

Determination of Optical Properties in Germanium-Carbon Coatings Deposited by Plasma Enhanced Chemical Vapor Deposition

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Abstract: In this research, Germanium-carbon coatings were deposited on ZnS substrates by plasma enhanced chemical vapor deposition (PECVD) using GeH_4 and CH_4 precursors. Optical parameters of the $\text{Ge}_{1-x}\text{C}_x$ coating such as refractive index, Absorption coefficient, extinction coefficient and band gap were measured by the Swanepoel method based on the transmittance spectrum. The results showed that the refractive index of the $\text{Ge}_{1-x}\text{C}_x$ coatings at the band of 2 to 2.2 μm decreased from 3.767 to 3.715 and the optical gap increased from 0.66 to 0.72 eV as $\text{CH}_4:\text{GeH}_4$ increases from 10:1 to 20:1.

Keywords: $\text{Ge}_{1-x}\text{C}_x$, PECVD, Optical Coatings, Optical Properties.

1. INTRODUCTION

Zinc Sulfide (ZnS), due to its low absorption coefficient, has been used as an infrared material since 1944 [1]. The real transmittance of the polished ZnS substrate is between 72% (in visible range) to 75% (in IR range) [2]. To improve the poor optical properties of ZnS window, coatings based on the available infrared materials such as diamond, boron phosphide (BP), diamond-like carbon (DLC), gallium phosphide (GaP) and germanium carbide ($\text{Ge}_{1-x}\text{C}_x$), have been developed [3-5]. Diamond-like carbon coatings include attractive mechanical, optical, electrical, chemical and tribological properties and can be used as antireflective coatings for solar cells, IR optical materials, wear resistant and low friction coatings, orthopaedic implants, etc [6-8]. DLC has relatively low refractive index around 1.7–2.3 and some extreme properties such as high hardness, chemical inertness, low friction coefficient and broad band IR transparency. However, it has high intrinsic compressive stress; these very high stress limit the maximum coating thickness [9]. $\text{Ge}_{1-x}\text{C}_x$ coating, an infrared coating material, has high durability, low absorption, low stress and nice adhesion with most substrates [10-12]. Furthermore, it has variable refractive index from 1.7 to 4.0 [9]. In

addition, the band gap of the coatings can also be changed with x in a very wide range, which makes them good semiconductive material candidates in the design of electronic devices and photovoltaic cells [13-15].

So far, there are very few reports on design of germanium carbon antireflection coating. As we know, access the values of the refractive index and thickness of the coating is necessary to design an antireflection coating. In this research, we have prepared $\text{Ge}_{1-x}\text{C}_x$ coatings on ZnS substrate by a PECVD method. Optical parameters of the $\text{Ge}_{1-x}\text{C}_x$ coating such as refractive index, thickness, absorption coefficient, extinction coefficient and band gap were measured by the Swanepoel method based on the transmittance spectrum.

2. EXPERIMENTAL PROCEDURE

$\text{Ge}_{1-x}\text{C}_x$ coatings were deposited on ZnS substrates by a PECVD technique with a gas mixture of germane (GeH_4 , 99.999%, Foshan Huate Gas, China) and methane (CH_4 , 99.995%, Technical Gas Services, China) as the precursor. To this end, a parallel-plates RF glow discharge stainless steel reactor (13.56 MHz) was employed. The substrates were cleaned in acetone. For the activation of substrate surface

Table 1. Deposition parameters of the germanium-carbon coatings.

| Parameter | Sample code | |
|--|--------------------|--------------------|
| | R ₁ | R ₂ |
| RF power (W) | 100 | 100 |
| Background vacuum (Torr) | 9×10 ⁻⁵ | 9×10 ⁻⁵ |
| Deposition pressure (Torr) | 0.05 | 0.05 |
| Flow rate of CH ₄ (sccm) | 0.8 | 1.2 |
| Flow rate of GeH ₄ (sccm) | 0.08 | 0.063 |
| Flow rate ratio of CH ₄ :GeH ₄ | 10:1 | 20:1 |
| Plate separation (mm) | 20 | 20 |
| Deposition time (min) | 30 | 30 |
| Deposition temperature (°C) | 25-100 | 25-100 |

and improvement of the coating adhesion, plasma etching process was done in argon plasma environment for 10 min with condition described here: flow rate: 30 sccm; work pressure: 0.3 Torr and RF power: 200 W. Then, after providing the background vacuum, at a given RF power and based on the deposition pressure and the flow ratio of gas precursors, germane and methane gases were fed into the deposition chamber under the precise control of digital mass flowmeters. The details of deposition parameters are listed in Table 1.

The transmission spectra were measured with a Nicolet 670 FTIR Spectrometer. Transmittance data were employed to evaluate the optical constants such as the refractive index (n), extinction coefficient (k), absorption coefficient (α), thickness, and band gap energy.

3. RESULTS AND DISCUSSION

Fig. 1, display the transmittance spectra of ZnS substrate and Ge_{1-x}C_x coatings prepared using CH₄:GeH₄, 10:1 (R₁) and 20:1 (R₂) in the visible and infrared regions.

Swanepoel is a very convenient method for estimating the optical constants of thin films, that have been mentioned in many studies [16-18]. The optical properties of the Ge_{1-x}C_x coatings can be evaluated from the transmittance data using the envelop method, which was proposed by Swanepoel. Various wavelengths can be calculated using the envelope curve for T_{max} (T_M) and T_{min} (T_m) in the transmission spectra

[19]. The expression for the refractive index is given by [19-21]:

$$n = \sqrt{(N + \sqrt{N^2 - N_s^2})} \tag{1}$$

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

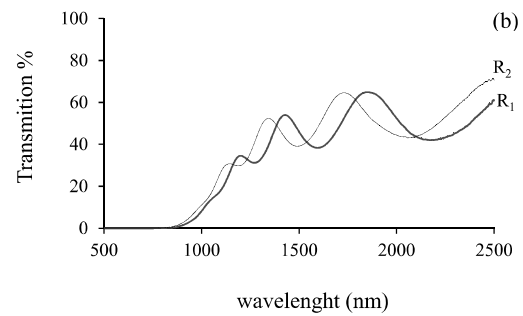
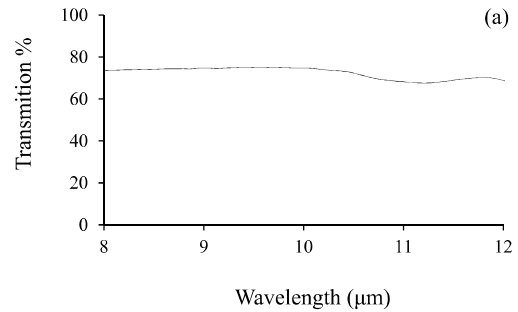


Fig. 1. Transmittance spectra of: (a) ZnS substrate and (b) Ge_{1-x}C_x coating with different gas flow rate on ZnS substrate.

T_M and T_m are the transmittance maxima and the corresponding minima at certain wavelengths. n_s is the refractive index of the substrate. The refractive index of the ZnS substrate can be calculated from the transmission spectrum of a clean substrate via the relation [22]:

$$n^2 = 8.393 + \frac{0.14383}{\lambda^2 - 0.2421^2} + \frac{4430.99}{\lambda^2 - 36.71^2} \quad (3)$$

The smooth envelopes of the $Ge_{1-x}C_x$ coatings are plotted by a computer program (Origin Pro 8.6) (Fig. 2).

Equation (1) leads to the refractive index of the coating at λ . If the refractive indices are obtained at the maxima or minima of the transmission spectrum, the thickness of the coating can be deduced. If n_1 and n_2 be refractive indices at two adjacent maxima (or minima) at λ_1 and λ_2 where, $\lambda_1 > \lambda_2$, then [23]:

$$2n_1d = m\lambda_1 \quad (4)$$

$$2n_2d = (m+1)\lambda_2 \quad (5)$$

where m is the interference order, λ is the wavelength, and d is the coating thickness. The interference order is an integer for maxima and a half-integer for minima [19]. Solving Eqs. (4) and (5) for d yields the coating thickness as [23]:

$$d = \frac{\lambda_1\lambda_2}{2(\lambda_1n_2 - \lambda_2n_1)} \quad (6)$$

Practically, there will be errors in the determination of extreme positions and the corresponding values of the smooth envelopes T_M and T_m . Therefore, the preliminary values of the refractive index calculated from Eq. (1) and the coating thickness obtained from Eq. (6), are erroneous. The more accurate thickness and refractive index (d_2 , n_2) can be obtained by further performing the following steps. Firstly, take the average value of d_1 . Secondly, use Eq. (4) to determine the estimated order number (m_0) for each extreme from the average value of d_1 and n_1 and round off each resulting m_0 to the closest integer for maxima or half integer for minima. These round values will be considered as the exact order number m corresponding to each maxima or minima. Thirdly, use m and n_1 again to calculate the accurate thickness d_2 for each maxima and minima. The average value of d_2 will be taken as the final thickness of the coating. Finally, from the exact value of m and the final thickness of the coating, the accurate refractive index n_2 can again be calculated for each maximum and minimum using Eq. (4) [23]. The average values of d_1 and d_2 ignoring the last values calculated, because errors have been affected. The values for the refractive index of the $Ge_{1-x}C_x$ are calculated and indicated in Table 2.

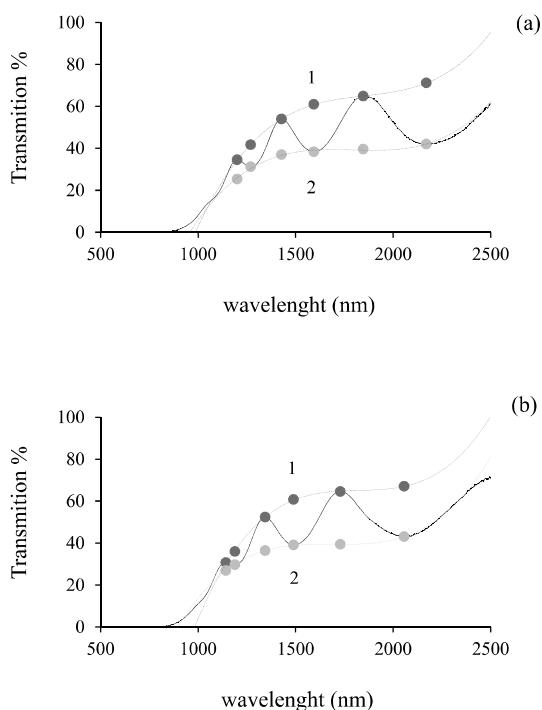


Fig. 2. T_M (1) and T_m (2) in different wavelengths: (a) R_1 and (b) R_2 .

The results show that the refractive index of $Ge_{1-x}C_x$ coatings at the band of 2 to 2.2 μm , decreases from 3.767 to 3.715 as $\text{CH}_4:\text{GeH}_4$

Table 2. Values of wavelengths corresponding to different maxima and minima.

| λ , nm | T_M | T_m | n_s | N_1 | n_1 | d_1 ,nm | m_0 | m | d_2 ,nm | n_2 |
|----------------|-------|-------|-------|-------|-----------------------------|----------------------------------|-------|-----|---------------------------------|-------|
| | | | | | Sample R₁ | | | | | |
| 2170 | 0.712 | 0.420 | 2.263 | 7.483 | 3.823 | - | 2.76 | 2.5 | 710 | 3.767 |
| 1846.5 | 0.649 | 0.396 | 2.267 | 7.533 | 3.836 | - | 3.25 | 3 | 722 | 3.846 |
| 1593.5 | 0.610 | 0.383 | 2.270 | 7.491 | 3.825 | 783 | 3.76 | 3.5 | 729 | 3.873 |
| 1428 | 0.540 | 0.370 | 2.274 | 6.956 | 3.678 | 1004 | 4.03 | 4 | - | 3.966 |
| 1270 | 0.417 | 0.312 | 2.279 | 6.775 | 3.627 | 1098 | 4.47 | 4.5 | - | 3.969 |
| | | | | | | $d_{1avg}=783$ | | | $d_{2av}=720$ | |
| | | | | | Sample R₂ | | | | | |
| 2056.5 | 0.671 | 0.431 | 2.264 | 6.824 | 3.642 | - | 2.36 | 2.5 | 706 | 3.715 |
| 1729.5 | 0.646 | 0.394 | 2.269 | 7.565 | 3.845 | - | 2.96 | 3 | 675 | 3.749 |
| 1489 | 0.608 | 0.391 | 2.273 | 7.232 | 3.755 | 666 | 3.36 | 3.5 | 694 | 3.766 |
| 1344 | 0.524 | 0.364 | 2.277 | 6.911 | 3.666 | 991 | 3.63 | 4 | - | 3.884 |
| 1189 | 0.360 | 0.297 | 2.282 | 5.793 | 3.334 | 1772 | 3.73 | 4.5 | - | 3.866 |
| | | | | | | $d_{1avg}=666$ | | | $d_{2av}=692$ | |

increases from 10:1 to 20:1. The refractive index of a material is closely correlated with the scattering of photons. The greater the atomic mass, the higher the refractive index [15]. Therefore, the refractive index decreases correspondingly with decreases of the average molecular weight of germanium-carbon, due to decreases of germanium content. The refractive index is usually defined in terms of the velocity of light, $n=c/v$, where v is the velocity in the medium. However, the velocity is related to the frequency and wavelength by, $v=\lambda_f$ so:

$$n = \frac{\lambda_0 f_0}{\lambda f} \tag{7}$$

In regions of the spectrum where the material does not absorb light, the refractive index tends to decrease with increasing wavelength, and thus increase with frequency. This called "normal dispersion", in contrast to "anomalous dispersion", where the refractive index increases with wavelength. Assuming that the interference is fully coherent, the locations of the interference maxima and minima are related to the real part $n(\lambda)$ of the complex refractive index, $n(\lambda) = n(\lambda) + jk(\lambda)$ with $k(\lambda)$ being the extinction coefficient, by the formula [19]:

$$k = \frac{\lambda \alpha}{4\pi} \tag{8}$$

where α is the absorption coefficient, which can be expressed as

$$\alpha = \left(\frac{-1}{d}\right) \ln X \tag{9}$$

where

$$X = \left\{ P + \left[P^2 + 2QT(1 - R_2R_3)^{\frac{1}{2}} \right] \right\} / Q,$$

$$P = (R_1 - 1)(R_2 - 1)(R_3 - 1),$$

$$Q = 2T(R_1R_2 + R_1R_3 - 2R_1R_2R_3)$$

$$R_1 = \left[\frac{1-n}{1+n} \right]^2, R_2 = \left[\frac{n-n_s}{n+n_s} \right]^2, R_3 = \left[\frac{n_s-1}{n_s+1} \right]^2,$$

and

$$T = (T_M T_m)^{\frac{1}{2}},$$

The values for the refractive index, absorption coefficient and extinction coefficient of the Ge_{1-x}C_x coatings are calculated and indicated in Table 3.

Table 3. Values of the Extinction Coefficient, Absorption Coefficient, and Refractive Index of Ge_{1-x}C_x coatings.

| λ , nm | T | R ₁ | R ₂ | R ₃ | Q | P | X | α (cm ⁻¹) | K |
|----------------|-------|----------------|----------------|-----------------------------|-------|--------|-------|------------------------------|-------|
| | | | | Sample R₁ | | | | | |
| 2170 | 0.547 | 0.337 | 0.062 | 0.150 | 0.071 | -0.529 | 0.962 | 538 | 0.009 |
| 1846.5 | 0.507 | 0.345 | 0.067 | 0.150 | 0.069 | -0.519 | 0.912 | 1279 | 0.019 |
| 1593.5 | 0.483 | 0.348 | 0.068 | 0.151 | 0.067 | -0.516 | 0.877 | 1823 | 0.023 |
| 1428 | 0.447 | 0.357 | 0.073 | 0.151 | 0.064 | -0.506 | 0.830 | 2588 | 0.029 |
| 1270 | 0.360 | 0.357 | 0.073 | 0.152 | 0.052 | -0.505 | 0.681 | 5336 | 0.054 |
| | | | | Sample R₂ | | | | | |
| 2056.5 | 0.537 | 0.332 | 0.059 | 0.150 | 0.068 | -0.534 | 0.940 | 894 | 0.015 |
| 1729.5 | 0.504 | 0.335 | 0.060 | 0.151 | 0.065 | -0.531 | 0.892 | 1652 | 0.028 |
| 1489 | 0.488 | 0.337 | 0.061 | 0.151 | 0.064 | -0.529 | 0.868 | 2046 | 0.024 |
| 1344 | 0.437 | 0.349 | 0.068 | 0.152 | 0.061 | -0.514 | 0.803 | 3170 | 0.034 |
| 1189 | 0.327 | 0.347 | 0.066 | 0.152 | 0.045 | -0.517 | 0.610 | 7143 | 0.068 |

Fig. 3 shows the refractive index, absorption coefficient, and extinction coefficient of the Ge_{1-x}C_x coatings as a function of wavelength.

The absorption coefficient as a function of photon energy can be expressed as [19, 24, 25]:

$$(\alpha h\nu)^m = A(h\nu - E_g), \quad (10)$$

where $h\nu$ is the photon energy, A is a constant, and E_g is the band gap energy. m is a constant which determines the type of the optical transition ($m = 2$ and $1/2$ for direct band gap and indirect band gap, respectively). The band gap energy of the Ge_{1-x}C_x coating can be estimated by assuming an indirect transition between the valence and conduction bands. The band gap value of the Ge_{1-x}C_x coating can be obtained by extrapolating the linear part of the plot relating $(\alpha h\nu)^{1/2}$ and $h\nu$ to $\alpha h\nu = 0$ as shown in Fig. 4 [23]. The optical gap increases from 0.66 to 0.72 eV as CH₄:GeH₄ increases from 10:1 to 20:1, respectively. Increasing of the carbon content, increases orbitals overlap. As a result, the optical gap increases with increasing the carbon content [26].

4. CONCLUSION

In the current study, germanium-carbon coatings were deposited on ZnS substrates at room temperature by plasma enhanced chemical vapor deposition using GeH₄ and CH₄ precursors.

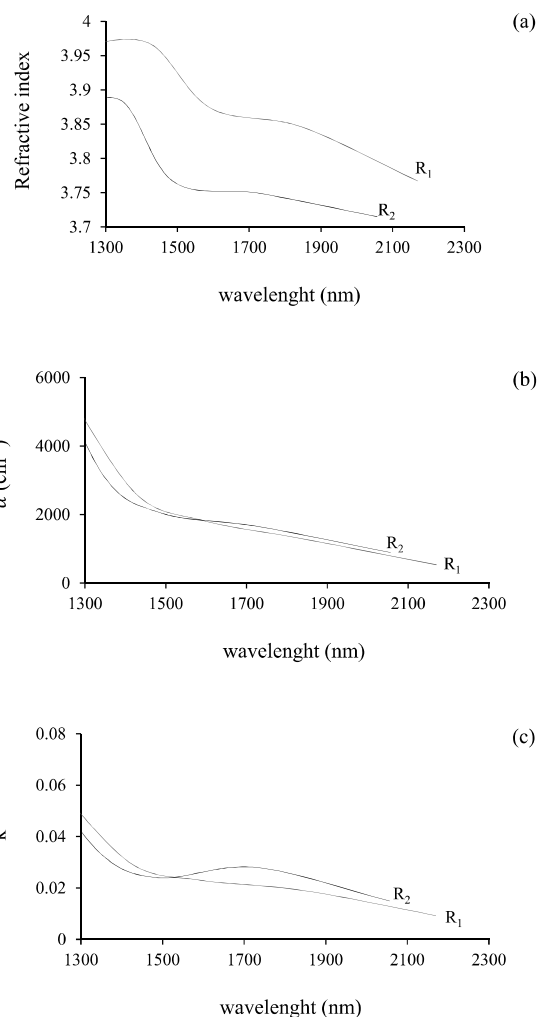


Fig. 3. (a) Refractive index, (b) Absorption coefficient and (c) Extinction coefficient of the Ge_{1-x}C_x coating as a function of wavelength for R₁ and R₂.

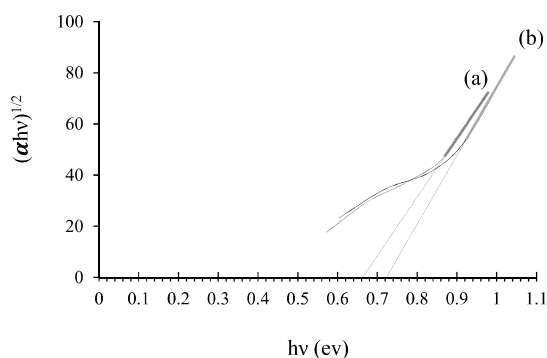


Fig. 4. The $(\alpha hv)^{1/2}$ versus hv plotted for $Ge_{1-x}C_x$ coating: (a) R_1 and (b) R_2 .

Optical constants of the $Ge_{1-x}C_x$ coatings as a function of wavelength, such as refractive index n , absorption coefficient α , extinction coefficient k , band gap E_g of the coating were evaluated from the optical transmission spectrum using Swanepoel's method. The results showed that the refractive index of the $Ge_{1-x}C_x$ coatings at the band of 2 to 2.2 μm decreases from 3.767 to 3.715 as $CH_4:GeH_4$ increases from 10:1 to 20:1. In addition, the coatings exhibited indirect optical transition with optical band gap of 0.66 and 0.72 eV as $CH_4:GeH_4$ increased from 10:1 to 20:1 respectively due to the increase of the carbon content.

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