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The infrared optical and mechanical properties of germanium carbide films prepared by ion beam sputtering

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Abstract: Germanium carbon ($Ge_{1-x}C_x$) thin films were deposited by ion beam sputtering deposition of Ge target in a CH_4/Ar discharge. The surface morphology, chemical structure, infrared optical and mechanical properties of the $Ge_{1-x}C_x$ films were investigated by atomic force microscopy (AFM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy and nano-indentation, respectively. The relationship between ion beam voltage and film properties was discussed. The results show that the surface roughness decreases with increasing of the ion beam voltage. The film deposited at a higher voltage has lower carbon content and higher fraction of Ge-C bonds. The film has excellent infrared optical and mechanical properties. The films show good transparent over a wide range. Due to the content of the carbon decreasing with increasing of voltage, the refractive index increases obviously as the ion beam voltage increases from 300 V to 800 V. The hardness of the film is above 8 GPa. With the Ge-C bonds instead of the C-C bonds and $C\text{-}H_n$ bonds, the hardness of the film increases with increasing ion beam voltage.

Key words: ion beam sputtering deposition, germanium carbon, infrared optical property, mechanical property
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离子束溅射法制备碳化锗薄膜的红外光学特性和力学特性

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摘要:采用离子束溅射法通过在 CH_4 和 Ar 的混合气体中溅射 Ge 靶材制备碳化锗($Ge_{1-x}C_x$)薄膜.分别通过原子力显微镜、拉曼光谱和 X 射线光电子能谱、傅里叶变换红外光谱以及纳米压痕测试研究了薄膜的表面形貌、化学结构、光学特性和力学特性.同时分析了制备薄膜时的离子源束压和薄膜性质之间的关系.结果表明,薄膜的粗糙度随束压的增大而减小.在较高束压下制备的薄膜含有较少的 C 元素和较多的 Ge-C 键.薄膜具有非常好的红外光学特性和力学特性.薄膜在较大波长范围内具有良好的透光性能.C 元素含量随着束压的升高而降低,进而导致薄膜的折射率在束压从 300 V 增大到 800 V 的过程中逐渐升高.薄膜的硬度大于 8 GPa.由于薄膜中的 Ge-C 键代替了 C-C 键和 $C\text{-}H_n$ 键,薄膜的硬度随束压的增加逐渐增加.

关　键　词:离子束溅射沉积;碳化锗;红外光学特性;机械特性

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Introduction

In recent years, more and more researches were focused on the applications of the $Ge_{1-x}C_x$ films for the hard protective thin films on infrared windows[1-2]. Concerning the applications of $Ge_{1-x}C_x$ films for protective films, there are four advantages as follows: (1) good adhesion on many infrared substrates[3-4]; (2) low extinction coefficient over a wide range[5]; (3) good mechanical properties[6-7]; (4) by varying the composition of the film, the refractive index can be widely changed in the range 2 ~ 4[8-9]. These excellent properties make the film having the great potential to be used as multilayer anti-reflective and protective coatings.

The film can be prepared by many deposition methods including molecular beam epitaxy technique[10], glow discharge[11], chemical vapor deposition[12-13] and radio frequency reactive magnetron sputtering[14-15]. Due to the excellent controllability and stability, chemical vapor deposition and radio frequency reactive magnetron sputtering are widely used. Chemical vapor deposition method uses the toxic germane and methane as reaction gas, which results in a relative high hydrogen content in the films since both reaction gases contain hydrogen. So the films are not suitable to be used as infrared optical thin film because the Ge-H bonds and $C\text{-}H_n$ bonds may cause the decrease in infrared transmittance of the films[2,16]. Radio frequency reactive magnetron sputtering method is an effective way to prepare $Ge_{1-x}C_x$ film in a high deposition rate. However, as the energy of the accelerated electrons is not high enough to decompose the CH_4 completely, the content of the carbon varies at a small range[17]. In recent years, ion beam sputtering deposition has also been used in a number of studies aimed to obtain high-quality optical films[18-19]. As the energy of the ion used for sputtering is higher than those in the two techniques mentioned above, films deposited by this process usually have excellent optical and mechanical properties. However there is no report on the $Ge_{1-x}C_x$ prepared by this method.

In this work, $Ge_{1-x}C_x$ films were prepared by ion beam sputtering deposition at different ion beam voltage. The focus was on the relationship between the chemical bondings and the properties of the films. The surface morphology, chemical bonding, infrared optical and mechanical properties were also investigated.

1 Experiments

The $Ge_{1-x}C_x$ films were deposited on polished Si and Ge substrate by ion beam sputtering of a single crystal Ge target (99.995%) in mixed discharge gases of Ar (99.999%) and CH_4 (99.99%). The base pressure of the deposition chamber was less than 1×10^{-3} Pa. In order to avoid the poison of the target, the CH_4 was introduced on the surface of the substrate. The Ar was introduced into the ion source. The gas flow rates of Ar and CH_4 were controlled by using mass flow controller. The Ar and CH_4 flow rates were 32 sccm and 80 sccm, respectively. The ion beam voltages were 300 V, 500 V and 800 V, respectively. The ion beam current was 150 mA. The films were deposited at room temperature.

The root mean squared (RMS) roughness and morphology were investigated with a Nanosurf easyscan 2 Flex atomic force microscope operating in tapping Mode. Raman spectroscopy of the deposited material was performed using a DXR Raman spectrometer with the laser line at 532 nm. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer). Prior to XPS analyses, argon ion cleaning lasting 120 s was accomplished by 5 keV ion beam energy for all samples. The XPS peak 4.1 was used to fit the XPS spectra. The line shape of each peak was assumed to be 90% Gaussian and 10% Lorentzian. The transmittance of the samples in the range 2000 ~ 10000 nm was obtained by a FTIR spectrometer (PE spectrum GX). The refractive index, extinction coefficient and the physical thickness of samples were determined from fitting the whole infrared optical transmittance spectrum by using the WVASE32 software (J. A. Woollam. CO.) The physical thickness of the films deposited at 300 V, 500 V and 800 V are 227 nm, 295nm and 354 nm, respectively. The film hardness was described by Nanoindentation measurement (Nano Indenter G200, Agilent Tech.), and Berkovich indenter was chosen during measurement. The films deposited on Si substrates were used for most of the measurements. In order to avoid the strong absorption from the silicon substrate, the $Ge_{1-x}C_x$ films deposited on the Ge substrates were used for FTIR test.

2 Results and discussion

AFM was used to investigate and measure the surface roughness of the films. The three-dimensional AFM images of the films deposited at different ion beam voltage are shown in Fig. 1. The average heights of clusters along the z-axis for the film deposited at different voltage are about 19.7 nm, 16.4nm and 9.74 nm, respectively.

The surface roughness of the $Ge_{1-x}C_x$ film is shown in Fig. 2. The surface roughness of the films deposited at 300 V, 500 V and 800 V are 2.520 nm, 1.274 nm and 0.606 nm, respectively. It can be seen that the surface roughness decreases with increasing of the ion beam voltage. The reasons for the phenomenon are as the following. Firstly, according to the growth theory, the thicker film could have the better continuous surface, resulting in lower surface roughness. As the physical thickness of the film increases with increasing of the ion beam voltage from 300 V to 800 V, the surface roughness decreases with increasing of the ion beam voltage. Secondly, as the ion beam voltage increases, the energy of Ar ions used for sputtering increases, which results in an increase of the average kinetic energy of Ge atoms sputtered from the target. It means the Ge atoms have more energy to move on the surface of film. So increasing the ion beam voltage will decrease the number of voids in the film and make the film smooth.

Raman spectrum for the $Ge_{1-x}C_x$ films in the range of 40 ~ 2 000 cm^{-1} is shown in the Fig. 3. It is obvious that there are three bands for each film in the spectrum. They are associated with Ge-Ge (50 ~ 350 cm^{-1}), Ge-C (500

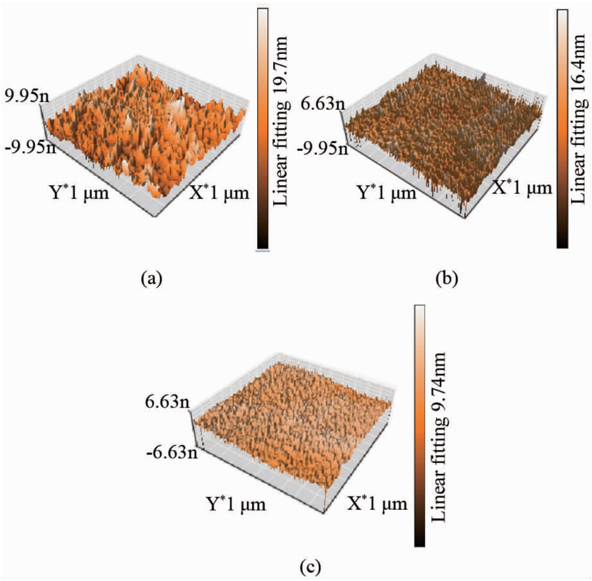

Fig. 1 AFM images of the $Ge_{1-x}C_x$ films deposited at different ion beam voltages, (a) 300 V, (b)500 V, and (c) 800 V
图 1 不同束压制备的 $Ge_{1-x}C_x$ 薄膜的 AFM 图像 (a) 300 V,(b)500 V,(c) 800 V

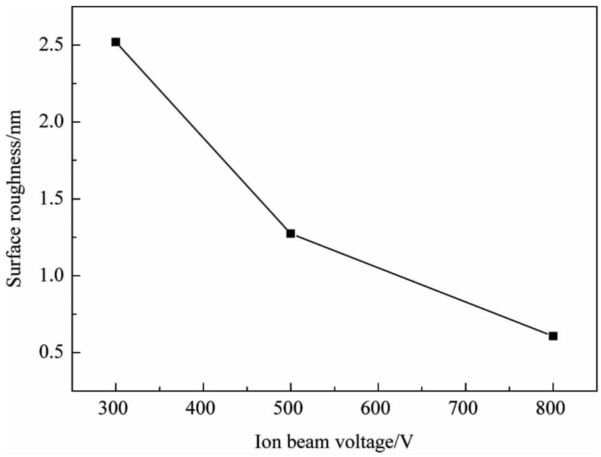

Fig. 2 Surface roughness of the $Ge_{1-x}C_x$ films deposited at different ion beam voltage
图 2 不同束压制备的 $Ge_{1-x}C_x$ 薄膜的表面粗糙度

~ 600 cm^{-1})[20] and C-C (1 200 ~ 1 700 cm^{-1}) bonds[21]. The sharp peaks around 80 cm^{-1} and 260 cm^{-1} may indicate the formation of Ge clusters in the film. It can be seen from Fig. 3 that there is only one peak in the range of 1 200 ~ 1 700 cm^{-1}. The center of the band is around 1 400 cm^{-1}. It cannot be fitted by G band (at 1 580 cm^{-1}) and D band (at 1 350 cm^{-1}). The peak stems from the vibration of sp^2 carbon sites[22]. The intensity of the band between 1 200 ~ 1 700 cm^{-1} decreases with increasing of the ion beam voltage, which may imply that the fraction of sp^2 C-C bonds in the films decreases as ion beam voltage increases. The variation of intensity of the sp^2 C-C bonds can also be described by the ratio (I_C/I_{Ge}). The I_C and I_{Ge} are the integrated area of C-C band and Ge-Ge band, respectively. The ratios (I_C/I_{Ge}) of the films prepared by different ion beam voltage are 0. 159, 0. 152 and 0. 063, respectively. It also implies that the fraction of sp^2 C-C bonds decreases with increasing of the ion beam voltage. As the kinetic energy of the argon ions used for sputtering increases with increase of the ion beam voltage, the sputtering yield of germanium will also increase. It means that the film prepared at a higher ion beam voltage could contain more germanium atoms and less carbon atoms, which results in decreasing of the fraction sp^2 C-C bonds in the $Ge_{1-x}C_x$ film.

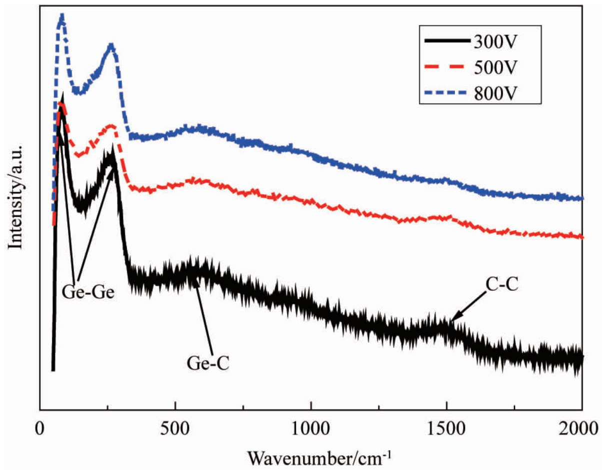

Fig. 3 Raman spectra for the $Ge_{1-x}C_x$ films deposited at different ion beam voltage
图 3 不同束压制备的 $Ge_{1-x}C_x$ 薄膜的拉曼光谱

XPS is an effective way to obtain quantitative information about composition and chemical bonding of the films. The contents of the C in the films prepared by different ion beam voltage are 80. 8% , 44. 7% and 42. 86% , respectively. It can be concluded that higher ion beam voltage could result in the increasing of the number of germanium atoms sputtered from the target.

The Narrow-scanning XPS spectra of C_{1s} for $Ge_{1-x}C_x$ films are shown in Fig. 4. It can be seen that the features of C_{1s} spectra gradually change as ion beam voltage increases. The C_{1s} peak positions of the films are located at 284. 8 eV, 284. 7 eV and 284. 6 eV with increasing of ion beam voltage from 300 V to 800 V, respectively. As shown in Fig. 4, the spectra of C_{1s} can be divided into three peaks around 283. 8, 284. 6 and 285. 7 eV. These peaks are ascribed to Ge-C bonds, C-C bonds and C-H_n bonds, respectively[23]. The binding Energy of the C_{1s}, Ge-C, C-C and C-H_n in $Ge_{1-x}C_x$ films deposited at different ion beam voltage are listed in Table 1. It can be seen from Table 1 that the binding Energy of C_{1s}, Ge-C, C-C and C-H_n in $Ge_{1-x}C_x$ films decrease with increasing ion beam voltage from 300 V to 800 V. It suggests that the chemical environment around C atoms can be significantly changed by varying the ion beam voltage.

The relative contents of the Ge-C bonds, C-C bonds and C-H_n bonds as a function of ion beam voltage are

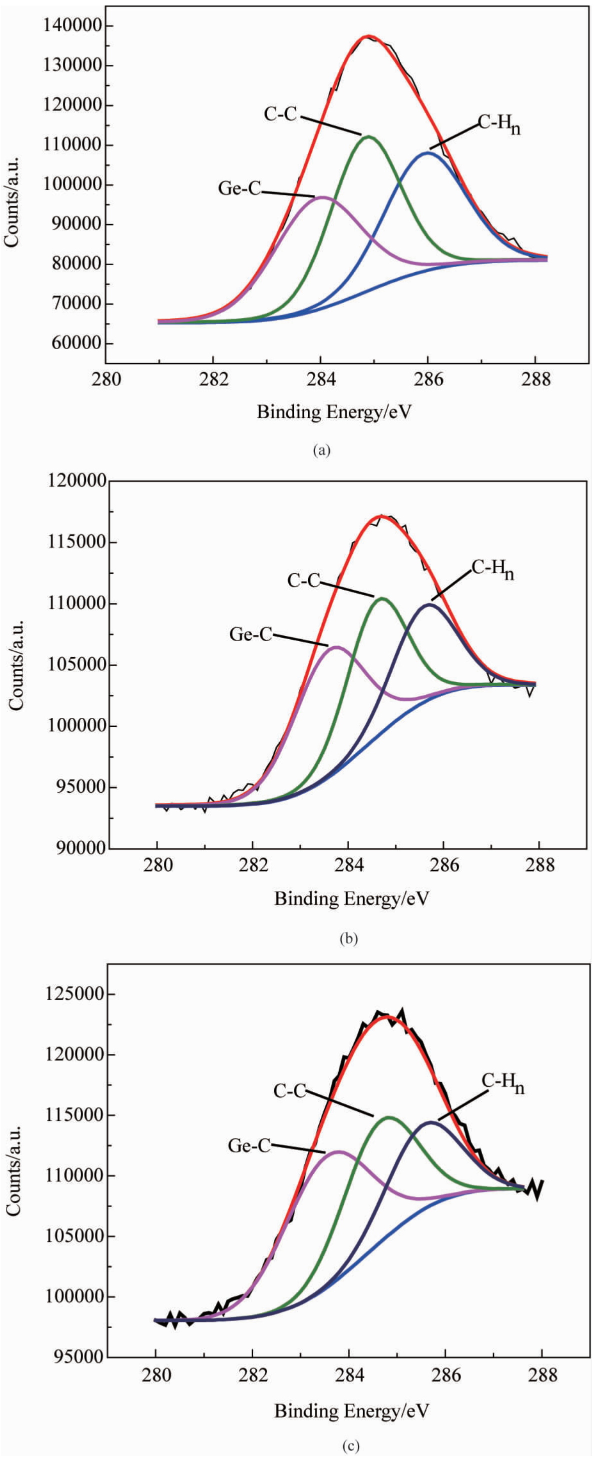

Fig. 4 The Narrow-scanning XPS spectra of C_{1s} for the $Ge_{1-x}C_x$ films deposited at different ion beam voltage (a) 300 V, (b) 500 V, and (c) 800 V

图 4 不同束压制备的 $Ge_{1-x}C_x$ 薄膜的 C_{1s}XPS 谱图 (a) 300 V, (b) 500 V, (c) 800 V

shown in Fig. 5. As ion beam voltage increases from 300V to 800V, the content of Ge-C bonds increase while the content of C-C bonds decreases. It was reported that the chemical environment surrounding the incorporated C atoms had great influence on the hybridized configuration of carbon atoms[24]. It is known to us that the germanium

Table 1 Binding Energy of the C_{1s}, Ge-C, C-C and C-H_n in $Ge_{1-x}C_x$ films deposited at different ion beam voltage

表 1 不同束压制备的 $Ge_{1-x}C_x$ 薄膜的 C_{1s}, Ge-C, C-C 和 C-H_n 的结合能

ion beam voltage/V	binding Energy of the C_{1s}/eV	binding Energy of the Ge-C /eV	binding Energy of the C-C /eV	binding Energy of the C-H_n/eV
300	284.8	283.9	284.8	285.9
500	284.7	283.6	284.6	285.6
800	284.6	283.5	284.6	285.5

only has the sp^3 hybridization. The carbon atom mainly bonds to germanium atom by sp^3 hybridization in the Ge-rich films. The content of the germanium increases with the increase of the ion beam voltage. Since the germanium atoms supply more tetrahedral configuration, the carbon atoms have more chance to bond with germanium atom in sp^3 hybridization. As a result, the relative content of Ge-C bonds increases while the content of C-C bonds decreases. It also can be seen from Fig. 5 that the content of C-H_n bonds decreases as the voltage increases from 300 V to 800 V. It is obvious that the C-H_n bonds in the film are from the CH_4 with the tetrahedron structure. Since the ion beam voltage increases, the energy of Ar ions used for sputtering increases, which lead to the increasing of sputtering yield and the energy of the Ge. It could promote the decomposition of the C-H_n bonds, resulting in the decrease of the fraction of C-H_n bonds.

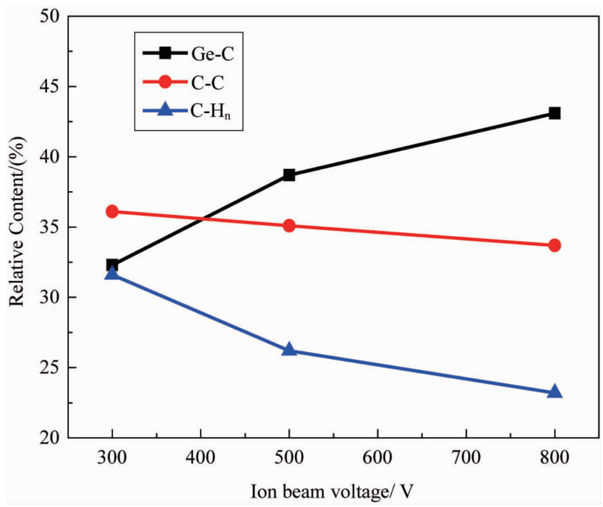

Fig. 5 The relative content of the Ge-C bonds, C-C bonds and C-H_n bonds for the $Ge_{1-x}C_x$ films deposited at different ion beam voltage

图 5 不同束压制备的 $Ge_{1-x}C_x$ 薄膜的 Ge-C 键, C-C 键和 C-H_n 键相对含量

Figure 6 shows the FTIR spectra of the $Ge_{1-x}C_x$ film deposited on Ge substrate at different ion beam voltage in the range of 2 000 ~ 10 000 nm. It can be seen from Fig. 6 that the transmittance for the Ge substrate is improved in the range of 2 000 ~ 10 000 nm. It means that the $Ge_{1-x}C_x$ films have low refractive index and extinction coefficient. This result suggests the films have the potential to be used as an antireflective film. It is shown in Fig. 6 that the maxim of the transmittance decreases with increasing of ion beam voltage. It also can be seen that as the ion beam voltage increases, the position of the peak in the spectra shifts to long wavelength. It implies that the optical thickness of thin films increases with increasing ion beam voltage. There is only one obvious absorption peak at 5100 nm in the spectra for each $Ge_{1-x}C_x$ film. The peaks can be attributed to the Ge-H stretching mode[25]. No strong absorption peaks around 3 400 nm or 6 900 nm for all the films are found. This result suggests that the films may have low content of the $C\text{-}H_n$ bonds. It can be concluded that the film prepared by ion beam sputtering has excellent infrared transparent property.

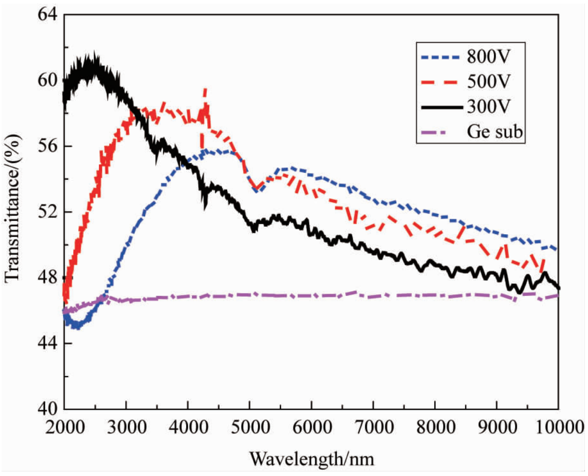

Fig. 6 The FTIR spectra of the $Ge_{1-x}C_x$ films
图 6 $Ge_{1-x}C_x$ 薄膜的傅里叶红外光谱

Figure 7 shows the optical constants of the $Ge_{1-x}C_x$ films obtained by fitting with transmittance spectrum. The dispersion characteristics of the optical constants of $Ge_{1-x}C_x$ films are obvious. Due to the absorption peaks at 5100 nm in the transmittance spectra, the peaks are at the same position in the dispersion curves of the optical constants. It can be seen that the film prepared by lower ion beam voltage exhibits a lower refractive index in the whole spectral range. The film with higher content of carbon will have more similar refractive index to a-C:H film, while the film with higher content of germanium will have more similar refractive index to Ge film. It is known to us that the refractive index of the Ge films is higher than that of the a-C:H films. As mentioned, the content of carbon in the film increases with decreasing of ion beam voltage. So the refractive index of the $Ge_{1-x}C_x$ films increases with increasing ion beam voltage. The extinction coefficients of $Ge_{1-x}C_x$ films are low, which is of practical significance for designing and preparing multilayer IR coatings.

Figure 8 displays the hardness of the $Ge_{1-x}C_x$ films prepared at different ion beam voltage. The hardness of the film is above 8 GPa, which is higher than those of the films prepared by chemical vapor deposition and radio frequency reactive magnetron sputtering (6 ~ 8 GPa)[17,24]. It can be seen that as the ion beam voltage

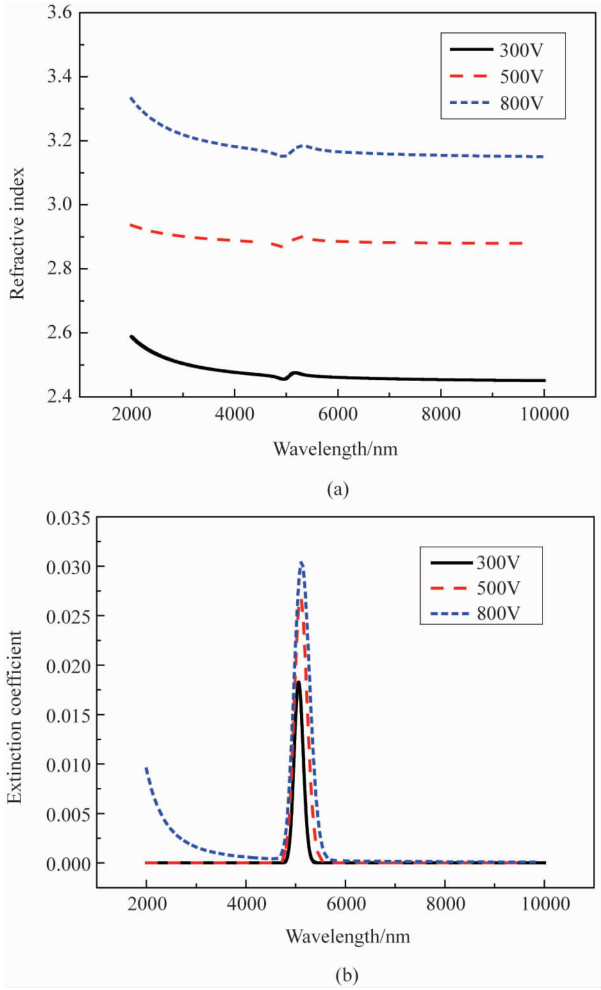

Fig. 7 The optical constants of the $Ge_{1-x}C_x$ films (a) refractive index, (b) extinction coefficient
图 7 $Ge_{1-x}C_x$ 薄膜的光学常数 (a) 折射率,(b)消光系数

increases, the hardness of the films increases. It is confirmed that the chemical structure has a great effect on the hardness of the $Ge_{1-x}C_x$ film. The structure of $Ge_{1-x}C_x$ is more similar to that of diamond-like carbon because of the higher content of Ge-C bonds, which results in the increasing of the hardness of the film. On the contrary, higher content of the sp^2 C-C bonds leads to the structure more similar to that of graphite which has much lower hardness. In addition, $C\text{-}H_n$ bonds are terminating bonds. The film with higher content of $C\text{-}H_n$ bonds will have lower hardness. XPS test indicates that the Ge-C bonds instead of the C-C bonds and $C\text{-}H_n$ bonds with increasing of ion beam voltage. So the hardness of the $Ge_{1-x}C_x$ the film increases with the increasing of the ion beam voltage.

3 Conclusions

$Ge_{1-x}C_x$ films have been prepared by ion beam sputtering a pure Germanium target at different ion beam voltage in a CH_4/Ar mixture. The films prepared by the new method exhibit good infrared optical and mechanical properties. It is found that the ion beam voltage has great

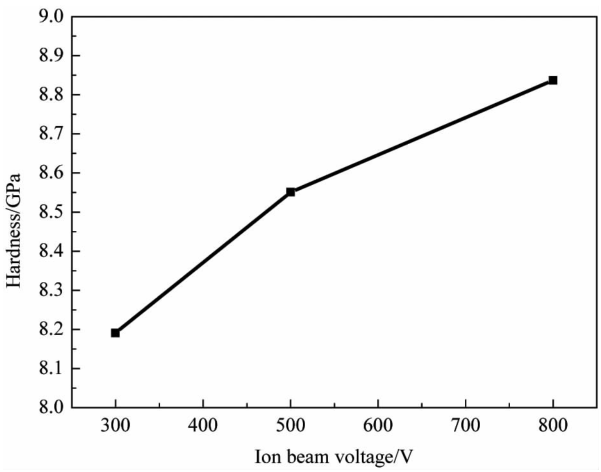

Fig. 8 The hardness of the $Ge_{1-x}C_x$ films
图 8 $Ge_{1-x}C_x$ 薄膜的硬度曲线图

influence on the properties of the $Ge_{1-x}C_x$ films. The surface roughness decreases while the ion beam voltage increases from 300 V to 800 V. The C atoms are more likely to bond in sp^3 hybridization at higher ion beam voltage. The film prepared at higher voltage has the higher refractive index. The extinction coefficient is low enough for the film to be designed and prepared for multilayer infrared coatings. The hardness of the film increases with increasing of the ion beam voltage. The films are the potential candidates to be used as antireflective and protective films.

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