Effect of laser irradiated silver doped polystyrene/polyethylene terephthalate (PET) thin film for solar cell applications

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In the current research, the resist action of silver-doped polystyrene/polyethylene terephthalate (PET) solar thin film towards laser irradiation was observed. Moreover, silver-doped polystyrene nanoparticles were synthesized via a chemical technique while the PET film was purchased from the commercial market. Nd:YAG pulsed laser has been used to irradiate the samples at 2 minutes, 4 minutes, and 6 minutes respectively. The XRD (X-ray diffraction) pattern shows that silver-doped polystyrene peak at around angle θ = 26° tends to decrease after the bombardment of Nd:YAG pulsed laser. This indicates that the crystallinity of PET film decreased after laser irradiation. The Raman spectra have revealed the zwitter characteristics of silver-doped polystyrene are shifting of bands at 1380 cm⁻¹ and 1560 cm⁻¹ upon laser irradiation. For PET film, the Raman spectra showed that the exposed regions tend to change to cross-linking/chain-scissoring at 2 minutes and 4 minutes of irradiation. The surface roughness first increases and decreases upon irradiation. These results indicate that silver-doped polystyrene/polyethylene terephthalate (PET) thin film is appropriate for solar cell applications.

1 Introduction

Lithography is defined as the patterning, etching, and coating of many layers of thin films. The most widely used form of lithography is photolithography. Photolithography is widely applied in semiconductor, capacitor, and IC (Integrated circuits) chip manufacturing industries. By using optical radiation, the desired pattern can be transferred from masks to the semiconductor wafers through photoresist layers. Photoresists can be divided into two types which are positive resist and negative resist. In the case of positive photoresist, the long chain polymer has broken into smaller and more soluble fragments and become chain scissoring. Examples of positive tone resistance are PMMA (polymethyl methacrylate) and ZEP520. In case of negative resists, the exposed regions will undergo cross-linking reaction (polymerization) to form three-dimensional structures which make it insoluble in developer solution. An example of negative tone resistance is polystyrene. Polystyrene resist is more etch resistance than PMMA, however, it has low sensitivity which limits its application to small-scale nano-patterning. It is found that when increasing the time of exposure, some of the resists exhibit a switching behavior, from positive resists to negative resists or vice versa. The switching behavior is known as the zwitter characteristic. The resists that show the zwitter characteristic include PMMA, PS, nitrocellulose, triphenylene, and poly(di-n-hexylsilane).

This modified polymer has wide applications in the medical, optoelectronic, and electronic fields. Polystyrene has been important nonmaterial’s in the area of materials science in the current decade. Polystyrene due to its low bandgap, quantum confinement effect, higher surface-volume ratio, and some exceptional physical and chemical characteristics have been examined in detail to use in electrical, optoelectronic, and solar cell thin film applications. As compared to semiconductors, polystyrene semiconductors exhibit environmentally friendly, high mobility, chemical and thermal stability, inexpensive, compatible, and easy processing with semiconductors for thin film solar cell applications. Silver Doped Polystyrene/
Polyethylene Terephthalate (PET) thin films has been deliber-
ated for several causes including higher theoretical capacity,
safety, environmentally friendly, radiation resistance, chemical
durability, non-toxicity, and also some exceptional characteris-
tics like the optical and electronic characteristics of solar cells.\(^{11}\)

EPS (expanded polystyrene) is a prominent and
environment-friendly material for packing and construction
moreover, EPS is a lightweight stiff soft foam with the best and
most efficient thermal lagging and efficient resistance. The
proficient electronic, thermal, and mechanical properties are
impervious to humidity therefore EPS materials are resistant to
water vapors.\(^{15,11}\) The life cycle assessment (LCA) of usually used
EPS is based on external thermal insulation systems (ETICS).
This assessment is a worldwide established method for
accessing the material’s effects on the environment. In the
present era, the concept of sustainable progress had the most
central part in thinking about future interrelationships between
the economy, society, and natural resources. In civilized societ-
ties, development and progress can be attained sustainably
which will ensure equal access to future generations. EPS is
a plastic material derived from crude oil used in a wide range of
applications. EPS (expanded polystyrene) is a green material. In
the production of EPS materials, any toxic raw products are not
utilized. The process of making EPS involves expanding the
polystyrene granules into a cellular shape using pentane a non-
CFC expansion agent. Moreover, support for its green environ-
ment friendly can be observed in the life cycle of expanded polystyrene. Expanded polystyrenes are 100% eco-friendly. EPS
does not pollute the water or air with gases or syroholuble
elements. EPS makes up only a tiny part of 0.1% of solid waste
materials.\(^{14}\) EPS is not friendly for the growth of bacteria and fungi. The transformation progression consumes very small
energy and does not produce waste. The EPS user and producer
do not bear any risk to the environment or health. EPS is
lightweight foam with good impact resistance, absolute water,
thermal insulation, load-bearing capacity at a light weight,
vapor barrier, air tightness for controlled environments,
extensive life, minimum cost maintenance, and economic and
efficient construction. EPS does not react with salt or alkali
solution as compared to other thin film materials such as nickel
oxide thin film. EPS thin film has a better temperature coeffi-
cient, small grain size, and efficient conductive feature as
compared to another thin films.\(^{15}\)

Numerous techniques are applied to fabricate silver nano-
particles, such as sol–gel, pyrolysis, magnetron sputtering,
hydrothermal, thermal oxidation, and co-precipitation. Among
these synthesis methods, the chemical is a well-known fast and
facile production method to fabricate silver-doped polystyrene
nanostructures due to its well-defined size and shape, scalable
fabrication, and easy manipulation. Though, the chemical
method is very rarely applied for the synthesis of nanomaterials.
The current literature explains the chemical production of
silver-doped polystyrene for solar cell applications.\(^{16}\)

An accurate description of the morphology and crystalline
behavior with Nd:YAG pulsed laser of polystyrene and poly-
ethylene terephthalate (PET) thin film is essential since it plays
a proficient role in solar cells. As a result, the primary aim of the
present work is to provide some important and significant
additional information to the presented data on polystyrene
and polyethylene terephthalate (PET) thin film. We have shown
the results of investigations on the resisting behavior of PET
and silver-doped polystyrene. The source that is used for expo-
sure is Nd:YAG pulsed laser. Each sample was irradiated for 2
minutes, 4 minutes, and 6 minutes respectively. The findings
reveal that there is a decreasing variation in the crystallinity of
PET film after laser irradiation. Furthermore, the XRD, FESEM,
SEM, and Raman spectroscopy results of polystyrene and poly-
ethylene terephthalate (PET) thin to determine is superior for
solar device applications.

2 Experimental details

The polystyrene nanoparticles had been successfully synthe-
size via the nano-precipitation method as clarified in previous
research\(^{12}\) while the silver nanoparticles were produced through
the chemical reduction method by using sodium borohydride
as the reducing agent.\(^{18}\) The silver-doped polystyrene (Ag-doped
PS) was prepared in two ratios, 1 (EPS) : 1 (Ag) and 1 (EPS) : 4
(Ag). The sample was made by putting the 20 µl EPS (expanded polystyrenes) and 20 µl Ag (silver) into the Eppendorf by using
a micropipette. Next, the sample was mixed by using Vortex
Mixer and ultrasonic cleaning machine for 5 minutes and 1
hour respectively. Vortex Mixer is a device used to mix a small
amount of liquid as shown in Fig. 1. The ultrasonic cleaning
machine is used to make sure that the sample is well mixing.
These steps were repeated to synthesis Ag-doped PS with ratio 1
(EPS) : 4 (Ag). These solutions were coating on a silicon
substrate by using drooping method and left to evaporate in
room temperature for one day.

Two commercial PET (Polystyrene/Polyethylene Tere-
phthalate) window tint solar films with a degree of shades of
70% (light shade) and 35% (black-out shade) were purchased.
Therefore, the samples were irradiated by using Nd:YAG
(neodymium-doped yttrium aluminum garnet; Nd:Y\(_3\)Al\(_5\)O\(_{12}\)
)pulsed laser. The samples were irradiated with different energy
densities which are manipulated by the time of exposure (2 min,
4 min, and 6 min). The laser irradiation parameters used in the
experiments are presented in Table 1. The samples that have
been irradiated were characterized by using several instru-
ments. Field emission scanning electron microscope (FESEM),
scanning electron microscope (SEM), Raman spectroscopy, and
powder X-ray diffraction (XRD) were employed to investigate the
surface morphology and structural properties before and after
laser irradiation.

3 Results and discussion

3.1 Structural analysis

The crystallinity of Ag-doped PS at different laser bombardment
times has been studied by using XRD. Fig. 2 shows the XRD
spectrum of pristine PET film with light shade (70%) and laser-
modified PET film with different bombardment times. The semi-crystal form of PET film had not been changed. However,
its is observed that the peak at around \(2\theta = 26^\circ\) tends to decrease
after being bombarded with Nd:YAG pulsed laser. This means that the crystallinity of PET film was decreased after laser irradiation.

The Debye–Scherrer formula can be used for the calculation of the average crystalline size from the peak.  

$D = \frac{K\lambda}{\beta \cos \theta}$  

(1)

where ‘$K$’ is the shape factor which has a constant value of 0.94, ‘$\lambda$’ is the wavelength of falling X-ray radiation and ‘$\beta$’ is the full width at half the maximum value of the diffraction angle $\theta$.

The X-ray density ($\rho_{XRD}$) can be calculated by following relation.$^{20,21}$

$\rho_{XRD} = \frac{ZM}{N_AV}$  

(2)

where ‘$Z$’ is some molecules per unit cell, ‘$M$’ is molecular weight, ‘$N_A$’ is Avogadro’s number and ‘$V$’ is unit cell volume, and by its value from eqn (2) can be put in eqn (3), then it will be obtained as:

$\rho_{XRD} = \frac{8A}{N_{abc} \sin \beta}$  

(3)

where $M$ is the molecular weight of the particular oxide and $abc$ sin $\beta$ is the volume of the monoclinic unit cell.

### 3.2 Morphological analysis

#### 3.2.1 Silver-doped polystyrene

Fig. 3 shows the FESEM images of the non-irradiated and laser-irradiated silver-doped polystyrene at different times. The average particle size of silver-doped polystyrene irradiated at 0 minutes, 2 minutes, 4 minutes and 6 minutes are 320 nm, 242 nm, 336 nm, and 304 nm respectively. Successively size degradation and promotion after irradiation proved that the Ag-doped PS has been modified by laser exposure. Besides that, at 2 minutes of exposure, the bonding between the nanoparticles becomes less tightly which may be suggested to undergo chain-scission (positive resist). However, the nanoparticles tend to bind more closely at 4 minutes of laser exposure which may indicate that cross-linking and polymerizing process (negative resist). At 6 minutes of laser exposure, the bonding between nanoparticles becomes significantly weaker which may be suggested to undergo polymerizing process (negative resist).

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**Table 1** Irradiation parameters for the laser exposure

| Irradiation parameters   | Value         |
|--------------------------|---------------|
| Energy                   | 700 mJ        |
| Wavelength               | 1064 nm       |
| Pulsed repetition rate (Hz) | 2 Hz         |
| Atmosphere               | Air           |
| Substrate temperature    | Room          |

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**Fig. 1** Experimental diagram of sample preparation of silver-doped polystyrene.

**Fig. 2** XRD spectrum of pristine PET and laser irradiated PET with a laser irradiation time of 2 min, (c) 4 min, and (d) 6 min.

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irradiation, the micrographs showed that there is a sign of a chain-scission process taking place because the nanoparticles dispersed much wider compared to the Ag-doped PS arrangement at 4 minutes of irradiation. Therefore, the Ag-doped polystyrene was suggested initially behaving as a positive resist and exhibiting successively negative and positive states.

Fig. 3  FESEM micrographs of (a) silver-doped polystyrene (1EPS:4Ag) and (b) with a laser irradiation time of 2 min, (c) 4 min, and (d) 6 min.

Fig. 4  SEM micrograph of the (a) pristine PET film and (b) modified PET film with a laser irradiation time of 2 min, (c) 4 min, and (d) 6 min.
3.2.2 Polyethylene terephthalate (PET) thin film. Fig. 4 shows the SEM micrograph of un-irradiated PET film and irradiated PET film at 2 minutes, 4 minutes, and 6 minutes of laser exposure respectively. The surface of the unirradiated PET film was flat and smooth as illustrated in Fig. 4(a). The surface roughness increased after 2 minutes of exposure and decreased when further bombarded the samples to 6 minutes which may be due to the change of chain bonding. These changes may be beneficial to the modification of wet ability and surface modification.

3.3 Raman analysis

3.3.1 Silver-doped polystyrene. Raman spectroscopy, which is a very sensitive probe to the vibrations of the material and its local atomic arrangements, has been usually employed for the examination of the microstructural nature of the nanomaterials. Raman scattering also gives important information about the bonds and structures of materials. More insight into the study of resist behavior was obtained by using Raman spectroscopy. Fig. 5(a) shows the Raman spectra corresponding to silver doped polystyrene (1EPS:4Ag) before and after irradiation at a different period while Fig. 5(b) shows the details of the bands at 1380 cm\(^{-1}\) and 1560 cm\(^{-1}\) upon irradiation. The changes of the bands at 1380 cm\(^{-1}\) and 1560 cm\(^{-1}\) upon irradiation were assigned to the forming of the carbonyl group. Two peaks were founded to shift closer at 4 minutes irradiation and become further apart at 6 minutes irradiation which may indicate the rearrangement of the polymer chains after irradiation. The band was broader and the intensity of scattered light increased as the laser irradiation time increased which may be due to the increasing carbonyl group forming and may be taken

![Fig. 5](image)

**Fig. 5** Raman spectra of (a) non-irradiated and irradiated silver-doped polystyrene (1EPS:4Ag); (b) bands at 1380 cm\(^{-1}\) and 1560 cm\(^{-1}\) in detail.

![Fig. 6](image)

**Fig. 6** (a) Raman spectrum of pristine PET and laser irradiated PET with different bombardment periods; (b) Raman spectra of bands at 1615 cm\(^{-1}\) in detail.
to represent a more crystalline state of the carbon resulting from an excessive laser dosage.

3.3.2 Polyethylene terephthalate (PET) thin film. Besides the morphological modification induced by laser irradiation, the chemical changes of the irradiated surface were inspected by Raman spectroscopy. Fig. 6(a) shows the Raman spectra for un-irradiated and irradiated PET film and Fig. 6(b) shows the details of the changes of bands at 1615 cm\(^{-1}\) (C-C ring stretching) upon laser bombardment. The Raman bands in the spectra of PET films were summarised in Table 2. It is observed that when the sample was irradiated for 2 minutes, this band shifted by around 2 cm\(^{-1}\) to a higher wave number and become narrower. Moreover, the intensity of scattered light detected become lower at 2 minutes of exposure. This may be due to the rearrangement of the polymer chains after irradiation. However, when the PET film was further irradiated for 6 minutes, the band tends to shift back to the lower wave number which is almost the same as the non-irradiated PET film. The bands become broadened and the intensity of scattered light detected become higher. These changes have shown the switching behavior of PET film to chain scission or cross-linking upon laser irradiation.

### Table 2  PET Raman bands

| Wavenumber (cm\(^{-1}\)) | Types of vibration                  |
|-------------------------|-------------------------------------|
| 1294                    | C(\(=\)O) stretching               |
| 1615                    | Stretching C-C vibration           |
| 1730                    | Stretching C=O vibration           |
| 2960                    | Methylene groups adjacent to oxygen atoms |
| 3077                    | Aromatic C-H bonds                 |

### Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Conflicts of interest

The authors declare that there is no conflict of interest.

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