

## Preparation and Study the Characteristics of Tungsten Trioxide Thin Films for Gas Sensing Application

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### ABSTRACT

In this study, Tungsten Trioxide thin films were successfully synthesized at different substrate temperatures by pulse laser deposition. Structural, morphological and electrical properties of  $WO_3$  thin films, were investigated by X-ray diffraction (XRD), Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM), Hall Effect and sensing measurements.

The results was indicated that  $WO_3$  thin films prepared at  $450^\circ C$  was optimum condition where sensitivity toward  $H_2S$  gas has been measured, sensitivity was higher than other films preparation at ( $250^\circ C, 350^\circ C$ ) temperature.

**Keywords:** Pulsed Laser Deposition (PLD),  $WO_3$  thin films, Electrical

### INTRODUCTION

Tungsten oxide ( $WO_3$ ) is one of the most important materials which show a spacious assortment of new characteristic, for developed technological operations, It showed structural conversions and sub-stoichiometric band transference, which have attracted the attentiveness of examiner through the ancient years to reach their possibility scientific and technological stratifications in the fields of show systems and microelectronic [1]. On the other hand, tungsten oxide is a very interesting n-type semiconducting materials with a band gap of 2.7 eV. Tungsten oxide, has characteristic in gas sensing, photocatalysis and electrochromic devices. [2]  $WO_3$  nanostructures were synthesized by pulse laser deposition. This is because of their advantages such as simple process, depressed-cost, possibility for large scale preparation and forming crystalline structure with perfect stability. Normal and minimum cost procedures for exactly nanostructured construction are preferred in gas-sensing and other applications [3].

In this research, we deal with detailed Hydrogen sulfide sensing characteristic of  $WO_3$  nanostructures prepared by pulse laser deposition process.  $H_2S$  is a standard reducing gas.  $H_2S$  is a heavier-than-air, colorless gas with a sweetish taste and characteristic odor of rotten eggs.

### Experimental procedure

$WO_3$  thin films were deposited by PLD using Nd:YAG laser as long as 600 mJ of 1064 nm wavelength of laser in 6 ns pulses at the repetition rate of 10 Hz (Huafei Tongda Technology—DIAMOND-288 pattern EPLS), ablation and rising clarity  $WO_3$  ceramic target. The  $WO_3$  films have been grown in an oxygen pressure of  $2 \times 10^{-1}$  mbar, with various substrate temperature ( $250-450$ )  $^\circ C$

The thickness of  $WO_3$  films have been measured by optical interferometer method (Fizeau fringes). An X-ray diffraction apparatus using Philips PW 1050 X-ray diffractometer was used to investigate the structure properties of the films. The surface morphology of the films was

studied by using, atomic force microscopy (AFM) (Digital Instruments Nanoscope II) Scanning Probe Microscope (AA3000) and Scanning Electron Microscopy (SEM, the VEGA easy probe). For electrical characteristic of the films were studied by employing Hall Effect (HMS-3000) and sensing measurement.

### The Result and Discussion

Fig. (1) shows the XRD pattern of  $\text{WO}_3$  films prepared at different substrate temperatures of  $250^\circ\text{C}$ ,  $350^\circ\text{C}$  and  $450^\circ\text{C}$  on glass substrate with laser energy of 600 mJ and Oxygen pressure  $2 \times 10^{-1}$  mbar. It can be seen that the films consists of amorphous phase and crystalline phase with low intensity for films depositing at  $T_s = 350^\circ\text{C}$  and  $250^\circ\text{C}$ , Fig. (1a, b) shows the dominant peaks on  $2\theta = 23.9765^\circ$ ,  $2\theta = 29.62^\circ$ ,  $2\theta = 33.2^\circ$ ,  $2\theta = 50.05^\circ$  and  $2\theta = 54.75^\circ$  corresponding to the (200), (111), (220), (112) and (420) planes respectively. The film was deposited at  $T_s = 450^\circ\text{C}$ . It is seen that increases in intensity of (200) orientation may be returning of temperature saving energy of film atoms to boost mobility that could reduce the impurity in the  $\text{WO}_3$  films and change for the bet equality of films. This leads to a lowering in (FWHM) of peak and rising in grain size of the films and shows dominant peaks on  $2\theta = 23.9765^\circ$ ,  $2\theta = 33.02^\circ$ ,  $2\theta = 38^\circ$ ,  $2\theta = 51.75^\circ$  and  $2\theta = 53.75^\circ$ , corresponding to the (200), (111), (220), (112) and (420) planes. The  $\text{WO}_3$  crystal structure was formed by (JCPDS card No. 72-0677), and with the previous study [4].

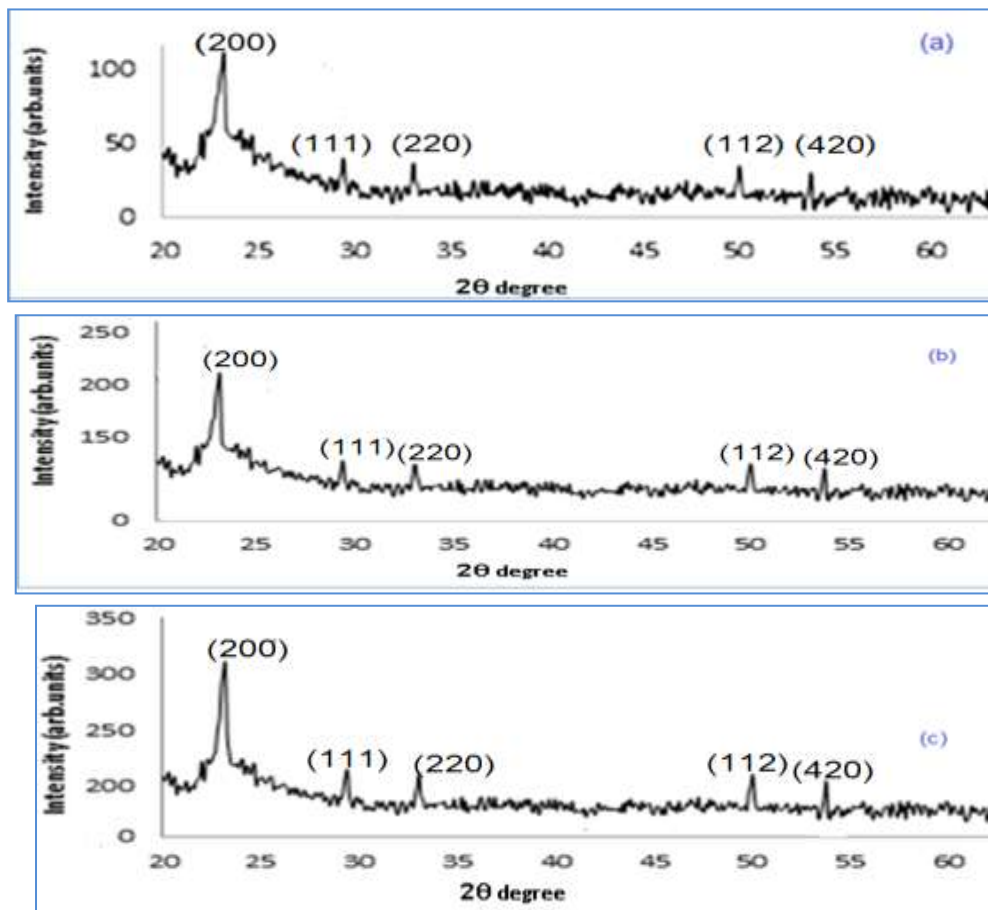
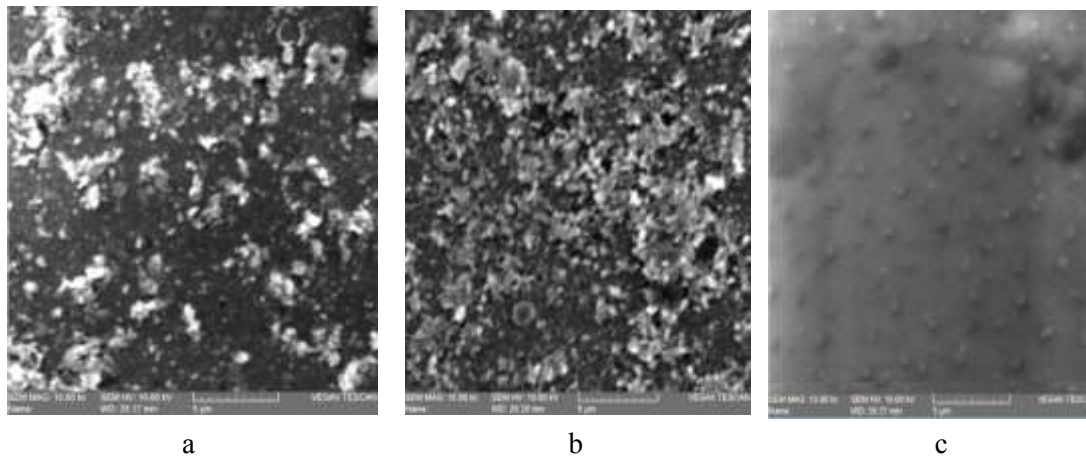


Figure (1):- XRD patterns of  $\text{WO}_3$  thin films prepared at various substrate temperatures (a)  $250^\circ\text{C}$ , (b)  $350^\circ\text{C}$ , (c)  $450^\circ\text{C}$ .

Fig. (2): shows the SEM images of the  $\text{WO}_3$  thin films deposited at substrate temperature of ( 250, 350 and 450) °C respectively,  $\text{WO}_3$  thin films were grown on silicon at fixed oxygen pressure  $2 \times 10^{-1}$  mbar and 600 mJ laser energy . The non-dense  $\text{WO}_3$  films are obtained at 250°C. When the substrate temperature rises to 350°C and 450°C the grain size obviously increase, especially the films at 450°C which have coarse grains. The surfaces of  $\text{WO}_3$  thin films were more planer and compact as the mobility of adsorbent atoms increased at higher temperatures. There are some bright spots on the surface of  $\text{WO}_3$  thin films. [5]



**Figure (2): SEM images of the  $\text{WO}_3$  thin films deposited at various temperatures of a) 250°C, b) 350°C, c) 450°C**

Fig. (3) shows the AFM picture of  $\text{WO}_3$  films deposited on silicon substrate at various substrate temperatures (250, 350, and 450 °C). The surface morphology varied with the different deposition temperatures. For the film deposited at 450 °C , the films' surface morphology was very coarse and rugged .The surface morphology of the  $\text{WO}_3$ films as observed from the AFM micrographs fig. (3)(a, b, c) show that the grains have uniformly diffused with individual columnar grains extending upwards. The root mean square (RMS) surface roughness of  $\text{WO}_3$  films are found to be 5.6nm, 8.4nm, 11.3nm, for substrate temperatures (250, 350, and 450) °C, respectively, The increase in grain size can be attributed to the enhanced mobility of ablated species at higher temperatures. Due to the increased mobility revealed in the Hall Effect measurement as shown in table 2, the adatoms can diffuse to form larger grains at higher temperatures. These result is in agreement with the work of S. Zhuiykov et al.[6]In films that can exist in more than one phase the simple relationship of increased surface roughness with increased substrate temperature does not hold. This is because the surface roughness and the grain size are also a function of the crystalline phase of the film [7].

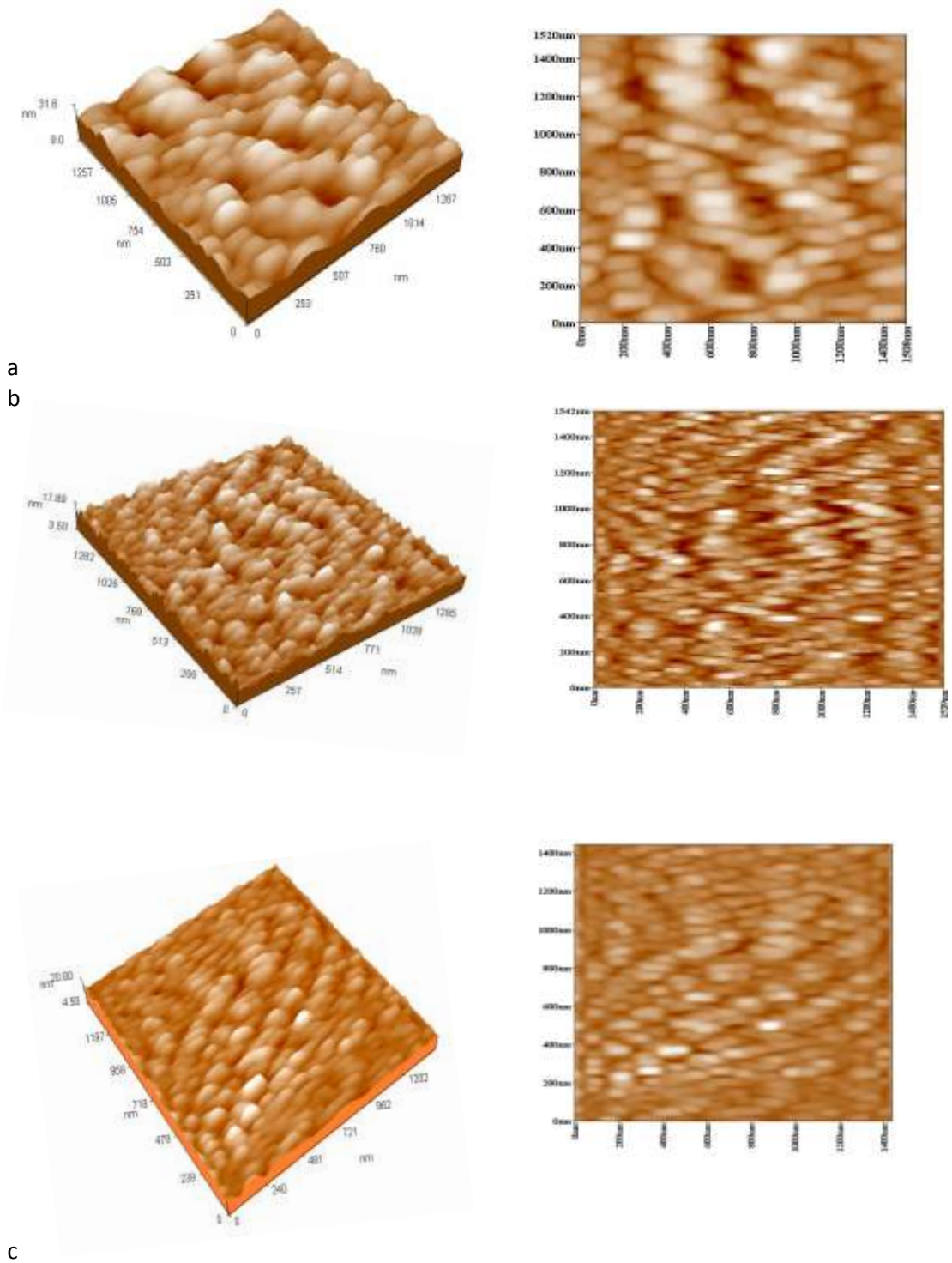
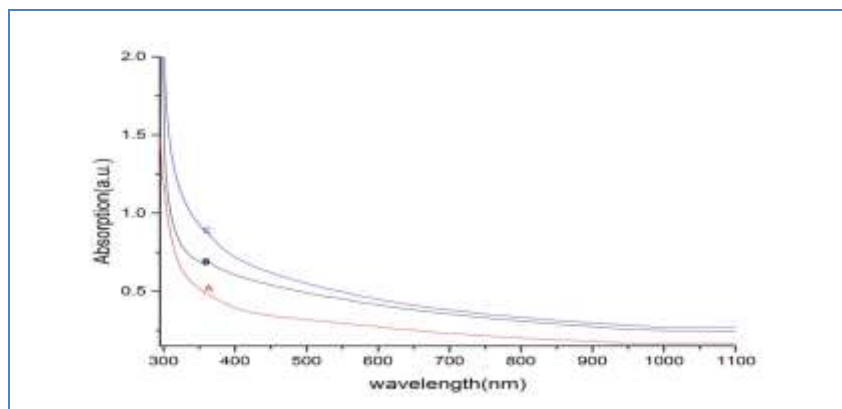


Figure (3): AFM images for films deposited at (a) 250°C, (b) 350°C, (c) 450 °C

Table (1) represents the values of RMS and main grain size taken from the AFM images.

Sample	Root Mean Square (nm)	Grain size(nm)
250°C	5.6	40
350°C	8.4	61
450°C	11.3	74

The optical absorbance of WO<sub>3</sub> thin films prepared by PLD was measured by UV-VIS spectrophotometer. The UV- VIS optical properties in the range from 300nm to 1100nm at various temperatures from 250°C to 450°C shows that the absorbance depends stronger on the temperature as shown in fig. (4) Further observation shows that the absorbance of the thin films increases with increasing substrate temperature and this is probably ascribed to the increase of particle sizes and surface roughness. Furthermore, the absorption edges of the thin films have a small red shift with increasing substrate temperature.



Figure(4): UV-VIS absorption spectra of the WO<sub>3</sub>/glass films at different substrate temperatures at a) 250°C, b) 350°C and c) 450°C

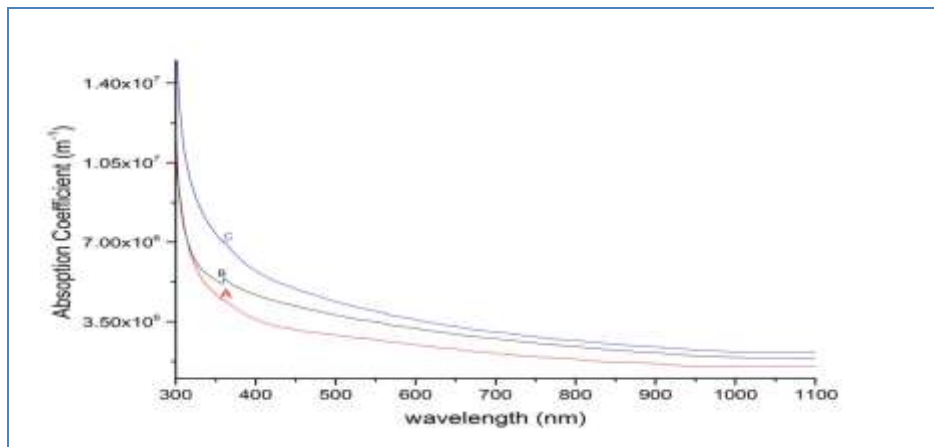
In the UV–VIS optical absorption spectra of the samples, the broad bands attributed to WO<sub>3</sub> have been observed at less than 370 nm and the bands grew with the sample different substrate temperature Figure (5) shows the absorption at wavelength of the WO<sub>3</sub> film samples with various substrate temperature .This confirmed that the PLD method is a very suitable method to fabricate substrate temperature of WO<sub>3</sub> thin films precisely. Absorption coefficient is calculated by using equation [6,7]

$$\alpha = \frac{1}{t} \ln \left[ \frac{(1 - R)^2}{T} \right] \quad \dots (1)$$

Where the absorption coefficient ( $\alpha$ ), the transmittance (T) , reflectance (R) and  $t$  is the film thickness data can be used to calculate absorption coefficients of the films at different wavelength.

Figure (5) show the variation of absorption coefficient ( $\alpha$ ) as a function of wavelength, ( $\alpha$ ) is decreasing with wavelength increase, its value is larger than ( $10^4 \text{ cm}^{-1}$ ), where as the absorption coefficient is increasing with substrate temperature increasing. The 450°C has the higher absorption coefficient due to it has a higher roughness, it may be attributed to the light scattering effect for its high surface roughness





**Figure (5) absorption coefficient as function of wavelength for different substrate temperature of same samples**

The results that were obtained from Hall Effect show that the WO<sub>3</sub> thin films are n-type and they have good conductivity. It can be seen that the increasing of laser fluency leads to an increase in the conductivity without changing the quality of the semiconductor.

The increase in conductivity is accompanied by a little increase in the value of Hall coefficient and an increase in both the number of carriers and mobility charge. ( $n_H$ ) increases one order of magnitude with increasing of  $T_s$ , this may be due to increasing of grain size or decreasing of grain boundary which increases both the number of charge carriers and their mobility essentially because of the reducing of grain boundary barrier height

This phenomenon can be explained as follows: with the increase in substrate temperature, best crystallization and increasing grain volume in the films this led to the reduce in impurities density and crystal-boundary Table (2) shows that drift velocity decreases with increasing of Substrate temperatures temperature. This behavior is caused by either increasing the trapping centers [8].

**Table: (2): Hall parameters for WO<sub>3</sub>films at different Substrate temperatures.**

Samples	$R_H$ (cm <sup>3</sup> /C)	Carrier type	$n(\text{cm}^{-3})$	$\sigma (\Omega.\text{cm})^{-1}$	$\mu_H$ (cm <sup>2</sup> /v.s)
250	-5.25	n	$2.32 \times 10^{18}$	3.15	3.85
350	-5.13	n	$4.32 \times 10^{18}$	5.15	1.15
450	-4.58	n	$4.51 \times 10^{18}$	4.15	7.15

Fig. (6) show the sensitivity as functions of operation time at different substrate temperature (250 °C, 350 °C, and 450 °C), film are placed under 80 ppm H<sub>2</sub>S gas concentration. A fast raise in sensibility is observed when the operation time increase the sensibility of the metal oxide semiconductor is at most fixed by the interaction, and increased surface roughness with increased substrate temperature.[9-10].The surface kind and the trapped electrons were returned to the conduction band causing by a raise in the conductivity of the film deposition 450 °C films and, respectively, the sensibility of the sensor

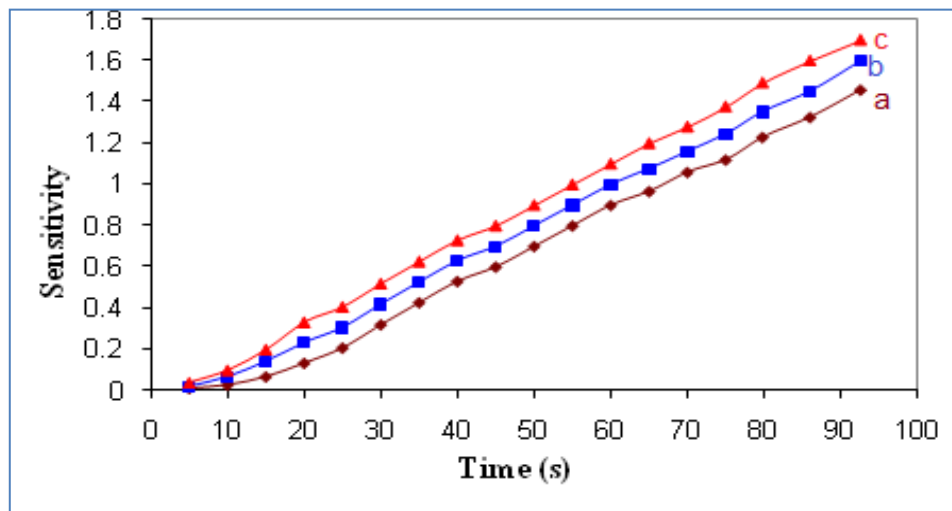


Figure (6): Gas sensitivity curve for  $\text{WO}_3$  thin films at different substrate temperature a) 250 °C b) 350 °C, and c) 450 °C

## CONCLUSION

In this study, the structural and morphological properties of nanostructure  $\text{WO}_3$  films deposited on Si (111) and glass substrates by pulsed laser deposition are directly influenced by the deposition temperature. The grain size and film thickness have been found to increase with increasing deposition temperature. SEM results showed that dense, homogeneous and fully crystalline film has been formed at higher deposition temperatures. XRD results indicate the structural changes induced with the variation of the deposition temperature of the substrate. AFM study reveals that the film surface becomes rougher at a higher deposition temperature (450 °C). The result of Hall Effect measurements, indicate that these films were n-type. Sensitivity is a function of operation time at different substrate temperatures.

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