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ARTICLE

Effect of Annealing Temperature on Optical Properties and Surface Structure of Germanium Thin Films

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Abstract: The influence of annealing temperature on optical properties and surface structure of Ge films prepared by electron beam evaporation was investigated. Ge films with a thickness of about 850 nm were prepared on silicon substrate and annealed at 350, 400, 450, and 500 °C. The transmittance of the film was measured by infrared spectrometer. The variation of refractive index and extinction coefficient of thin films was obtained by spectral inversion method. The crystal properties and surface morphology of the specimens were analyzed by X-ray diffraction and atomic force microscope. Results show that compared with the properties of films before annealing, the transmittance of films after annealing is increased, while the refractive index and extinction coefficient become decreased. When the annealing temperature increases from 350 °C to 500 °C, the transmittance and refractive index gradually decrease, while the extinction coefficient gradually increases. Crystallization occurs in the films after annealing above 400 °C and the Ge(111) crystal plane is the preferred growth orientation. With increasing the annealing temperature, the grain size becomes larger, the granular particles appear on the film surface, and the surface roughness is increased.

Key words: annealing; germanium thin films; optical properties; surface structure

In order to improve the stealth performance of materials, various kinds of photonic crystal stealth materials have been developed in recent years. One-dimensional photonic crystal materials are widely used due to their advantages of simple design and adjustable stealth band, and most of them in infrared band are designed and prepared based on Ge/ZnS materials[1,2]. Ge thin film materials have important applications in photonic crystal stealth materials. Ge has excellent infrared properties and is widely used in infrared optoelectronic devices as an important film material with high refractive index. In addition, Ge coupled with materials of low refractive index such as ZnS, ZnSe, and SiO_2 is commonly used to prepare infrared filters, high reflective films, and anti-reflection films[3-6].

Preparation methods of germanium films include electron beam evaporation[7,8], magnetron sputtering[9,10], and chemical vapor deposition[11]. Electron beam evaporation has excellent characteristics such as high deposition rate and can achieve uniform films, so it was adopted in this research to prepare Ge films.

Optical properties and surface structure of thin films can be affected by preparation conditions. The optical properties normally include transmittance which can be measured directly by spectrometers, refractive index, and extinction coefficient, both of which are usually calculated through spectral inversion method. The surface structure often affects the surface adhesion, mechanical strength, and stress of the films. Yasutaka et al[12] prepared Ge thin films on flexible substrate by chemical vapor deposition (CVD) and realized crystallization at low temperature by introducing Cu/Ti. Furlan et al[13] compared effects of direct current magnetron sputtering and high-power pulsed magnetron sputtering (HPPMS) on the performance of Ge films, and the results showed that the films prepared by HPPMS are more prone to crystallization and have higher thermal conductivity. Li et al[14] prepared Ge films by magnetron sputtering and studied the effect of annealing on the properties of the films, and the results showed that the infrared absorption of the films is increased after annealing. Liu[15] and Xu[16] et al studied the variation law of the optical properties of Ge films at high/low

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temperature by in-situ tests, and obtained the expression of the refractive index of films and temperature. However, few researchers reported the effect of annealing temperature on the optical properties and surface structure of Ge films prepared by electron beam evaporation.

The optical properties of Ge films at high temperature were investigated by annealing treatment. In this research, the variation of refractive index, transmittance, extinction coefficient, crystallization characteristics, and surface morphology of the thin film at different annealing temperatures was studied.

1 Experiment

Fig. 1 shows the schematic diagram of incident light which is vertical to a single-layer film. N and N_S represent the complex refractive index of thin film and substrate, respectively. Usually, N_S is given, and $N=n+ik$, where n is the refractive index, i is an imaginary singular, and k is the extinction coefficient. n and k change significantly with different preparation states of thin film.

When incident light perpendicularly hits the surface of single-layer film, the variation of each parameter needs to meet the transmission matrix equation, as shown in Eq.(1) [17]:

$$\begin{bmatrix} B \\ C \end{bmatrix} = \begin{bmatrix} \cos\delta & i\sin\delta/N \\ i\sin\delta N & \cos\delta \end{bmatrix} \begin{bmatrix} 1 \\ N_S \end{bmatrix} \quad (1)$$

where $\delta=2\pi/\lambda Nd$ (λ is the wavelength of the incident light; d is the film thickness); B and C are elements of a second-order matrices composed of film parameters. According to Eq. (1), the relationship between reflectance R or transmittance T of the film with the wavelength can be obtained, as expressed by Eq.(2) and Eq.(3), respectively:

$$R = \left(\frac{B-C}{B+C}\right)\left(\frac{B-C}{B+C}\right)^* \quad (2)$$

$$T = \frac{4N_S}{(B+C)(B+C)^*} \quad (3)$$

Considering the effect of back reflection, the above transmittance expression should be further modified. The reflectance and transmittance of the substrate are R_s and T_s, respectively. After correction, the transmittance of the film and the substrate can be obtained, as follows:

$$T_1 = \frac{TT_S}{1-RR_S} \quad (4)$$

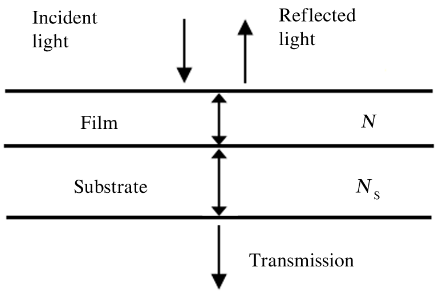

Fig.1 Schematic diagram of light penetrating single-layer film

According to the above calculation process, if the refractive index, extinction coefficient, and thickness of the film are given, the film transmittance can be obtained; if the film transmittance is directly measured by the spectrometer, the refractive index, extinction coefficient, thickness, and other optical parameters of the film can be obtained through the inversion formulae. In this study, the Cauchy equation was used as the dispersion model for the index which is an exponential model, as expressed by Eq.(5) and Eq.(6) [18,19]:

$$n(\lambda) = A_n + B_n/\lambda^2 + C_n/\lambda^4 \quad (5)$$

$$k(\lambda) = A_k \exp\left(B_k/\lambda\right) \quad (6)$$

where A_n, B_n, C_n, A_k, and B_k are the constant terms calculated by inversion formulae.

The Ge films were prepared by electron beam evaporation on Leybold automatic optical evaporation coating machine. The germanium particle with purity of 99.999% was used as evaporating material and the substrate was double-side-polished silicon wafer. Before coating, the silicon wafer was ultrasonically cleaned by the mixture solution of ethanol and acetone (analytical pure) with the volume ratio of 1:1 for more than 10 min to remove the oil and impurities, and then it was blow-dried with high-pressure nitrogen. The back pressure was 2.0×10^{-3} Pa, the evaporation rate was 0.5 nm/s, and the film thickness was 850 nm. The deposition rate and thickness of thin films were controlled and monitored by a quartz crystal system. After deposition, the specimens were placed in the annealing furnace at an atmospheric press. The annealing temperature was 350, 400, 450, and 500 °C, and the annealing duration was 2 h.

Fourier transform infrared spectrometer was used to test the film transmittance. The surface morphology of the specimens was characterized by AR MFP-3D atomic force microscope (AFM). Rigaku Smartlab X-ray diffractometer (XRD) was used to analyze the crystalline properties of the germanium films.

2 Results and Discussion

2.1 Effect of annealing temperature on optical properties of Ge films

The transmittance of the thin film determines the imaging quality of the photoelectric detection system, and thereby is an important index to evaluate the optical properties of the thin film. The transmittance of Ge films before and after annealing is shown in Fig.2. It can be seen that the transmittance of the film after annealing is significantly improved compared with that of the one before annealing, namely the as-deposited specimen. For example, the peak transmittance near the wavelength of 2500 nm is 51.4%, 53.8%, 53.2%, 52.9%, and 52.1% for as-deposited specimen, specimens annealed at 350, 400, 450, and 500 ° C, respectively. With increasing the annealing temperature, the crests of transmittance curves shift to the short wave area, which indicates that the optical thickness of the film is decreased after annealing.

The refractive index reflects the optical dispersion property

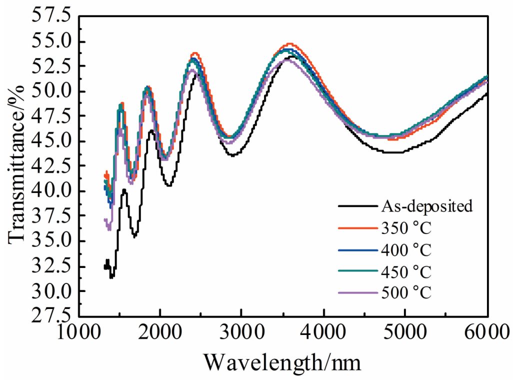

Fig.2 Effect of annealing temperature on transmittance of Ge film

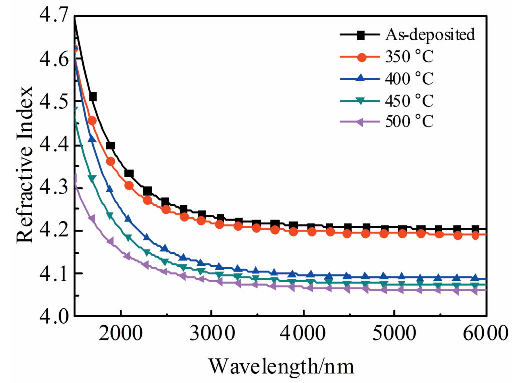

Fig.3 Effect of annealing temperature on refractive index of Ge film

of the film, and the extinction coefficient represents the optical absorption property of the film. Therefore, these two optical indices need to be studied and can be calculated by inversion method through the transmittance curves in Fig. 2. The values of each constant in the expressions are listed in Table 1. For example, the expressions of refractive index and extinction coefficient of the as-deposited film obtained by inversion calculation are as follows:

$$n(\lambda) = 4.203 + 2.476/\lambda^4 \tag{7}$$

$$k(\lambda) = 2.766 \times 10^{-4} \exp(7.974/\lambda) \tag{8}$$

According to Table 1, the relationship of refractive index and extinction coefficient with wavelength can be obtained, as shown in Fig. 3 and Fig. 4, respectively. It can be seen from Fig. 3 that the refractive index of Ge films after annealing is significantly smaller than that before annealing. The higher the annealing temperature, the smaller the refractive index. At the wavelength of 4000 nm, the refractive index of the as-deposited thin film is 4.213, while that of specimens after annealing at 350, 400, 450, and 500 °C is 4.200, 4.098, 4.083, and 4.068, respectively. This is because with increasing the annealing temperature, the particles in Ge film are aggregated, resulting in the increase in surface roughness and the decrease in film density. The denser the film, the greater the refractive index. After annealing, the compactness of the film becomes worse, so the refractive index is decreased accordingly.

Fig.4 shows the change of extinction coefficient of Ge film before and after annealing. It can be seen that the extinction coefficient of the as-deposited film is relatively large, which

Table 1 Related constants for calculation of refractive index and extinction coefficient

Annealing temperature/°C	$n(\lambda)$			$k(\lambda)$	
	A_n	B_n	C_n	$A_k/\times10^{-4}$	B_k
As-deposited	4.203	0	2.476	2.766	7.974
350	4.189	0.041	2.012	0.560	8.085
400	4.088	0	2.597	1.034	8.005
450	4.072	0.064	1.839	1.465	7.904
500	4.055	0.156	0.943	2.489	7.883

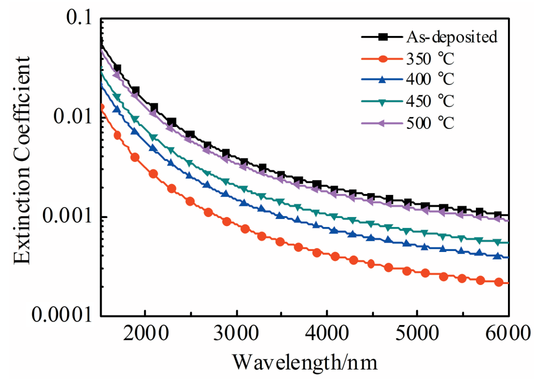

Fig.4 Effect of annealing temperature on extinction coefficient of Ge film

indicates that the as-deposited film has strong absorption. After annealing at 350 °C, the extinction coefficient of the film decreases greatly, indicating that the absorption of the film decreases after annealing, and thereby the transmittance of the film increases. After all, the extinction coefficient is decreased after annealing, and that of specimen annealed at 500 °C is the closest to that of the as-deposited specimen. The change rule of extinction coefficient is consistent with that of transmittance, which indicates that the change of extinction coefficient has a greater influence on the film transmittance.

2.2 Effect of annealing temperature on crystallization characteristics of Ge films

Annealing temperature has a significant effect on the crystallization state of Ge film. Fig.5 shows XRD patterns of Ge films annealed at different temperatures. It can be seen that the XRD patterns of the films before and after annealing at 350 and 400 °C have no obvious diffraction peaks, indicating that the Ge films are in amorphous state. When the annealing temperature is 400 °C, a diffraction peak appears at 2θ=27.3°, which is corresponding to the crystal plane of Ge(111), indicating that the film has been crystallized in this case. When the annealing temperature further increases to 450 °C, two obvious diffraction peaks appear at 2θ=45.3° and 2θ=53.7°, which correspond to Ge(220) and Ge(311) crystal planes, respectively. After annealing at 500 °C, the intensity of

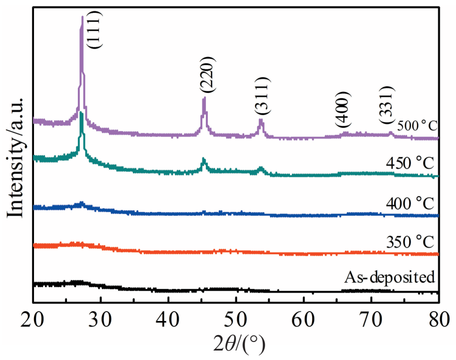

Fig.5 XRD patterns of Ge films before and after annealing at different temperatures

the (111) diffraction peak is the strongest, and that of (220) and (311) diffraction peaks also becomes more obvious. In addition, the diffraction peaks of Ge(400) and Ge(331) crystal planes appear. When the annealing temperature is 450 and 500 °C, the intensity of (111) diffraction peak is the strongest. The higher the annealing temperature, the stronger the intensity of (111) diffraction peak, which indicates that the film is more likely to grow along (111) crystal plane after annealing.

Scherrer formula[20] was used to calculate the grain size in this research, as follows:

$$D = \frac{0.89\lambda}{B\cos\theta} \tag{9}$$

where D is the average grain size, λ is the wavelength of incident light, B is the full width at half maximum (FWHM) of the diffraction peak, and θ is the diffraction angle. In this case, the wavelength is 0.154 nm (Cu K). The calculated grain size is listed in Table 2.

According to Table 2, the crystallization occurs on the surface of Ge film after annealing at 400 °C. With increasing the annealing temperature, the grain size of Ge films is increased gradually. When the annealing temperature reaches 500 °C, the maximum grain size of 19.1 nm for Ge films can be obtained.

2.3 Effect of annealing temperature on surface morphology of Ge films

Annealing treatment can change the crystal state and microstructure of the material surface, thus further affecting the properties of material[21]. In order to characterize the change of surface morphology, AFM was used to study the surface morphology of the thin Ge film before and after annealing. As shown in Fig.6, the AFM surface morphologies of the thin films change dramatically with increasing the annealing temperature. Ge films prepared by electron beam evaporation have smooth and dense surface without obvious particles before annealing. After annealing at 350 °C, the film surface is relatively smooth and dense. After annealing at 400 °C, some fine particles begin to appear on the film surface. When the annealing temperature is further increased to 450 and 500 °C, more granular particles appear on the film surface, which is ascribed to the obvious crystallization on the film surface.

Table 2 Calculated grain size of Ge films after annealing at different temperatures

Annealing temperature/°C	2θ/(°)	FWHM(111)/(°)	Grain size/nm
400	27.273	0.698	11.8
450	27.298	0.532	15.6
500	27.270	0.441	19.1

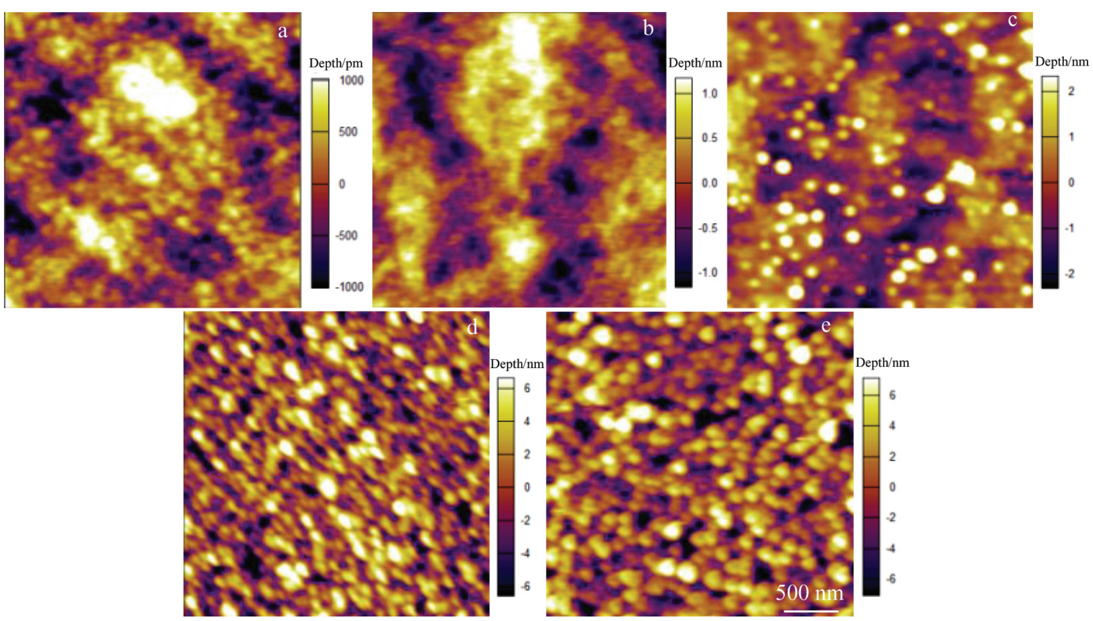

Fig.6 AFM morphologies of Ge films before (a) and after (b~e) annealing at different temperatures: (b) 350 °C, (c) 400 °C, (d) 450 °C, and (e) 500 °C

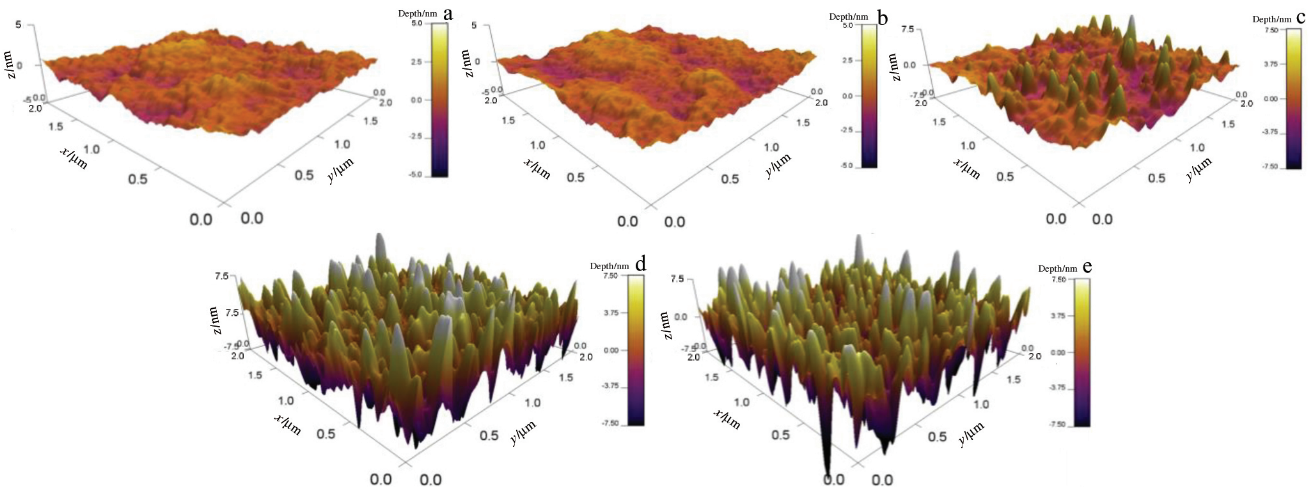

Fig.7 3D morphologies of Ge films before (a) and after (b~e) annealing at different temperatures: (b) 350 °C, (c) 400 °C, (d) 450 °C, and (e) 500 °C

Fig. 7 shows the three-dimensional surface morphologies of the Ge films before and after annealing at different temperatures. Before annealing or after annealing at 350 °C, the film surface has less humps and is relatively flat. After annealing at 400 °C, there are spikes on the film surface in the test range of 2 μm×2 μm. This is because the recrystallization occurs on the film surface with increasing the annealing temperature. The recrystallization also leads to the fact that the film surface changes from the original smooth state to uneven state, and the surface roughness is significantly increased. When the annealing temperature is further increased, the film surface becomes uneven significantly, and the surface roughness is greater, as shown in Fig. 7d and 7e. This is because the particles on the film surface re-migrate after annealing at a higher temperature, and the grains are easily formed in some regions. However, the process of the secondary condensation is not completed, which eventually leads to the increase in film roughness and the deterioration of the compactness. From the three-dimensional AFM analysis, the higher the annealing temperature, the worse the compactness of the film. In general, the lower the film density, the smaller the refractive index. These results also explain the fact that the refractive index of the film is decreased with increasing the annealing temperature.

3 Conclusions

1) Optical properties and surface structure of Ge films are greatly affected by the annealing temperature. The transmittance of the film is increased after annealing, compared with that of the as-deposited film. The transmittance decreases gradually when the annealing temperature increases from 350 °C to 500 °C. The refractive index and the extinction coefficient are decreased after annealing. However, among these annealed specimens, with increasing the annealing temperature, the refractive index is decreased while the extinction coefficient is gradually increased.

2) The as-deposited film and the film annealed at 350 °C are in amorphous state. After annealing at 400 °C, the diffraction peak of (111) crystal plane begins to appear. The crystallization of the film becomes more obvious after annealing at 450 and 500 °C, and other diffraction peaks such as (220) and (311) crystal planes begin to appear. The higher the annealing temperature, the larger the grain size of the film surface.

3) Surface morphology shows that with increasing the annealing temperature, more granular particles appear on the film surface, the humps become obvious, and the surface roughness of the film is increased. Therefore, the effect of annealing temperature on the optical properties, crystallization characteristics, and surface morphology of Ge films should be considered comprehensively in the preparation of Ge films and selection of the appropriate annealing temperature to obtain the film with optimal performance.

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退火温度对锗薄膜光学性能和表面结构的影响

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摘　要：研究了退火温度对电子束蒸发制备的锗薄膜光学性能和表面结构的影响规律。在硅基底上制备了厚度约850 nm的Ge薄膜，分别在350、400、450和500 ℃下进行退火。通过红外光谱仪测试了薄膜的透射率变化，采用光谱反演法得到了薄膜折射率和消光系数的变化规律，使用X射线衍射和原子力显微镜测试了样品的结晶特性和表面形貌。结果表明，与退火前的薄膜各项参数相比，退火后薄膜的透射率升高，而折射率和消光系数下降。当退火温度从350 ℃升高到500 ℃，透射率和折射率均逐渐减小，而消光系数逐渐变大。在400 ℃以上进行退火处理的薄膜出现结晶现象，Ge(111)晶面为择优生长取向。随着退火温度的升高，晶粒尺寸变大，薄膜表面出现颗粒状物质，并且表面粗糙度升高。

关键词：退火；锗薄膜；光学性能；表面结构

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