



Characterization of SiO₂/ LDPE Composite Barrier Films

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Abstract

Silicon dioxide, SiO₂ has been deposited on Low-Density Polyethylene (LDPE) surface using Physical Vapor Deposition (PVD) technique. Several thickness films (200, 500, 700 and 1500 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. The morphological characterization emphasized the homogeneity of the prepared films surface and the uniform of grains size with the following order 500, 700, 450 and 525 nm as observed by AFM. Optical measurements show that, the coated films prevent the transmission of IR radiation near 10μm and allow UV-VIS transmission during sun-shining time.

1. Introduction

The excellent performance of silicon dioxide film has attracted attention in academia and industry. Due to its anti-resistance, hardness, corrosion resistance, dielectric properties, optical transparency etc [1]. Silicon dioxide as a thin film is widely used to improve the surface properties of materials. This is why silicon dioxide thin films are used in many fields as in antireflection coating film field [2]. In packaging industry, silicon dioxide films are used as barrier layers in polymer packaging materials. Most of the modern packaging materials do not provide an efficient barrier against the permeation of gases. This leads to food and drink not to get rotten quickly. Just because of this, a silicon dioxide film deposited on the surface of polymer packaging becomes popular and indispensable. Besides, silicon dioxide films can be also used as corrosion protective layers of metals. Because of the universal application of silicon dioxide films in various fields, the preparation of silica with high quality is always an important aim of scientific research. Silicon dioxide films can be produced by different methods, such as sol-gel [3], liquid phase deposition [4], sputtering [5], Chemical Vapor Deposition (CVD) [6], thermal oxidation [7], Plasma Enhanced Chemical Vapor Deposition (PECVD) [8], atmospheric pressure plasma deposition [9], and Physical Vapor Deposition (PVD) [10],...etc. PVD is one of the most traditional vacuum deposition techniques. It includes vacuum evaporation, ion plating and sputtering deposition. 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. The development of Physical Vapor Deposition (PVD) coating technologies started in the mid-1980s [11].

Nowadays, polymeric materials are widely used in food packaging and in greenhouses. Typical examples of such materials are polypropylene (PP), polyethylene (PE), and polyethylene terephthalate (PET) [12-13].

One way to protect many materials is by applying a protective coating, such as an ion painting or a plasma-deposited layer on the material to be protected. For fire protection, even very thin layers of silica deposited onto a polymer surface can lower heat release and delay polymer ignition as well [14-15].

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 [11] [16].

Currently, Silicon is in demand for manufacturing photovoltaic (PV) devices [17] masking layer [18] dielectric films deposition [19]. It is also used as an insulating layer in metal-insulator structures [20].

This work represents the results of experiments on silicon dioxide insulation films deposited on LDPE to prevent the transmittance of IR domain and to allow the transmittance of UV-VIS domains, so we can keep the thermal radiation of the ground in the greenhouse.

1-1 SiO_2 Complex Refractive Index:

The simulation of optical proprieties of coated LDPE demand the complex refractive index of silicon dioxide values which is given as follows: $N=n_r-i.k$ ($i=\sqrt{-1}$). 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.

We notice that the imaginary part of the refractive index is 1.5, (for the wavelength in the vicinity of $10\mu\text{m}$) which fits well with the transmittance value measured by the FT-IR Spectrometer, while the real part is ($n_r=1.43$).

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 [21] 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 black body 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 example, can be approximated as black-body 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 $10\mu\text{m}$ (9 to 11) μm , because at the temperatures near 0°C (273 k), the thermal radiation from the ground is maximum at $10\mu\text{m}$, while at the temperature 300 (303 K) thermal radiation from the ground is maximum at $9.5\mu\text{m}$.

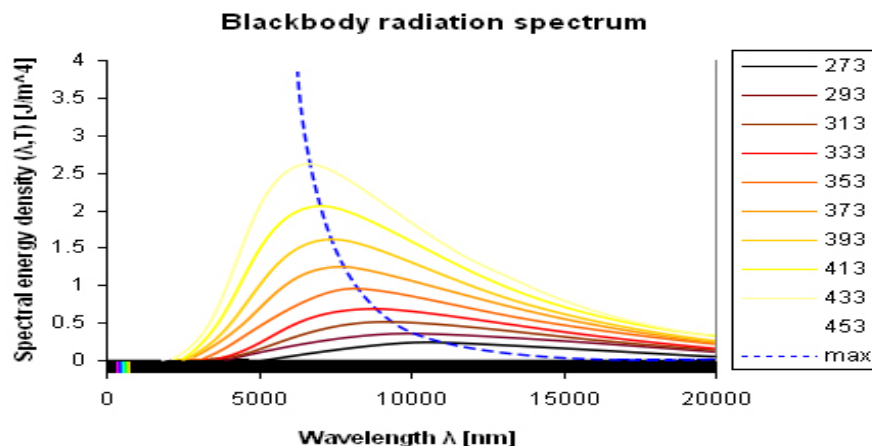


Figure 1: Blackbody radiation spectra at 273, 293, 313, 333, 373, 393, 413, 433 and 453 K.

2. Material and Methods

2.1. materials

The materials used were Silicon dioxide (SiO_2) from Technolab, Low-density polyethylene (LDPE) which is a thermoplastic made from the monomer ethylene from Saudi Basic Industries Corporation (SABIC).

2.2. Sample preparation

samples of polymeric substrates of LDPE used in greenhouses. SiO_2 films were deposited on polymeric substrates ($12\text{cm} \times 12\text{cm} \times 120\mu\text{m}$) by PVD technique. Prior to deposition, the polymeric substrates were cleaned in methanol for 5 minutes. For accurate thickness measurement, we used the TF1 glass ($n=1.64$) where the roughness is less than 10 \AA . The optical thickness and geometrical thickness were measured by spectral refraction measurement [22] and the used of the Alpha Step 200 profilometer.

The TF1 glass substrates were cleaned by calcium carbonates (CaCO_3). The evaporation of SiO_2 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_2). 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 figure 2).

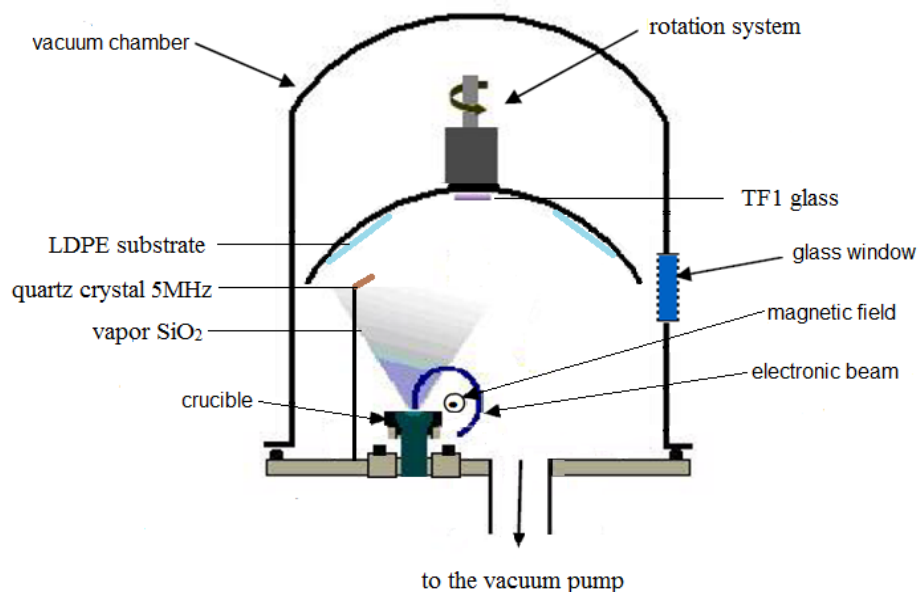


Figure 2: Evaporation device.

2.3. Infrared spectroscopic study

The transmittance of SiO_2 films with different thicknesses (200-500-700-1500 nm) 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 (3) shows the transmittance spectra of the LDPE films on which a layer of SiO_2 with different thicknesses was deposited.

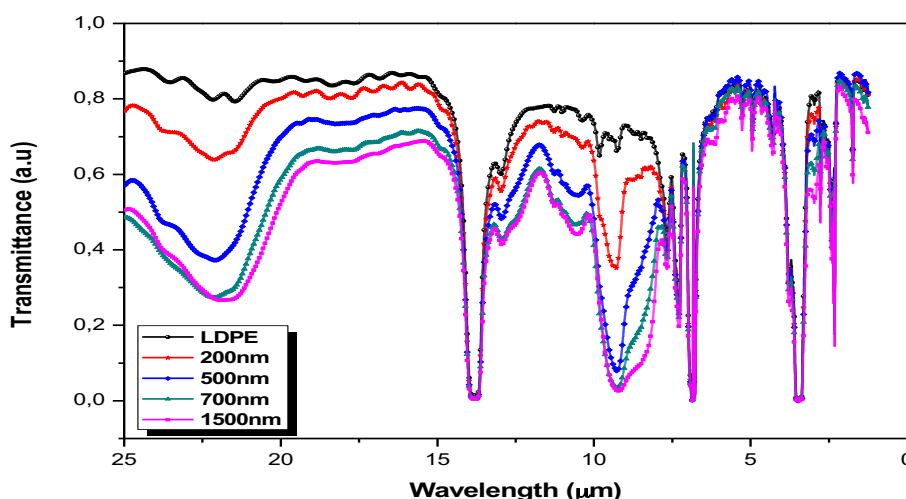


Figure 3: FTIR spectra deposited for different thicknesses of SiO_2 thin film.

Different absorption peaks could be identified in the MIR range. The first one at $\sim 3 \mu\text{m}$ caused by OH group, other peaks at $\sim 9.3 \mu\text{m}$, $\sim 13 \mu\text{m}$ and $\sim 21 \mu\text{m}$, due to Si—O—Si resonance mode of vibrations [23]. Some of these peaks also involve the LDPE substrate in the IR absorption spectra. The peak at $9.3 \mu\text{m}$ give the SiO_2 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 $10.5 \mu\text{m}$ are shown in (figure 4). We notice a sharp decline in transmittance when deposition thickness increases.

2.4. Ultraviolet–visible spectroscopy study

Optical characterization of SiO₂ thin films is very important due to their increasing applications as protective and ion barrier layers in electronic and optoelectronic devices. The optical transmittance measurements of LDPE/SiO₂ 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, 700 and 1500nm). The UV spectra show that the deposited films of thicknesses (200-500-700 nm) have no significant effect on the transmittance. On the other hand, a significant decrease in the transmittance is observed comparing to the LDPE without coating, when the deposition thickness is 1500 nm. This decrease is addressed in the “Results and discussion” section.

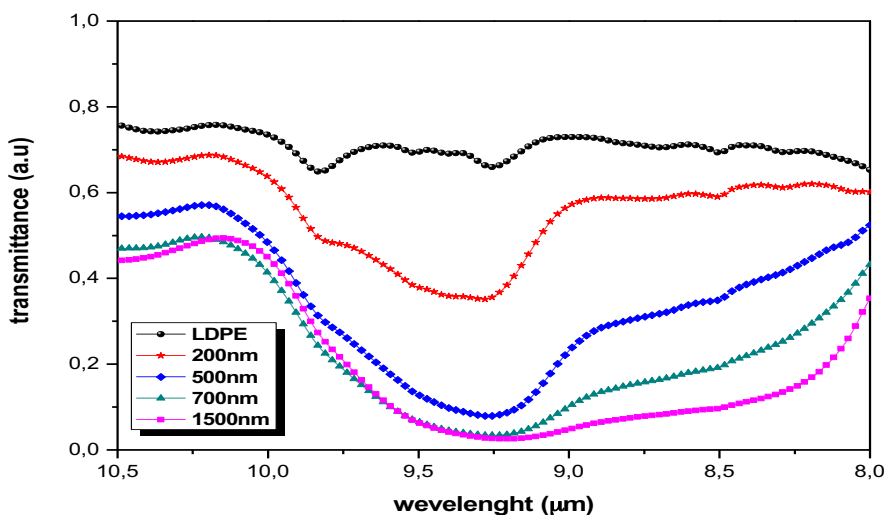


Figure 4: FTIR spectra in the range (8-10.5) μm .

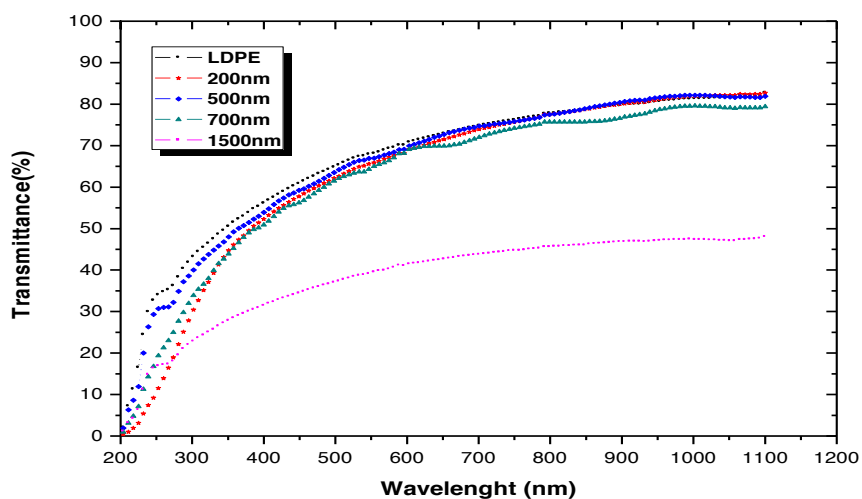


Figure 5: UV-visible spectra of SiO₂ films deposited on LDPE for different thicknesses.

2.5. AFM Analysis

The surface profile, particle sizes and surface roughness of the SiO₂ were examined using Atomic Force Microscopy (AFM, Nanosurf easyScan2, Switzerland). AFM measurements were performed in contact mode in the air at room temperature. Silicon cantilevers (Tap190 Al-G, NanoSensors™, Neuchatel, Switzerland) with 30-nm thick aluminium reflex coating were used. AFM microphotograph (10 μm x 10 μm) images recorded on samples of SiO₂/LDPE thin films deposited with different thicknesses (200, 500, 700 and 1500 nm) are shown in (figure 6). The image of the resulting SiO₂ particles shows spherical nano- microstructure with mean diameters ranged from 450 to 700 nm approximately, whereas the mean height grain varied from 98 nm to 115 nm approximately.

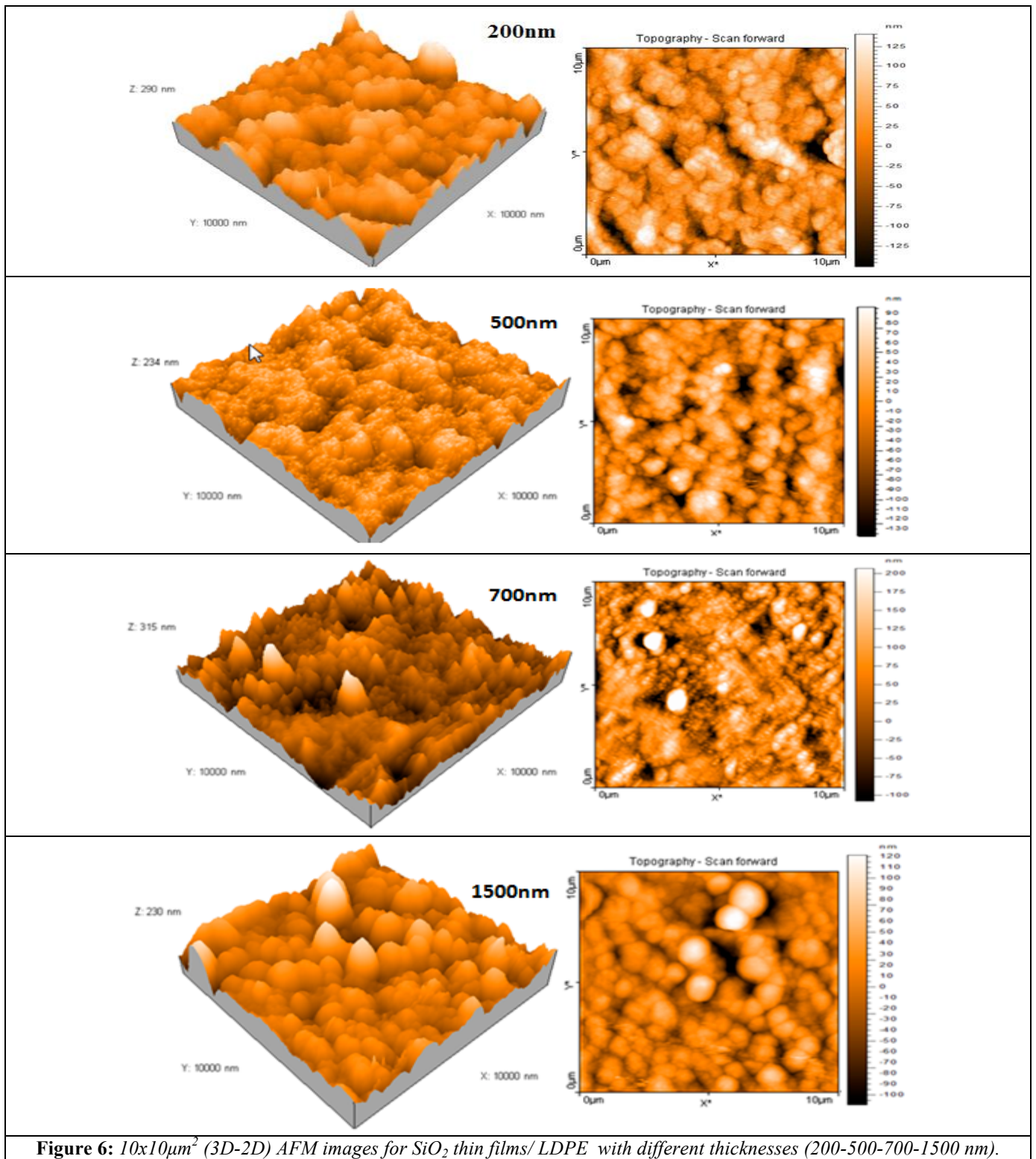


Figure 6: $10 \times 10 \mu\text{m}^2$ (3D-2D) AFM images for SiO_2 thin films/ LDPE with different thicknesses (200-500-700-1500 nm).

The evolution of the microstructure for the SiO_2 film may be related to the reorganization of the SiO_2 molecules during the PVD evaporation process [24]. From the topographic images, it can be seen that the films deposited at 1500 nm appear to be more uniform than the films deposited at other thicknesses topography (see figure 7). The root mean square (RMS) roughness also decreased with increasing the thickness (t). The analysis section shows that RMS roughness values for thin films deposited at 200, 500, 700 and 1500 nm are 47, 45, 28 and 23 nm, respectively. the decrees of roughness with increasing thicknesses can be explained by the formation of new bigger domed spherical grains.

Grain diameters and height distribution were measured for each thickness (see figure 7). A narrow distribution of grain diameters and heights was observed for 1500nm thickness, while a broader distribution in the grain diameter and height was obtained for the 500 nm thickness.

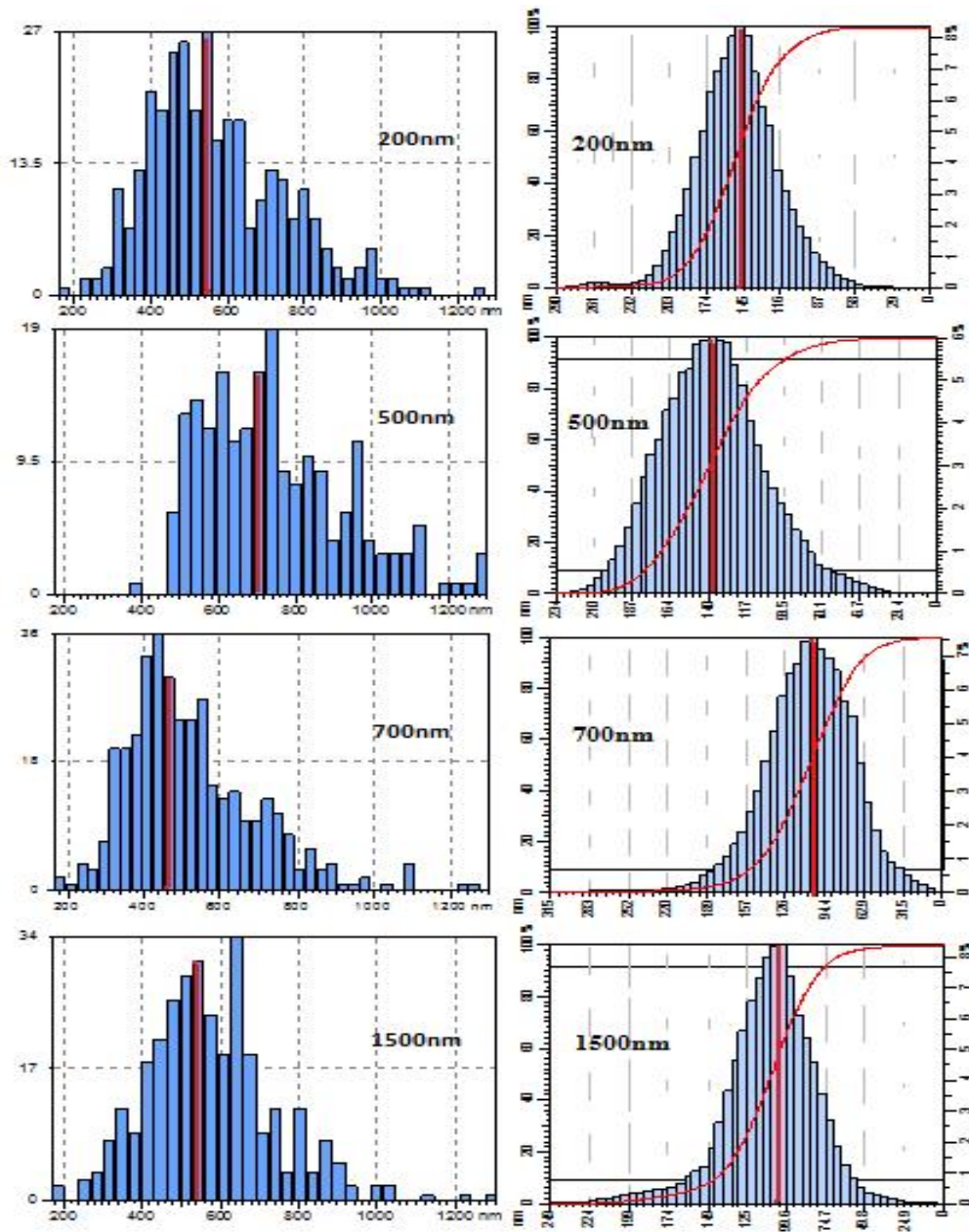


Figure 7: Statistical histograms of SiO₂ grain diameter (left) and height dispersions (right) for different thicknesses (200-500-700-1500 nm).

The mean diameter, height and the RMS of the roughness of the surface of SiO₂ films are tabulated in Table 1 for the 200-500-700-1500 nm thicknesses. Table 1 reveals that the surface roughness of SiO₂ thin films decreases with increasing thickness.

Table1: Variation of particle size (diameter and height) and root mean square (RMS) of the roughness of the surface according to the thickness.

S. NO	Thickness (nm)	diameter Particle (nm)	Particle height (nm)	R MS (nm)
1	200	500	115	47
2	500	700	140	45
3	700	450	108	28
4	1500	525	98	23

3. Results and discussion

We built a mini greenhouse of LDPE without coating and another of LDPE coated with a 700nm SiO₂ layer. We also built a third mini greenhouse of window silka glass (glass thickness is 6 mm, the transmittance 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 SiO₂ film or LDPE. We considered the complex refractive index of SiO₂ near 10μm as follows :

$$N=n_r-i.k=1.43-i.1.5 \quad (i=\sqrt{-1})$$

Then we calculated the value of the reflection coefficient using the matrix method [21] in the following cases:

- 1-Incident medium is air – SiO₂ layer – substrate is LDPE: The reflection coefficient is R=33%.
- 2-Incident medium is LDPE – SiO₂ layer – substrate is air: The reflection coefficient is R=18%.

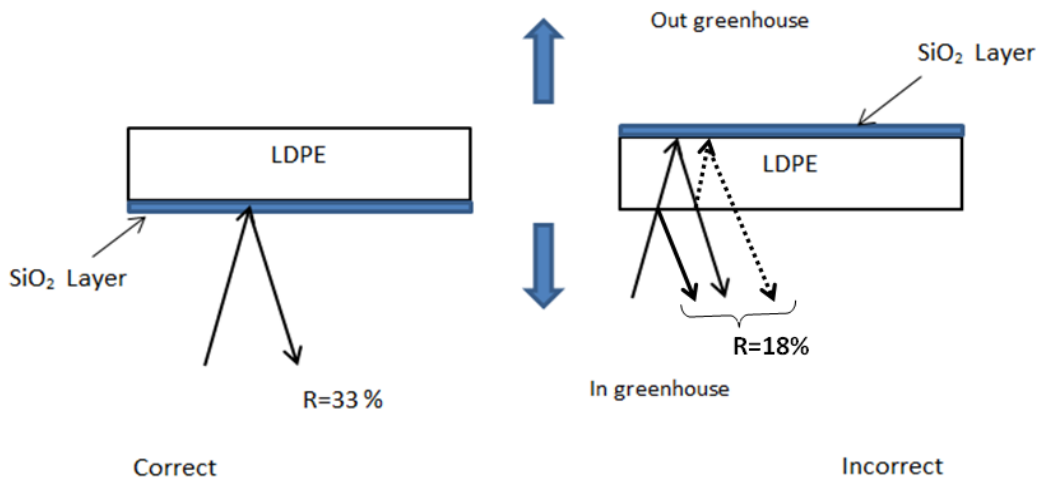


Figure 8: Correct use of Coated LDPE

The side facing the ground (inside the greenhouse) should be the SiO₂ 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. 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 SiO₂ layer is noticed. This increase is estimated to be more than 1°C compared with the without coating greenhouse LDPE (1.2 °C overall and 1.3 °C between 11 PM and 5 AM). We also notice that the transmittance of the greenhouse coated with the 700 nm SiO₂ 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 0.25 °C overall and the two temperatures between 11 PM and at 5 AM match each other very well.

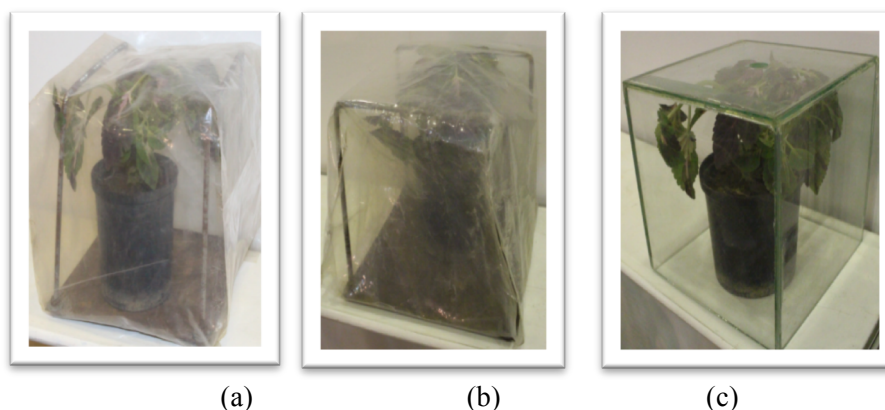


Figure 9: Three green houses (a) LDPE without coating, (b) LDPE coated with 700nm SiO₂, (c) silica glass.

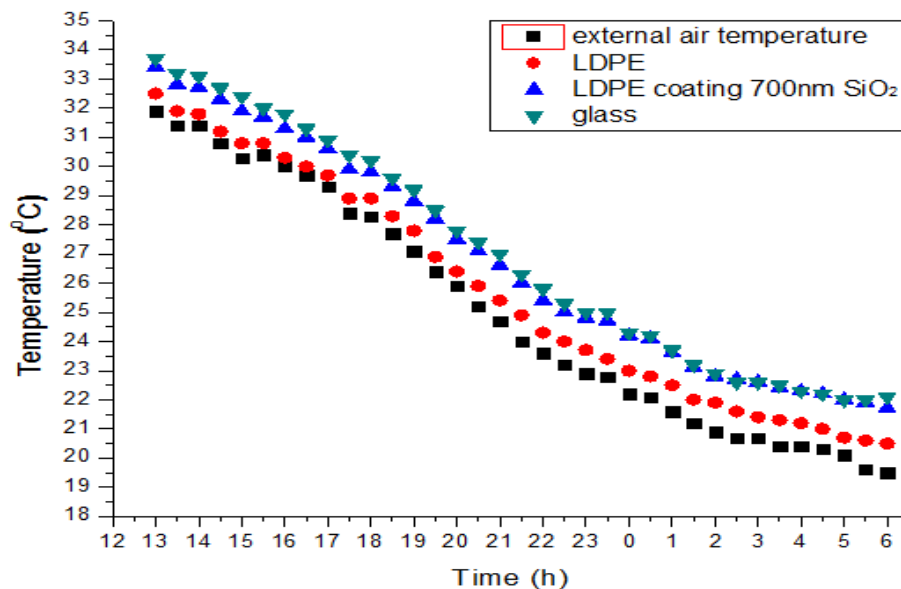


Figure 10: The variations of difference temperature (ΔT), between the temperature inside the greenhouse and the temperature in the external air, during the time.

By studying the IR transmission in figures (3, 4, 11), A decrease in the transmittance near $10\ \mu\text{m}$ 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 $10\ \mu\text{m}$, the transmittance of the sample with a thickness of $1500\ \text{nm}$ is very close to that with a thickness of $700\ \text{nm}$. We deduce that it may not be very beneficial to go beyond $700\ \text{nm}$.

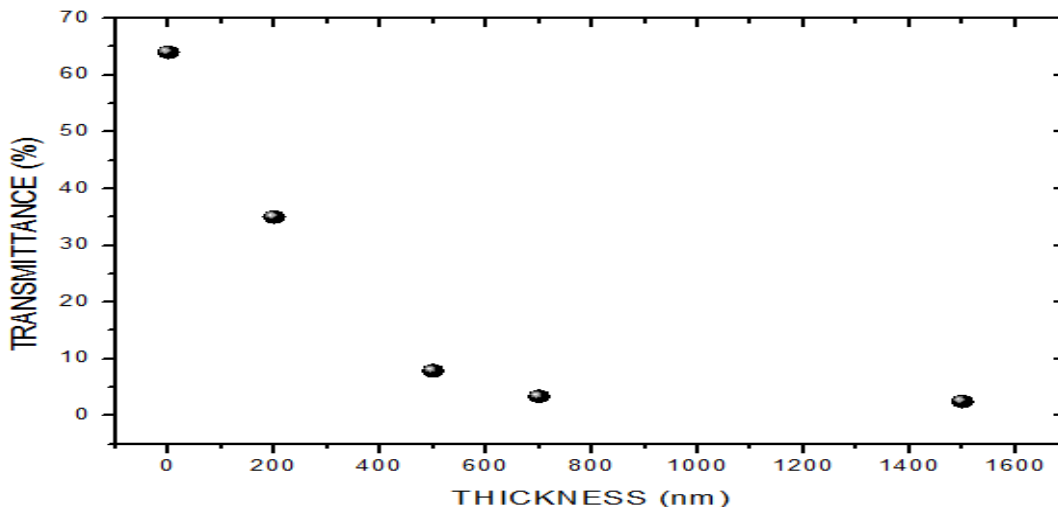


Figure 11: Transmittance at $10\ \mu\text{m}$ as a function of different thicknesses of SiO_2 .

By studying the UV-VIS transmission in (figure 5), A significant decrease is noticed in the transmittance of the film with a thickness of $1500\ \text{nm}$, compared with the other films of less thicknesses ($200, 500$ and $700\ \text{nm}$). These three films do not have any significant effect on the transmittance compared with that of the LDPE without coating. Thus, the film with a $700\ \text{nm}$ SiO_2 layer was adopted to build the mini greenhouse. It has no effect on the UV-VIS transmission but its reduces a maximum the transmission of the IR radiation around $9.3\ \mu\text{m}$.

The refractive index of LDPE in the visible domain is 1.51 while the imaginary part ($k=0$) [25]. It is very close to the real part value of the refractive index of SiO_2 which is equal to 1.43 [26]. Therefore, there should not be any significant change in the transmittance of the LDPE, in the visible range, when coated with SiO_2 . This is clearly seen in (figure 5) except for the last case where the thickness of the SiO_2 layer is $1500\ \text{nm}$. Consequently, there should not be any significant change in the greenhouse temperature during sun-shining time. The significant

reduction in the transmittance in the case where the thickness of the SiO₂ layer is of 1500 nm is probably due to Mie scattering [27], since the dimensions of the deposited particule, as the study of the surface by AFM, is of the order of the wavelength or to the evaporation of some contaminants during the deposition of such a large thickness of SiO₂.

Conclusion

Throughout this study, silicon dioxide films with different thicknesses (200, 500, 700 and 1500 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. SiO₂ 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 1 °C, compared with the same greenhouse without coating. The temperature inside the SiO₂ coated LDPE greenhouse was found to be almost identical to that inside the glass greenhouse.

Statistically speaking the conclusions are acceptable because the experiment were replicated many time. The main gain is the fact that the SiO₂ Coated LDPE greenhouse has the same temperature as Glasse made greenhouse.

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