Hardness and optical gap enhancement of germanium carbon films by nitrogen incorporation

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ABSTRACT

Low hardness and optical gap of amorphous germanium carbon films limit their applications as antireflective and protective coatings (APC). This study reports that incorporating suitable amount of nitrogen into the films during the sputtering process effectively enhances the hardness and optical gap without significant sacrifice of the original far-infrared transmission. Our first-principle calculations show that the observed hardness and optical gap enhancement arises from transition from weak Ge–C to strong Ge–N bonds with nitrogen incorporation. These nitrogen-incorporated germanium carbon films are good as APC on high-speed far-infrared windows.

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1. Introduction

An increasing number of military applications in recent years are associated with high-speed windows operating in the far-infrared region of 8–11 μm [1]. Germanium carbon films have attracted much attention because of their excellent properties: low stress, low light absorption, good adhesion on many far-infrared substrates, etc. This makes them promising candidate for application as antireflective and protective coatings (APC) on far-infrared windows [2,3]. However, there are two problems associated with germanium carbon films as APC. One is the relatively low hardness (about 6.0–8.5 GPa depending on Ge/C atomic ratio) [4], which makes the films difficult to resist impact of raindrops and sands flying at high speed. Another is the narrow optical gap (approximately 0.60–1.16 eV depending on Ge/C atomic ratio) [1], which may cause free-carrier optical absorption and emission in infrared wavebands under aerodynamic heating. These shortfalls largely limit their further application as APC on hypersonic far-infrared windows. Though germanium carbon films' key properties have been reported, such as optical [5,6] electrical [7,8], mechanical [9,10] and structural [11–13], the improvement of hardness and optical gap for these films has not yet been attempted.

In this work, nitrogen is incorporated into germanium carbon films during magnetron sputtering. It is found that suitable amount of nitrogen into germanium carbon films enhances the hardness and optical gap without significant sacrifice of the original far-infrared transmission. The mechanism behind these enhancements is elucidated by means of chemical bonding measurements and the first-principle calculations.

2. Experimental & computational 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 was kept at 7.2 and 57.6 sccm with 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 containing Ar and CH_4, whereas the flow rate of N_2 increased from 0 to 24 sccm, the flow rate of CH_4 and Ar gradually decreased with an unchanged ratio of 1/8. During film deposition process, the deposition time, substrate temperature, radio-frequency power and total sputtering gas pressure were kept at 20 min, 200 °C, 150 W and 0.9 Pa, respectively. The films were deposited on single-crystal Si (001) wafer and optical glass at the same time. No-nitrogen films were also deposited as control. 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

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Si and glass substrates were cleaned ultrasonically in acetone and petroleum ether, consecutively. The flow rate of Ar, CH_4 and N_2 was accurately controlled by D08-1A/ZM mass flow controllers. The film thicknesses were found to be 993, 996, 1003, 802, 824, 938 and 772 nm, respectively, for the N-incorporated germanium carbon films with the nitrogen content C_N = 0, 1.7, 4.5, 8.4, 9.7, 11.1 and 17.6%.

The films deposited on Si (001) substrates were subjected to Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and nanoindentation for chemical bonding, composition and hardness measurements, and those on glass underwent UV–VIS–NIR transmittance tests (to avoid absorption rendered by silicon substrate). The IR transmittance was measured with an FTIR spectrometer (PerkinElmer Spectrum One B type) at a resolution of 4 cm^{-1}. The absorption spectra were calculated from transmission spectra by applying Lambert–Beer's law [14]. XPS measurements were carried out using a monochromatized Al Kα (1486.6 eV) X-ray source (VG ESCA LAB MKII). Ar$^+$ cleaning procedure was applied to all samples for 180 s prior to XPS quantitative analysis. The nitrogen (C_N), carbon (C_C) and germanium content (C_{Ge}) of the films were obtained from the integrated area of the corresponding narrow-scanning peaks of XPS N1s, C1s, and Ge3d, which were calculated from the following equation.

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

$$C_{Ge} = \frac{\frac{I_{Ge3d}}{S_{Ge}}}{\frac{I_{Ge3d}}{S_{Ge}} + \frac{I_{N1s}}{S_N} + \frac{I_{C1s}}{S_C}}$$

where I_{N1s}, I_{C1s} and I_{Ge3d} represent the integrated area of the N1s, C1s, and Ge3d peaks, and S_N, S_C and S_{Ge} denote sensitivity factors of nitrogen, carbon and germanium, which are equal to 0.42, 0.25 and 0.38, respectively. The transmittance in the range of 300–2500 nm was obtained with a UV–VIS–NIR spectrometer (PerkinElmer Lambda 900). The absorption coefficients (α) of samples were determined from the transmission spectra using a well-known procedure described by Swanepoel [15]. The optical gap of the films was determined by plotting $(\alpha h\nu)^{1/2}$ against the photon energy $h\nu$ according to the Tauc equation. The film hardness and elastic modulus were measured using Nano-Indenter XP equipment with a Berkovich diamond tip. The film thicknesses were determined by using a Dektak3 surface profile measuring system.

The electronic structures of bulk GeC (space group $F\bar{4}3m$, prototype β-SiC) and Ge_3N_4 (space group $P6_3/m$, β-Ge_3N_4) were calculated using CASTEP code [16] (Module of Materials Studio 5.0) based on density functional theory using Vanderbilt-type ultrasoft pseudopotentials [17] and plane-wave expansion of wave functions. The generalized gradient approximation in the scheme of Perdew–Burke–Ernzerhof [18] was used to describe the exchange and correlation potential. The plane wave energy cutoff was set to 500 eV for GeC and Ge_3N_4 in our calculations. The Brillouin zone was sampled by $8 \times 8 \times 8$ special k-point meshes for cubic GeC and hexagonal Ge_3N_4 using the Monkhorst–Pack method [19]. The Brodyden–Fletcher–Goldfarb–Shanno optimization scheme was used to optimize the lattice parameters [20]. Based on these settings, the convergence tolerance of energy, maximum force, and maximum displacement became 2×10^{-5} eV/atom, 0.05 eV/Å, and 2×10^{-3} Å, respectively. The average bond energy E_b for Ge–C and Ge–N bonds were calculated as follows:

$$E_b(GeC) = \frac{a\mu(Ge) + b\mu(C) - E(GeC)}{k} \tag{1}$$

$$E_b(Ge_3N_4) = \frac{a\mu(Ge) + c\mu(N) - E(Ge_3N_4)}{k} \tag{2}$$

where a, b, and c are the numbers of Ge, C, and N atoms in the unit cell of GeC or Ge_3N_4, k is the number of Ge–C or Ge–N bonds in the unit cell, E(GeC) and E(Ge_3N_4) are the total energies of cubic GeC and hexagonal Ge_3N_4 unit cell, μ(Ge), μ(C) and μ(N) are the total energies of single Ge, C, and N atoms.

3. Results and discussion

3.1. Nitrogen-induced changes in mechanical and optical properties

Fig. 1 displays the hardness, optical gap and absorption edges of germanium carbon films. With N incorporation, the hardness of the films almost doubles (increased from 6.3 to 11.7 GPa from C_N = 0% to C_N = 17.6%, Table 1). Meantime, the optical gap widens from 1.16 to 1.63 eV (an increase of 41%, Table 1). These results suggest that N incorporation is effective in improving the hardness and optical gap of germanium carbon films. High hardness is necessary in resisting high-speed impact deformation when the window is in a particle-impacting environment. At the same time, wide optical gap is more favorable to reducing free-carrier optical absorption and emission of the films in infrared wavebands under aerodynamic heating [21]. As such, N incorporation renders improvements in both hardness and optical gap thus makes germanium carbon films suitable for applications as APC on high-speed far-infrared windows.

Fig. 2a plots FTIR absorption spectra of germanium carbon films with varying nitrogen. Without nitrogen (C_N = 0%), the center of absorption bands is located in ~16.5 μm, which is far away the application concerned region of 8–11 μm, indicating the film without nitrogen is optically transparent in that region. As nitrogen is incorporated into the film, the lattice-vibration absorption band continuously shifts to shorter wavelengths (the peak values in Fig. 2a or explicitly plotted in Fig. 2b). When C_N is not more than 9.7%, no remarkable optical absorption appears in the 8–11 μm region. However, as C_N goes over 9.7%, considerable optical absorption occurs in the interested region, causing decreased optical transmission. Therefore, excessive nitrogen incorporation needs to be avoided.

3.2. Nitrogen-induced transition from Ge–C to Ge–N bonds

In order to understand why nitrogen incorporation causes hardness increase and at the same time optical gap widening, we have investigated the composition and bonding properties of the films by employing XPS and FTIR measurements.

Fig. 2c plots carbon and germanium content in the films as a function of nitrogen content (C_N). Without nitrogen (C_N = 0%), the carbon and germanium contents in the film are 21.0% and 79.0%, respectively. As nitrogen is incorporated, the carbon content in the film experiences linear reduction while the germanium content remains almost unchanged. The increase in the nitrogen content and at the same time a decrease in the carbon content are due to the enhancement in nitrogen gas supply and simultaneously reduction in methane gas supply. The unchanged germanium content is mainly due to the constant total sputtering pressure and RF power, which causes the sputtering yield of germanium target keep basically unchanged. Because the germanium content is almost constant and a sum of germanium, carbon and nitrogen content is equal to 100%, the increase in nitrogen content in the films results in an almost linear reduction in the carbon content. This observation indicates that nitrogen incorporated into Ge–C network "squeezed out" some of the carbon, forming Ge–N bonds as is further confirmed by FTIR measurements.

From the FTIR spectra shown in Fig. 2a and b, the dominant absorption peak appears at ~16.5 μm (~605 cm^{-1}) for the film without nitrogen. Based on our previous studies [4], this absorption peak is assigned to the Ge–C bond. However, as nitrogen is introduced into the film, the absorption peak consistently shifts to shorter wavelengths (or higher wavenumbers) (Fig. 2b). As the nitrogen content is increased