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

**F. Sousani*, A. Eshaghi, R. Mozafarinia and H. Jamali**

* *f_sousani@mut-es.ac.ir*

**Received: August 2017 Accepted: January 2018**

**Faculty of Materials Science and Engineering, Malek Ashtar University of Technology, Esfahan, Iran.**

**DOI: 10.22068/ijmse.15.1.24**

***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 Ge1-xCx 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 $Ge_{1-x}C_x$ 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 $CH_4$:$GeH_4$ increases from 10:1 to 20:1.*

***Keywords:*** *Ge1−XCx, 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 ($Ge_{1-x}C_x$), 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]. $Ge_{1-x}C_x$ 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 $Ge_{1-x}C_x$ coatings on Zns substrate by a PECVD method. Optical parameters of the $Ge_{1-x}C_x$ 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

$Ge_{1-x}C_x$ 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



[ Downloaded from sarbaz.iust.ac.ir on 2025-07-19 ]

[ DOI: 10.22068/ijmse.15.1.24 ]

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

| Parameter | Sample code | |
|---|---|---|
| | **$R_1$** | **$R_2$** |
| RF power (W) | 100 | 100 |
| Background vacuum (Torr) | $9\times10^{-5}$ | $9\times10^{-5}$ |
| 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 $CH_4$:$GeH_4$, 10:1 (R1) and 20:1 ($R_2$) 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 Tmax ($T_M$) and Tmin ($T_m$) in the transmission spectra [19]. The expression for the refractive index is given by [19-21]:

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

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \quad (2)$$

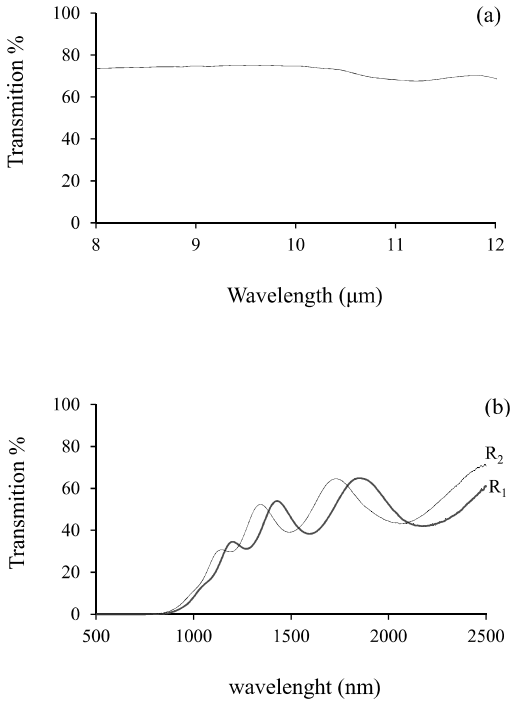


**Fig. 1.** Transmittance spectra of: (a) ZnS substrate and (b) Ge1-XCX coating with different gas flow rate on ZnS substrate.

[ Downloaded from sarbaz.iust.ac.ir on 2025-07-19 ]

[ DOI: 10.22068/ijmse.15.1.24 ]

$T_M$ 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 envelops 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 $\lambda_1$ and $\lambda_2$ where, $\lambda_1 > \lambda_2$, then [23]:

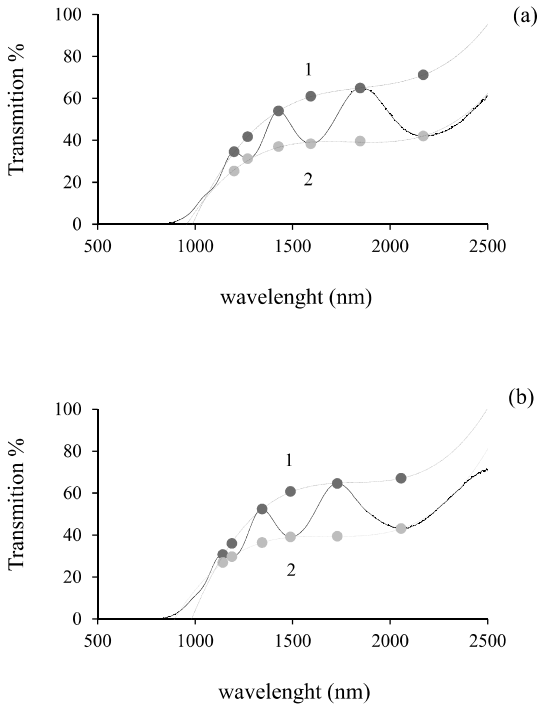


**Fig. 2.** $T_M$ (1) and $T_m$ (2) in different wavelengths: (a) $R_1$ and (b) $R_2$.

$$2n_1 d = m\lambda_1 \quad (4)$$

$$2n_2 d = (m+1)\lambda_2 \quad (5)$$

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]:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (6)$$

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.

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 $CH_4$:$GeH_4$



[ Downloaded from sarbaz.iust.ac.ir on 2025-07-19 ]

[ DOI: 10.22068/ijmse.15.1.24 ]

**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 $R_1$** | | | | | |
| 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 $R_2$** | | | | | |
| 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/ν, where ν is the velocity in the medium. However , the velocity is related to the frequency and wavelength by, $\nu=\lambda_f$ 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(λ) of the complex refractive index, n(λ) = n(λ) + jk(λ) with k(λ) 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

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

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.

[ Downloaded from sarbaz.iust.ac.ir on 2025-07-19 ]

[ DOI: 10.22068/ijmse.15.1.24 ]

**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 | $\alpha$ ($cm^{-1}$) | K |
|---|---|---|---|---|---|---|---|---|---|
| | | | | **Sample $R_1$** | | | | | |
| 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 $R_2$** | | | | | |
| 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]:

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

where hυ 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 $(\alpha h\upsilon)^{1/2}$ and hυ to αhυ=0 as shown in Fig. 4 [23]. The optical gap increases from 0.66 to 0.72 eV as $CH_4$:$GeH_4$ 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 $GeH_4$ and $CH_4$ precursors.

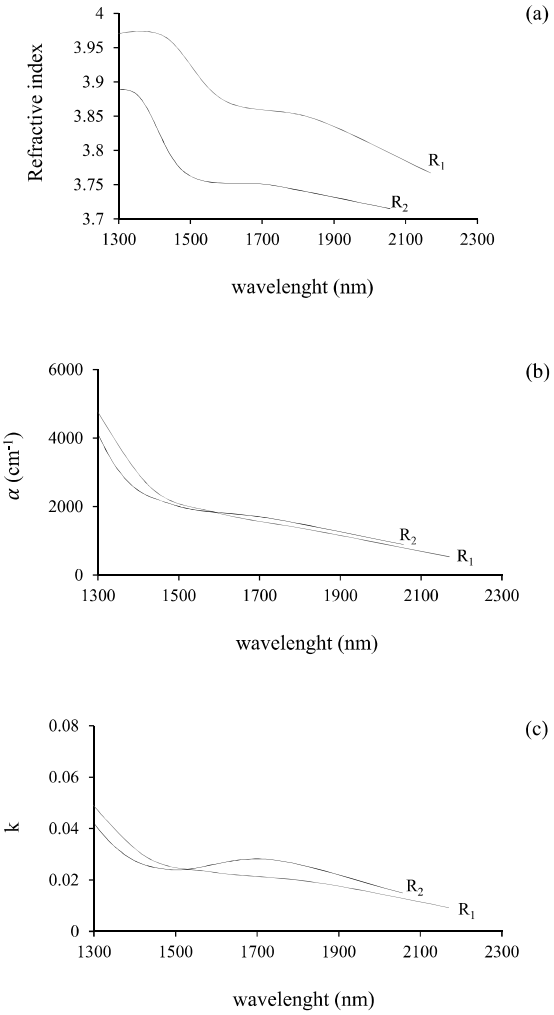


**Fig. 3.** (a) Refractive index, (b) Absorption coefficient and (c) Extinction coefficient of the $Ge_{1-X}C_X$ coating as a function of wavelength for $R_1$ and $R_2$.



[ Downloaded from sarbaz.iust.ac.ir on 2025-07-19 ]

[ DOI: 10.22068/ijmse.15.1.24 ]

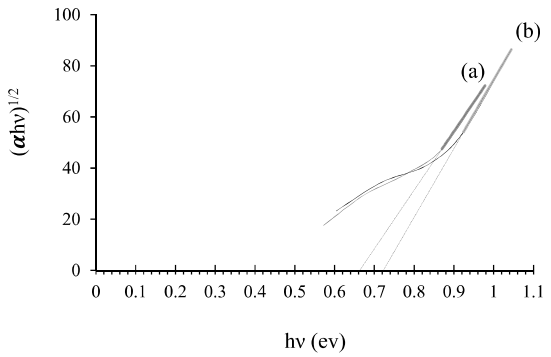


**Fig. 4.** The $(\alpha h\nu)^{1/2}$ versus hν plotted for $Ge_{1-X}C_X$ coating: (a) $R_1$ and (b) $R_2$.

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.

## REFERENCES


1. Wu, X., Zhang, W., Yan, L. and Luo, R., "The deposition and optical properties of Ge1-xCx thin film and infrared multilayer antireflection coatings", Thin Solid Films., 2008, 516, 3189–3195.
2. Zhu, J. Q., Jiang, C. Z., Han, X, Han, J. C., Meng, S. H., Hu, C. Q. and Zheng, W. T., "Multilayer antireflective and protective coatings comprising amorphous diamond and amorphous hydrogenated germanium carbide for ZnS optical elements," Thin Solid Films., 2008, 516, 3117–3122.
3. Hu, C. Q., Zheng, W. T., Li, J. J., Jiang, Q, Tian, H. W., Lu, X. L., Liu, J. W., Xu, L. and Wang, J. B., "Ge1-xCx double-layer antireflection and protection coatings," Appl. Surf. Sci., 2006, 252, 8135–8138.
4. Ping, L., Ning, W. X., Ch, Ch, Sen, Bo. and Tang, L., "Infrared transmissive and rain-erosion resistant performances of GeC/GaP double-layer thin films on ZnS substrates," Appl. Surf. Sci., 2013, 264, 538–544.
5. Jamali, H., Mozafarinia, R. and Eshaghi, A., "Evaluation of chemical and structural properties of germanium carbon coatings deposited by plasma enhanced chemical vapor deposition," J. Alloy Compd., 2015, 646, 360-367.
6. Reddy, K., Varadea, A., Krishnaa, A., Joshuab, J., Sasenc, D., Chellamalaia, M. and kumar, P. V., "Double side coating of DLC on silicon by RF-PECVD for an application," Procedia Engineering., 2014, 97, 1416–1421.
7. Safaie, P., Eshaghi, A. and Bakhshi, S., "Optical properties of oxygen doped diamond-like carbon thin films," J. Alloy Compd., 2016, 672, 426-432.
8. Varade, A., Reddy, K. N., sasen, D., Krishna, A., Chellamalai, M. and Shashikumar, P. V., "Detailed raman study of DLC coating on Si (100) made by RFPECVD," Procedia Engineering., 2014, 97, 1452–1456.
9. Li, Y., Liu, Z., Zhao, H. and Feng, L., "Infrared transmission properties of germanium carbon thin films deposited by reactive RF magnetron sputtering,Vacuum" 2009, 83, 965–969.
10. Harrise, D. C., "Materials for infrared windows and domes properties and performance," SPIE, Washington, 1999.
11. Hu, C., Zheng, W., Tian, H., Xu, L. and Jiang, Q., "Effects of the chemical bonding on the optical and mechanical properties for germanium carbide films used as antireflection and protection coating of ZnS windows," J. Phys., 2006, 18, 4231–4241.
12. Hu, C. Q., Xu, L., Tian, H. W., Jin, Z. S., Lv, X. Y. and Zheng, W. T., "Effects of radio frequency power on the chemical bonding, optical and mechanical properties for radio frequency reactive sputtered germanium carbide films," J. Phys., 2006, 39, 5074–5079.
13. Che, X. S., Liu, Z. T., Li, Y. P. and Wang, N, "Effects of hydrogen and substrate temperature on the chemical bonding and optical properties of germanium carbon films deposited by reactive sputtering," Appl. Surf. Sci., 2012, 258,


[ Downloaded from sarbaz.iust.ac.ir on 2025-07-19 ]

[ DOI: 10.22068/ijmse.15.1.24 ]

6212–6216.
14. Zhua, J. Q., Jianga, C. Z., Hana, J. C., Yua, H. L., Wanga, J. Z., Jia, Z. C. and Chenb, R. R., "Optical and electrical properties of nonstoichiometric a-Ge1−xCx films prepared by magnetron co-sputtering," Appl. Surf. Sci., 2012, 258, 3877–3881.
15. Mahmood, A. Shah, A., Castillon, F. F., Araiza, L. C., Heiras, J., Yasin, M. and Khizar, M., "Surface analysis of GeC prepared by reactive pulsed laser deposition technique," Curr. Appl. Phys., 2011, 11. 547-550.
16. Shaaban, E. R., Yahia, I. S., and El-Metwally, E. G., "Validity of Swanepoel's method for calculating the optical constants of thick films", ACTA PHYSICA POLONICA A., 2012, 121, 628-635.
17. Sanchez-Gonzalez, J., Dıaz-Parralejo, A., Ortiz, A. L. and Guiberteau, F., "Determination of optical properties in nanostructured thin films using the Swanepoel method", Applied Surface Science, 2006, 252, 6013–6017.
18. Manifaciar, J. C., Gasiot, J. and Fillard, J. P., "A simple method for the determination of the optical constants n, k and the thickness of a weakly absorbing thin film," Journal of Physics. 1976, 9, 1002–1005.
19. Eshaghi, A. and Aghaei, A. A., "Determination of optical properties in nanostructured $TiO_2$ thin film fabricatedby electron beam physical vapor deposition," J. Opt. Technol., 2016, 83, 36-39.
20. Gholami, M., Nazari, A., Azarin, Kh., Yazdanimeher, S. and Sadeghniya, B., "Determination of the thickness and optical constants of metal oxide thin films by different methods," J. Basic Appl. Sci. Res., 2013, 3, 597-600.
21. Swanepoel, R., "Determination of the thickness and optical constants of amorphous silicon," J. Phys. E., 1983, 16, 1214-1222.
22. Debenham, M., "Refractive indices of zinc sulfide in the 0.405-13-μm wavelength range," Appl. Opt., 1984, 23, 2238-2239.
23. Pimpabute, N., Burinprakhoni, T. and Somkhunthot, W., "Determination of optical constants and thickness of amorphous GaP thin film," Opt. Appl., 2011, 1, 257-268.
24. Eshaghi, A. and Hajkarimi, M., "Optical and electrical properties of aluminum zinc oxide (AZO) nanostructured thin film deposited on polycarbonate substrate," Optik., 2014, 125, 5746–5749.
25. Davoodi, A., Tajally, M., Mirzaee, O. and Eshaghi, A., "Fabrication and characterization of optical and electrical properties of Al-Ti Co-doped ZnO nano-structured thin film," J. Alloy Compd., 2016, 657, 296-301.
26. Che, X., Liu, Z., Li, Y., Wang, N. and Xu, Z., "Effects of methane flow rate on the optical properties and chemical bonding of germanium carbon films deposited by reactive sputtering," Vacuum., 2013, 90, 75-79.

[ Downloaded from sarbaz.iust.ac.ir on 2025-07-19 ]

[ DOI: 10.22068/ijmse.15.1.24 ]