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Photoconductivity Study of Spray Pyrolized STO Thin Films

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Abstract: ***The Strontium Titanate (STO) thin films are prepared by using spray pyrolysis technique with optimised parameters. The 0.1M films are prepared by spraying the aqueous solution of strontium chlorite hexahydrate [Sr (Cl_2) $6H_2O$] and Titanium trichloride [$TiCl_3$] for 9:1, 1:1, and 1:9 volumetric ratios at 350^0C temperature on to the preheated glass substrate. The films were characterized by XRD, FE-SEM, and UV-Vis. The films are used to measure the dark and photocurrent. Initially film was kept unexposed to light i.e. AC voltage of 100W tungsten filament bulb (which is source of radiation) at zero volt; now applied voltage is increased with step of 25V and corresponding dark current (Id) measured up to 150V. Thereafter the same film is exposed to light by increase of AC voltage thereby increase intensity of light and corresponding photocurrents (Ip) are recorded. It was observed that Dark current (Id) was greater than photocurrent (Ip).The dark current is more than that of photocurrent therefore negative photoconductivity exhibited by the material film. The cause of negative photoconductivity is described.***

Keyword: STO films, Spray pyrolysis, DC conductivity, XRD, FE-SEM, UV, Negative Photoconductivity

I. INTRODUCTION

As silicon is the basis of conventional electronic and photovoltaic applications, strontium titanate (STO) is the workhorse in the emerging technologies based on complex oxides [1–3] besides being a popular substrate for growing other perovskites [4]. Although the pure STO is a transparent band insulator with a band gap of 3.2 eV, electron doping can be achieved by either thermal reduction in vacuum or ion irradiation.

As the name implies, photoconductivity is the effect whereby the electrical conductivity of a solid changes under the action of light. This effect, which was first observed in 1873 on selenium and which subsequently found application in the well known selenium cells. When the dark current is greater than photocurrent, the resultant conductivity is known as negative photoconductivity. This property has been used advantageously in several branches of science and technology. Photoconductivity studies on the films give information about the charge transport mechanism. It is important to determine the charge transport mechanism in order to improve the material properties for photo refractive applications. Photoconductivity is an elementary processing solid, and as the name suggests, it involves the generation and recombination of charge carriers and their transport to the electrodes.

Recent interesting findings in STO have triggered many attempts to search for new physics in these material and related perovskite oxides. Current thinking is that the nature of its oxygen vacancy is closely related to the physical properties of STO. Although many experimental and theoretical efforts have been made, the role of this oxygen vacancy is not yet well understood. However, new insights into the atomistic and electronic structure of the oxygen vacancy in STO have been obtained through first-principle calculations. The researchers, based at Kyoto University in Japan, found that the oxygen vacancy induces a local antiferrodistortive-like oxygen octahedron rotation, even in the cubic phase [5-6]. This feature leads to in-gap localized electronic states, giving a convincing explanation for the thermal ionization and optical transition that are observed experimentally. The oxygen-octahedron rotation around the oxygen vacancy thus plays a key role in the physical properties of STO.

II. SYNTHESIS OF STO THIN FILMS

The thin films were prepared by spraying aqueous solution as mixture of 0.1M Strontium chlorite hexahydrate [Sr (Cl_2) $6H_2O$] and 0.1M Titanium trichloride [$TiCl_3$]. All solvents were completely miscible, in a volume ratio of 9:1, 1:1, and 1:9.This solution was prepared by dissolving appropriate amount of [Sr (Cl_2) $6H_2O$], powder of white colour with molecular weight of 266.62 g/mol, in d-ionized water and appropriate amount of $TiCl_3$ liquid of violate in color with molecular weight of 154.23 g/mol in d-ionized water too. Mixing the solutions was carried out by using magnetic stirrer and leaving the solution for 30 minutes to make sure that no residues were left and to ensure the homogeneity of the resultant solution. The resultant solution was sprayed on glass substrate kept at 350ºC ± 50ºC. When the solution was sprayed, the reaction takes place at the surface of the heated substrate. The resultant films were stable and have good adhesive properties. Film thickness was estimated by employing the weight loss method.

III. CHARACTERISTICS OF THIN FILMS

A. XRD of STO Thin Films

The X-ray diffraction (XRD) studies were carried out to study the structural properties using X-ray diffractometer with CuKα radiation (λ = 1.54406 Å); the range of 2θ was 20-80º. Comparing the obtained spectra of the prepared STO thin films with that of JCPDS data, it is observed that the structure of the prepared thin films was cubic having lattice parameter equal to 3.905Å.

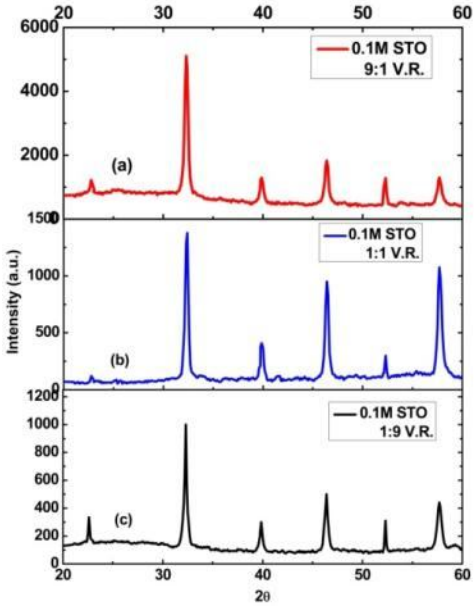

Fig. 1. XRD of STO thin film of (a) 9:1, (b) 1:1 and (c) 1:9 V.R.

It is observed that it possesses the dominant diffraction peaks at 2θ angle for STO of volumetric ratio 9:1 (Fig.1(a)) are 32.26, 39.84, 46.39 and 57.71 representing (110),(111), (200), (211) lattice planes respectively. In case of 1:1 VR (Fig.1 (b)) same indices of reflection are observed for respectively. Also same indices of reflection are observed at 32.40, 39.88, 46.39, and 53.70 for 1:9 VR (Fig.1(c)). The XRD patterns are well matched with the JCPDS data (card number 350734) for four (present) indices. The obtained XRD patterns reveal that as-synthesized STO films which exhibited as a mixture of phases, which were identified as predominant of STO and impurity phases. Intensities of all peaks were changed with change in volumetric ratio. The XRD patterns show films are of polycrystalline in nature. The numbers of observed peaks are related to the symmetry of the unit cell. Higher is the symmetry fewer are the peaks. From the XRD pattern in case of polycrystalline films the XRD shows various peaks at different angles of diffraction and diffraction pattern. The single crystal material exhibits sharp reflections (sharp peaks). For the amorphous films material, the diffraction does not exhibit any sharp peaks [7-8].

B. Morphology study of STO Thin Films

1) FE-SEM images of STO Thin Film:

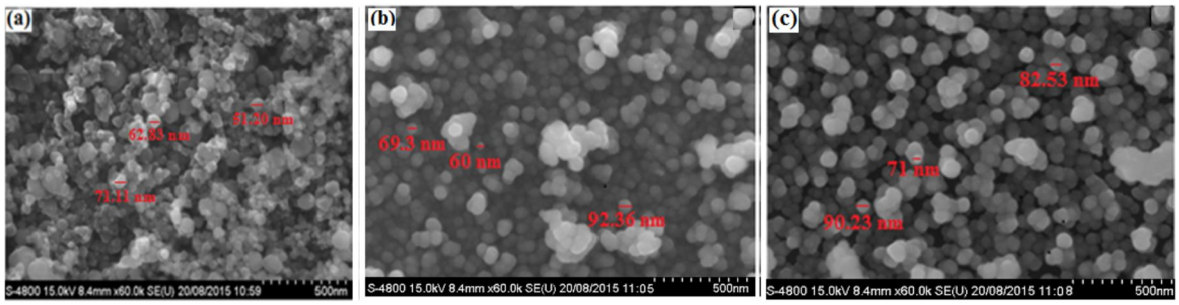

Fig. 2 FE-SEM images of STO thin films of volumetric ratio (a-9:1), (b-1:1) and (c-1:9)

The FE-SEM micrographs of pure STO films with different concentrations are presented in Fig.2.The surface morphology of the STO thin films has been studied by FE-SEM. From Fig.2.(a) shows morphology of agglomeration of nanosized

grains.Fig.2(b) shows that voids are present; some large, non-uniforms grains are coming out to the front Fig.2.(c) shows Bajra like uniform nanosized grains.

TABLE I

THE VALUES OF PARTICLE SIZE FROM FE-SEM IMAGES

Volumetric Ratio	Concentration (Mole)
	0.1M
(a) 9:1	51.2 nm
(b) 1:1	69.3 nm
(c)1:9	90.23 nm

2) Elemental Analysis of STO thin films:

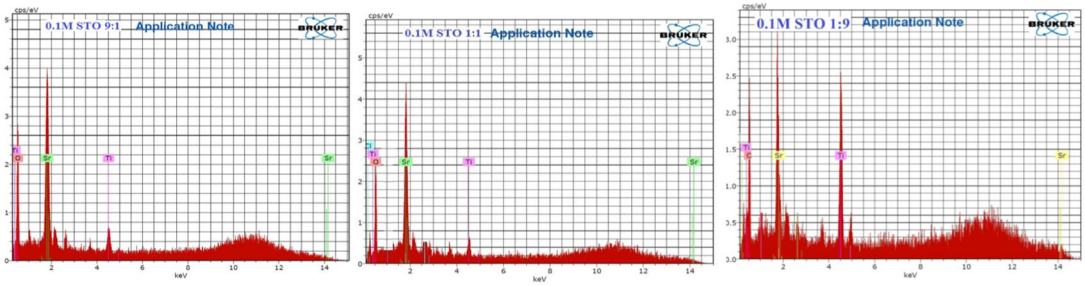

Fig .3 EDS spectrum of STO thin films

Fig.3.Show the EDS spectrum of STO thin films of (a) 9:1, (b) 1:1 and (c) 1:9 volumetric ratio. From elemental analysis (EDS), thin films fabricated with different concentration with Sr: Ti volumetric ratios, all films contain the elements Sr and Ti as expected. The atomic percentage of Strontium, Titanium and Oxygen are presented in Table 4.2.

TABLE: II

ATOMIC PERCENTAGE OF SR, TI AND O FROM EDS ANALYSIS

Element	Sample	Concentration and Volumetric Ratio		
		0.1M		
		9:1	**1:1**	**1:9**
Sr	Strontium	49.84	4932.09	14.21
Ti	Titanium	18.12	31.12	40.97
O	Oxygen	32.04	36.79	44.82

C. Electrical properties of STO thin films

1) DC Conductivity of STO thin films

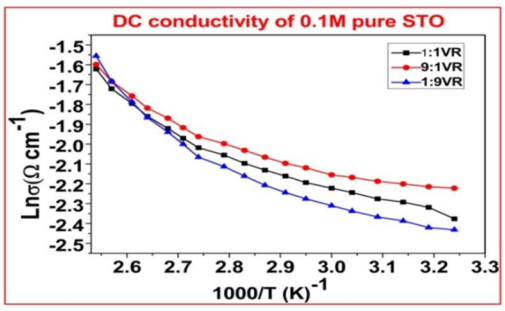

Fig.4 The Variation of conductivity with temperature of STO thin films.

The activation energy is the minimum energy that must be possessed by reacting molecules before the reaction will occur i.e. energy possessed by reacting molecules for getting them converted into products. Lower the value of activation energy higher the will be the rate at which reaction will proceed and higher the value of activation energy lower will be the rate at which the reaction proceeds. The conduction mechanism of the STO films is believed to be related to the concentration of the electrical carriers, which is the oxygen vacancy existed in the structure. The change of conductivity with temperature and thickness indicates that all the film samples have negative temperature coefficient (NTC) of resistivity which suggests their nature. In order to study the conductivity mechanism, it is convenient to plot the logarithm of conductivity (Ln σ) as a function of 1000/T. It is noticed that conductivity displays two mechanisms of charge carrier's transport, yielding two activation energies at two thermal ranges. In the range of (308-333) K (Ea_1) and (334-393) K (Ea_2). The following table shows dc conductivity and activation energy of different concentration with different volumetric ratio.

TABLE III
D.C CONDUCTIVITY AND ACTIVATION ENERGY OF STO THIN FILMS

Concentration	**Volumetric Ratio**	**(308 to 333)K**	**(334 to 393)K**	**σRT (Ω cm -1)**
		Ea1(eV)	**Ea2(eV)**	
0.1M	9:1	0.1847	0.1521	5.191X10-6
	1:1	0.1323	0.1150	3.783X10-6
	1:9	0.0575	0.0945	1.529X10-6

D. Optical Study of STO thin films

1) Absorption Coefficient (α): Absorption coefficient is characteristic of the particular semiconductor material; furthermore, it varies with the incident photon energy (hv) and semiconductor property.

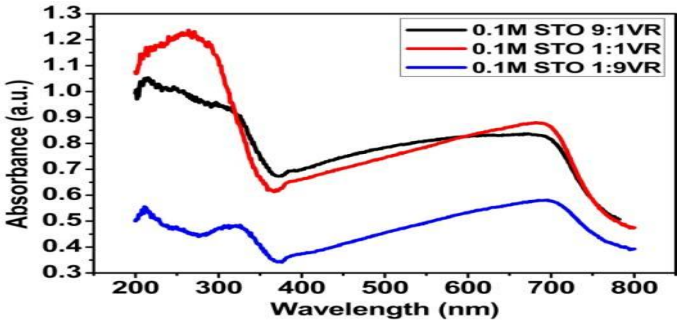

Fig 5 Variation of absorbance with wavelength to STO thin film for 9:1, 1:1 and 1:9 volumetric ratios.

The absorbance decreases rapidly at short wavelengths (high energies) corresponding to the energy gap of the film. This evident increase of energy is due to the interaction of the material electrons with the incident photons which have enough energy for the occurrence of electron transitions. The transitions occur between localstates inside the forbidden energy gap (Eg) in the low absorption region. This region depends on the nature of the material depending on its preparation and purity.

2) Optical band gap energy of STO thin films: The energy gap for allowed direct transition materials can be estimated by plotting a graph between $(\alpha h\nu)^2$ and (hv) in eV, a straight line is obtained and the extrapolation of this line to $(\alpha h\nu)\ 2 = 0$ gives the value of the direct band gap of the material [9].The thickness of the thin films are measured using micro gravimetric method.

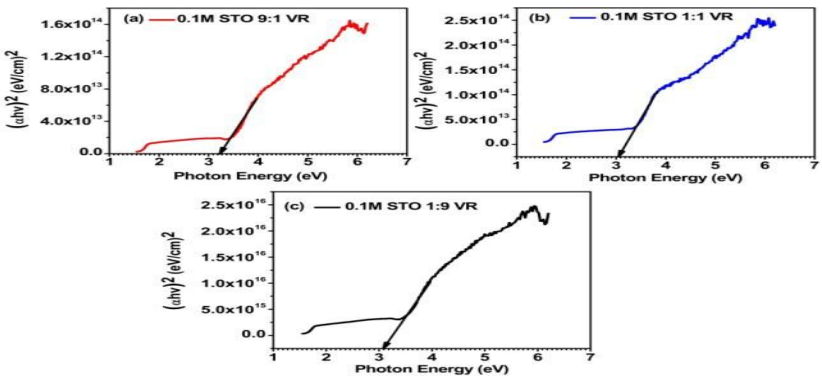

Fig 6 Tauc plot according to the absorption coefficient to estimate the band gap of the STO thin films.

TABLE IV
THE VALUES OF BAND GAP FOR DIFFERENT CONCENTRATIONS.

Concentration (Mole)	Volumetric ratio	Band gap (eV)
0.1	9:1	3.2
	1:1	3.1
	1:9	3

E. Photoconductivity Study of STO Thin Films

1) Field Dependence of Dark Current:

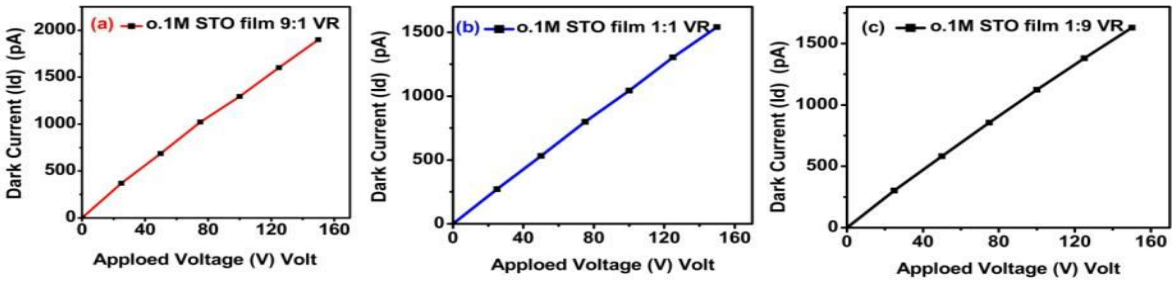

Fig 7 Value of dark current for the applied DC voltage

Fig.7 show the variation of dark current (Id) with applied field. It is seen from the plots that Id of the sample increase linearly with applied field. It is observed from the plots that the dark current is always higher than the photo current, thus confirming the negative photoconductivity.

2) Field Dependence of Photocurrent: Fig.8 shows current-voltage characteristics of STO under intensity of illumination. The ln (I) against ln (V) curves are straight line having different slopes with respect to varying voltage according to power law, I α Vm, where 'm' represents slope of different straight line segments and different for lower and higher voltages of the curves and may increases with increasing voltage.

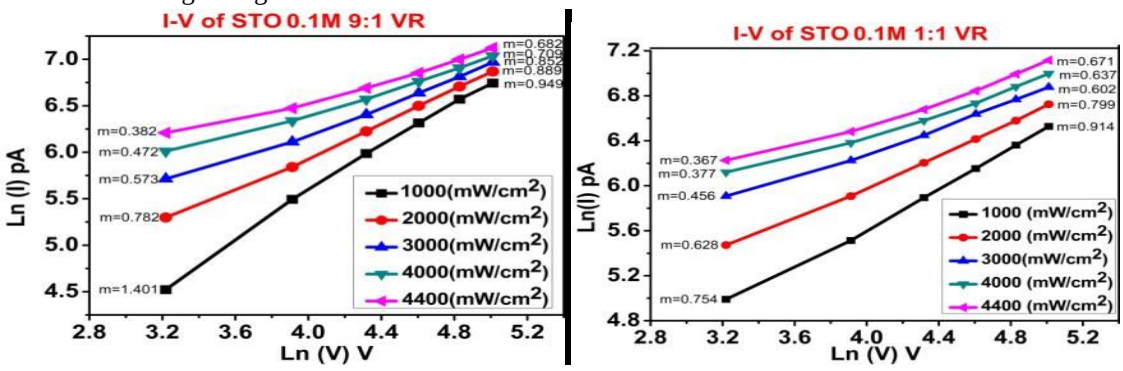

Fig.8.(a) Fig.8.(b)

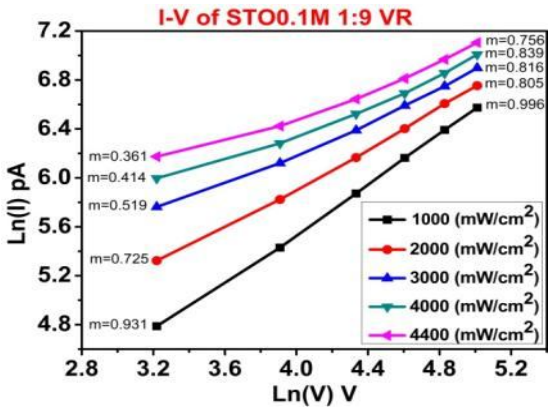

Fig.8. (c)

Fig 8 Variation of photocurrent (Ip) with applied voltage.

The photocurrent (Ipc) varies super-linearly at lower and upper voltage range. The super-linear (m>1) variation may be attributed to flow of trap as well as space charge current inside the material. Super-linear behavior with m >1 suggests that some charge carriers are being injected into the sample from one of the electrodes. As the intensity of illumination increases, the variation of photocurrent with voltage remains super-linear.

3) Intensity Dependence of Photocurrent:

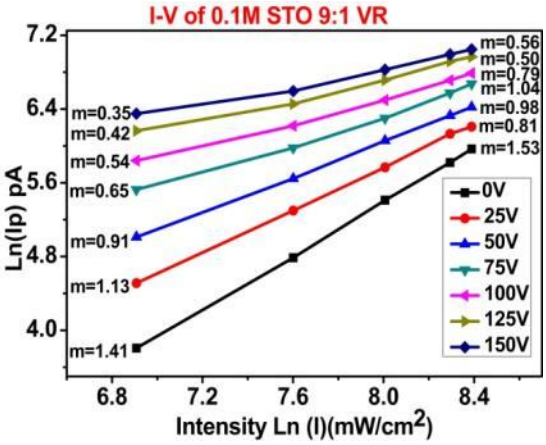

Fig.9 (a)

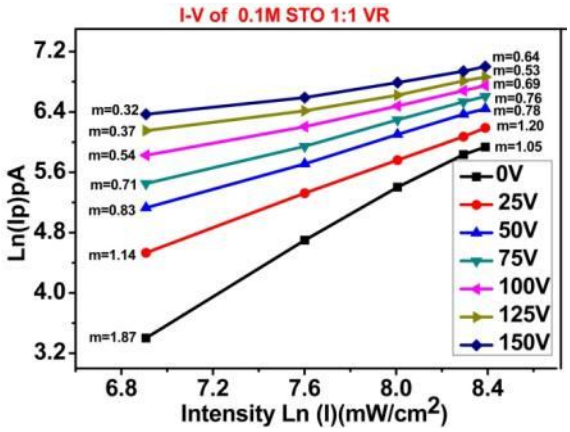

Fig.9 (b)

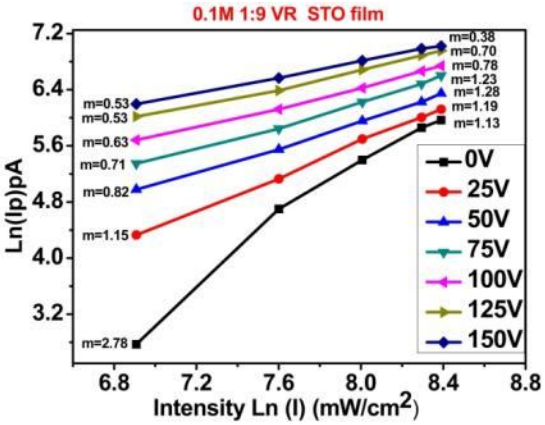

Fig.9 (c)

Fig 9 Variation of photocurrent with applied voltage for different intensity of illumination

The STO thin film of 0.1M of 9:1, 1:1 and 1:9 volumetric ratios were employed for the measurement of photocurrent. Initially applied voltage was 70 V (bulb was glow) and intensity of light was not considerable then intensity was increased gradually and corresponding photocurrent was recorded. The linear increase of photocurrent with intensity was observed.

The variations of photocurrent with light intensity for different samples are shown in Fig. 9 Figure show straight line curves having different slopes in different intensity region. Thus the variation can be represented by relation Ip α Lm the value of m is < 1 for the some region of intensity of illumination. This shows that photocurrent varies sub-linearly with the light intensity.

F. Photoconductivity

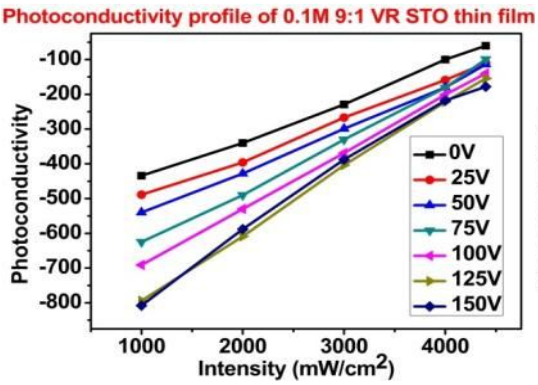

Fig.10.(a)

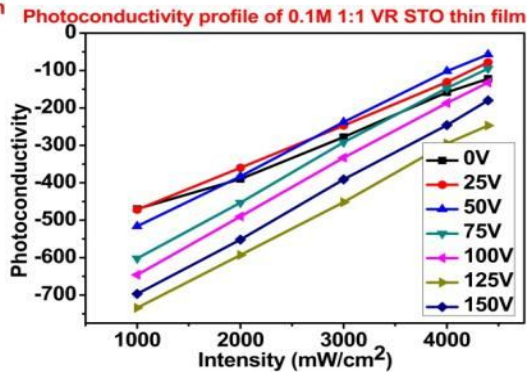

Fig.10.(b)

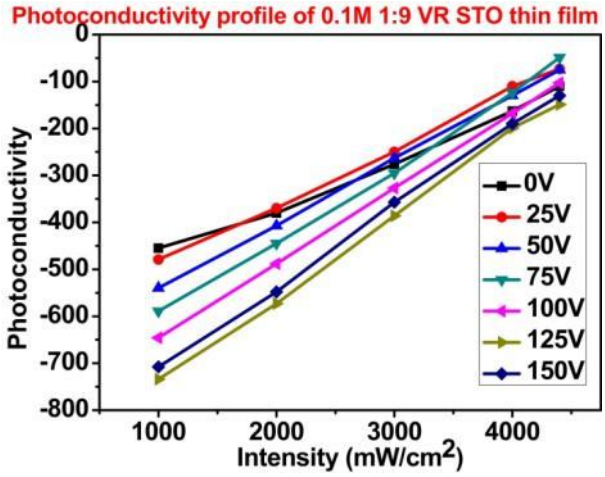

Fig.10. (c)

Fig 10 Variation of photoresponse with intensity of light

Fig.4.15 (a-i) depicts the photoconductivity effect of intensity and dark and photocurrent. Photo response Iph, was the photoconductivity of the excess number of photogenerated charge carriers under steady-state illumination, which was gained by subtracting dark conduction from the conduction of lumination, Ip,

$$Iph = Ip\text{-}Id$$

From Fig.10, it is observed that the difference of photocurrent and dark current is found to be negative. The STO films under test are found to be exhibiting negative photoconductivity (NPC) property. The NPC exhibited by the STO thin films may be due to the reduction in the number of charge carriers or their lifetime in the presence of radiation [10-11].

IV. CONCLUSIONS

The spray pyrolysis technique used for the preparation of thin films of STO is a relatively simple and low cost method. From FE-SEM studies, as prepared thin film of STO is nanostructured. Optical studies of the films revealed that increasing Ti content increase the absorbance of the films. Absorbance spectra obtained from the films were used to evaluate the optical band gaps. The prepared films were show negative photoconductivity. The STO thin films have negative temperature coefficient (NTC) of resistivity which suggests that the STO is n-type material. The activation energy for 308 to 333K temperature decreases and for 334 to 393 K temperature are increases according to composition of Sr and Ti in the chemical reaction during the pyrolysis of STO.

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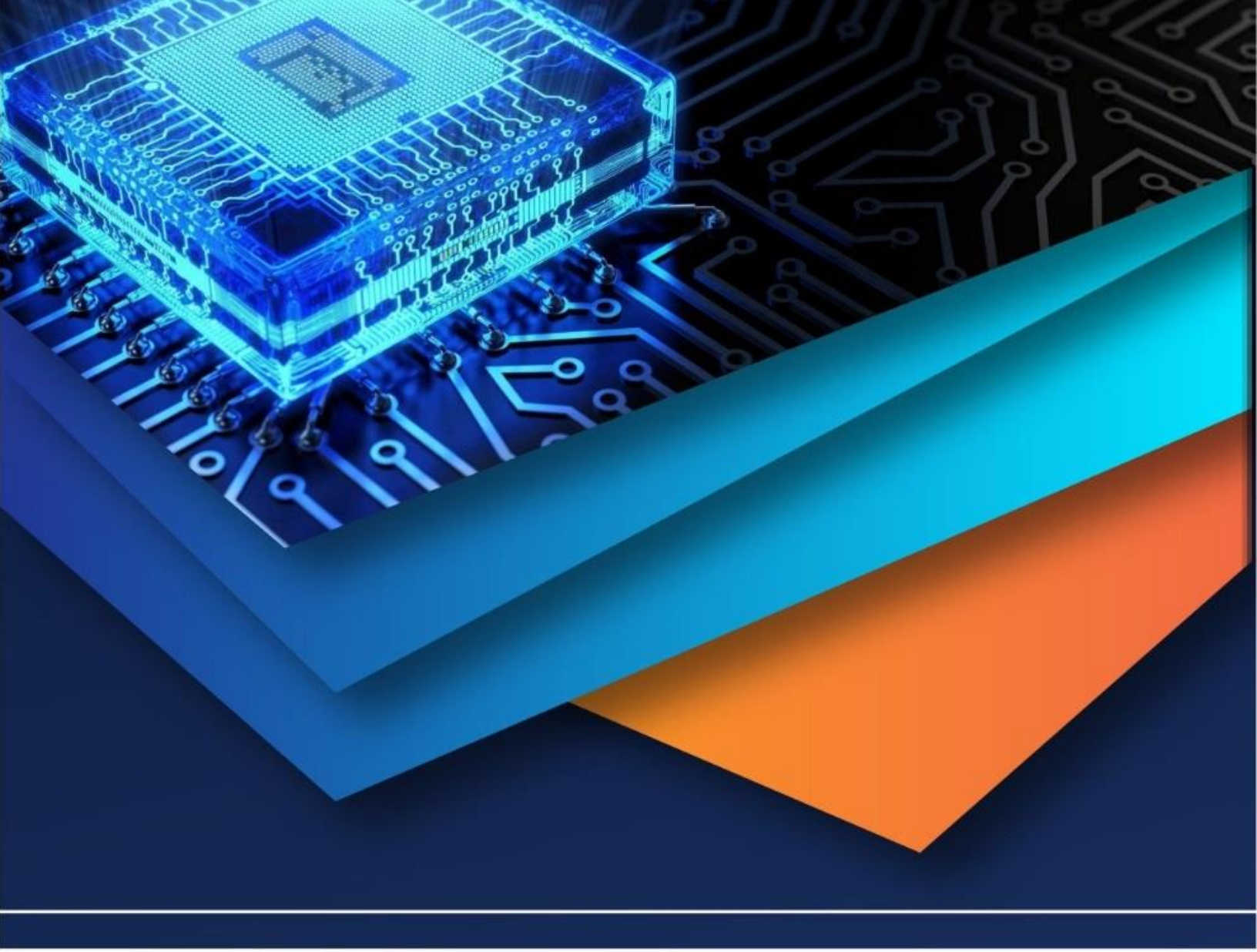

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