm, with gradual decreasing flow of CH_4 and Ar while maintaining the ratio of 1/8. During the deposition process, the deposition time, substrate temperature, RF power and the total chamber pressure were kept at 20 min, 200 °C, 150 W and 0.9 Pa, respectively. No bias voltage was applied. The films were deposited on single-crystal Si (001) wafer and optical glass at the same time in the same chamber. The distance between the target and substrate holder was fixed at 80 mm. The chamber was evacuated by a turbomolecular pump to 6×10^{-4} Pa prior to deposition. Before introduction into the vacuum chamber, the Si wafer and glass substrates were cleaned ultrasonically in acetone and petroleum ether, consecutively. The flow rates of Ar, CH_4 and N_2 were accurately controlled by D08-1 A/ZM mass flow controllers. The film thickness was 993, 996, 1003, 802, 824, 938 and 772 nm, determined using a Dektak^3 surface profile measuring system, for the $GeC_{1-x}N_x$:H films with the nitrogen content $C_N = 0$, 1.7, 4.5, 8.4, 9.7, 11.1 and 17.6 atomic %.

The films on Si (001) wafer were examined using Atomic Force Microscopy (AFM, Dimension Icon, Bruker, Germany), Scanning Electron Microscopy (SEM, JSM-6700F, JEOL Inc., USA), Fourier Transform Infra-red spectroscopy (FTIR, Spectrum One B type, Perkin Elmer, USA), X-ray Photoelectron Spectroscopy (XPS, ESCALAB 250, Thermo Electron, USA) for surface morphology, chemical bonding and composition measurements. Those on glass were tested for Ultraviolet-visible-near infrared transmittance (UV-VIS-NIR, Lambda 900, Perkin Elmer, USA) (to avoid absorption rendered by silicon substrate). AFM images were obtained using RTESP probe with a resonance frequency of 300 kHz. The scanning range was $2 \times 2\mu$m. Each measurement was conducted for three times and an average of roughness was calculated with error less than 0.2 nm. The SEM observations were obtained at an acceleration voltage of 8 kV and working distance of 9.1 mm. The IR transmittance was measured with an FTIR spectrometer at a resolution of 4 cm^{-1}. The absorption spectra were calculated from transmission spectra by applying Lambert-Beer's law [21]. XPS measurements were carried out using a monochromatized Al Kα (1486.6 eV) X-ray source (VG ESCA LAB MKII). During XPS experiments, the energy of the Ar^+ beam was set at 3 keV, and an electron flood gun was used for charge compensation. All spectra were collected using the C1s spectra of contaminated carbon with a binding energy of 284.6eV. We used Origin 8.5 software for peak fitting, where the background type was User Defined mode. The position of Gaussian peaks was constrained during the whole fitting process. Ar^+ cleaning procedure was applied to all samples for 180 s prior to XPS quantitative analysis. The content of nitrogen (C_N), carbon (C_C) and germanium (C_{Ge}) were obtained from the integrated area of the corresponding narrow-scanning peaks of N1s, C1s and Ge3d, which are calculated from the following equations:

$$C_N = \frac{\frac{I_{N1s}}{S_N}}{\frac{I_{Ge3d}}{S_{Ge}} + \frac{I_{N1s}}{S_N} + \frac{I_{C1s}}{S_C}}, C_C = \frac{\frac{I_{C1s}}{S_C}}{\frac{I_{Ge3d}}{S_{Ge}} + \frac{I_{N1s}}{S_N} + \frac{I_{C1s}}{S_C}}, C_{Ge} = \frac{\frac{I_{Ge3d}}{S_{Ge}}}{\frac{I_{Ge3d}}{S_{Ge}} + \frac{I_{N1s}}{S_N} + \frac{I_{C1s}}{S_C}} \tag{1}$$

Where, I_{N1s}, I_{C1s} and I_{Ge3d} represent the integrated area of N1s, C1s and Ge3d peaks, respectively. S_N, S_C and S_{Ge} denote sensitivity factors of nitrogen, carbon and germanium, which are 0.42, 0.25 and 0.38 [22], respectively. Since H atoms are bonded with Ge, C and N atoms, the total concentration of bonded H per unit volume (C_H) in the film should be the sum ($C_{Ge-H} + C_{C-H} + C_{N—H}$) of the concentration of H bonded to Ge, C and N per unit volume. To describe the variation of bonded H quantitatively, we applied the relation $C_H = AI_a$, where I_a is the integrated intensity of the absorption band and the constants A are 1×10^{20} cm^{-2} [23] for the Ge—H bands, 1×10^{21} cm^{-2} [24] for C—H bands, and 4.7×10^{20} cm^{-2} [25] for N—H bonds. Wide-angle X-ray diffraction measurements (XRD, D8tools, Bruker, Germany) were carried out at a scan speed of 0.2°/s. The transmittance in the range of 300–2500 nm was obtained with a UV-VIS-NIR spectrometer. According to the envelope method [26], the refractive index of weak absorption band (1300–1700 nm) was calculated by the following equations:

$$n = \left[N + \left(N^2 - S\right)^{1/2}\right]^{1/2} \tag{2}$$

$$N = 2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \tag{3}$$

Where n is the refractive index of films, s is the refractive index of substrate, T_M and T_m represent the upper and lower transmittance, respectively. Dielectric constant ε was calculated by $\varepsilon = n^2$. Urbach tail width was extrapolated from the inverse slope of $ln\alpha \sim h\nu$ line in the region of exponential absorption, where α and $h\nu$ being the absorption coefficient and incident photon energy, respectively.

3. Results and discussion

3.1. Composition and structure

Fig. 1a plots a typical full-scanning XPS spectrum of $GeC_{1-x}N_x$:H films, where the appearances of Ge3d, Ge3p, Ge3s, Ge Auger, C1s and N1s peaks suggest germanium, carbon and nitrogen exist in the film. Fig. 1b plots the content of nitrogen, carbon and germanium (C_N, C_C and C_{Ge}) in the films as a function of nitrogen flow rate (R_{N2}).