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Development of Optical barrier films on flexible polymer substrates

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Abstract

Silicon monoxide, SiO has been deposited on Low-Density Polyethylene (LDPE) surface using Physical Vapor Deposition (PVD) technique. Several thickness films (200, 500 and 700 nm) were prepared. The obtained films were identified and characterized by Fourier transform infrared spectroscopy (FTIR), ultraviolet–visible spectroscopy (UV-VIS) and atomic force microscopy (AFM). At specific coating thickness, far infrared radiation transmittance was prohibited while the ultraviolet–visible transmittance is allowed and that will be explained in details. AFM results showed homogenous and smooth silicon mono oxide thin films. The mean grain size, average roughness (Ra) and root mean square (RMS) roughness values for SiO films were estimated from AFM. Optical measurements show that the coated films prevent the transmission of IR radiation near 9.5µm and allow UV-VIS transmission during the sun-shining time.

Keywords: *Silicon monoxide (SiO). Physical Vapor Deposition (PVD). Low-Density Polyethylene (LDPE). Selective Coating, Atomic Force Microscopy (AFM).*

1.Introduction

Barrier films deposited on flexible substrates are indispensable for a lot of applications. These are, for example, flexible displays based on LCD or OLED devices, flexible solar modules, materials for thermal insulation (e.g., vacuum insulated panels) or food packaging [1]. Silicon oxide is used as a coating material in industry owing to its attractive optical, chemical, mechanical properties, anti-resistance, hardness, corrosion resistance and dielectric properties etc [2,3]. Silicon monoxide (SiO) is another stoichiometric silicon oxide material. Silicon monoxide films can be produced by Physical Vapor Deposition (PVD) methods, sputtering [4], Thermally Evaporated [5] and Electronic Beam Vapor Deposition [6,7],…etc. PVD is one of the most traditional vacuum deposition techniques.These techniques allow better control of the film thickness and the ensure that the deposited film has a good adhesion performance. Due to this aspect, the PVD approach was adopted in this study. A number of different barrier coating technologies is currently being developed. Theoretically, a barrier function can be incorporated into a plastic-based packaging material via two different means, either by coating a layer of the barrier material or by mixing a barrier material with the base polymer [8] [9]. This work represents the results of optical and thermal experiments on silicon monoxide insulation films deposited on LDPE at different thickness (200, 500 and 700 nm). The aim is to achieve a composite material that prevents the transmittance of IR and allows the transmittance of UV-VIS. So that most of the thermal radiation of the ground and plants in the greenhouse are conserved.

1-1- SIO COMPLEX REFRACTIVE INDEX:

The simulation of optical proprieties of coated LDPE demand the complex refractive index of silicon oxide values which is given as Eq. 1.

$$N = n_r - i.k \quad (i = \sqrt{-1}) \qquad (1)$$

The real part of the refractive index (n_r) expresses the speed of the radiation wave in the film relative to the speed of radiation in the vacuum, while the imaginary part (k) expresses the extinction coefficient of radiation. It denotes the presence of absorption inside material. The imaginary part of the refractive index is 1.43, (for the wave length in the vicinity of 10µm) which fits well with the transmittance value measured by the FT-IR spectrophotometer, while the real part is (n_r=1.85).

1-2- OPTICAL THIN FILM CALCULATION:

To calculate optical proprieties of thin film system(transmittance reflectance ..etc), we need the refractive index of the incident medium, refractive index and optical thickness of layer (s) to build the equivalent matrix of the layer(s), and refractive index of substrate, then we can use the standard matrix method [10] or other methods.

1-3- BLACK-BODY THERMAL RADIATION:

All objects with a temperature above absolute zero emit energy in the form of electromagnetic radiation. A blackbody is a theoretical or model body which absorbs all radiation falling on it, It is a hypothetical object which is a “perfect” absorber and a “perfect” emitter of radiation. The electromagnetic radiation emitted by a blackbody has a specific spectrum and intensity that depends only on the body's temperature, the thermal radiation spontaneously emitted by ordinary objects, land and plants for exemple, can be approximated as blackbody radiation. Figure.1 shows the blackbody radiation spectrum at 273, 293, 313, 333, 373, 393, 413, 433 and 453 K. We are interested in the vicinity of 10µm (9 to 11) µm, because at the temperatures near 0ºC (273 K),the thermal radiation from the ground is maximum at 10µm , while at the temperature 30°C (303 K) thermal radiation from the ground is maximum at 9.5µm.

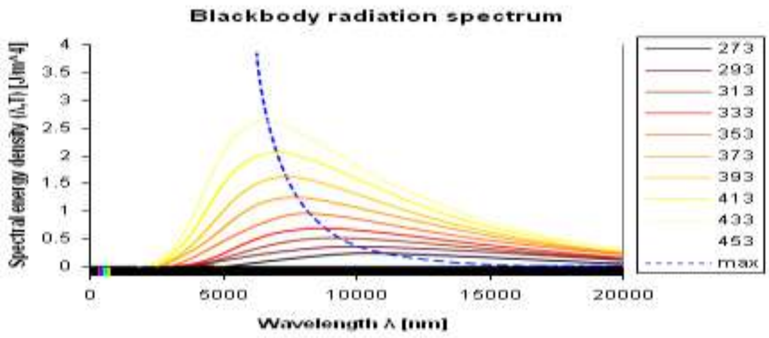

Figure 1. *Blackbody radiation spectra at 273, 293, 313, 333, 373, 393, 413, 433 and 453 K.*

2-MATERIAL AND METHODS

2-1-MATERIALS

Low-density polyethylene (LDPE) which is a thermoplastic made from the ethylene monomer with a density of 0.922 g/cm^3 was purchased from Saudi Basic Industries Corporation (SABIC). Silicon monoxide (SiO) from SIGMA ALDRICH with product number 262951. Table 1 shows the basic physical and chemical properties of the silicon monoxide used in the present work.

Table 1: Basic physical and chemical properties of silicon monoxide.

Properties	**value**
Color	Brown
Form	powder
particle size	−325 mesh
density	2.13 g/mL at 25 °C(lit.)

2-2-SAMPLE PREPARATION

Samples were prepared by depositing silicon monoxide films on LDPE at a different thickness (200, 500 and 700 nm). Silicon monoxide films were deposited on LDPE substrates (12cm × 12cm × 120µm) by PVD technique. Prior to deposition, the polymeric substrates were cleaned in methanol for 5 minutes. For accurate thickness measurement, we used the BK7 glass (n=1.52) where the roughness is less than 10 A°. The optical thickness and geometrical thickness were measured by spectral refraction measurement [11] and the user of the Alpha Step 200 profilometer. The BK7 glass substrates were cleaned by calcium carbonates ($CaCO_3$). The evaporation of SiO takes place under a pressure of the order of 10^{-5} mbar at room temperature. The evaporation process was done by using an electron beam. A magnetic field is used to focus and scan the electron beam on the substance to be evaporated (SiO). The substrate is placed on a spherical holder and rotated at a speed of 30 rounds per minute during evaporation to ensure a homogeneous film growth. The reference thickness of the thin film was measured during the deposition by an 5MHz-quartz sensor head (see fig.2).

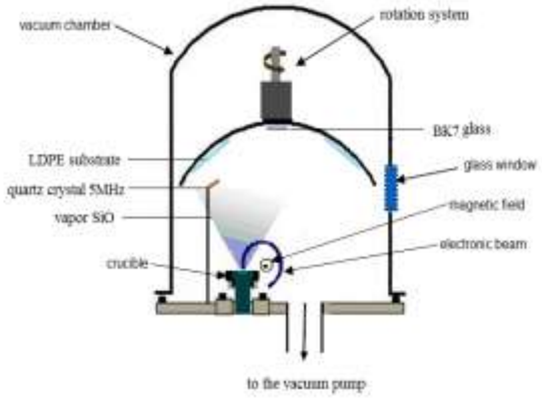

Figure 2. *Schematic diagram of a thermal-PVD machine.*

3-RESULTS AND DISCUSSION

3-1-Optical study

3-1-1- INFRARED SPECTROSCOPIC STUDY

The transmittance of samples was examined by Fourier Transform Infrared (FTIR) Spectroscopy (FT-IR Spectrometer - VERTEX 70/70v from Bruker™ Optics) in the wavelength range of 1-25 µm. Figure (5) shows the transmittance spectra of the SiO/LDPE films with different thicknesses. Different absorption peaks could be identified in the MIR range. The peaks at ~ 9.6 µm, ~ 13 µm and ~ 21 µm, due to Si—O resonance mode of vibrations [12]. Some of these peaks also involve the LDPE substrate in the IR absorption spectra. The peak at 9.6 µm give the SiO its importance and allow it to be used in this application. We observe a decrease in transmittance when the deposition thickness increases. The changes in the average transmittance for wavelengths ranging from 8. to 11.5 µm are shown in fig.4. We notice a sharp decline in transmittance when deposition thickness increases.

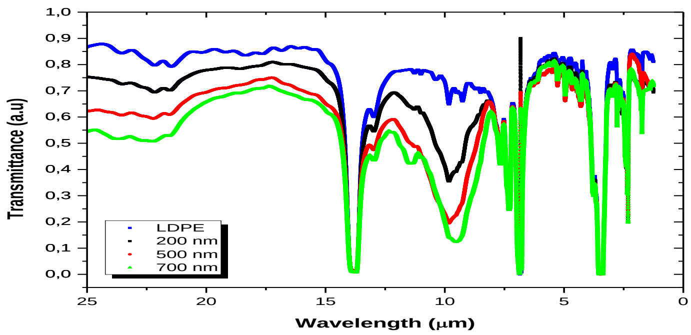

Figure 3. *FTIR spectra deposited for different thicknesses of SiO thin film.*

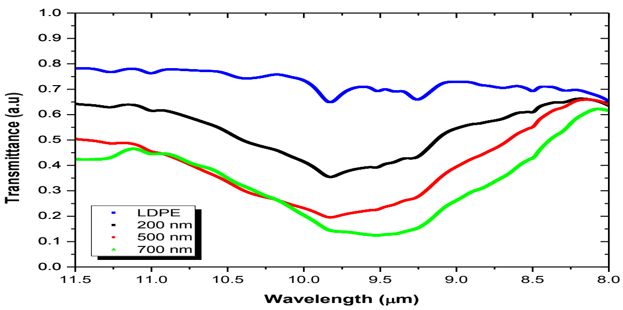

Figure 4. *FTIR spectra in the range (8-11.5) µm.*

3-1-2- ULTRAVIOLET–VISIBLE SPECTROSCOPY STUDY

The optical transmittance measurements of SiO/LDPE thin films were carried out with a UV-Vis-NIR spectrophotometer ((UV Spectrophotometer –A560AOE instruments) at normally incident of light in the wavelength range of 200-1100 nm. Figure 5 shows the transmittance spectra of the samples deposited with different thicknesses (LDPE without coating, 200, 500, and 700nm). The UV spectra show that the deposited films of thicknesses (200-500-700 nm) have a little decrease in the transmittance is observed comparing to the LDPE without coating. This decrease is addressed in the “Results and discussion” section.

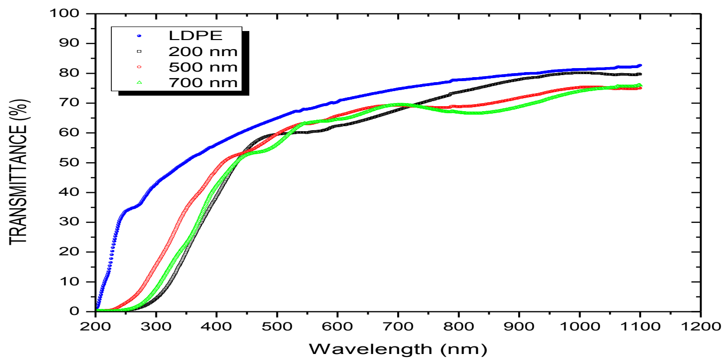

Figure 5: *UV-visible spectra of SiO films deposited on LDPE for different thicknesses.*

3-2- SURFACE PROFILE AND ROUGHNESS CHARACTERIZATION USING ATOMIC FORCE MICROSCOPY (AFM)

In this study, an atomic force microscope (AFM, Nanosurf easyScan2, Switzerland) was used to examine the surface morphology and topography of the SiO. All the AFM scans were acquired in tapping mode using a standard Si3N4 tip (Tap190 Al-G, NanoSensors™, Switzerland), at a scan resolution of 256×256 points.

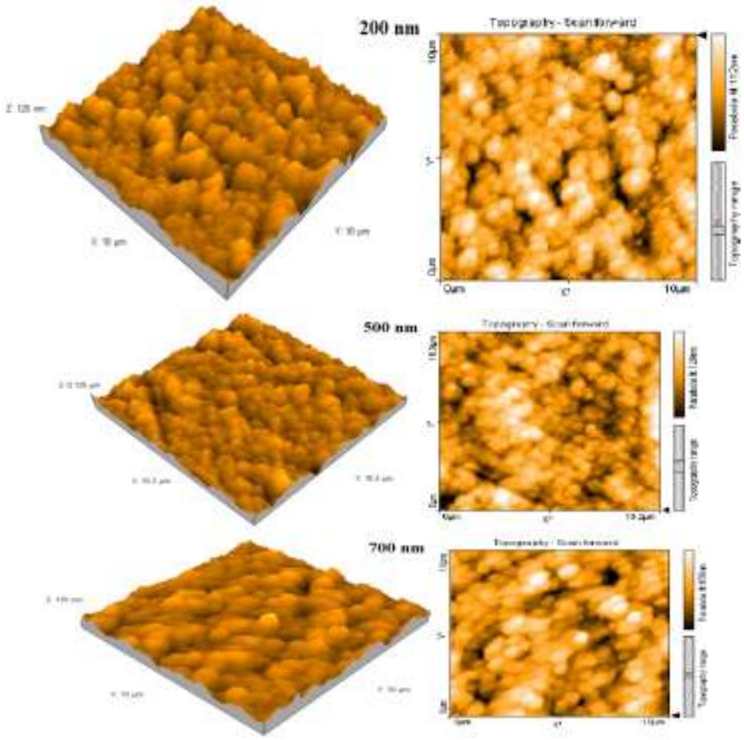

Figure 6: *l0xl0µm^2 AFM images of SiO samples presented in 3D view on left and 2D view on right, displaying the granularity of the films.*

All scans size were chosen as (10μm x 10μm) recorded on samples of SiO/LDPE thin films deposited with variation the thickness of layers in the thickness of the layers (200, 500 and 700 nm). Collected images of topography were processed in Nanosurf report expert and presented as a 3D and 2D view of the selected surface area (see figure 6). As can be noticed from these images, the grain SiO thin films have a high degree of homogeneity and the large grains have the uniform distribution on the LDPE. The mean diameter and height grains of the samples were minimum (500 and 75nm respectively) at thickness 200nm (S1) compared with thickness 500nm (S2) and 700nm (S3) could be perceived (mean diameter grain range of 580-570nm, whereas the mean height grain varied from 83nm to 105nm approximately). The evolution of the microstructure for the SiO film may be related to the reorganization of the SiO molecules during the PVD evaporation process [13]. Grain diameters and height distribution were measured for each thickness (see figure 7)Software-based image processing of AFM data can generate quantitative information from individual grains or group of grains. Quantitative analysis through histogram plots is shown in Fig. 7 for SiO films deposited at different thicknesses. It is found from the histogram that a narrow distribution of grain diameters and heights was observed for 200nm thickness, while a broader distribution in the grain diameter and height was obtained for another thickness.

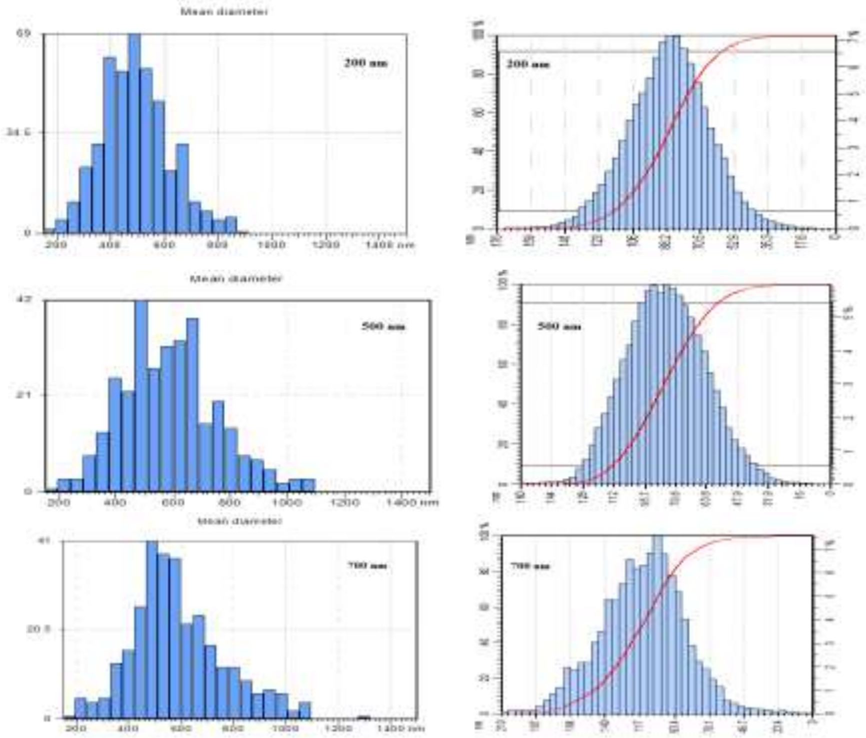

Figure 7: *Quantitative analysis of SiO grain diameter (left) and height dispersions (right) for different thicknesses (200-500-700 nm).*

Table 2 contains the mean diameter, mean hight, average roughness values (Ra) root mean square height (RMS), Surface Skewness (Ssk) and Surface Kurtosis (Sku) values for the films, computed for the $10x10μm^2$ scans in order to consider the influence of the large casual defects which appear in the AFM images. Table 2 illustrates that the variations of the average roughness (Ra) values have the same trend as the variations of RMS roughness (Rq) values for all SiO films. For a Gaussian distribution of asperity height, statistical theory shows that the ratio of Rq to Ra should be 1.25 [14]. As shown in Table 2, the values of Rq/Ra using data collected from AFM imaging are reasonably close to the value of 1.27 predicted by theory. This result is significant since it indicates that, at the imaging scale, the asperity height distribution of these surfaces are approximately Gaussian. Table 2 also shows that values of skewness

Roughness (Rsk) and Roughness kurtosis (Rku) using data collected from AFM imaging. the skewness describing the asymmetry of height distribution of topography of a surface varies from one film to another. S1 and S2 samples having good bearing surface as have negative values of the skewness indicates that the valleys are dominant over the scanned area, the while S3 sample has a positive Rsk value that reveals the domination of peaks on the topography of a surface. The distribution of positive and negative values indicates the existence of protruding grains. Kurtosis is used to measure the distribution of the spikes above and below the mean line/plane. Roughness kurtosis (Rku) describing the flatness of height distribution in surface topography varies as well from one sample to another. spiky surfaces, Rku > 3; for bumpy surfaces, Rku < 3; perfectly random surfaces have kurtosis 3 [15] . All SiO film deposited had the value of Rku more than three (Rku> 3), the distribution will have relatively higher numbers of high peaks and low valleys with a spiky surface.

Table2: Morphological characteristics from image for SiO thin film with three different thickness.

Thickness (nm)	Mean diameter (nm)	Mean height (nm)	RMS (nm)	Ra (nm)	Surface Skewness (Rsk)	Surface Kurtosis (Rku)
S1: 200nm	500	75	15.4	12.1	- 0.104	3.39
S2: 500nm	580	83	15.4	12.2	-0.187	3.18
S3: 700nm	570	105	28.3	22.3	0.014	3.42

3-3- Thermal Study

We built a mini greenhouse of LDPE without coating and another of LDPE coated with a 700nm SiO layer. We also built a third mini greenhouse of window silka glass (glass thickness is 6 mm ,the tansmittance in from 350 -1100 nm is 88 % approximately) , (see figure 9). All the three greenhouses are cubic with a side of 20 cm. Inside each greenhouse, we put a small plant. These plants previously grown under similar conditions. We need to determine whether the side facing the thermal radiation, whether it is the SiO film or LDPE. We considered the complex refractive index of SiO near 10µm as follows :

$N = n_r - i.k = 1.85 - i.1.43 \ (i = \sqrt{-1})$

Then we calculated the value of the reflection coefficient using the matrix method [10] in the following cases:

1-Incident medium is air – SiO layer – substrate is LDPE : The reflection coefficient is R=34%.

2-Incident medium is LDPE – SiO layer – substrate is air : The reflection coefficient is R=19%.

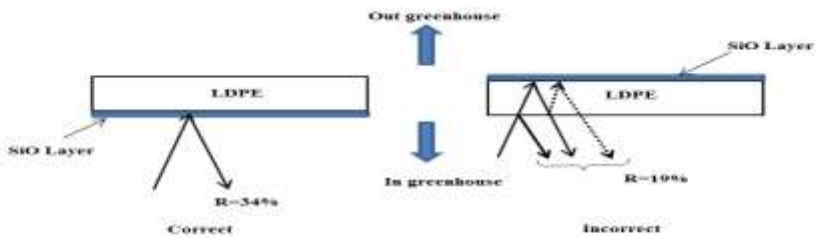

Figure 8: *Correct use of Coated LDPE*

The side facing the ground (inside the greenhouse) should be the SiO film, because this choice leads to a better reflection coefficient of the thermal radiation emitted from the earth and plants (See figure 8.). The temperature inside each greenhouse was measured using identical temperature sensors (Tecnologic with resolution 0.1°C). The external

temperature was also measured using an identical sensor. All the measurements were made at the same moment every thirty minutes starting from 1 pm until 6 am the next day.

(a) (b) (c)

Figure 9: *Three green houses (a) LDPE without coating, (b) LDPE coated with 700nm SiO (c) silica glass.*

Figure 10 shows the temperature variations inside the three greenhouses along with the external air temperature. An increase in the temperature inside the greenhouse coated with the 700 nm SiO layer is noticed. This increase is estimated to be more than 0.5°C compared with the without coating greenhouse LDPE (0.6 °C overall and 0.8 °C between 11 PM and 5 AM). We also notice that the transmittance of the greenhouse coated with the 700 nm SiO layer approaches that of the glass house very much (See the green and blue triangles in figure 10). In fact, the average temperature difference is about 0.6 °C overall and the two temperatures between 11 PM and at 5 AM match each other very well.

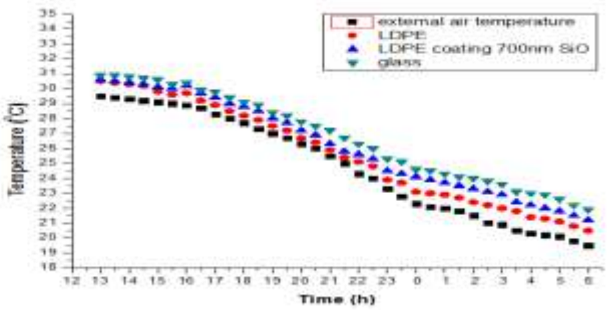

Figure 10: *The variations of difference temperature (ΔT), between the temperature inside the greenhouse and the temperature in the external air, during the time.*

By studying the IR transmission in fig (3, 4, 11), A decrease in the transmittance near 10 µm with increasing deposition thickness is noticed. This result explains the rise in temperature inside the mini greenhouses (shown in figure 11.) The coating of LDPE preserves thermal radiation of the ground. Thus, the internal temperature inside the greenhouse is maintained. One can also notice that in the vicinity of 10 µm, the transmittance of the sample with a thickness of 700 nm is very close to that with a thickness of 500 nm. We deduce that it may not be very beneficial to go beyond 700 nm. The refractive index of LDPE in the visible domain is 1.51 while the imaginary part (k=0) [16]. It is not close to the real part value of the refractive index of SiO which is equal to 1.85 [17]. Therefore, there is significant change in the transmittance of the LDPE, in the visible range, when coated with SiO. This is clearly seen in (figure 5). By studying the UV-VIS transmission in (figure 5), A small decrease is noticed in the transmittance of the film with thicknesses (200, 500 and 700 nm) compared with that of the LDPE without coating.(because THE SiO refractive index is approximately 1.85 > 1.51 refractive index of LPDE. Thus, the film with a 700 nm SiO layer was adopted to build the mini greenhouse. It has a little effect on the UV-VIS transmission but it is reduces a maximum the transmission of the IR radiation around 9.5 µm.

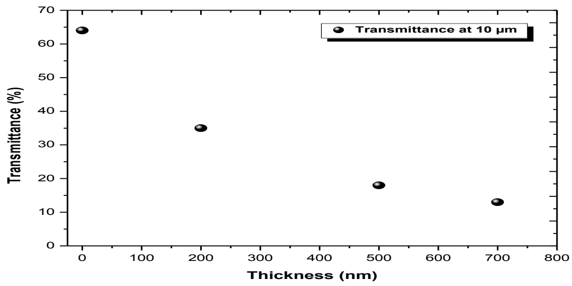

Figure 11: *Transmittance at 10 µm as a function of different thicknesses of SiO.*

4- CONCLUSION

Throughout this study, silicon oxide films with different thicknesses (200, 500 and 700 nm) were deposited on Low-Density Polyethylene (LDPE) polymer, using Physical Vapor Deposition (PVD) method technique. By using these coated LDPE to build a mini greenhouse. SiO coating reduces the transmission of radiation near 10 µm and allow the transmission of the ultraviolet and visible radiations to pass through them during daytime (period of sunshine, without being exposed to direct sunshine.) Thus, we were able to preserve the thermal radiation of the ground by raising the internal temperature of the greenhouse up to more than 0.5 ºC, compared with the same greenhouse without coating. The temperature inside the SiO coated LDPE greenhouse was found to be almost identical to that inside the glass greenhouse. Statiscaly speaking the conclosions are acceptable because the expirement were replicated many time. The main gain is the fact that the SiO Coated LDPE greenhouse has the same tempreture as Glasse made greenhouse. AFM results showed homogenous and smooth SiO thin films, the root mean square (RMS) roughness for SiO thin films, estimated from AFM. The thickness (700 nm) has highest average grain size and RMS roughness, and the thickness (200 nm) has minimum average grain size and RMS roughness of the SiO thin films.

5- REFERENCES

1. Charton, C., Schiller, N., Fahland, M., Holländer, A., Wedel, A. and Noller, K., 2006. Development of high barrier films on flexible polymer substrates. Thin Solid Films, 502(1-2), pp.99-103.
2. Jin, S. B., Kim, S. I., Choi, Y. S., Choi, I. S., & Han, J. G. Current Applied Physics, 11(4) (2011) 1107-1110.
3. Delimi, A., Coffinier, Y., Talhi, B., Boukherroub, R., & Szunerits, S. Electrochimica Acta, 55(28) (2010) 8921-8927.
4. Andersen, S.V. and Pedersen, K., Optics express, 20(13) 2012 pp.13857-13869.
5. Yang, L., Wang, H., Zhang, X., Li, Y., Chen, X., Xu, X., Zhao, X. and Song, A., IEEE Transactions on Electron Devices, 64(4) 2017.1846-1850.
6. Sasaki, M., & Ehara, T. In Journal of Physics: Conference Series 417, 1, (2013). 012028. IOP Publishing.
7. Pivot, J., Morelli, D., Tardy, J., Roger, J.A. and Dupuy, C.H.S., Thin Solid Films, 28 (1975) 357-368.
8. Liu, Z., Sun, Z., Ma, X., & Yang, C. L. Packag Technol Sci, 26(S1) (2013) 70-79.
9. Lange, J., & Wyser, Y. Packag Technol Sci, 16(4) (2003) 149-158.
10. Macleod, H.A. and Macleod, H.A. Thin-film optical filters. CRC press (2001) 171.
11. A.Piegari, E. Masetti, Thin solid films. 124 (1985) 249-257.
12. Kitamura, R., Pilon, L., & Jonasz, M. Appl. Opt, 46(33) (2007) 8118-8133.
13. Petrov, I., Barna, P. B., Hultman, L., & Greene, J. E. Sci. Technol., A. 21(5) (2003) S117-S128.
14. B.rajsh Kumar, T. Subba Rao, Vol. 7, No. 4, p. 1881-1889, 2012.
15. S. Trabishi, R. Abou S. and I. Asaad, Journal of New Technology and Materials, 03(1) (2013) 43-49.
16. Mitchell, B. S. John Wiley & Sons. (2004) 901.
17. Miyazaki, H., Journal of Glass Science and Technology Part B, 51(2) (2010)136-137.