Aerosol assisted dielectric barrier discharge plasma jet for Silver\ PMMA nanocomposite thin films preparation

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Abstract

Silver Poly (methyl methacrylate) PMMA nanocomposite thin films deposited on glass substrates by in-situ aerosol assisted plasma polymerization at atmospheric pressure and room temperature, from methyl methacrylate monomer in the presence of different concentrations of Ag nanoparticles (3%, 5%, 7%, and 9wt%). The average particles size for the silver nanoparticles was within 50nm. Metal polymer nanocomposite thin films were characterized by UV-VIS, XRD, and SEM the optical studies show that the energy band gap will be different according to the silver PMMA concentration. The XRD pattern indicates that the pure PMMA is amorphous where The XRD pattern of Ag nanoparticles in PMMA, all the refractions corresponded to the pure silver metal with cubic symmetry. SEM and the XRD reveal the presence of silver nanoparticle embedded into PMMA. It can be concluded that it can be prepared Ag\ PMMA nanocomposite thin films by aerosol assisted dielectric barrier discharge DBD plasma jet polymerization and control the optical energy band gap irregulars by controlling the experiment variables.

Keywords: PMMA, nanocomposite, plasma jet.

بلازما نفث بالتفريغ الكهربائي عبر حاجز عازل والمعززة بالرذاذ لتحضير متراكبات فضة - PMMA

الخلاصة

تم ترسيب اغشية رقيقة نانوية لمتراكبات Ag/ PMMA على قواعد من الزجاج وذلك بانجاز البلمرة موضعيا بالبلازما المعززة بالرذاذ وبدرجة حرارة الغرفة وعند الضغط الجوي ،من مونيمر MMA وبوجود تراكيز مختلفة من جسيمات الفضة النانوية .(3%, 5%, 7%, and 9wt%).معد قطر الجسيمات النانوية للفضة هي 50nm .الاغشية الرقيقة النانوية لمتراكبات معدن بوليمر شخصت بال UV-VIS, XRD وSEM ،دراسة الخواص البصرية بينت ان فجوة الطاقة البصرية تتغير مع تغير تركيز الفضة في PMMA. حيود الشعة السينية بين ان PMMA ذو تركيب بنائي عشوائي بينما نمط حيود الاشعة السينية للفضة في PMMA كانت ناتجة عن فضة نقية ذات تركيب بلوري مكعب .فحوصات المجهر الالكتروني والاشعة السينية بينت ان جسيمات الفضة النانوية مزروعة بصورة متجانسة داخل الPMMA .

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من هذا نستنتج امكانيت تحضير اغشية رقيقة لمتراكبات Ag/PMMA بالبلمرة الموضعية بالبلازما نفث الملولدة بالتفريغ الكهربائي عبر حاجز عازل DBD والتحكم بفجوة الطاقة البصرية بشكل منتضم وذلك بالتحكم بمتغيرات التجربة.

INTRODUCTION

In several last year plasma polymers containing small metal, particles have been intensively studied due to their novel physical properties and promising application. Plasma is often done by means of a dielectric barrier discharge (DBD). This is mostly worked out through a parallel plate electrode system. At least one of the electrode surfaces is covered with a dielectric. A carrier gas is brought between the two electrodes to be ionized for creating the discharge. Commonly used carrier gasses are inert gasses like helium, argon and nitrogen. The layer that is deposited originates from a precursor that is injected into plasma[1]. Different precursor systems can be used: gasses, liquid vapors, and aerosols. Most often gasses and/or aerosols are used. This work deals with the atmospheric plasma jet deposition technique using aerosols. Plasma can split up molecular particles. Only elements and components with a low molecular weight can be utilized as gas precursor in plasma depositing applications. As there are much more liquid than gaseous precursors available, the number of possible material is clearly higher when working with aerosol precursors. Various nanoparticles and monomer systems can be simultaneously applied in aerosol form during plasma treatment. So working with aerosol precursors offers more flexibility [2]. Different techniques can be used for aerosol production: ultrasonic piezoelectric technology and nozzles. Nozzles are the most stable system in case of constant production. Important parameters are the distribution of the drop size and the average drop diameter. The smaller the drop size, the higher the interaction precursor-plasma [3].

In this work special nozzle was used to generate an aerosol. One of the main challenges in preparation high-performance nanometalparticle/polymer composite thin films is achieving homogeneous dispersion of the nanoparticles in a polymer matrix. This criterion is vital because good dispersion of the individual nanoparticles in a polymer matrix is the basis for obtaining promising material properties [4]. In this work, the in-situ polymerization process was used to prepare Ag PMMA nanocomposite thin films. Selected PMMA among different polymers because of its simple synthesis procedure, good environmental and thermal stability, low-cost price, good optical and chemical properties[5]. The motivation behind this investigation is to study the characteristic change in optical properties of PMMA when silver nanoparticles are embedded in it. Here PMMA plays the role of a dielectric medium. Silver nanoparticles are of current importance because of its easy preparation process and unique optical, electrical and thermal properties. These nanoparticles are best suited for application in surface plasmon optics, photonics, photography, surface enhanced Raman scattering, surface enhanced florescence, catalysis, data storage, random laser etc [6]. Hence the synthesis of PMMA–silver nanoparticle composite is receiving wide attention.

Experimental details

The Dielectric Barrier Discharge (DBD) plasma jet system used for the thin films deposition consist of alternating high voltage power supply, generates high voltage of sinusoidal shape of 7.5 kV peak to peak and fixed frequency of 28 kHz, plasma jet torch, gas supply and fiting. Fig.1 shows a photograph at working of the non-thermal atmospheric pressure plasma torch. Silver nanoparticles from Nanjing nano Technology co, ltd, China its particle size was 50nm and purity of 99.9%, with concentration of 3%, 5%, 7% and 9wt% were mixed with Methyl Methacrylate Monomer (MMA) product from Vertex-Dental Netherlands. The mixer dispersed by ultrasonic to ensure a homogeneous distribution of nanoparticles. Then silver PMMA nanocomposite thin films deposited by DBD plasma jet system on ultrasonically cleaned glass substrate of standard size 10 x 10 mm. Fig.2 shows a photografe for the non-equilibrium atmospheric pressure plasma system for Silver/PMMA nanocomposite thin films preparationis.

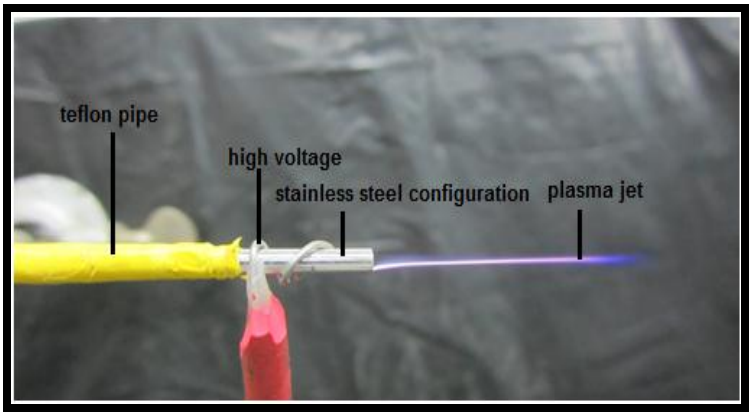


Figure (1) Photograph at working of the non-thermal atmospheric pressure plasma torch.

Whene the Argon gas passes through the nobilizer which contains the mixture, the mixture convert to aerosol. This aerosol was guided by the Ar gas to the plasma jet. the plasma was ignited by using an electric source at a fixed frequency of 28 kHz. The plasma was generated downstream to the substrate which was positioned along the plasma jet at a fixed distance from the plasma torch (1.5cm). The film deposition was carried out for 5min.the levels of gas flow rate was 1 l/min.

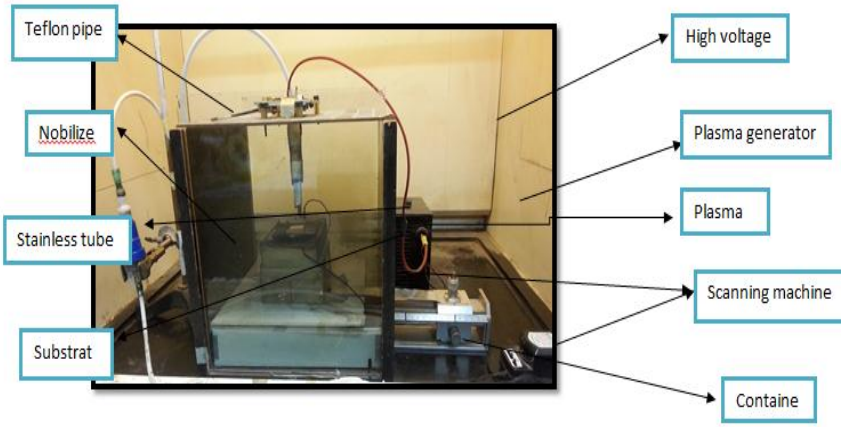


Figure (2) Photograph for the non-equilibrium atmospheric pressure plasma system for Silver/PMMA nanocomposite thin films preparations.

UV-Visible absorption spectra of pure PMMA and Ag/PMMA nanocomposite thin films were obtained by using a double beam UV-VIS-NIR 210A Spectrophotometer.the fluorescence measurements were obtained by using SL 174 spectrofluorometer. The thin films surface morphological analysis is carried out by SEM and the structure analysis are achived by X-ray diffractometer system type SHIMADZU 6000. The thickness of the films was measured by optical interferometric method.

Results and discussion

Absorption spectrum

Fig.3 shows the absorption spectrum of Ag/PMMA nanocomposite thin films with the four concentration of Ag nanoparticles (3, 5, 7, and 9wt%) and also the absorption spectrum of pure PMMA thin films and Table 1 shows the thin films preparation conditions and its thickness, all prepped at the same gas flow rate 1 L/min. The absorption spectra of Ag/PMMA films shows the effect of Ag nanoparticles and the enhancement of SPR which is represented by the peaks around 400nm while pure PMMA films have peak at 294nm and transparent from 300 to 900nm.

Absorption coefficient(α)

Fig.4 shows the absorption coefficient of Ag/PMMA nanocomposite at the known four concentrations and pure PMMA calculated from the following equation [7]

$$\alpha = 2.303\ A/t \qquad \ldots (1)$$

where A the absorbance and t the sample thickness we can see that it has the same behavior of absorption that the effect of SPR for silver NPs appear clearly.

Table (1)The experimental condition for the preparation of pure PMMA thin films and Ag/PMMA nanocomposite thin films.

Sample	Thickness (nm)
Pure PMMA	275
Ag 3wt%	330
Ag 5wt%	228
Ag 7wt%	311
Ag 9wt%	323

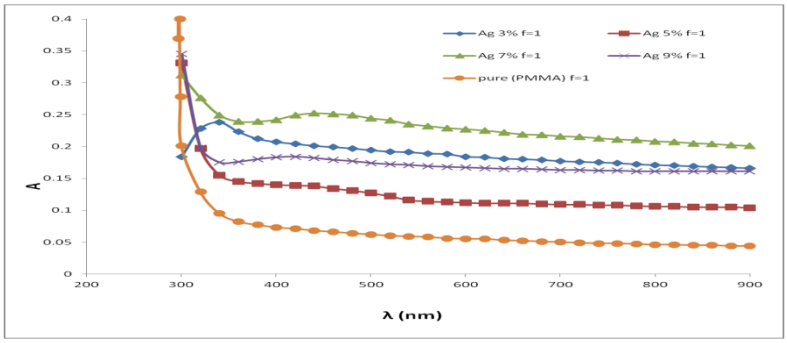


Figure (3) Absorption spectrum for pure PMMA. Ag/PMMA nanocomposite with 3,5,7, and 9wt% silver NPs.

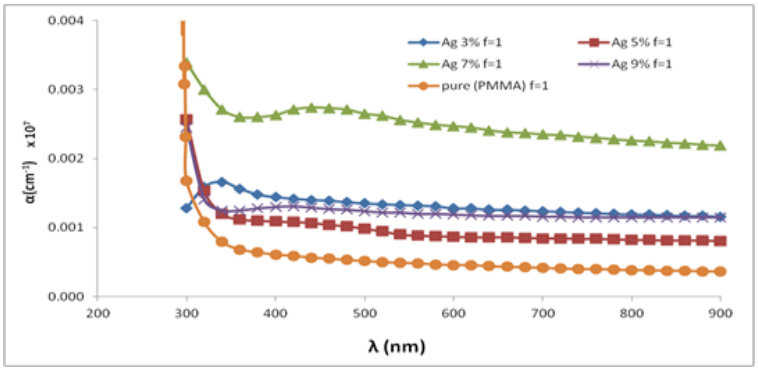


Figure (4) Absorption coefficient for pure PMMA, Ag/PMMA nanocomposite with 3,5,7and 9wt% silver NPs.

Optical energy band gap E_g

The optical energy band gap represented in Fig.5 it has been determined by plotting the variation of $(\alpha hv)^2$ versus hv (eV) for direct energy gap transition. The increasing in silver NPs concentration lead to decrease of E_g from 2.715 eV for 3wt% Ag concentration to 2.36 eV for 9wt% Ag concentration while for pure PMMA film was 4.0556 eV. The decreasing in E_g is properly due to the modification of polymer structure

and also the addition of metal NPs to polymer matrix induces a structural ordering of the polymers and these changes are supporting by UV-Vis spectra, so the optical band gaps vary with silver concentration.

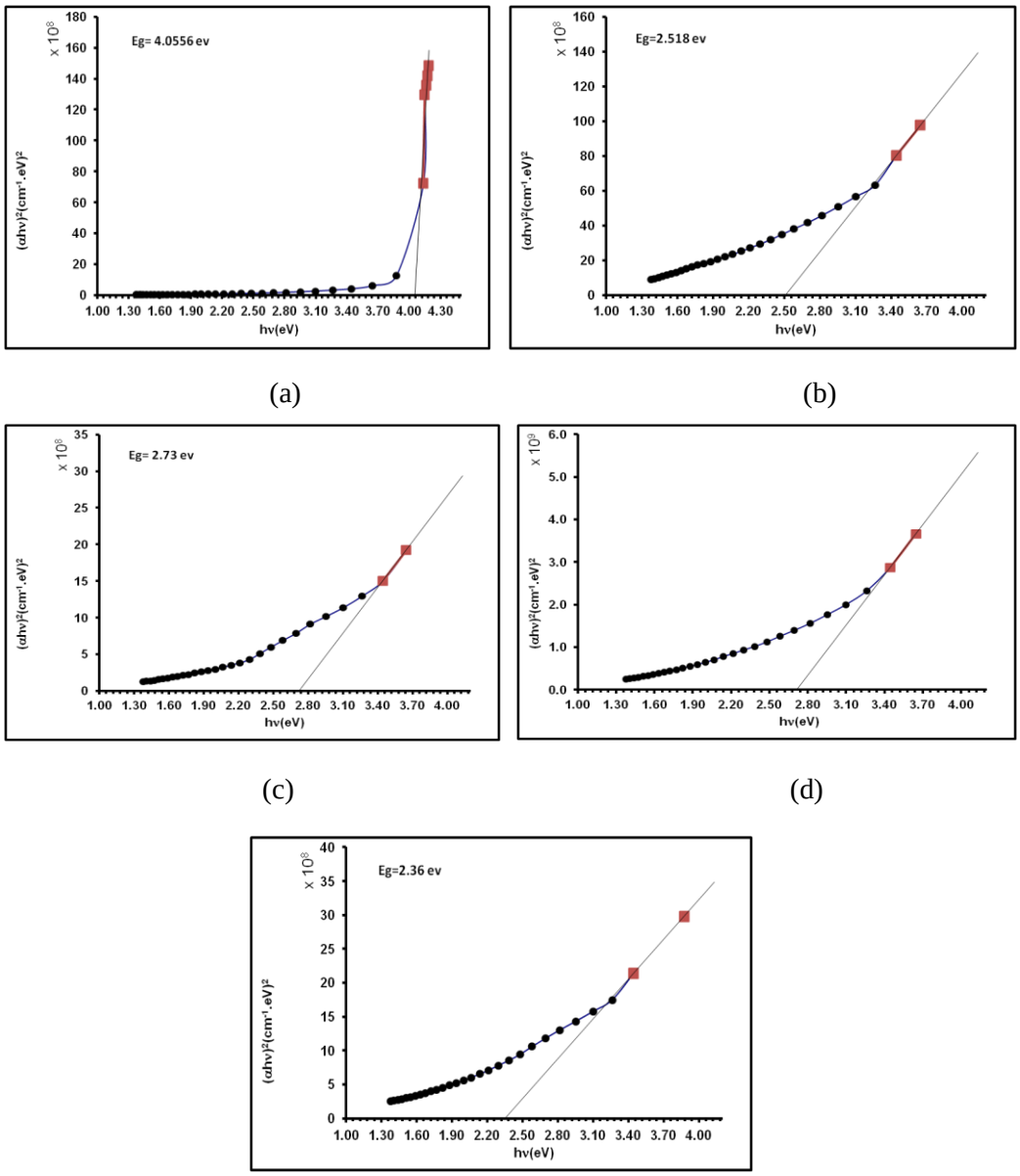


Figure (5) The E_g for (a) pure PMMA film,(b) 3wt% silver concentration, (c) 5wt%, (d) 7wt% and (e) 9wt%.all at constant gas flow rate 1L/min.

Refractive index

Fig.6 shows the variation of refractive index calculated from the relation[8]

$$n = \left(\frac{4R}{(1-R)^2} - {K_0}^2\right)^{\frac{1}{2}} + \frac{(1+R)}{(1-R)} \quad \text{.... (2)}$$

where

R (the reflectance and K_0 the extinction coefficient) with wavelength for pure PMMA and Ag/PMMA nanocomposite thin films at the four concentration of silver NPs, the increasing in silver NPs concentration lead to increase in refractive index.

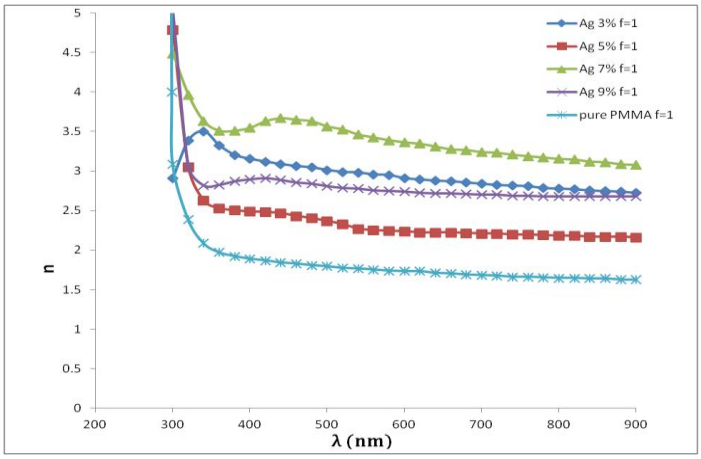


Figure (6)The variation of the refractive index (n) with wavelength for pure PMMA Ag/PMMA nanocomposite with 3,5,7,9 wt% silver NPs.

X-Ray Diffraction

Fig.7 shows the XRD pattern of the prepared PMMA thin film and Fig.8 for Ag/PMMA nanocomposite films at two silver NPs concentration 7 and 9 wt%, for pure PMMA the film has an amorphous structure. The XRD pattern of Ag nanoparticles in PMMA, all the refractions corresponded to the pure silver metal with cubic symmetry. The refractions presented by four main peaks at 2θ= 38.160, 44.320, 64.440, 77.420 and 81.540° which are assigned to the lattice planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) this agree with [9, 10].

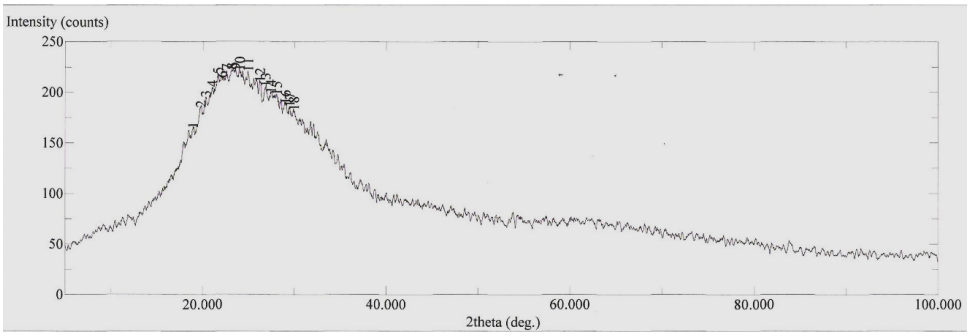
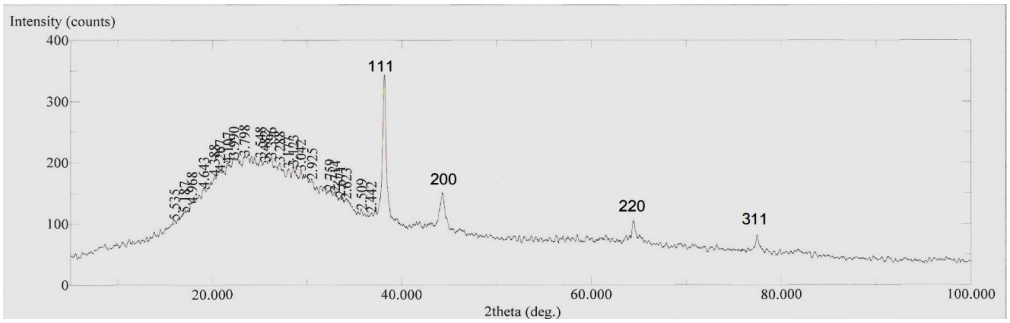
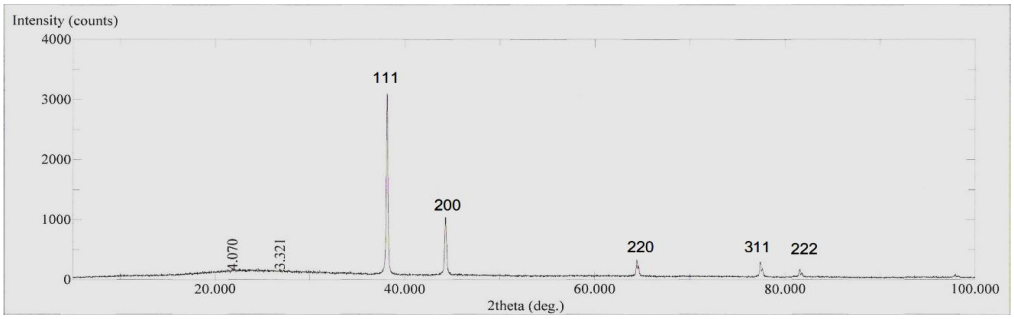


Figure (7) XRD for pure PMMA thin film.



(a)



(b)

Figure (8) XRD (a) for Ag/PMMA nanocomposite film at 7wt % (b) Ag/PMMA nanocomposite film at 9wt %.

Surface morphology

The distribution and shape of Ag NPs were found by performing scanning electron microscopy. Fig.9 shows the SEM image of Ag/PMMA nanocomposite thin film at 9wt% silver NPs concentration and for 5wt% is shown in Fig.10. The SEM images indicate that Ag NPs disperse in the PMMA matrix with a relatively uniform distribution and formed mostly spherical NPs. The silver nanoparticles are homogeneously dispersed in the polymer matrix.

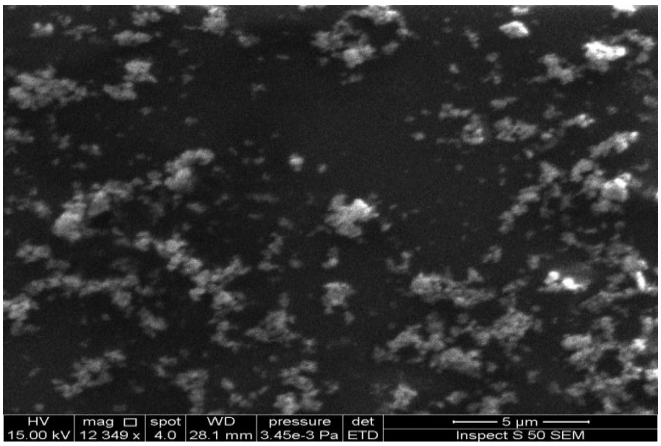


Figure (9) SEM image for Ag/PMMA nanocomposite thin film at 9wt% silver NPs concentration.

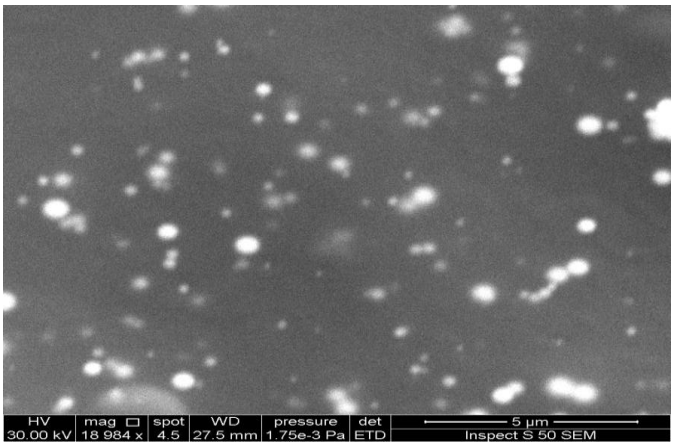


Figure (10) SEM image for Ag/PMMA nanocomposite thin film at 5wt% silver NPs concentration.

Conclusions

As is clear, the preparation of nanocomposite films by plasma polymerization made a new material with different chemical structure. The polymer polymerized by plasma different from conventional polymer that it has high cross linked, highly branched and high density and this effect on the linear refractive index. The silver particles are uniformly distributed in the PMMA matrix. Increasing the weight percentage of the silver in the nanocomposite thin films lead to decreases the optical energy bandgap, and modifies the polymer structure.

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