Cumhuriyet Sci. J., 45(4) (2024) 598-603
DOI: https://doi.org/10.17776/csj.1482632

Cumhuriyet Science Journal

| csj.cumhuriyet.edu.tr | Founded: 2002 ISSN: 2587-2680 e-ISSN: 2587-246X Publisher: Sivas Cumhuriyet University

Production of GeOx Films at Different Oxygen Flow Rates and Different Annealing Temperatures and Examination of Energy Band Gaps using Kubelka Munk Method

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Research Article

History
Received: 12/05/2024
Accepted: 21/08/2024

ABSTRACT

In this study, GeO_x films were grown on silicon substrates using the Radio Frequency (RF) Magnetron Sputtering method at different oxygen flow rates and annealing temperatures. The films were produced at a substrate temperature of 250°C and a working pressure of 13 mTorr. Subsequently, the films were annealed at temperatures of 300°C, 500°C, 600°C, 700°C, 900°C, and 1000°C. Total and diffuse reflection measurements were performed to investigate the optical properties of the films. Energy band gaps were determined using diffuse reflection measurements and they were calculated using the Kubelka-Munk method. It was observed that the energy band gap increased with increasing oxygen ratio. Additionally, annealing temperatures were found to cause changes in the energy band gaps.

Keywords: GeO_2, Reflectance, RF Magnetron.

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Introduction

Due to its small difference between indirect and direct bandgap, high carrier mobility, and strong photon absorption, Germanium's optical properties are highly attractive compared to other semiconductors [1]. Furthermore, its large exciton Bohr radius, lower bandgap, and smaller effective carrier mass [2], along with its unique energy bandgap structure, make it appealing for scientific research and open up new possibilities for next-generation applications [3]. However, electronic devices based on narrow bandgap materials suffer from being unsuitable for operating at high temperatures and having high power consumption during processing [4]. The high processing cost and chemical instability of pure semiconductors also limit their application areas [5].

Therefore, in recent years, the production and engineering of semiconductor oxide materials at the nano scale have gained significant importance due to their exceptional physical and chemical properties and have attracted great interest due to their potential applications in modern nano-scale electronic and optical devices. Among various semiconductor oxides, Germanium oxide (GeO_2) is a promising material exhibiting interesting properties such as high transparency, wide energy bandgap (> 5 eV), good mechanical strength, high dielectric constant, high thermal stability, high carrier concentration, and refractive index [6,9]. The unique properties of crystalline GeO_2 make it suitable for optoelectronic and memory applications [8, 10-12]. Additionally, GeO_2 finds various uses in optical applications such as infrared lenses, prisms, spectroscopy devices, electronic memory devices [13], fiber optics [14], piezoelectric material [15,16], and potential anode materials for high-energy Li-ion batteries [17,18]. Apart from these, GeO_2 is used as the main material in devices emitting photoluminescence emission in the visible region [10]. However, the technological importance of films in optical fields strongly depends on quality and structural properties that can be adjusted with varying growth conditions and growth parameters [19,20].

In recent years, various techniques have been developed for the growth of GeO_2 thin films, including the sol-gel technique [21], hydrothermal technique at different synthesis pressures and temperatures [22], electron beam evaporation [23], RF and DC magnetron sputtering [24,25], and pulsed laser deposition (PLD) technique [26]. Yin and Garside [27] produced GeO_2 thin films through radio frequency (RF) sputtering and reactive direct current (DC) sputtering. In both techniques, high deposition rates were achieved. Valligatla et al. prepared GeO_2 planar waveguides on v-SiO_2 substrates using an RF magnetron sputtering system with GeO_2 target, applying 80 W rf power at a pressure of 5.4×10^{-3} mbar with Ar gas, and then annealed with a pulsed CO2 laser. They examined the effects of this annealing on the optical and structural properties of the produced material using m-line and micro-Raman spectroscopy and AFM measurements. When they looked at the Raman spectroscopy and AFM results after pulsed CO2 laser annealing [28], they found that the materials produced showed a crystalline environment that changed with the varying irradiation time. Xie et al. [29] grew GeO_2 with a thickness of 300 nm on n-type Ge (100) using radio frequency magnetron sputtering method with a GeO_2

target in Ar/O_2 at a base pressure of 6×10^{-6} Pa at room temperature. Chiasera et al. [30] grew GeO_2 planar waveguides on a silica substrate of size 7.5 × 2.5 cm under an Ar atmosphere at a pressure of 5.4×10^{-3} mbar using the Radio Frequency Sputtering (RFS) technique with 80 W RF power and then annealed with a pulsed CO2 laser.

The aim of this study is to optimize the performance of germanium dioxide (GeO_2) annealed at different temperatures and produced at different oxygen flow rates by examining its optical properties. Understanding the effects of annealing temperature and oxygen flow rates on the energy band gap of GeO_2 in detail is critical to increase the efficiency of the material in various high-tech applications. Our motivation for this study is the increasing importance of GeO_2, especially in optoelectronic and sensor technologies. However, studies on the properties of GeO_2 produced by RF magnetron sputtering at different annealing temperatures and different oxygen flow rates are limited in the current literature. This research was carried out to address this deficiency and to maximize the potential of GeO_2 in applications. In our study, the effects of changes in the optical properties resulting from the annealing of GeO_2 at different temperatures and different oxygen flow rates were comprehensively analyzed. In addition, this study provides valuable information for future research and applications by revealing the effects of different annealing temperatures and different oxygen flow rates on the performance of GeO_2 in detail.

Materials and Methods

In this study, GeO_x films were produced on silicon using the RF magnetron sputtering method. The NANOVAK NVTS-400 Thermal and Sputter combined system was utilized to fabricate the films. Germanium with a purity of 99.999% was used as the target material, and GeO_x thin films with different oxygen ratios of 7%, 8%, and 9% were obtained. The films were produced at a substrate temperature of 250°C, with a rotation speed of 10 rpm, a power of 100 W, a growth rate of 0.4-0.6 Å/s, and a working pressure of 13 mTorr.

Subsequently, the films were annealed at temperatures of 300°C, 500°C, 600°C, 700°C, 900°C, and 1000°C. Reflection measurements for the optical study of the GeO_x semiconductor films, produced under different growth conditions on silicon substrates, were performed using a Cary 5000 UV-VIS-NIR Optical spectrophotometer. Total and diffuse reflection measurements were taken in the wavelength range of 250-800 nm using the spectrophotometer. The diffuse reflection measurements allowed us to determine the energy band gap.

Result and Discussion

Figure 1 (a, b, c) shows the total reflection measurements of the films produced at three different oxygen ratios and annealed at different temperatures.

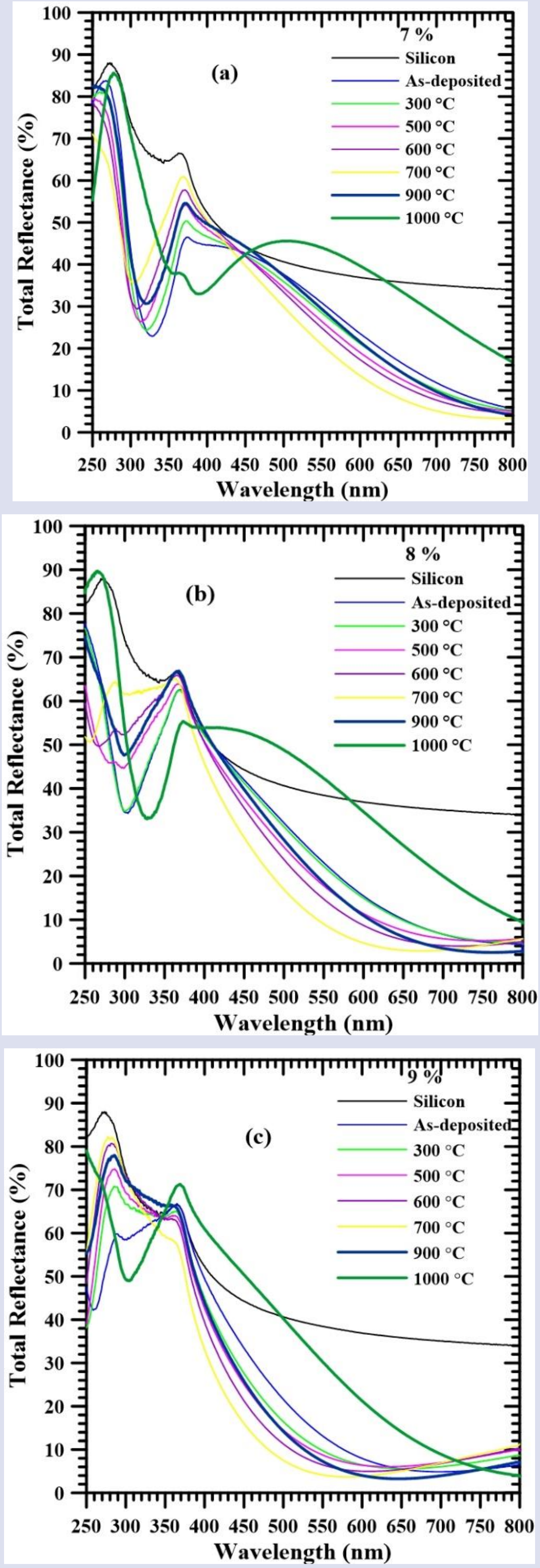


Figure 1. Variation of total reflectance as a function of wavelength **(a)** 7% oxygen flow **(b)** 8% oxygen flow **(c)** 9% oxygen flow.

It has been observed that there is a shift towards shorter wavelengths in thin films with oxygen ratios of 7% and 8% up to 700°C, followed by an increase again. In the case of the thin film with a 9% oxygen ratio, there is a shift towards shorter wavelengths up to 600°C, followed by an increase. After 600°C, it can be said that the surface properties of the film have changed. Films produced with different oxygen percentages were annealed at different annealing temperatures and as annealing increased, total reflection first increased and then decreased. The decrease in reflection with annealing is thought to be related to the removal of defects. Accordingly, the energy band gap first increased and then decreased. It was observed that the energy band gap first increased and then decreased with the increase in annealing temperature. The shift in the energy band gap is generally related to oxygen deficiencies in the crystal phase.

The graphs of diffuse reflection measurements are provided in Figure 2. When examining the graphs, it is observed that as the temperature increases in the ultraviolet region, the diffuse reflection also increases. Although there is a gradual decrease in diffuse reflection after 700°C for thin films with oxygen ratios of 7% and 8%, a decrease is observed after 600°C for the film with a 9% oxygen ratio. The energy band gap of the produced thin films was determined using diffuse reflection measurements. For this purpose, the Kubelka-Munk method was employed [31]. The diffuse reflection of the film is related to the Kubelka-Munk function denoted as F(R). Calculation of the reflection data is performed using the Kubelka-Munk method as follows:

$$F(R) = \frac{(1-R)^2}{2R} \tag{1}$$

This equation relates the film's diffuse reflection (R) to the Kubelka-Munk function (F(R)). From here, graphs of $(F(R) \times E)^2$ are plotted against energy to determine the energy band gap. In the Cary 5000 device, there is a transition from the Deuterium lamp to the halogen lamp at a wavelength of 350 nm. Therefore, the fluctuations seen in Figure 3 (b) have occurred.

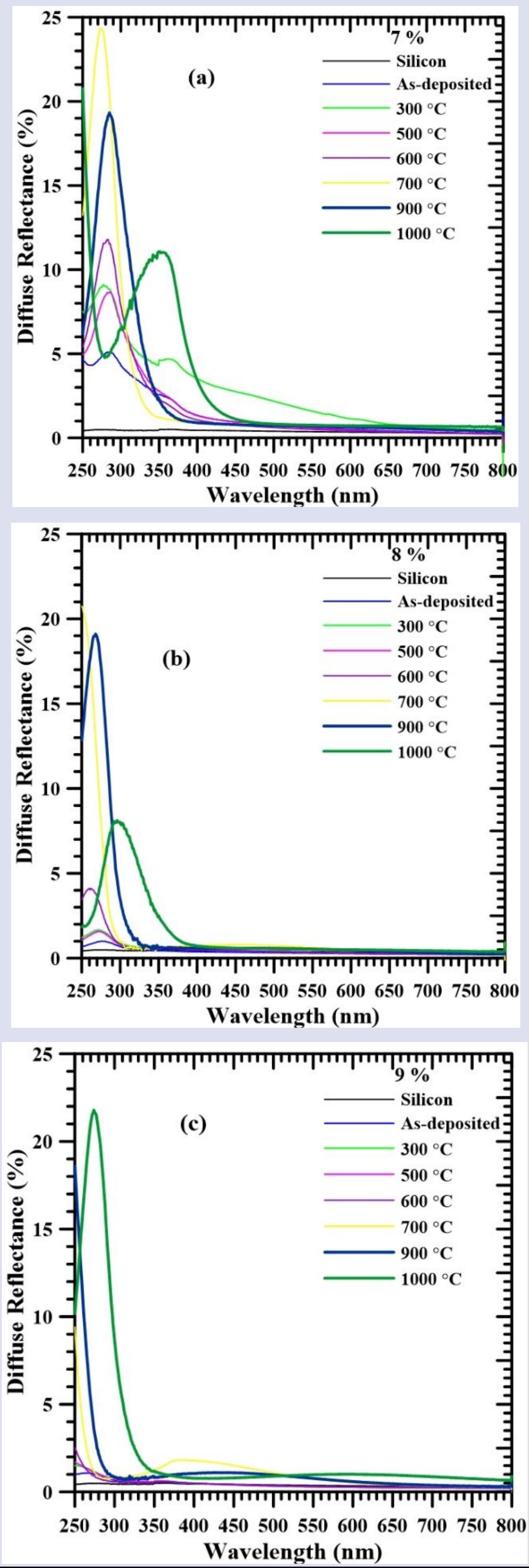


Figure 2. Variation of diffuse reflectance as a function of wavelength **(a)** 7% oxygen flow **(b)** 8% oxygen flow **(c)** 9% oxygen flow

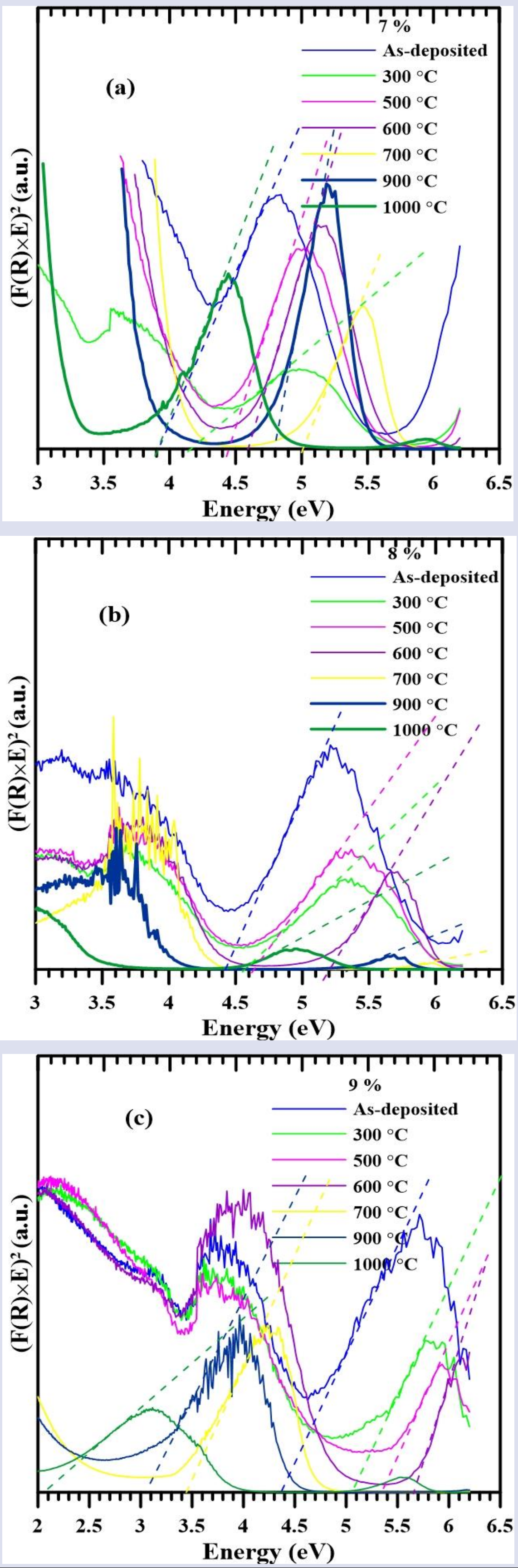
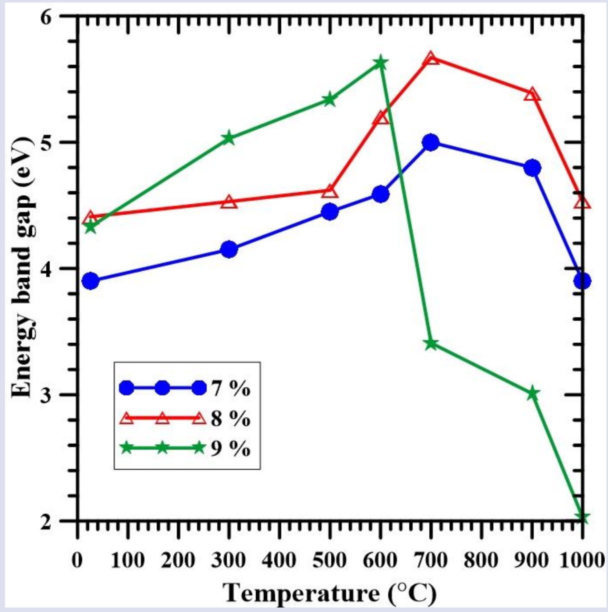


Figure 3. Variation of $(F(R)\times E)^2$ of the film with 7% oxygen content according to energy **(b)** Variation of $(F(R)\times E)^2$ of the film with 8% oxygen content according to energy **(c)** Variation of $(F(R)\times E)^2$ of the film with 9% oxygen content according to energy

In Figure 3 (a), tangents are drawn at the absorption edges based on the first peaks (absorption edge). The points where these tangents intersect the x-axis provide the energy band gap. It is observed that the energy band gap increases up to 600°C. The highest increase in the energy band gap is also observed at 700°C. After this temperature, a decrease in the energy band gap is observed. It has been visually observed that the color of the films changes after 700°C. As seen in Figure 4, the energy band gap of the as-annealed samples with a substrate temperature of 250°C varied with increasing oxygen flow. Up to annealing temperatures of 300°C, 500°C, and 600°C, the energy band gap of all three samples increased. However, at higher temperatures the energy band gap decreased. When comparing films produced at 7% and 8% oxygen ratios, there was no decrease in the energy band gaps. However, for the film produced at a 9% oxygen ratio, a decrease was observed after 600°C.



Figüre 4. Energy Band Gaps of Thin Films Produced at 7%, 8%, and 9% Oxygen Ratios

This is because the produced film maintains its structure up to a certain temperature. After a certain value of the annealing temperature, there may be a decrease in the band gap values, a decrease in the number of oxygen vacancies and/or defects that may be grain boundaries. This leads to a decrease in the carrier concentration in the conduction band of the material. At the same time, the annealing process improves crystallinity and increases the average grain size. Ultimately, this results in the reduction of defects. It reduces the tension in films. As a result, high-temperature annealing improves the crystal structure of the material and increases the ordering at the atomic level. This can cause a narrowing of the energy band gap. This change is related to the crystallization and defect correction that occurs during the annealing process [32,33,34].

Conclusion

GeO_x films produced on silicon substrates with different oxygen percentages were successfully produced by the RF magnetron sputtering method at different annealing temperatures. It has been observed that there is a shift towards shorter wavelengths in thin films with oxygen ratios of 7% and 8% up to 700°C, followed by an increase again. In the case of the thin film with a 9% oxygen ratio, there is a shift towards shorter wavelengths up to 600°C, followed by an increase. It is observed that the energy band gap increases up to 600°C. The highest increase in the energy band gap with a 7% oxygen ratio is also observed at 700°C. After this temperature, a decrease in the energy band gap is observed. For the film produced at a 9% oxygen ratio, a decrease was observed after 600°C. This is because the produced film maintains its structure up to a certain temperature.

Acknowledgement

This study is supported by TÜBİTAK 2209-A University Students Research Projects, No. 2209-A Tübitak-1919B012108759.

Conflicts of interest

There are no conflicts of interest in this work.

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