SERS on mesostructured thin films with silver nanoparticles

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ABSTRACT

Mesostructured 2d-hexagonal sol-gel films were prepared by dip-coating method. Their structures were detected by X-ray diffraction. Silver nanoparticles reduced from Ag^+ ion (silver nitrate) to Ag^0 were deposited into the channels of the structure produced by the neutral surfactant Brij58. Surface enhanced raman spectroscopy technique was used to characterize the films. Spectra of films without metallic particles were compared to those with silver nanoparticles; the earliest exhibit an increased intensity on the 885, 955, 1061, 1129, 1230,1429, 1521, and 1796 cm^{-1} bands. This enhancement due to SERS is the result of the surface plasmon excitation inside the silver particles causing a reactivation of the Raman scattering from the molecules on the surface colloids. Photoconductivity studies were performed on mesostructured films with silver colloids. ϕl_0 and $\phi\mu\tau$ parameters are bigger than those from photorefractive crystals $KnbO_3:Fe^{3+}$. The photovoltaic effect increases with $AgNO_3$ concentration. Mesostructured film without silver colloids shows a small photovoltaic parameter.

KEYWORDS: Dip coating, thin films, surfactant, surface plasmon.

1. Introduction

Raman spectroscopy is a widely used technique for the characterization of solids by their optical phonon frequencies[1]. Surface-enhanced Raman scattering (SERS) is a modified version of this technique. It is a process in which the Raman scattering cross-section of molecules absorbed onto the surfaces of metals such as silver, copper and gold is increased by as much as six orders of magnitude compared with the cross-section for normal Raman scattering. Two possible mechanisms are responsible for this phenomenon. One mechanism is associated with large electric fields that can exist on the surfaces of the metal particles with small radii and it is obtained in case of metals for which the complex part of the dielectric function is small[2]. The second mechanism is related to polarizability distortions of the absorbed molecules by formation of charge-transfer complexes with the metal surface[2]. SERS has two important features: a very large enhancement and short range[3].

Most SERS studies employ the same instrumentation as that used for conventional Raman spectroscopy. This consists of a laser light source (Ar or Kr laser); beam steering optics, 90º or backscattering collection optics, and a double monochromator with either a photomultiplier tube or diode array detector.

In this work, mesostructured sol-gel thin films were prepared using an oligo (ethylene oxide) surfactant (Brij58) as a template for silica polymerization in the synthesis of uniformly distributed silver-ion-containing mesostructured silica material. Silver ions in mesostructured silica material were reduced to silver colloids spontaneously, by keeping the samples in the darkness at room temperature. This effect was detected by the sequence of color changes on the film from colorless/white to black. Optical absorption gave a broad absorption band in the visible region of the spectrum between 400 and 500 nm due to the plasmon mode of metallic silver particles. A 2d-hexagonal phase[4] was detected by X-ray diffraction. Raman spectroscopy was used to determine the Raman signal of the Brij copolymer on the films.

Photoconductivity studies were done on the mesostructured sol-gel films with nanoparticles to determine the charge transport parameters and to compare them with those from photorefractive crystals of $KnbO_3:Fe^{3+}$.

2. Experimental

Glass substrates were boiled in an acidic solution of sulfuric acid with hydrogen peroxide. Films were dip coated to the glass substrates at rate of 3.5 cm/min. The films were drawn with the equipment described previously that uses hydraulic motion to produce a steady and vibration-free withdrawal of the substrate from the sol[5]. Convection-free drying was critical to obtaining high optical quality films.

All reagents were Aldrich grade. An initial solution was prepared with $AgNO_3$ (silver nitrate) dissolved in a small quantity of deionized water and nitric acid. Then was added 1 g of methanol, 5.4 g of TMOS (Tetramethyl

orthosilicate), and 1.3-4 g of the neutral surfactant $C_{16}H_{33}PEO_{20}$. This initial solution was mixed and heated to 50-70 ºC for 20 minutes to homogenize the mixture. The final molar ratio concentrations were Ag^{+}/ $C_{16}H_{33}PEO_{20}$ = 0.5-0.7.

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The structure of the final films was characterized with X-ray diffraction (XRD) at low and high angle. X-ray diffraction was recorded on a Siemens D500 difractometer using Ni-filtered CuKα radiation with an integration time of 1 sec at low angle.

A Coherent 190-6 Kr laser was used with 476 nm, 514 nm, and 530 nm lines for silver. The laser beam was focused on the sample by using a lens with 150 mm focal length. The scattered light was collected with a Spex 1401 double monochromator. A PMT cooled tube RCA C31034 and a photon counter Standford Research Systems SR 400 were used to detect the signal. The data were captured on a PC (Figure 1).

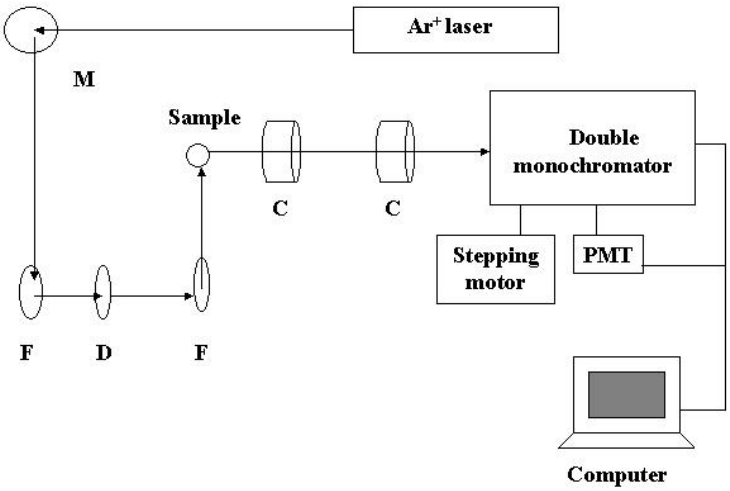

Figure 1. Raman spectroscopy setup used to detected the SERS signal. The components are M=mirrors, F=focusing lens. C=collecting lens, D=diaphragm, PMT= photomultiplier tube.

For photoconductivity studies[6] silver electrodes were painted on the sample. It was maintained in a 10^{-5} Torr vacuum cryostat at room temperature in order to avoid humidity. For photocurrent measurements, the films were illuminated with light from an Oriel Xe lamp passed through a 0.25m Spex monochromator. Currents were measured with a 642 Keithley electrometer connected in series with the voltage power supply. The applied electrostatic field E was parallel to the film. Light intensity was measured at the sample position with a Spectra Physics 404 power meter[7].

3. Results

Silver colloids were produced by spontaneous reduction of Ag^{+} ions stored in the darkness at room temperature for three months. Figure 2 shows the absorption band from two concentrations, $AgNO_3$/Brij58= 0.5 and 0.7 molar ratios. A broad absorption band was formed between 400 and 500 nm. It corresponds to the electron surface plasmon resonance from silver.

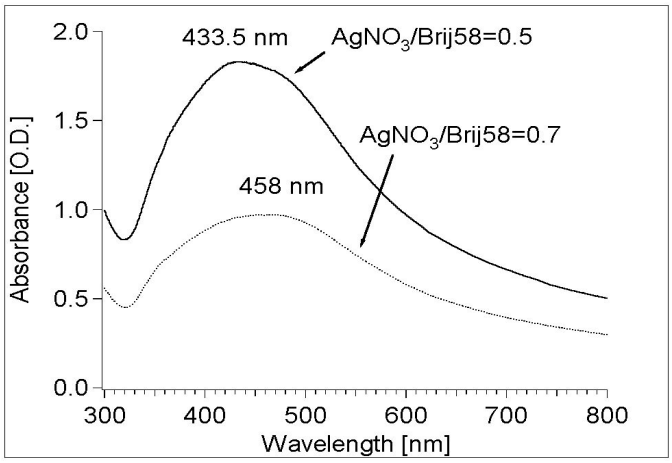

Figure 2. Absorption spectra of mesostructured sol-gel thin films with two silver nitrate concentrations. The absorption band was located between 430-460 nm.

The X-ray diffraction patterns of mesostructured sol-gel thin films with $AgNO_3$/Brij58= 0.5 and 0.7 molar ratio concentration are shown in the figure 3. The *d*-spacing for the hexagonal phase (100) peak is 53.5 Å.

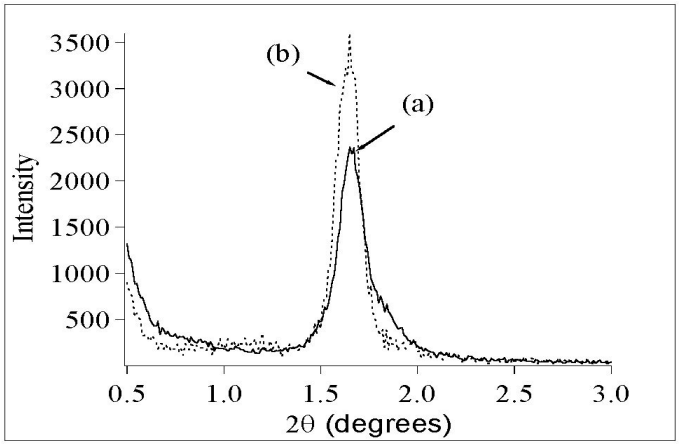

Figure 3. X-ray diffraction patterns of mesostructured sol-gel thin films of (a) $AgNO_3$/Brij58= 0.5 molar ratio, and (b) $AgNO_3$/Brij58= 0.7 molar ratio.

The withdrawal speed affects the structure of the final mesostructured film. Figure 4 shows the XRD patterns for withdrawal speeds of 4.3 cm/min, 6.1 cm/min, and 9.3 cm/min. The best structure corresponds to the highest intensity; it was obtained with the smallest value of the withdrawal speed.

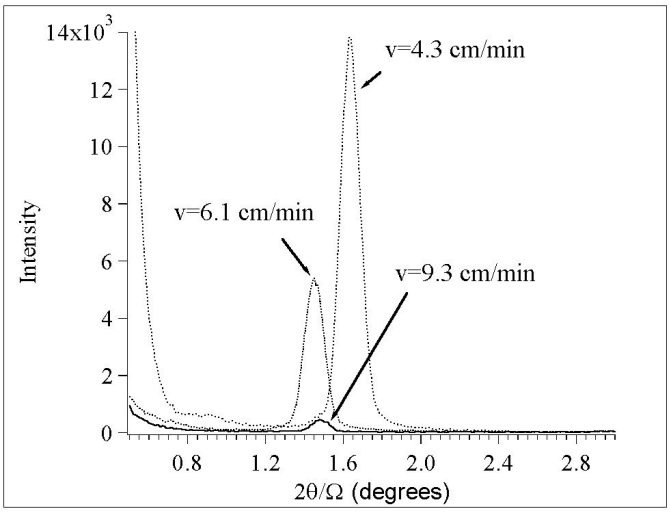

Figure 4. XRD patterns of mesostructured sol-gel thin film with different speed withdrawal.

The Raman spectrum of the block copolymer Brij58 is shown on the figure 5, the most intense bands are located at 885, 955, 1061, 1129, 1230,1429, 1521, and 1796 cm^{-1}. Figure 6 shows the Raman spectrum of mesostructured sol-gel thin film with the block copolymer Brij58 alone, the bands are located around the similar values as those from figure 5. The Raman spectrum of mesostructured sol-gel thin film with $AgNO_3$/Brij58=0.5 molar ratio without silver colloids is shown on figure 7, the Raman signal is weak in comparison with the Raman signal from the figure 8 (a), which shows the Raman spectrum of mesostructured sol-gel thin film with $AgNO_3$/Brij58=0.5 molar ratio, and the figure 8 (b) from the Raman spectrum of $AgNO_3$/Brij58=0.7 molar ratio, both having silver colloids. There is a clear enhancement of the Raman signal from the Brij 58 compared with that from figure 7. Thus, block copolymer must be located on the surface of the silver colloids and there is a resonance from its vibrational modes with the plasmons from the silver colloids.

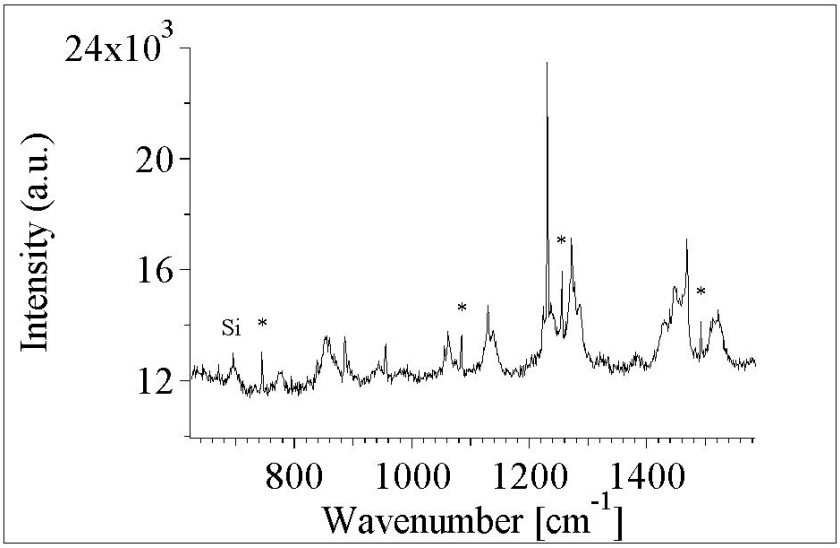

Figure 5. Raman spectrum of Brij58 powder. * corresponds to the Kr lines laser. Si corresponds to the silica (glass substrate).

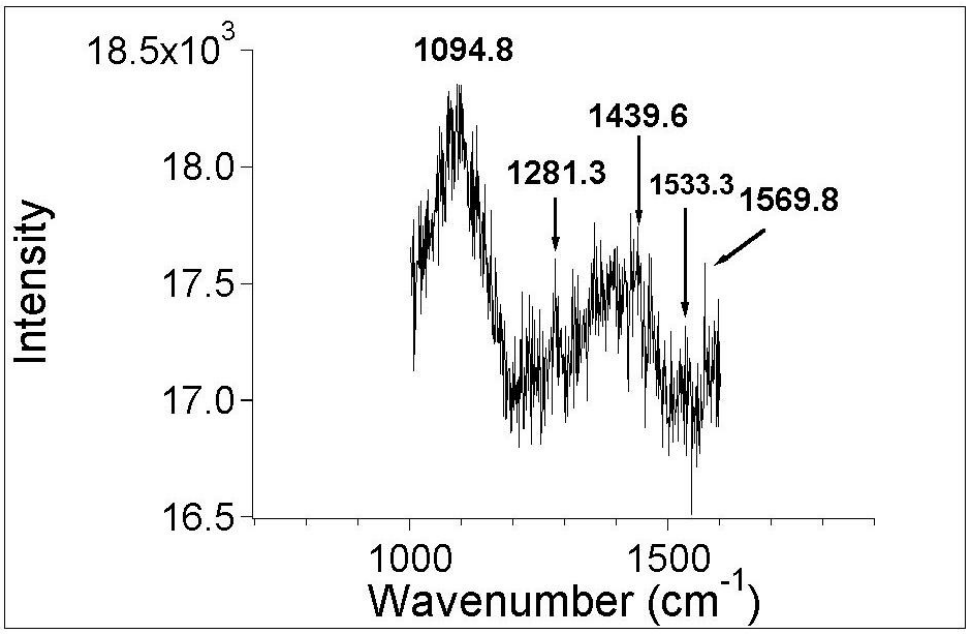

Figure 6. Raman spectrum of mesostructured sol-gel thin film prepared with block copolymer Brij58. It has a hexagonal mesophase.

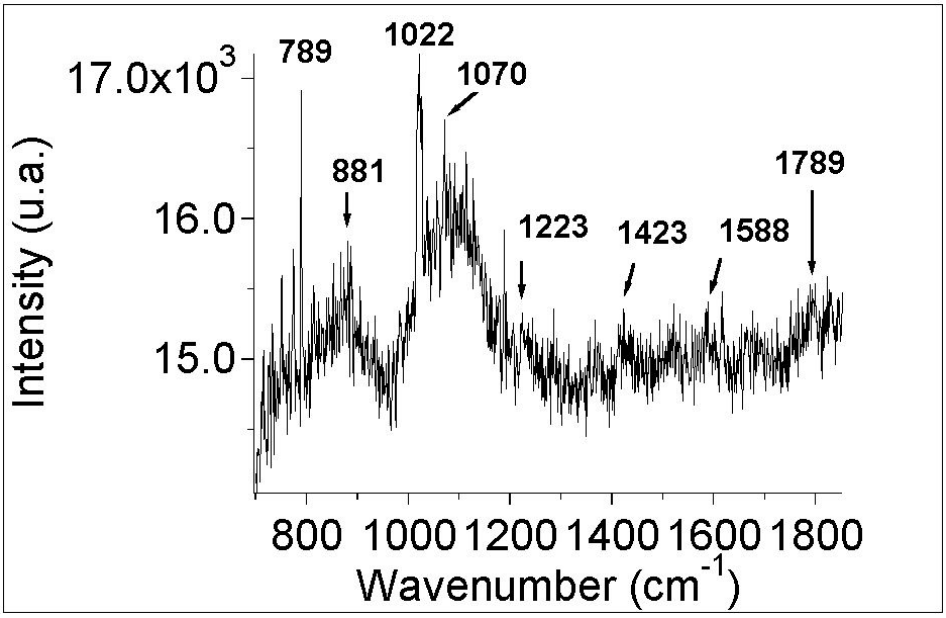

Figure 7. Raman spectrum of mesostructured sol-gel thin film without silver colloids.

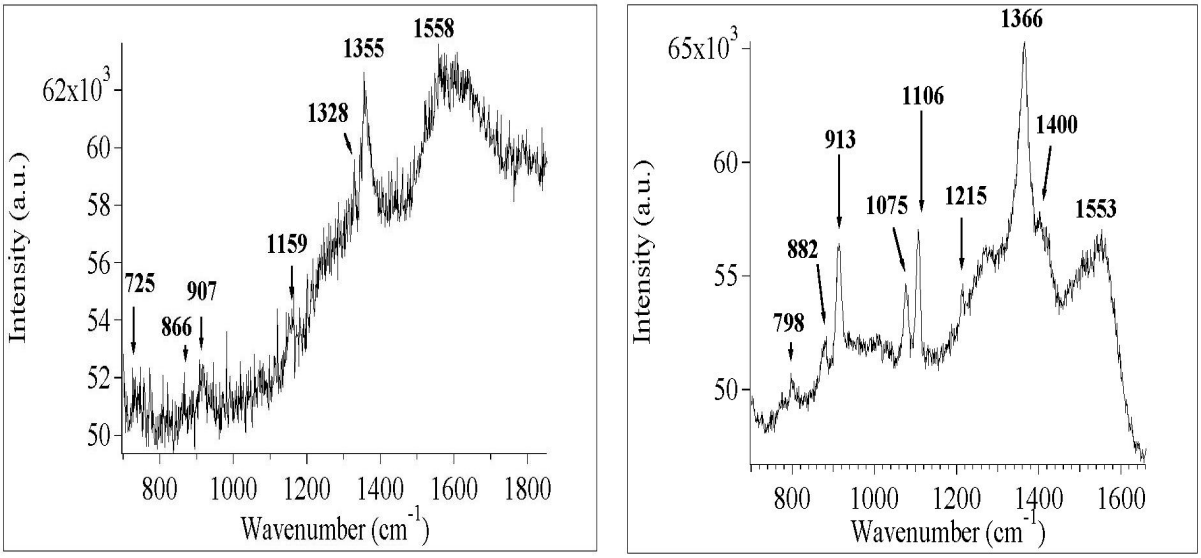

Figure 8. (a) Raman spectrum of mesostructured thin film with $AgNO_3$/Brij58=0.5 molar ratio at λ=476.2 nm. (b) Raman spectrum of mesostructured thin film with $AgNO_3$/Brij58=0.7 molar ratio λ=530.9 nm. Both films have silver metallic colloids.

Table I contains the main bands identified from each Raman spectrum from the silica, methanol and the block copolymer Brij58.

Table I. Identified bands from the Raman spectrum that were observed in each figure.

SAMPLE	λ(nm)	Silica	B1	B2	Methanol	B3	B4	B5	B6	B7	B8	B9	Figure
Brij58 powder	530.9		885	955	1033	1061	1129	1230	1271	1429	1521	1796	5
Brij58 film	530.9					1094		1281	1395	1439	1569		6
$AgNO_3$/Brij58= 0.5 (No silver colloids)	476.2	789	881		1022	1070		1223		1423	1558	1789	7
$AgNO_3$/Brij58= 0.5	476.2	725	866	907			1159		1355		1558		8 (a)
$AgNO_3$/Brij58= 0.5	514.5	802	914		1014	1077	1108	1215	1365	1436	1548		
$AgNO_3$/Brij58= 0.5	530.9	776		964		1081			1325		1541		
$AgNO_3$/Brij58= 0.7	476.2	763	838	918	1027		1170		1370	1426	1539	1762	
$AgNO_3$/Brij58= 0.7	530.9	798	882	913		1075	1106	1215	1366	1400	1553		8 (b)

Photoconductivity results of mesostructured sol-gel thin films with $AgNO_3$/Brij58=0.7 molar ratio and silver nanoparticles are shown on Figure 9. Current density as function of electric field applied on the film was plotted. The linear behavior means the samples have an ohmic response. The experimental data were fitted by least squares with straight lines at darkness, under illumination at 633 and 420 nm. When the film is illuminated the slope decreases, this indicates a noticeable photovoltaic behavior, i.e. an electric potential difference is produced on the sample when the illumination is applied. Photoconductivity on samples without colloids had a less photovoltaic response (not shown). The decrement in the photoconductivity on the mesostructured thin films with silver colloids can be explained thinking that metallic colloids screen locally the external electric field and then the charge carriers inside the sample see an effective field lesser than that without the colloids.

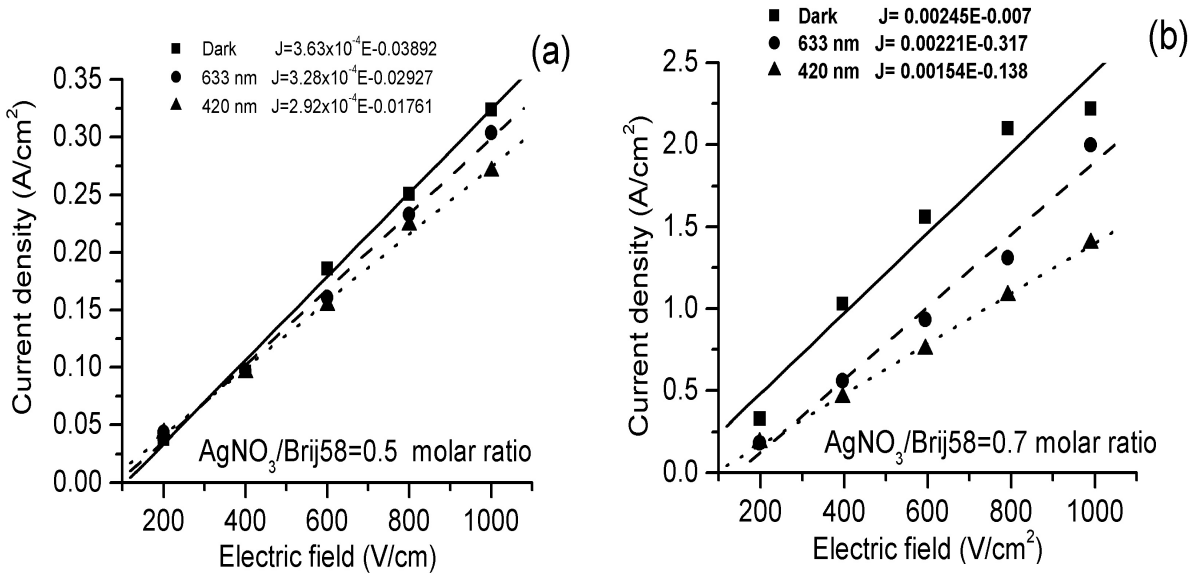

Figure 9. Photoconductivity results on (a) mesostructured thin sol-gel film with $AgNO_3$/Brij58=0.5 molar ratio with silver nanoparticles, (b) mesostructured thin sol-gel film with $AgNO_3$/Brij58=0.7 molar ratio with silver nanoparticles.

Photoconductive and photovoltaic parameters were calculated. They are reported in Table I. These were compared with those from photorefractive crystals of potassium niobate reported by Garcia et al.[6]. Our results in the present work are bigger than these values for at least two orders.

Table I. Obtained photovoltaic and photoconductive parameters.

Sample	Parameter	633 nm	488 nm	420 nm
$KNbO_3:Fe^{3+}$	ϕl_0 (cm) $\phi\mu\tau$ (cm^2/V)	$0.85x10^{-8}$ $23.4x10^{-11}$	$0.58x10^{-8}$ $7.1x10^{-11}$	
$AgNO_3$/Brij58=0.5	ϕl_0 (cm) $\phi\mu\tau$ (cm^2/V)	$8.4x10^{-7}$ $3.0x10^{-9}$		$5.6x10^{-7}$ $1.9x10^{-9}$
$AgNO_3$/Brij58=0.7	ϕl_0 (cm) $\phi\mu\tau$ (cm^2/V)	$2.4x10^{-5}$ $2.0x10^{-8}$		$3.6x10^{-6}$ $2.2x10^{-8}$

4. Conclusions

Mesostructured sol-gel thin films were produced with an excellent 2D hexagonal mesophase. Silver nanoparticles were spontaneously reduced at room temperature from Ag^+ ion (silver nitrate) to Ag^0 and they were deposited into the channels of the structure produced by the neutral surfactant Brij58. The absorption spectrum shows the characteristic band from surface plasmon mode at 410 nm.

Raman spectra of mesostructured sol-gel thin film with silver nanoparticles contain four bands localized on 885, 955, 1061, 1129, 1230,1429, 1521, and 1796 cm^{-1}, which corresponds to block copolymer Brij58. This signal is much more intense than that from the Raman spectra of mesostructured sol-gel thin film without silver nanoparticles.

On photoconductivity studies, the mesostructured thin films with silver nanoparticles are more photovoltaic than those without nanoparticles. These films are more photoconductive than the photorefractive crystals by two orders, approximately.

Acknowledgments

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