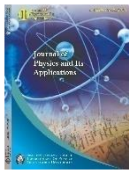
Journal of Physics and Its Applications

Journal homepage : https://ejournal2.undip.ac.id/index.php/jpa/index



Influence of annealing on the physical and optical properties of Ge thin films deposited using thermal evaporation

Isom Hilmi[1]*, Muhammad Kevin Adam[1], Joko Purwadi[2], Qidir Maulana Binu Soesanto[3], and Damar Yoga Kusuma[1]

[1]*Department of Physics, Faculty of Applied Science and Technology, Universitas Ahmad Dahlan, Tamanan, Banguntapan, Bantul, Yogyakarta, Indonesia*

[2]*Department of Mathematics, Faculty of Applied Science and Technology, Universitas Ahmad Dahlan, Tamanan, Banguntapan, Bantul, Yogyakarta, Indonesia*

[3]*Department of Physics, Faculty of Sciences and Mathematics, Diponegoro University, Semarang, Indonesia*

**Corresponding author: isom.hilmi@fisika.uad.ac.id*

ARTICLE INFO

Article history:
Received: 24 September 2024
Accepted: 23 December 2024
Available online: 31 May 2025

Keywords:
Annealing
Ge
XRD
Absorbance
bandgap

ABSTRACT

Germanium (Ge) is extensively utilized in various technological applications, particularly in optoelectronic devices due to its favorable electronic properties. In this study, Ge thin films were deposited onto soda-lime glass substrates using the thermal evaporation technique. The deposited films were subsequently subjected to annealing at temperatures ranging from 200 to 700 °C. Comprehensive characterization of the films was performed using XRD to analyze crystallinity, UV-Vis spectroscopy to evaluate optical properties, and SEM to investigate surface topography. The annealing process induced a significant phase transformation from an amorphous state to a co-existing Ge and GeO2 structures, as evidenced by XRD measurements. This structural evolution was accompanied by notable changes in the optical properties of the films. Specifically, an increase in annealing temperature resulted in a higher absorbance in the longer wavelength regions of the UV-Vis spectrum. These findings highlight the possibility of a controlled manipulation on the structural and optical characteristics of Ge thin films by thermal treatment, with potential applications in optoelectronic devices.

1. Introduction

Germanium (Ge) and its oxide derivatives (GeOx) have garnered substantial research interest over the past decade due to their significantly favorable properties for a wide range of devices, including semiconductors [1], photodetectors [2-4], photovoltaics [5-7], optoelectronics [8-10], and microelectromechanical systems (MEMS) [11]. In contrast to silicon (Si), which has an indirect bandgap, pure elemental germanium possesses a direct bandgap of approximately 0.67 eV. This characteristic renders it particularly suitable for those aforementioned applications. Although Ge has a lower bandgap than that of Si , the melting point of Ge is however much lower than that of Si, which could reduce the purification cost making it interesting for its applications [12].

Ge and GeO_x in the form of thin films have been fabricated using various techniques, including RF magnetron sputtering [13], pulsed laser deposition (PLD) [14], wet-chemical processes [15], and both e-beam and thermal evaporation techniques [16, 17]. Among these, thermal evaporation is particularly versatile for fabricating different types of thin films. It offers several advantages over other deposition methods, including procedural simplicity, the capability for large-area deposition, and scalability for device fabrication. Additionally, thermal evaporation provides precise control over film thickness and uniformity. Despite these advantages, there remains a need for comprehensive investigations into the properties of Ge films produced via thermal evaporation. Specifically, a detailed analysis of the structural, optical, and electronic characteristics of evaporated Ge films, including also thermally-treated films, is essential for optimizing their performance and expanding their application in its advanced technological domains. The thermal treatment of Ge films are commonly performed in order to improve their optical properties for their application in e.g. optoelectronic devices [18]. A comprehensive investigation on physical properties of Ge films upon annealing process are then of outmost importance.

This study aims to provide a comprehensive analysis of the fabrication of Ge films using thermal evaporation and the subsequent transformation of the phase of the films into germanium oxide, GeO_x, through an annealing process. The primary objective is to elucidate the effects of annealing on the physical properties of the deposited Ge films with a particular focus on optimizing them for specific applications such as laser sources, photodetectors, and waveguides. In these applications, achieving the optimum temperature for getting optimum UV-Vis absorptions are critical factors. To illustrate, in photodetectors, the film's thickness and optical absorption properties significantly influence its ability to detect and respond to light in the UV-Vis range, in the context of laser applications, the properties of Ge and GeO_x films, including their bandgap and optical absorption, are key to improving efficiency and performance. Furthermore, in waveguides, the thin film's refractive index and uniformity are crucial for light propagation and confinement. Therefore, understanding the impact of annealing on these properties will provide essential insights for optimizing Ge films for these advanced technological applications.

To achieve the primary objective outlined above, a series of experiments were conducted, focusing on the influence of annealing on the films' structural and optical characteristics. Some annealing experiments on Ge films have been reported by various means such as direct thermal treatments and also using laser beam [4, 18]. The physical properties of the films were evaluated using multiple analytical techniques. Specifically, the crystallinity, the microstructure, and the optical properties of the films were investigated by means XRD, SEM, UV-Vis spectroscopy, respectively. Through this systematically work, the study aims to offer a thorough understanding of how thermal evaporation and subsequent annealing influence the properties of Ge and GeOx films, thereby contributing to their optimization for advanced technological applications.

2. Methods

Ge films were deposited by means of the thermal evaporation technique on soda-lime glass substrates (see Fig. 1(a)). Prior to each deposition of the film, each of the substrates was cleaned with freshly prepared acetone for 10 min in the ultrasonic bath. The depositions took place in the vacuum chamber of ≤1×10-5 mbar with the substrate-target distance of ~8 cm. Each of the depositions took place at RT, using a current and voltage of 80 A and ~1 V, respectively, for evaporating the Ge powder source.

The annealing experiments were then performed for the as-deposited Ge films in order to crystallize the films and to oxidize the Ge film into GeO_x. The annealing was done by increasing the temperature by ramping it up at 30 ^{0}C per minute and maintaining a constant temperature for 15 minutes at the desired temperature. The cooling was done by removing the film from the annealing tool and leaving it at room temperature (AC room conditions 18-20 ^{o}C). See Fig. 1(b) for the schematic.

The physical properties of the films were evaluated using multiple analytical techniques. To characterize the structural properties of the films, XRD measurements were performed using the x-ray diffractometer with CuKα radiation (λ = 0.15418 nm, Bruker). The XRD measurements were performed using thin film type of measurement. The 2θ scans were performed to assess the crystallinity of the film using grazing incident angle. The optical properties of the films were obtained by measuring UV-Vis spectroscopy. To analyze the microstructures of the films, SEM measurements were performed. SEM was employed to obtain high-resolution images of the film's surface morphology and microstructure, revealing detailed information about surface uniformity and textures. UV-Vis spectroscopy was used to analyze the optical properties of the films, including their absorption spectra. Through these analytical methods, the study aims to offer a thorough understanding of how thermal evaporation and subsequent annealing influence the properties of Ge and GeOx films, thereby contributing to their optimization for advanced technological applications.

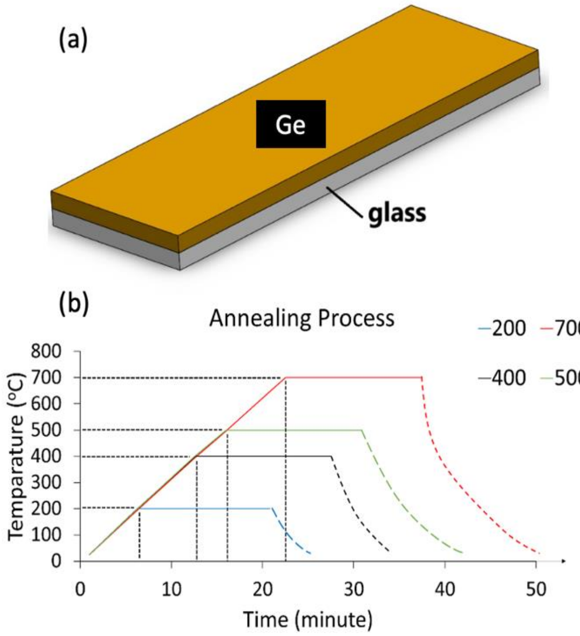


Fig. 1: The schematics of (a) the Ge/GeO_x layer on a glass substrate, and (b) the annealing process at different temperatures.

3. Results and discussions

As detailed in the experimental section, XRD measurements were conducted to evaluate the crystalline phases and degree of crystallinity of the films. Fig. 1 displays representative XRD patterns for films annealed at temperatures of 500 °C and 700 °C, indicated by the red and black curves, respectively. For films annealed at lower temperatures (≤500 °C), the XRD patterns (not shown) predominantly feature broad peaks, such as the peak at approximately 2θ = 27.3°, which corresponds to the (111) crystallographic plane of cubic germanium (Ge) [19, 20]. The broadness of these peaks suggests that films annealed at these temperatures are predominantly amorphous. Despite this, an estimation of the degree of crystallization can be made. Calculations reveal that the film deposited at 200 °C exhibits the lowest degree of crystallization, which increases to approximately 20.4% for the film annealed at 500 °C. At this temperature, an additional broader peak is observed at 2θ ≈ 12.6° [21], associated with the (100) crystallographic plane of cubic Ge [22]. This indicates that, at 500 °C, partial crystallization has occurred, and the film exhibits a more complex phase composition compared to those annealed at lower temperatures.

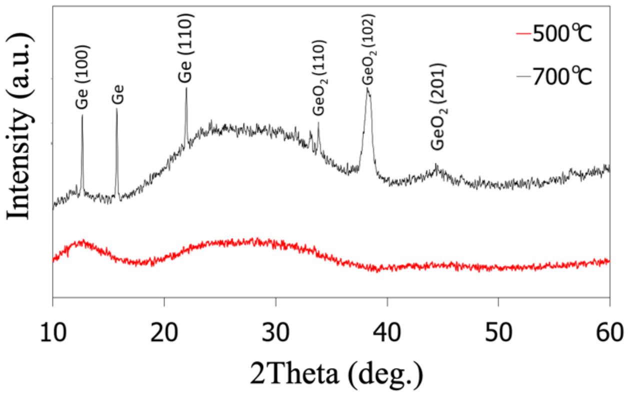


Fig. 2: XRD patterns of the Ge thin films annealed at different temperatures.

The film annealed at a higher temperature of 700 °C exhibits distinct characteristics as evidenced by the XRD pattern shown by the black curve in Fig. 2. Analysis of this curve reveals the emergence of sharp XRD peaks, which indicate significant crystallization of the film. The sharpness and intensity of these peaks confirm the predominant crystallization of the film following high-temperature annealing. The XRD data shows peaks corresponding to the diffraction patterns of both cubic germanium (Ge) and tetrahedral germanium dioxide (GeO_2) phases. Specifically, peaks observed at approximately 2θ values of 12.6° and 22.0° are associated with the Ge(100) and Ge(110) crystallographic planes, respectively [22]. Additional peaks at around 33.8° and 28.2° correspond to the GeO_2(110) and GeO_2(201) planes, respectively [23]. The presence of diffraction peaks from both Ge and GeO_2 phases suggests that at the annealing temperature of 700 °C, both phases coexist within the film [23-25]. This coexistence of Ge and GeO_2 phases can be attributed to the annealing and subsequent cooling processes being conducted under ambient pressure, rather than in a vacuum or an inert gas environment such as argon. Under these conditions, the high-temperature annealing likely facilitated oxidation, resulting in the formation of GeO_2 alongside the crystalline Ge.

As detailed in the experimental section, varying the mass of the Ge powder was employed to produce thin films with different thicknesses. To assess the optical properties of these films within the UV to visible wavelength range, UV-Vis spectroscopy was performed. The data obtained from UV-Vis spectroscopy are presented in absorbance mode to elucidate the optical absorption spectrum of the thin films. Fig. 3 illustrates the optical characteristics of Ge thin films deposited from Ge powder with masses of 0.006 g, 0.012 g, and 0.018 g, represented by the red, green, and blue curves, respectively. The data reveal that as the mass of the Ge source powder increases, resulting in thicker films, there is a corresponding increase in optical absorption across the UV-Vis spectrum. Additionally, the absorption spectrum indicates that optical absorption decreases with increasing wavelength, with higher absorption observed in the shorter wavelength (UV) region compared to the longer wavelength (visible) region. This behavior reflects the material's wavelength-dependent absorption characteristics and highlights the impact of film thickness on optical performance.

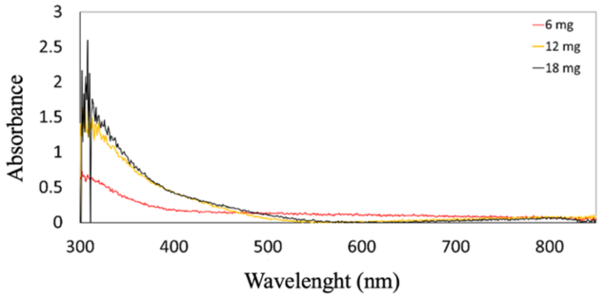


Fig. 3: Optical absorptions of the films deposited by means of the thermal evaporation technique using Ge source powders with different masses: 0.006 g, 0.012 g, dan 0.018 g.

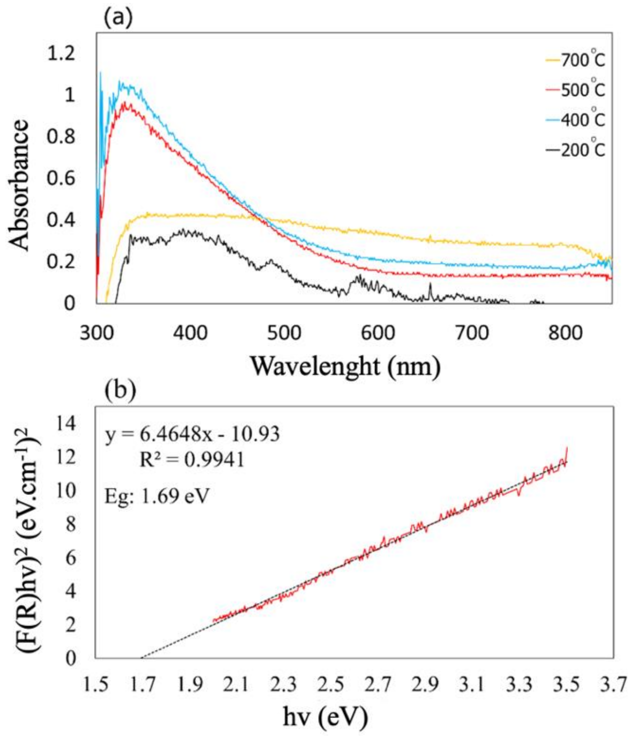


Fig. 4: (a) The optical absorption of the films annealed at 200, 400, 500, and 700 °C. (b) The Tauc's plot of the film annealed at 700°C

UV-Vis spectroscopy was also employed to investigate the optical properties of films annealed at various temperatures. Fig. 4(a) presents the UV-Vis optical absorption spectra for films deposited using 0.018 g of Ge powder and subsequently annealed at temperatures of 200 °C, 400 °C, 500 °C, and 700 °C, as indicated by the black, blue, red, and yellow curves, respectively. The data reveal a notable transformation in the absorption spectra with increasing annealing temperature. All samples exhibit absorption peaks in the UV region, specifically between 300 and 400 nm. The spectrum for the film annealed at 200 °C (black curve) demonstrates the lowest average absorption compared to films annealed at higher temperatures. In contrast, the sample annealed at 700 °C (yellow curve) shows a stable average absorption above wavelengths of 320 nm. Significant variations are observed in the spectra of films annealed at intermediate temperatures of 400 °C and 500 °C (blue and red curves). These films display more intense absorption in the UV region (λ ≤ 400 nm), with pronounced absorption peaks around λ ≈ 400 nm. This variation in absorption characteristics underscores the influence of annealing temperature on the optical properties of the Ge thin films, reflecting changes in their structural and electronic properties.

Band gap energy measurements of the film annealed at 700 °C, using Tauc's plot i.e. by analyzing $h\nu^2$ (photon energy squared) against $(\alpha h\nu)^2$ curve, where α is the absorption coefficient. From Fig. 4(b), we can observe that the relationship between $(\alpha h\nu)^2$ and hν (photon energy) is linear, which is consistent with the characteristics of semiconductor materials with a direct band gap with the energy gap (Eg) of 1.69 eV. The changes in the UV-Vis spectrum of the films that have been annealed at different temperatures can occur for two reasons. The first can be due to the crystallization process in the thin film, which greatly affects the magnitude of the dielectric constant of the thin film. The higher the annealing temperature, the higher the degree of crystallinity of the thin film. The second is the degree of oxidation that occurs during heating. Oxidation will lead to the formation of GeOx oxide which has different optical absorption properties from the pure Ge layer.

To analyze the microstructural features of the surface of annealed films at various temperatures, SEM was employed. Fig. 5 presents the SEM images of films annealed at 400 °C, 500 °C, and 700 °C. As depicted in Fig. 5(a), the SEM image of the film annealed at 400 °C reveals a predominantly smooth surface. At this lower annealing temperature, the degree of crystallization is limited, as corroborated by XRD measurements. In contrast, annealing at 500 °C leads to a more pronounced crystallization, as evidenced by the SEM image in Fig. 5(b). The surface of the film annealed at this temperature displays a distinctive morphology characterized by interconnected spherulite structures with diameters exceeding 5 μm. This snowflake-like pattern indicates active nucleation and crystal growth during the annealing process, which is predominantly surface growth [26]. The homogeneous distribution of these spherulites across the film surface suggests uniform crystallization. At the higher annealing temperature of 700 °C, as shown in Fig. 5(c), the SEM image reveals the development of larger crystallites forming a flower-like structure. This pattern suggests a transition from surface growth to volume growth [26], reflecting more extensive crystal development. The observed structure indicates that the crystallization process at this temperature involves substantial volume growth rather than just surface growth. Overall, the SEM images demonstrate that the surface topography of the thin films evolves with increasing annealing temperature, transitioning from a smooth surface to more complex morphologies. The crystallization process appears to be homogeneous, with temperature-dependent changes in crystal growth mechanisms. The nature of crystal growth, whether surface or volume, is influenced by factors such as the ratio of surface to bulk contaminant gas elements during substrate and holder degassing [26].

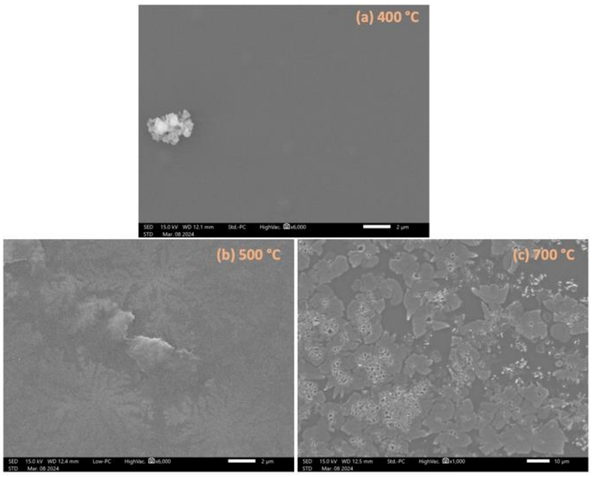


Fig. 5: SEM images of the Ge thin films annealed at (a) 400, (b) 500, and (c) 700 °C.

5. Conclusions

In this study, Ge films were deposited onto low-cost soda-lime glass substrates using thermal evaporation. The films were subsequently annealed at temperatures ranging from 200 to 700 °C. To characterize the films, we employed a combination of XRD, UV-Vis spectroscopy, and SEM. The XRD analysis reveals that the phase of the film transitions from an amorphous state to a predominantly cubic diamond-like structure of Ge, with a concurrent presence of a tetragonal GeO_2 phase at the highest annealing temperature of 700 °C. This phase transition significantly affects the optical properties of the films, as observed through UV-Vis spectroscopy. Specifically, higher annealing temperatures correlate with increased optical absorbance at longer wavelengths, indicating a shift in the films' optical absorption characteristics due to the formation of GeO_2 and the evolution of the Ge crystal structure.

Acknowledgment (Optional)

The authors acknowledge the generous financial support from Penelitian Internal UAD 2023 through Penelitian Dosen Pemula with contract number PDP-259/SP3/LPPM-UAD/VIII/2023.

References

[1]. L. Wind, M. Sistani, Z. Song, X. Maeder, D. Pohl, J. Michler, B. Rellinghaus, W. M. Weber, and A. Lugstein, "Monolithic metal-semiconductor-metal heterostructures enabling next-generation germanium nanodevices" ACS Applied Materials & Interfaces, 13(10), 12393-12399, (2021).

[2]. L. Wang, Y. Zhang, B. Wang, Y. Wei, B. Zhang, L. Meng, T. Liu, B. Wang, B. Han, and Z. Jiang, "High-performance infrared Ge-based plasmonic photodetector enhanced by dual absorption mechanism" APL Photonics, 5(9), (2020).

[3]. B. Zheng, Z. Wu, F. Guo, R. Ding, J. Mao, M. Xie, S. P. Lau, and J. Hao, "Large-area tellurium/germanium heterojunction grown by

molecular beam epitaxy for high-performance self-powered photodetector" Advanced Optical Materials, 9(20), 2101052, (2021).
[4]. K. Kumari, S. Kumar, M. Mehta, A. Chatterjee, S. K. Selvaraja, and S. Avasthi, "Laser-crystallized epitaxial germanium on silicon-based near-infrared photodetector" IEEE Sensors Journal, 22(12), 11682-11689, (2022).
[5]. F. Zhao, X. Chen, Z. Yi, F. Qin, Y. Tang, W. Yao, Z. Zhou, and Y. Yi, "Study on the solar energy absorption of hybrid solar cells with trapezoid-pyramidal structure based PEDOT: PSS/c-Ge" Solar Energy, 204, 635-643, (2020).
[6]. S. Moon, K. Kim, Y. Kim, H. K. Kang, K.-H. Park, and J. Lee, "Ultrathin Flexible Ge Solar Cells for Lattice-Matched Thin-Film InGaP/(In) GaAs/Ge Tandem Solar Cells" Solar RRL, 7(22), 2300387, (2023).
[7]. L. Tang, S. E. Kocabas, S. Latif, A. K. Okyay, D.-S. Ly-Gagnon, K. C. Saraswat, and D. A. Miller, "Nanometre-scale germanium photodetector enhanced by a near-infrared dipole antenna" Nature Photonics, 2(4), 226-229, (2008).
[8]. D. Benedikovic, L. Virot, G. Aubin, J.-M. Hartmann, F. Amar, X. Le Roux, C. Alonso-Ramos, É. Cassan, D. Marris-Morini, and J.-M. Fédéli, "Silicon-germanium receivers for short-wave-infrared optoelectronics and communications: High-speed silicon-germanium receivers (invited review)" Nanophotonics, 10(3), 1059-1079, (2021).
[9]. Y. Yang, X. Wang, C. Wang, Y. Song, M. Zhang, Z. Xue, S. Wang, Z. Zhu, G. Liu, and P. Li, "Ferroelectric enhanced performance of a GeSn/Ge dual-nanowire photodetector" Nano Letters, 20(5), 3872-3879, (2020).
[10]. M. Oehme, J. Werner, M. Kaschel, O. Kirfel, and E. Kasper, "Germanium waveguide photodetectors integrated on silicon with MBE" Thin Solid Films, 517(1), 137-139, (2008).
[11]. B. G. Dimez, "Al-Ge eutectic bonding for wafer-level vacuum packaging of MEMS devices" Middle East Technical University, (2022).
[12]. X. Geng, Q. Xie, Y. Zhu, G. Yao, and L. Wang, "An improvement for enrichment and purification of germanium using carbonyl acid extractants" Separation and Purification Technology, 356, 129770, (2025).
[13]. D. Baghdedi, H. Hopoğlu, S. Sarıtaş, İ. Demir, İ. Altuntaş, N. Abdelmoula, E. Gür, and E. Ş. Tüzemen, "Comprehensive growth and characterization study of GeOx/Si" Journal of Molecular Structure, 1274, 134398, (2023).
[14]. P. G. Nalam, D. Das, V. Shutthanandan, and C. Ramana, "α-Quartz Phase Stabilization, Surface Texturing, and Tunable Optical Properties of Nanocrystalline GeO2 Films Made by Pulsed-Laser Deposition: Implications for Optical and Optoelectronic Applications" ACS Applied Optical Materials, 1(11), 1761-1776, (2023).
[15]. L. Xu, S. Watariguchi, T. Takahashi, and H. Watanabe, "Investigation into Tin-Germanium Oxide Films Deposited from Aqueous Solutions and Their Application to Metallizations on Glass" Journal of The Electrochemical Society, 164(14), D1066, (2017).
[16]. M. S. Rathore, A. Vinod, and N. S. Rao, "Structural and Optical Properties of GeO2 Thin Films Prepared by E-Beam Evaporation" Advanced Science Letters, 22(11), 3798-3801, (2016).
[17]. K. M. Sulieman, M. Jumidali, and M. Hashim, "Blue Emission Peak of GeO2 Particles Grown Using Thermal Evaporation" AIP Conference Proceedings, 121-124, (2010).
[18]. Y. Cho, M. Jiang, D. Ahn, and W. Choi, "Effect of Deposition Temperature on the Electrical Properties of Solid-Phase Crystallized Ge Thin Films" Electronic Materials Letters, 1-8, (2024).
[19]. K. Hatano, Y. Asano, Y. Kameda, A. Koshio, and F. Kokai, "Formation of germanium-carbon core-shell nanowires by laser vaporization in high-pressure Ar gas without the addition of other metal catalysts" Materials Sciences and Applications, 8(12), 838-847, (2017).
[20]. R. Islamgaliev, R. Kuzel, E. Obraztsova, J. Burianek, F. Chmelik, and R. Valiev, "TEM, XRD and Raman scattering of germanium processed by severe deformation" Materials Science and Engineering: A, 249(1-2), 152-157, (1998).
[21]. K. Vijayarangamuthu, S. Rath, D. Kabiraj, D. Avasthi, P. K. Kulriya, V. Singh, and B. Mehta, "Ge nanocrystals embedded in a GeOx matrix formed by thermally annealing of Ge oxide films" Journal of Vacuum Science & Technology A, 27(4), 731-733, (2009).
[22]. H. Ninomiya, N. Itoh, S. Rath, S. Nozaki, and H. Morisaki, "Study of growth process of germanium nanocrystals using a grazing incidence x-ray diffraction method" Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena, 17(5), 1903-1905, (1999).
[23]. X. Wang, L. Duan, G. Dong, P. Wei, W. Wang, L. Wang, and Y. Qiu, "Synthesis and characterization of nano/micro-structured crystalline germanium dioxide with novel morphology" Chinese Science Bulletin, 54(16), 2810-2813, (2009).
[24]. K. Takemura, U. Schwarz, K. Syassen, M. Hanfland, N. Christensen, D. Novikov, and I. Loa, "High-pressure Cmca and hcp phases of germanium" Physical Review B, 62(16), R10603, (2000).
[25]. C. Ramana, G. Carbajal-Franco, R. Vemuri, I. Troitskaia, S. Gromilov, and V. Atuchin, "Optical properties and thermal stability of germanium oxide (GeO2) nanocrystals with α-quartz structure" Materials Science and Engineering: B, 174(1-3), 279-284, (2010).
[26]. A. Barna, P. Barna, and J. Pocza, "Crystallization processes in a-Ge thin films" Journal of Non-Crystalline Solids, 8, 36-44, (1972).