

Optical and Electrical Properties of Glass/Graphene Oxide Thin Films

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Abstract

The work studies the effect of Graphene oxide on the optical and electrical properties of glass prepared on glass substrates using sol-gel dip-coating technique. The deposited film was of about (60-100 \pm 5%) nm thickness. Optical and electrical properties of the films were studied under different graphene oxide concentrations of 2%, 4%, 6% and 8% wt. The results show that the optical band gap for glass-graphene oxide films decreased after adding the graphene oxide. Calculated optical constants, such as transmittance, extinction coefficient, have changed after adding graphene oxide. The structural morphology and composition of elements in the samples was demonstrated using SEM and EDX. The electrical properties of films include DC electrical conductivity increase in current as graphene oxide concentration increases was noticed.

Key words

Glass – Graphene oxide thin films, optical properties, electrical properties, SEM, EDX.

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الخصائص البصرية والكهربائية للأغشية الرقيقة الزجاج / أكسيد الكرافين

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الخلاصة

تم دراسة تأثير اوكسيد الكرافين على الخواص الضوئية والكهربائية للزجاج المحضر على ركائز الزجاج باستخدام تقنية الطلاء بالغمس. الفيلم المترسب يبلغ سمكه حوالي (60-100 \pm 5%) نانومتر. تمت دراسة الخواص البصرية والكهربائية للأغشية تحت ظروف تحضير مختلفة مثل تركيز اوكسيد الكرافين 2، 4، 6 و 8 بالوزن%. أظهرت النتائج أن فجوة الطاقة البصرية لأغشية اوكسيد الكرافين الزجاجية تتناقص بعد إضافة اوكسيد الكرافين. تتغير الثوابت الضوئية المحسوبة، مثل معامل النفاذية والخمود بعد إضافة اوكسيد الكرافين. تم توضيح البنية التركيبية وتكوين العناصر للعينات باستخدام المجهر الإلكتروني الماسح و مطيافية تشتت الطاقة بالأشعة السينية. تشمل الخواص الكهربائية الموصلية الكهربائية للتيار المستمر، وجدنا زيادة في التيار مع زيادة تركيز اوكسيد الكرافين.

Introduction

Graphene is a chemical compound consisting of carbon, oxygen, and hydrogen in various proportions. Graphite consists of layers of graphene. Graphene oxide can be obtained through several methods, including the Hummer's method and the modified Hummer's method, which are chemical methods used to produce graphene oxide by adding graphite to a solution of sulfuric acid (H₂SO₄) with sodium nitrate (NaNO₃) and potassium permanganate (KMnO₄) at room temperature. The mixture is stirred for 3 days in order to achieve the highest degree of oxidation. One of the important features of graphene oxide is its versatility in many applications, especially nanoelectronics. Graphene oxide used in the process of filtering water and organic solutions play an important role in some applications such as water purification [1-5].

Graphene is an allotropic substance of carbon, with a two-dimensional hexagonal crystal structure (also called honeycomb or chicken wire). It is the thinnest substance ever known so far, its thickness is equivalent to only one carbon atom, yet it is considered one of the strongest materials known. In addition, the material of graphene is almost completely transparent, and despite this, it is very dense to the extent that it does not allow the smallest atom (helium) to pass through its hexagonal structure [6-10].

Two Russian scientists, Andrei Geim and Konstantin Novoselov, from the University of Manchester in 2004, developed graphene and both are winners of the Nobel Prize in Physics in 2010, Andrei Geim and Konstantin Novoselov. The substance is a plate 50 atoms long and 1 atom wide. The most prominent advantage of this material is the high velocity of its electrons, which reach ($44,000 \text{ cm}^2/\text{s}$) at room temperature. Graphene material is expected to help raise the speed of computers and touch screens to higher levels. Researchers from IBM reported in Safar 2010 that they achieved speeds of up to 100 GHz using a transistor of graphene [11].

There are many applications that are included in the composition of graphene, and in various fields such as: energy storage and transfer, and electronic devices, including: it is considered an alternative to silicon, especially as it is a very thin and solid material at the same time, as it is an appropriate price. It is used as a single film in paint applications and the production of modified surfaces to improve structural integrity, transparency and protection from corrosion. Graphene Oxide can replace the "plastic" nylon in many industries. It enters in many modern technological industries. It can be used in the manufacture of touch screens in addition to possessing optical properties and applications as it consists of a thin layer with two dimensions that can be used in optical and electronic devices such as transistors [12-15].

In this paper, graphene oxide with different concentrations and glass-graphene oxide thin films dissolved in Hydrofluoric acid (HF) solution have been prepared successfully by sol-gel (dip-coating) technique in room temperature. Structural, surface morphology, optical and electrical properties of samples were analyzed.

Experimental work

1. Materials

The primary precursors for the synthesis of glass-graphene oxide thin films include glass powder (microscopic slides) from RS with grain size (0.04-0.125) mm, Graphene 20 μm , and Hydrofluoric acid (HF) with concentration of 20% from sigma-Aldrich.

2. Preparation glass substrates and solutions

Glass substrates were prepared from the Chinese origin "microscope slide" type-RS, with 1.1 mm thick. The glass substrates were cut into pieces each of area of (2×2.5) cm^2 . These were cleaned thoroughly very well in order to extract any them of the impurities and unwanted materials attached to them. Otherwise, these impurities affect the structural and optical properties of the films deposited on them and thus this leading to a change of their properties and their physical and chemical characteristics. These cut glass substrates were first washed with a very pure solution of acetone ($\text{C}_3\text{H}_6\text{O}$), which is a fine organic solvent used as a paint remover, as it easily removes the deposits formed on the glass. Then, a solution of very pure absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) was used. This solution is a colorless and volatile liquid, after which dichloromethane (CH_2Cl_2) was used. This solution is a colorless liquid that evaporates easily to give a toxic gas with a strong smell and is not flammable, and it is a good

chemical solvent for various organic compounds (must wear masks when using it). It is considered one of the best glass cleaners ever, as it is used to remove difficult stains, colors and everything that may be stuck on glass. Finally, distilled water was used to remove stains deposited on the glass.

At each cleaning stage, the glass samples were placed in an ultrasonic cleaning bath for a period of 20 minutes. Then the glass bases were dried in the laboratory oven for 10 minutes, and then these substrates were dried with cleaning papers so as not to leave any impurities or unwanted traces on these glass substrates after wiping them with smooth, soft paper, to be ready for use and work.

3. Preparation of graphene oxide and glass-GO solutions

The glass pieces were crushed using a quartz mortar, and then 2 gm of this glass powder was dissolved in 5 ml of pure hydrofluoric acid solution at 99% purity. In addition, different ratios of graphene 2, 4, 6 and 8 wt% were used in order to dissolve in 5 ml of pure hydrofluoric acid solution at 99% purity).

The two solutions (GH) and (GRH) were mixed together, in order to obtain four different solutions $a=2\%$, $b=4\%$, $c=6\%$ and $d=8\%$ of glass-graphene oxide solutions. These solutions, they were placed on a (magnetic Stirrer) for a period of one hour at $70\text{ }^{\circ}\text{C}$ with the use of paramagnetic magnets to ensure that the materials were mixed and dissolved well. Then the solutions were placed in an (ultrasound bath) for a period of 3 days until the graphene oxide is completely dissolved in these four solutions, so that no large particles remain in the solution.

The resulting solutions were deposited on the previously prepared glass bases using a dip coating device, where the glass bases were placed in the solution with continuous up and down movement. Then, the samples were dried using a laboratory oven for drying for 10 minutes at $100\text{ }^{\circ}\text{C}$ or $80\text{ }^{\circ}\text{C}$ for 30 min. Finally, prepared samples are taken to make the required laboratory measurements.

4. Preparation and deposition of thin films

The substrates are prepared and cleaned first with different chemical solutions. Films from the sol-gel are preferred for use in dip-coating technique. All substrates were dipped into the gel; they were slowly withdrawn from the bath at a fixed speed of (80 mm/min).

5. XRD analysis

The crystal structure of the glass-graphene oxide films were analyzed with X-ray diffraction analyzer (XRD, Shimadzu) Voltage 40 kV, Current 30 mA, scanning speed 5 deg./min. The sample was scanned at $2\theta = (20-80)^{\circ}$.

6. Thickness of film measurements

To measure the thickness of the thin films prepared and deposited on glass substrates, the weight method was used. As this method only needs a sensitive electronic balance (4 digits) to measure the mass of the precipitated material on the substrate and through the product of the difference between the mass of the substrate before and after deposition of thin films. The thickness of the film can be found from the following relationship

$$t = \frac{\Delta w}{\rho \times A} = \frac{w_2 - w_1}{\rho \times (L \times W)} \quad (1)$$

where: t is the film thickness (cm), $\Delta w = w_2 - w_1$ is mass of the glass in gram before and after deposition, ρ is the density of the deposited material = 0.44 g/cm^3 , and

$A = L \times W$ is the area of the sample in cm^2 , in our case L is the length of the sample, W is the width of the sample (rectangle sample).

7. Optical properties measurements

Optical properties of thin films deposited by sol-gel method have been studied with double beam spectrophotometer (T80+ UV/VIS spectrometer). UV-visible spectroscopy was performed at room temperature and at a region from (200 to 1000) nm.

8. Electrical properties measurements

The electrical properties of glass-graphene oxide films depend on several factors. Electrical measurements were carried out to measure the electrical Current–Voltage with the use of a DC power supplied (0-10) V and the output current was measured with Keithly Electrometer (type 4830).

The electrical properties of glass-graphene oxide thin films and the effect of adding graphene oxide on the electrical properties of samples have been investigated.

Results and discussion

1. Measuring thickness of films

By applying Eq. (1), the results obtained are shown in Table 1.

Table 1: Thickness of (G-GO) samples using weight method.

No.	GO weight (gm)	Thickness Before Deposition (μm)	Thickness After Deposition (μm)
a: GO-2%	0.2	4.758974	4.819511
b: GO-4%	0.12	2.810938	2.891722
c: GO-6%	0.09	2.072954	2.168775
d: GO-8%	0.06	1.345101	1.445853

2. Structural measurements

The importance of using the X-ray diffraction technique lies in knowing the nature of the crystal structure of solids and thin films. Using this technique, it was proved that the films prepared in this work are pure and have a multicrystalline structure.

The X-ray diffraction spectrum Fig.1, shows that the graphene sample has a sharp crystal peak of about ($2\theta=26.320^\circ$), which corresponds to Miller's indices (002), thus, the intermediate distance of it is ($d=3.357$ nm), (according to $n\lambda = 2d\sin\theta$). Upon oxidation of graphite to graphene oxide, the X-ray diffraction spectrum was characterized by the appearance of a sharp peak at the angle ($2\theta= 11.42^\circ$) in all the GO samples which corresponds to Miller's indices (002). The intermediate distance has an amount of ($d=0.77$ nm). This is the result of the presence of oxygen, which has a number of functional groups that make up graphene oxide. This result indicates the formation of graphene oxide.

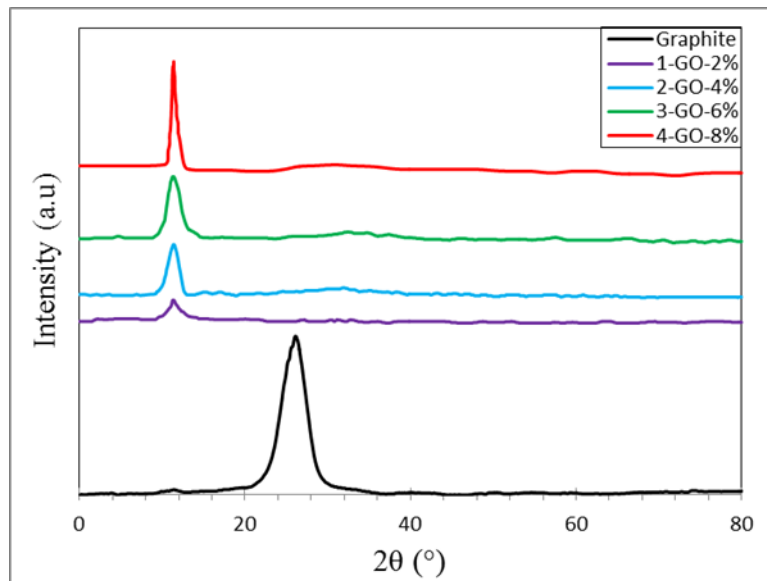


Fig.1: X-ray diffraction spectra of graphite powder and graphene oxide thin films.

3. Optical measurements

Optical analysis of samples deposited on glass was performed using UV-Vis spectroscopy. This technique is generally used for band gap determination and purity approximation. Transmittance spectra of films before and after adding graphene oxide is shown in Fig.2.

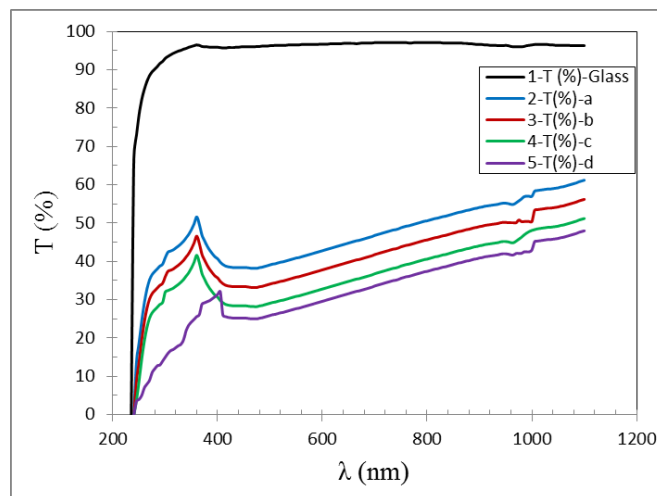


Fig.2: Variation of transmittance with wavelength of (1) glass pure (2) glass for different doping concentrations of graphene oxide thin films ((a) 2%, (b) 4%, (c) 6% and (d) 8% wt.

It is seen in Fig.2 that the transmittance edge shifts to higher wavelengths with increasing the concentrations of graphene oxide suggesting a decrease in the optical band gap.

The absorption coefficient is calculated using the following relation [16-18]:

$$\alpha = \frac{2.303 \times A}{t} \quad (2)$$

where: t is the thickness (cm), A is absorbance.

Fig.3 shows the relationship between the absorption coefficient and energy of glass thin films for different doping concentrations of graphene.

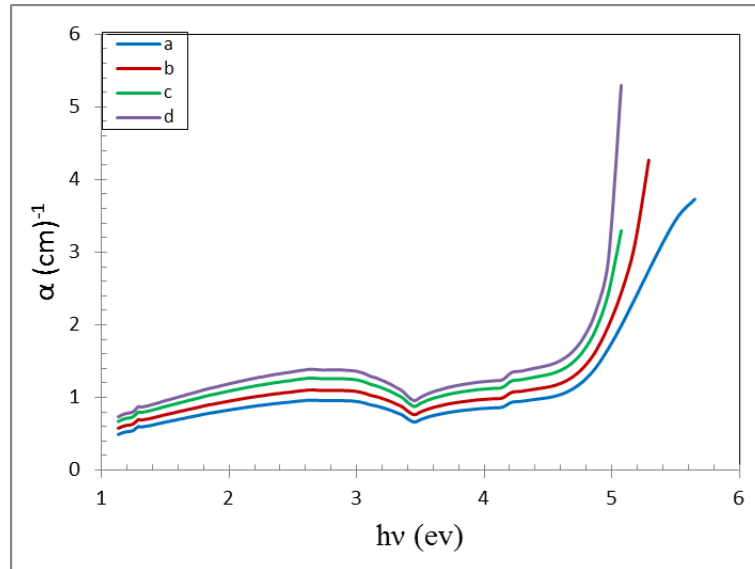


Fig.3: The absorption coefficient as a function of photon energy of glass for different doping concentrations of graphene oxide thin films ((a) 2%, (b) 4%, (c) 6% and (d) 8% wt.

From this figure, it is noticed that the absorption coefficient increased with the increase of the doping concentrations of graphene.

The refractive index calculation of the samples was achieved by the following equation [16-18]:

$$n = \frac{(1+\sqrt{R})}{(1-\sqrt{R})} \quad (3)$$

where: R is the reflectance of the sample.

The change in refractive index as a function of photon energy for glass with different doping concentrations of graphene oxide thin films is shown in Fig.4. It is observed that the refractive index values decreases with the increase of doping concentrations of graphene.

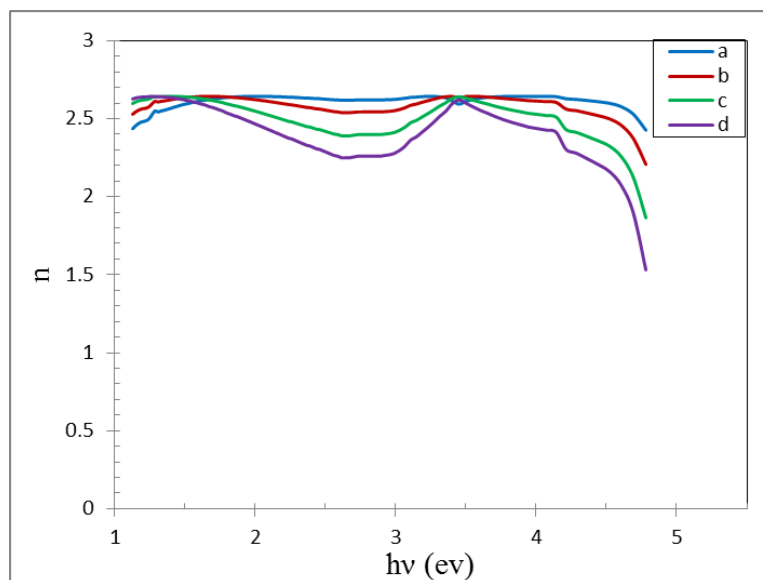


Fig.4: The refractive index as a function of photon energy incident on glass for different doping concentrations of graphene oxide thin films ((a) 2%, (b) 4%, (c) 6% and (d) 8% wt.

Extinction coefficient (unitless) of samples can be calculated using the following equation [16-18]:

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

Fig.5 shows the extinction coefficient of the samples as a function of photon energy. The results show that the extinction factor of the samples increased with increasing the concentration of graphene oxide. The value of the extinction coefficient of the sample with 8% wt of graphene is larger than the other concentrations of graphene.

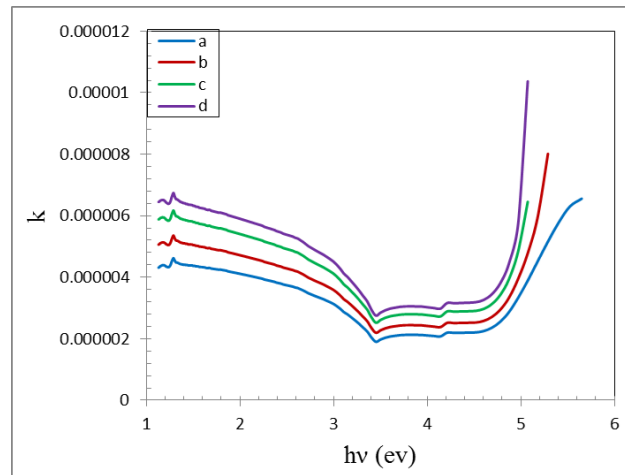


Fig.5: Extinction coefficient as a function of photon energy of glass for different doping concentrations of graphene oxide thin films ((a) 2%, (b) 4%, (c) 6%, (d) 8% wt.

$[(\alpha h\nu)]^2$ versus $(h\nu)$ Extrapolating the straight part of the plot to the photon energy axis, gives the energy gap of glass which is 7 eV, as shown in Fig. 6. This method can be used to know the energy gap of glass thin films of different doping concentrations of graphene. This was found to be 5 eV for 2% wt doping concentrations and was and 4.25 eV for concentrations of 8% wt. It can be concluded that as the concentration of graphene for glass increases; the energy gap has been reduces as shown in Figs. 6 and 7.

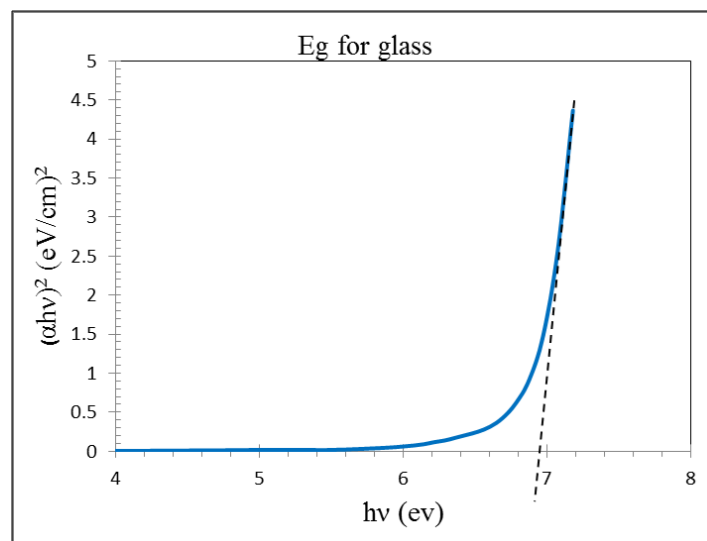


Fig.6: The optical band gap for glass-graphene thin films.

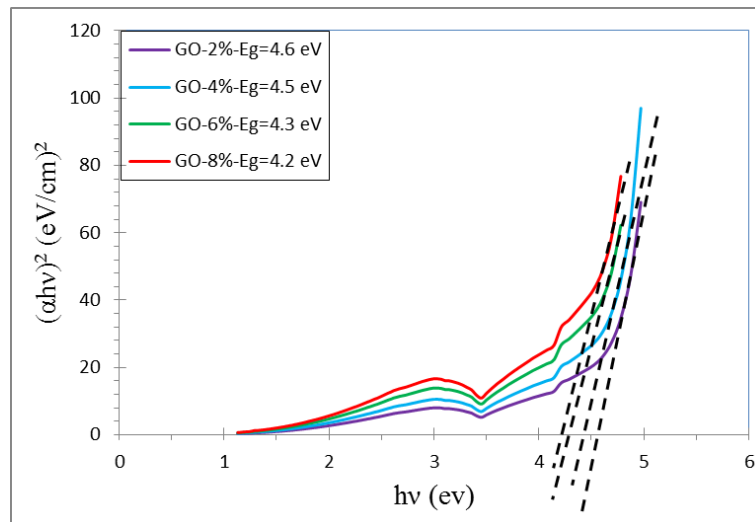


Fig.7: The optical band gap for glass for different doping concentrations of graphene oxide thin films (2, 4, 6 and 8) % wt.

This result agrees with that of Shen et al. [19]. In addition, the refractive of films was calculated based on the following equation as shown in Fig.8.

$$T + R + A = 1 \tag{5}$$

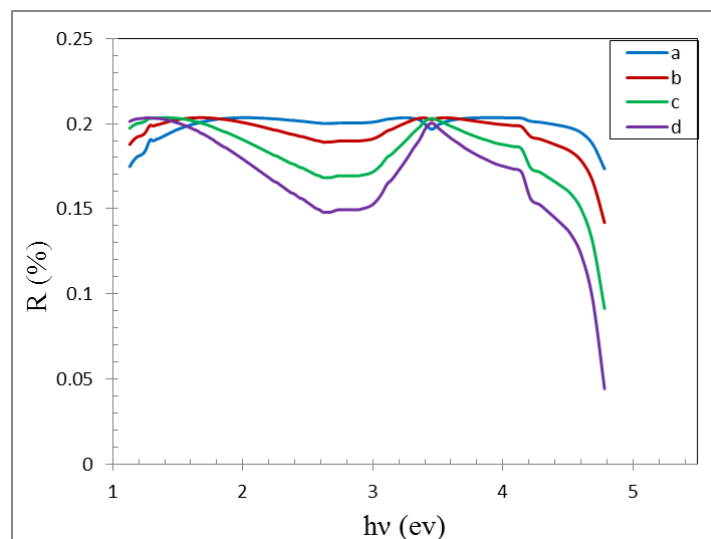


Fig.8: The reflectivity as a function of photon energy of glass for different doping concentrations of graphene oxide thin films ((a) 2%, (b) 4%, (c) 6%, (d) 8% wt.

From the Fig.8, it is noticed that the reflectivity decreases slightly as the concentration increases because of the effect of doping graphene oxide on the brightness of the films. As the films become coarse and non-glossy with the increase of the doping concentration.

4. EDX Analysis

Fig.9 shows EDX spectrum of sample GO-2%. It is noted that the quantity of the graphene oxide in sample a (GO-2%) is the largest compared to the rest of the samples. In addition, Table 2 shows the composition (elements) of the samples. One can see that the glass elements were silicon Si, oxygen O and fluorine F.

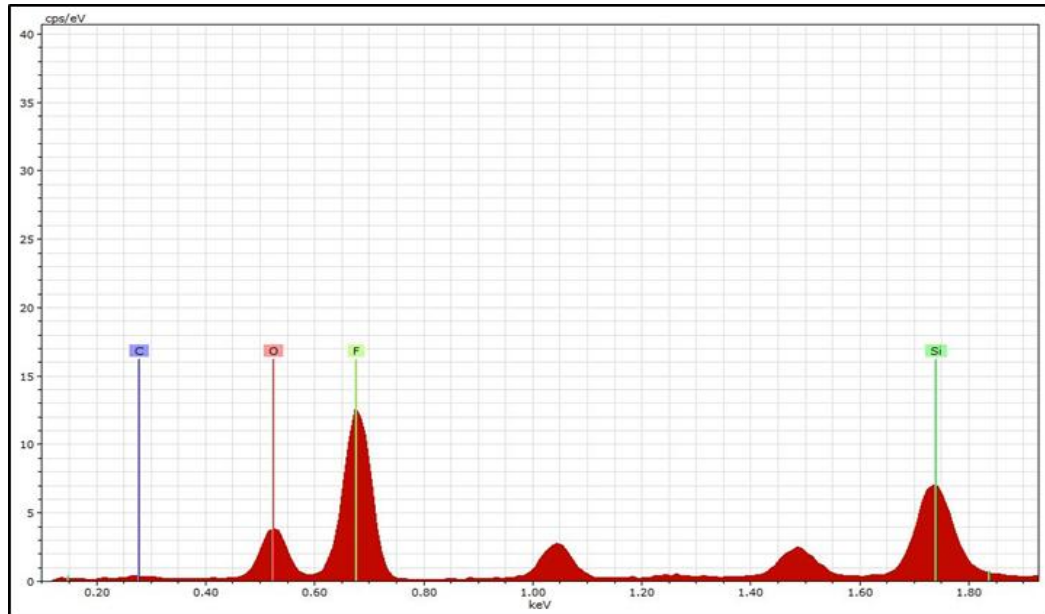


Fig.9: EDX spectra of sample b.

Table 2: Composition of elements for the samples using EDX.

	Elements								Total	
	F		O		Si		C		Total Mass (%)	Total Atomic (%)
	Mass (%)	Atomic (%)	Mass (%)	Atomic (%)	Mass (%)	Atomic (%)	Mass (%)	Atomic (%)		
a: GO-2%	56.65	44.15	30.23	42.11	6.90	4.425	6.22	9.32	100	100
b: GO-4%	76.51	75.40	4.99	5.84	11.30	7.54	7.20	11.22	100	100
c: GO-6%	62.20	58.87	20.30	22.81	9.21	5.90	8.30	12.42	100	100
d: GO-8%	73.66	81.46	4.16	38.0	11.35	9.83	10.83	20.70	100	100

5. Morphological Properties (SEM)

Fig.10 shows SEM images of the samples prepared by dip-coating technique. These images provide direct information of the microstructure and morphology of the samples. A smooth cylindrical surface of GO with glass powder is noticed. In addition increasing the concentration of graphene oxide leads to an increase in surface roughness of the (Fig. 10 (d)). In some areas of the sample, GO sheets agglomerated and extended on the surface of samples.

Electrical properties

Fig.11 shows the I-V characteristics of glass-graphene thin films. From the curves, it is clear that the increase of current with the applied voltage at high graphene concentration is much greater than that at low graphene concentrations. This could be due to the increase in quantum collection efficiency of graphene oxide – generated charge carriers. It has already been noticed that the crystalline size is higher in samples of high graphene concentration. Hence, the density of their grain boundaries is less, which in terms increases the mobility of charge carriers.

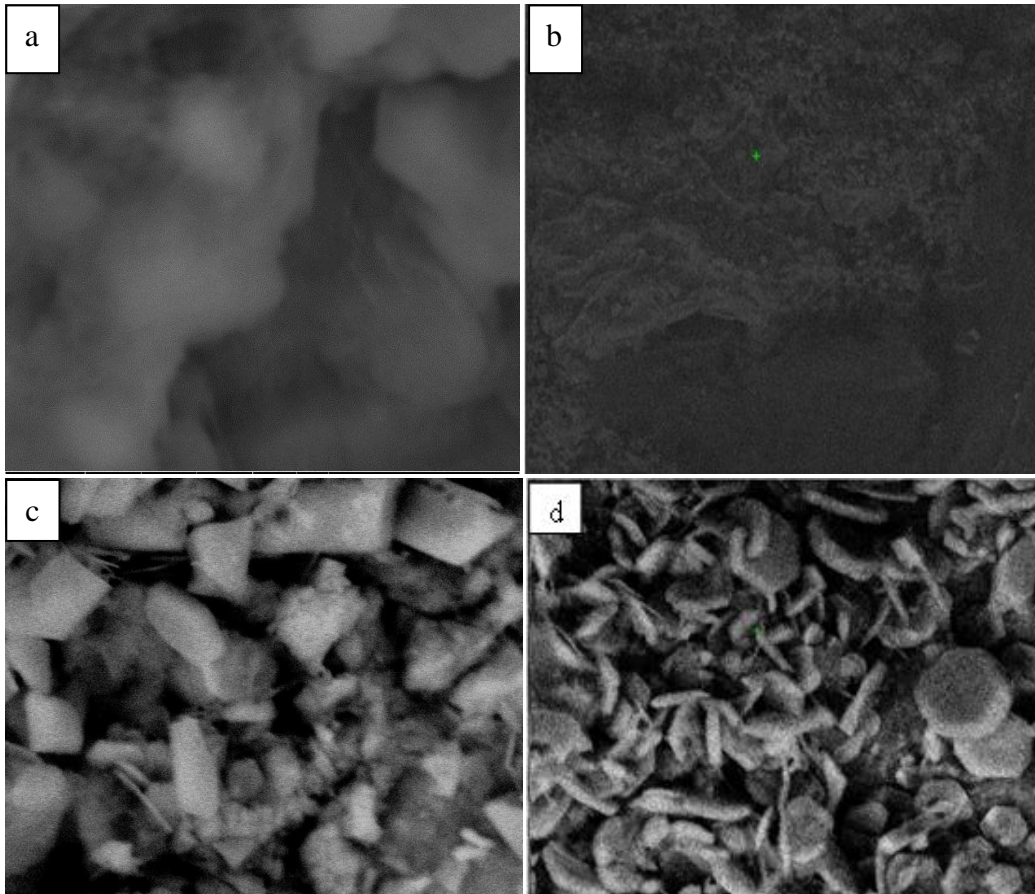


Fig.10: SEM photograph of glass for different doping concentrations of graphene oxide thin films (a) 2%, (b) 4%, (c) 6% and (d) 8% wt.

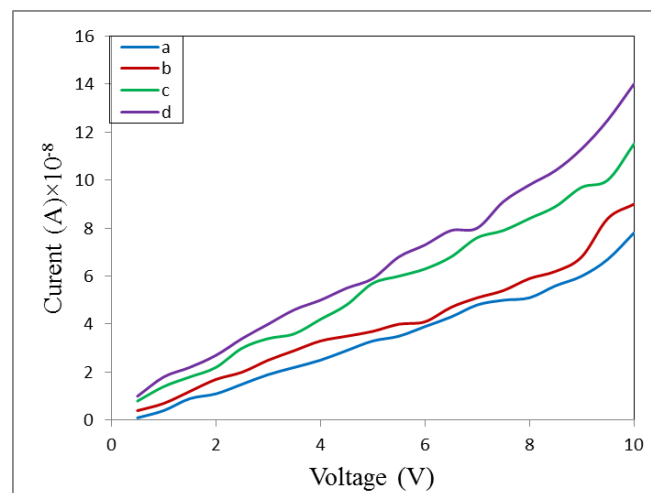


Fig.11: The I-V characteristics of glass for different doping concentrations of graphene oxide thin films ((a) 2%, (b) 4%, (c) 6%, (d) 8% wt).

Conclusions

After studying and analyzing the results of measurements of the graphene oxide-glass thin films prepared using a solution of hydrofluoric acid (HF), the following was found out:

The effects of graphene oxides on glass to obtain thin films are: Graphene oxide of crystalline structure has been successfully prepared using hydrofluoric acid. Demonstration of graphene oxide formation based on X-ray diffraction spectrum,

absorbance spectrum, and energy gap value. Energy gap values of the glass-graphene films decreased after adding graphene oxide to the glass, as the energy gap value of the glass was 7 eV, and when graphene oxide was added in different concentrations 2%, 4%, 6% and 8% wt. it becomes 4.6, 4.5, 4.3 and 4.2 eV respectively. Increase the value of absorbance coefficient of the samples in the ultraviolet region and the decreases in the visible region. As for the I-V characteristics, it was noticed that increasing the concentration of graphene oxide will increase the current.

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References

- [1] N.I.Zaabaa, K.L.Fooa, U.Hashimad, S.J.Tanbc, Wei-WenLiua, C.H.Voon, *Procedia engineering* 184 (2017) 469-477.
- [2] Gao W (Ed.) "Graphene oxide: reduction recipes, spectroscopy, and applications", Springer, 61-95, (2015).
- [3] S. N. Alam, N. Sharma, L. Kumar, *Graphene*, 6, 1 (2017) 1-18.
- [4] D. C. Marcano, D. V. Kosynkin, J .M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, J M. Tour, *ACS Nano*, 4, 8 (2010) 4806-4814.
- [5] A. T. Smith, A. M. La Chance, S. Zeng, B. Liu, L. Sun, *Nano Materials Science*, 1, 1 (2019) 31-47.
- [6] R. Zeynali, K. Ghasemzadeh, A. B. Sarand, F. Kheiri, A. Basile, *Separation and Purification Technology*, 200 (2018) 169-176.
- [7] S. Pei, J. Zhao, J. Du, W. Ren, H.M. Cheng, *Carbon*, 48, 15 (2010) 4466-4474.
- [8] J.W. S. Hummers, 1957 U.S. Patent No. 2,798, 878 Washington DC: U.S. Patent and Trademark Office.
- [9] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J. R. Potts, R. S. Ruoff, *Advanced Materials*, 22, 35 (2010) 3906-3924.
- [10] P. Avouris, C. Dimitrakopoulos, *Materials Today*, 15, 3 (2012) 86-97.
- [11] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, A. K. Geim, *Science*, 320, 5881 (2008) 1308-1308.
- [12] C. Xu, Y. Xu, J. Zhu, *ACS Applied Materials & Interfaces*, 6, 18 (2014) 16117-161123.
- [13] Z. Bo, X. Shuai, S. Mao, H. Yang, J. Qian, J. Chen, J. Yan, K. Cen, *Scientific Reports*, 4, 4684 (2014) 1-8.
- [14] H. Zhou, J. Yin, Z. Nie, Z. Yang, D. Li, J. Wang, X. Liu, C. Jin, X. Zhang, T. Ma, *Journal of Materials Chemistry, A* 4, 1 (2016) 67-73.
- [15] M. L. Yola, T. Eren, N. Atar, *A Sensors and Actuators B: Chemical*, 210 (2015) 149-157.
- [16] Rasheed M, Barillé R, *Optical and Quantum Electronics*, 49, 5 (2017) 1-14.
- [17] Rasheed M, Barillé R, *Journal of Non-Crystalline Solids*, 476 (2017) 1-14.
- [18] Rasheed M, Barillé R, *Journal of Alloys and Compounds*, 728 (2017) 1186-1198.
- [19] Y. Shen, S. Yang, P. Zhou, Q. Sun, P. Wang, L. Wan, J. Li, L. Chen, X. Wang, S. Ding, DW. Zhang, *Carbon*, 62 (2013) 157-164.