Preparation of Bi$_2$Sr$_2$CaCu$_2$O$_x$ Thin Film by Pulsed Laser Deposition for Optoelectronic Devices Application

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Abstract
We report on the fabrication of Bi$_2$Sr$_2$CaCu$_2$O$_x$ (BSCCO) nanostructure films by pulsed laser deposition technique (PLD). The structural and optical properties of nanostructured Bi$_2$Sr$_2$CaCu$_2$O$_x$ film were investigated. X-ray diffraction (XRD) studies of the films prepared at 6.5 and 8 J/cm$^2$ showed that the films are crystalline in nature with orthorhombic phase. Scanning electron microscopy (SEM) investigation confirmed that the deposited film has spherical grains and the mean grain size of the film was found to be increased from 150 nm to 250 nm as laser energy density increased from 6.5 to 8 J/cm$^2$. The value of the optical energy gap of the film decreased from 2.24 to 1.7 eV when the energy density increased. The optoelectronic properties of the Bi$_2$Sr$_2$CaCu$_2$O$_x$/Si heterojunction photodetector have been investigated. The photodetectors exhibited rectification properties and the ideality factor of the photodetectors deposited at 6.5 and 8 J/cm$^2$ were 2.3 and 4.2, respectively. The on/off ratio of the photodetectors was found to be 761 and 385 for the photodetectors prepared at 6.5 and 8 J/cm$^2$, respectively. A responsivity of 514 mA/W at 860 nm was obtained for photodetector prepared with 6.5 J/cm$^2$.

Keywords BSCCO film · Laser deposition · Laser energy density · Photodetector

1 Introduction

Since the discovery of the bismuth-based superconductors Bi-Sr-Ca-Cu-O (BSCCO) compound [1], have considered being a significant for many industrial applications bulk or thin films due to their superior electrical and magnetic properties [2–7]. The advantage of Bi-based oxides is available, not poisonous, also contains no rare-earth element, relatively stable in atmosphere pressure, thermally and chemical stable, not deformed on cooling and less sensitive with water. Though BSCCO is high temperature superconductor materials; the phenomenon of superconductivity [8] is exhibited in vanishing electrical resistivity of the material when it is cooled to a certain temperature called critical temperature ($T_c$) [9]. The critical temperature of BSCCO is in the range (105) k and (80–85) k for Bi-2212 and Bi-2232, respectively. Therefore, it is essential to fabricate a thin film for the growth of each pure phase for BSCCO thin film applications [10, 11]. Beside the electrical properties of the BSCCO film, the energy gap of BSCCO film was around to be 2 eV at room temperature which can be useful for optoelectronic applications. Many methods were used to deposit BSCCO thin film, for example, metal organic chemical vapor deposition, molecular beam epitaxy (MBE), co-evaporation, non-vacuum route, and pulsed laser deposition (PLD) [12, 13]. The main advantages of PLD route are: simplicity, inexpensive, multi-components film deposition, good adhesion of film to the substrate, and good control on film thickness [14]. It is reported that the laser parameters such as energy density, wavelength and pulse duration affecting the properties of the deposited films [15, 16]. To date, no data have been reported on the optoelectronic properties of BSCCO film. Herein, we report on fabrication of Bi$_2$Sr$_2$CaCu$_2$O$_x$/Si photodetector by pulsed laser deposition (PLD) technique. The properties of BSCCO as well as the figures of merit of the BSCCO/Si photodetector were estimated.

2 Experimental Work

Bi$_2$Sr$_2$CaCu$_2$O$_x$ thin film have been deposited by using PLD system. The main parts of PLD system are glass bell jar,
Nd:YAG laser and rotary pump. The laser used for deposition of the BSCCO films was Nd:YAG operating at 532 nm (second harmonic generation Nd:YAG) and pulsed duration of 7 ns. The target that we used is Bi(Pb)-Sr-Ca-Cu-O of adding 5 wt% PbO, to the compound. The deposition was carried out in the vacuum using brings vacuum bellow than $2.0 \times 10^{-3}$ mbar. The laser beam was focused onto a BSCCO target (99.99% purity) of using positive lens (10 cm focal length). The substrates used in this work were glass and silicon, the silicon was p-type with orientation of (100) and electrical resistivity of 1–3 Ω cm. The distance between the substrate and the target and was 5 cm. The values of laser energy density used to prepare the films were 6.5 and 8 J/cm² and the substrate temperature fixed at 60 °C. X-ray diffractometer (XRD-6000, Shimadzu) was employed to examine the structure of the deposited films. To investigate the morphology of the film, a scanning electron microscope SEM (Tscan Vega III Czech) was used. The optical transmission of the film was measured using UV-Vis spectrophotometer (Metertech, SP8001). BSCCO/p-Si photodetector was fabricated by depositing a thin film of BSCCO on Si substrate with area of 1 cm² and the ohmic contacts were made by evaporating aluminum film on the BSCCO film and indium film on the silicon substrate, respectively, using thermal evaporation technique through mask. The schematic diagram of cross sectional view of BSCCO/p-Si with electrical configuration is shown in Fig. 1. Dark and illuminated current-voltage characteristics were studied. The responsivity of the photodetector was investigated using monochromator (Jobin Yvon).

### 3 Results and Discussion

Figure 2a shows the XRD patterns of BSCCO thin films prepared at laser energy density of 6.5 and 8 J/cm² with the same thickness (350 nm). The XRD of BSCCO film deposited at 6.5 J/cm² showed the presence of five peaks at 17.4, 39.4°, 45.6°, and 66° corresponds to (006), (0014), (0016), and (0020) plane, respectively. These peaks are indexed to well-crystallized BSCCO film with orthorhombic phase. The observed peaks confirmed that the grains of the BSCCO film are highly oriented along the c-axis [17, 18]. The XRD pattern also shows the presence of a small peak related to the Bi-2201 phase located at 13.8°. Increase in the laser energy density from 6.5 J/cm² to 8 J/cm² leads to a remarkable increase in the intensity of (006) peak and appearance of a new peak at 25.6° corresponded to (008) plane was observed. Moreover, the XRD peaks at 39.4°, 45.6°, and 66° were disappeared. This result ascribes to the preferred orientation along (006) plane which comes from varying the growth.

![Fig. 1](image1.png)

![Fig. 2](image2.png)
mechanism with increasing the laser fluence. The XRD pattern confirms that no peaks related to the impurities or nonstoichiometric phases were detected.

The mean crystallite size of the BSCCO film was estimated for (006) plane by using Scherrer equation and found to be 66 and 100 nm for film grown with 6.5 and 8 J/cm², respectively. Figure 3 shows the SEM images with two magnifications of BSCCO film deposited on the silicon substrate with 6.5 and 8 J/cm². The film grown at 6.5 J/cm² shows the existence of complete spherical grains with different sizes that distributed randomly on the film surface. The average size of the grain of the film that determined by image J software was 150 nm. No change in the surface morphology of the film deposited at 8 J/cm² was observed and the average grain size was 250 nm. With increase the laser energy, the evaporated volume increased and the grains agglomeration is increased. Micro-sized grains with spherical shape were detected on the surface of the film deposited with 8 J/cm². As clearly seen from Fig. 3, the agglomerated and the clustering grains have larger sizes and irregular shapes.

Figure 3 shows the SEM images with two magnifications of BSCCO/Si film deposited with 6.5 and 8 J/cm². Presence of particulates and/or droplets due to the effect of laser splashing is also observed on the film surface.

Figure 3 shows that the films have no microcracks and porosities. The EDX spectra of the films is shown in Fig. 4. It shows the presence of Bi, Sr, Ca, Cu, and O elements which all indexed to the BSCCO film and the origin of the other elements C, Na and Mg is the SEM chamber.

Figure 5a displays the optical absorption of BSCCO film. The film deposited at 6.5 J/cm² has lower optical absorption than that deposited at 8 J/cm² with the same thickness due to the droplets and agglomeration formed at 8 J/cm². These structures act as scattering centers which lowering the film transmission. As it is obvious from Fig. 5a, a distinct absorption peak located at 415 nm for film deposited at 6.5 J/cm² and 450 nm for film deposition at 8 J/cm² were observed. The origin of this peak can be attributed to quantum size effect [19, 20].

A yellowish color is observed for BSCCO film deposited on the glass substrate as depicted in Fig. 5b. The reflectance spectra of BSCCO films are illustrated in Fig. 6a. The films reflectance is shown in Fig. 6a revealed that...
the film prepared at 8 J/cm² has higher reflectance than that prepared at 6.5 J/cm². This can ascribe to particulates and droplets formed at higher laser energy density. The film reflectance decreased sharply after 300nm and then tends to saturate. The variation of the refractive index with wavelength is depicted in Fig. 6b.

To obtain the optical energy gap ($E_g$) of BSCCO film, $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) was plotted as revealed in Fig. 7. The energy gap can be determined from the extrapolation of the straight line of Fig. 6 to $(\alpha h\nu)^2 = 0$ point according to Tauc plot for direct transition type

\[ (\alpha h\nu)^2 = A(h\nu - E_g) \]  

(1)

Where $\alpha$ is the absorption coefficient, $h$ is Plank constant, $\nu$ is the frequency, and $A$ is a constant.

As shown in Fig. 7, the energy gap of BSCCO films deposited at 6.5 and 8 J/cm² were 1.65 and 2.25 eV, respectively. We attributed the reduction in the film energy gap after increasing the laser energy density to increasing the grain size as well as to the grains agglomeration effect. The obtained values of $E_g$ are consistent with reported data [21].

Figure 8a illustrates the dark current-voltage characteristics of BSCCO/Si heterojunction at room temperature at forward and reverse bias directions. The figure shows that the devices have rectification characteristics. The current transport mechanism in both heterojunctions is a recombination-tunneling. The forward current increases as bias voltage increase due to the decreasing the depletion layer width. The forward current of BSCCO/Si heterostructure deposited at 6.5 J/cm² is larger than that of heterojunction prepared with 8 J/cm² at same bias voltage.

This result could be attributed to the grains agglomeration found for film deposited at 8 J/cm² and also due to the high resistivity of BSCCO film. The electrical resistivity of the films was measured using Hall effect and it found to be 0.4 $\Omega$cm for film deposited at 6.5 J/cm² and 1 $\Omega$cm for film deposited at 8 J/cm². Figure 8b showed that the forward current of the heterojunction prepared at 8 J/cm² tends to saturate after 4 V as a result of high series resistance effect. The ideality factor (n) of the BSCCO/p-Si was found using simple diode equation

\[ n = \frac{q}{KT} \left( \frac{\partial V}{\partial \ln I} \right) \]  

(2)

where $I_s$ is the saturation current of the photodetector which can determine from semi-logarithmic $I_f$-$V$ plot as shown in Fig. 8b. The values of n were 2.3 and 5 (region 1) for heterojunction prepared with 6.5 and 8 J/cm², respetively. The main reason for $n > 1$ can be ascribed to the domination the recombination current over the diffusion current and due to the surface states at BSCCO-Si interface [22, 23].

Figure 9 Illustrates the illuminated current-voltage characteristics at room temperature and illuminated at different white light intensities. As the incident light incident hits the photodetector, it results in the increasing of the photocurrent due to the absorption of light in the depletion region, which leads to produces electron-hole pair. The presence of the internal and external electric fields prevent electron-hole recombination. The on/off ratio of the photodetector deposited with 6.5 J/cm² was $2.3 \times 10^2$ at 7.5 V bias and at light intensity of 10 mW/cm². Increasing the bias voltage leads to increasing the photocurrent because of widening of the depletion width.
Figure 10 shows that the photocurrent increases with increasing the light intensity because of increasing the number of e-h pairs generated in the depletion region. This result indicates that the prepared photodetectors have reasonable linearity characteristics (large dynamic range). The on/off ratio of the photodetector prepared at 8 J/cm$^2$ was $1.7 \times 10^2$ at 7.5 V bias and at light intensity of 10 mW/cm$^2$. We have ascribed the decrease in the on/off ratio of the photodetector deposited with 8 J/cm$^2$ to the structural defects, surface states and recombination centers [24].

Figure 11 shows the spectral responsivity of the BSCCO/Si photodetector. The responsivity of the photodetector ($R_\lambda$) is calculated from

$$R_\lambda = \frac{I_{ph}}{P}$$

Where $I_{ph}$ is the photodetector photocurrent and $P$ is the power of the light at certain wavelength. As shown in Fig. 9, the responsivity of the photodetector prepared with 6.5 J/cm$^2$ is larger than that prepared with 8 J/cm$^2$. The response peak of the photodetector deposited with 6.5 and 8 J/cm$^2$ is found to be at 560 and 760nm, respectively. The shift in peak response could be ascribed to the film absorption edge. The photodetector responsivity fabricated with 6.5 J/cm$^2$ increased with wavelength up to 860nm, while it decreases after 760nm wavelength for photodetector prepared with 8 J/cm$^2$. The depletion region extended toward the substrate (silicon side) in the case of photodetector prepared with 8 J/cm$^2$ which leads to improvement in the responsivity of the photodetector for near infrared wavelengths. Figure 11 confirmed that the maximum responsivity is 0.514 A/W at 860 nm for hetrojunction prepared with 6.5 J/cm$^2$.

The external quantum efficiency (EQE) of the photodetector was determined from

$$EQE = \frac{1240I_{ph}}{\lambda P} \times 100$$ (4)

Figure 12 shows the EQE versus wavelength plot of the photodetector. The value of EQE of the photodetector prepared with 6.5 J/cm$^2$ was larger than that prepared with 8 J/cm$^2$. The maximum value of EQE is 74 % at 860 nm which is comparable to the silicon based hetrojunction photodetector [25–27].
The specific detectivity ($D^*$) of the photodetector considers the most important figures of merit of the photodetectors. It is a function of responsivity and noise current ($I_n$) as shown in the following relationship

$$D^* = \frac{R_A (A \Delta f)^{0.5}}{I_n}$$  \hspace{1cm} (5)$$

where $A$ is the photodetector area and $(\Delta f)$ is the bandwidth of the photodetector. Figure 13 shows the $D^*$ of the photodetectors deposited at 6.5 and 8 J/cm$^2$ at bias voltage of 7.5 V. The detectivity of the photodetector prepared with 6.5 J/cm$^2$ is higher than that deposited with 8 J/cm$^2$ due to its lower noise current and high responsivity. The maximum detectivity of the photodetector prepared at 6.5 J/cm$^2$ is $2.57 \times 10^{11}$ Jones at 860 nm, while the maximum detectivity of the photodetector prepared at 8 J/cm$^2$ is $2.35 \times 10^{11}$ Jones at 860 nm.

![Fig. 6](image_url) (a) The reflectance spectra and (b) refractive index of BSCCO films deposited with 6.5 J/cm$^2$ and 8 J/cm$^2$.

![Fig. 7](image_url) Optical energy gap of BSCCO film deposited with 6.5 J/cm$^2$ and 8 J/cm$^2$. 

Fig. 6 (a) The reflectance spectra and (b) refractive index of BSCCO films deposited with 6.5 J/cm$^2$ and 8 J/cm$^2$.
prepared with 8 J/cm² is $9.4 \times 10^{10}$ Jones at 760nm. This due to the defects and surface traps [28] formed at the interface between the BSCCO film and silicon for the photodetector prepared at 8 J/cm². The values of the noise equivalent power NEP of the detectors prepared with 6.5 and 8 J/cm² are 3.8 pW and 11 pW, respectively.

### 4 Conclusions

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ film has been prepared by pulsed laser deposition route, and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$/Si heterojunction photodetectors were fabricated. Results of XRD showed that the structural properties of the deposited films were strongly depending on the laser energy density. The XRD data revealed that the film prepared with 8 J/cm² was highly oriented along (006) plane. The energy gap of the film decreased from 2.2 eV to 1.6 eV when the laser energy density increased from 6.5 to 8 J/cm². Results of
SEM confirmed that the grown film consisted of spherical grains with different sizes and the grains agglomeration and aggregation were found to be increased as laser energy density increased. The electrical properties of BSCCO/Si heterojunction revealed that current transport mechanism is recombination-tunneling type. The ideality factor of the heterojunction increased and rectification factor decreased as laser energy density decreased. The responsivity, quantum efficiency, detectivity and NEP were estimated as a function of energy density. The best photodetector has responsivity of 0.514 A/W, EQE of 74 % and D* of $2.57 \times 10^{11}$ Jones at 860 nm. Based on the obtained results, the BSCCO film can be suggested to be good materials for high photosensitivity Vis-NIR heterojunction photodetector.

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Author Contributions

Raid and Noor conceived the presented idea.

Raid and Noor supervised the finding of this work.

All authors discussed the results and contributed equally to the final manuscript.

Raid and Suaad conducted the experiments.

All authors provided critical feedback and helped shape the research, analysis and manuscript.

Data Availability

Not applicable

Declarations

Ethics Approval and Consent to Participate

Not applicable.

Consent for Publication

Not applicable.

Competing interests

The authors have declared that no competing interests exist.

Conflict of Interest

The authors have declared no conflict of interest.

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![Fig. 11 Spectral responsivity of the BSCCO/Si heterojunction fabricated with 6.5 J/cm² and 8 J/cm²](image1)

![Fig. 12 EQE of the photodetector as a function of wavelength for thin film deposited with 6.5 J/cm² and 8 J/cm²](image2)

![Fig. 13 Detectivity of BSCCO/Si film photodetector prepared at 6.5 J/cm² and 8 J/cm²](image3)
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