

Research Article

PLD Grown Polycrystalline Tungsten Disulphide (WS_2) Films

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Polycrystalline WS_2 films were grown by pulsed laser deposition (PLD) system at relatively low temperature. The main objective of this study is to optimize the growth conditions for polycrystalline WS_2 films at relatively low temperature to use them for photovoltaics (PVs). Different growth conditions and substrates are used and examined systematically. It is found out that films grown on strontium titanate SrTiO_3 (STO) substrate have the best structural properties when compared to other substrates examined in this work. X-ray diffraction and optical characterizations of these films reveal crystallographic growth and very promising optical properties for PVs. Furthermore, it was observed that higher growth temperature ($>300^\circ\text{C}$) has an unfavorable effect on the layers by creating some tungsten metallic droplets.

1. Introduction

The rising interest and research on alternative, abundant, and nontoxic absorber materials like tungsten disulfide (WS_2) could play a major role to advance the photovoltaics field and renewable energy market [1–7]. WS_2 is layered transition metal dichalcogenide (TMDC) material. For decades [8, 9], it has been known to be a promising alternative solar cell material to replace the conventional ones such as Si, CIGS, and CdTe due to its matching optical and electrical properties. However, WS_2 has been investigated mainly for non-optoelectronic applications [10] such as using it as lubricant. For electronics and optoelectronics devices, the TMDC materials start gaining very growing attention recently [2, 9, 11].

The p-type WS_2 is an indirect band gap material (1.29 eV) with direct transitions start about 1.7 eV. Along the layers, it has excellent transport properties; some reports estimated the diffusion length to be in the range of $200\ \mu\text{m}$ [12, 13]. Yet, its transport is anisotropic and is very small between the layers. Optically, it has absorption coefficient of greater than $10^5\ \text{cm}^{-1}$ for photon energies above 1.75 eV [14, 15]. The required absorption length to catch most of the absorbable

photons from solar radiation is less than $1\ \mu\text{m}$ [1]. This is much less than the measure diffusion length and exhibits WS_2 strong potential for PVs. In 1982, an efficiency of 6% (the short circuit current $J_{\text{sc}} = 26\ \text{mA cm}^{-2}$, the open circuit voltage $V_{\text{oc}} = 0.42\ \text{V}$, and fill factor $FF = 60\%$) was achieved from WS_2 photoelectrochemical cell [16].

In thin-film form, WS_2 has been grown by various techniques like sputtering [17], pulsed laser deposition (PLD) [18], chemical bath deposition (CBD) [19], electrodeposition technique [20], and many others. The growth of polycrystalline films with large grain sizes in inclined orientation at relatively low growth temperature is necessary to make efficient solar cells [21]. For most TMDC, the substrates play important role in the crystal growth for them [22] as they have a tiny tolerance for lattice mismatch. It is not uncommon to end up with amorphous films. Furthermore, the high lattice mismatch at the junction results in high defect.

In this work, good-quality polycrystalline WS_2 thin films have been grown at relatively low temperatures of 250°C and 300°C using PLD technique on STO substrates. XRD data shows preferred orientation for the as deposited films. The measured structural and optical properties are presented and discussed.

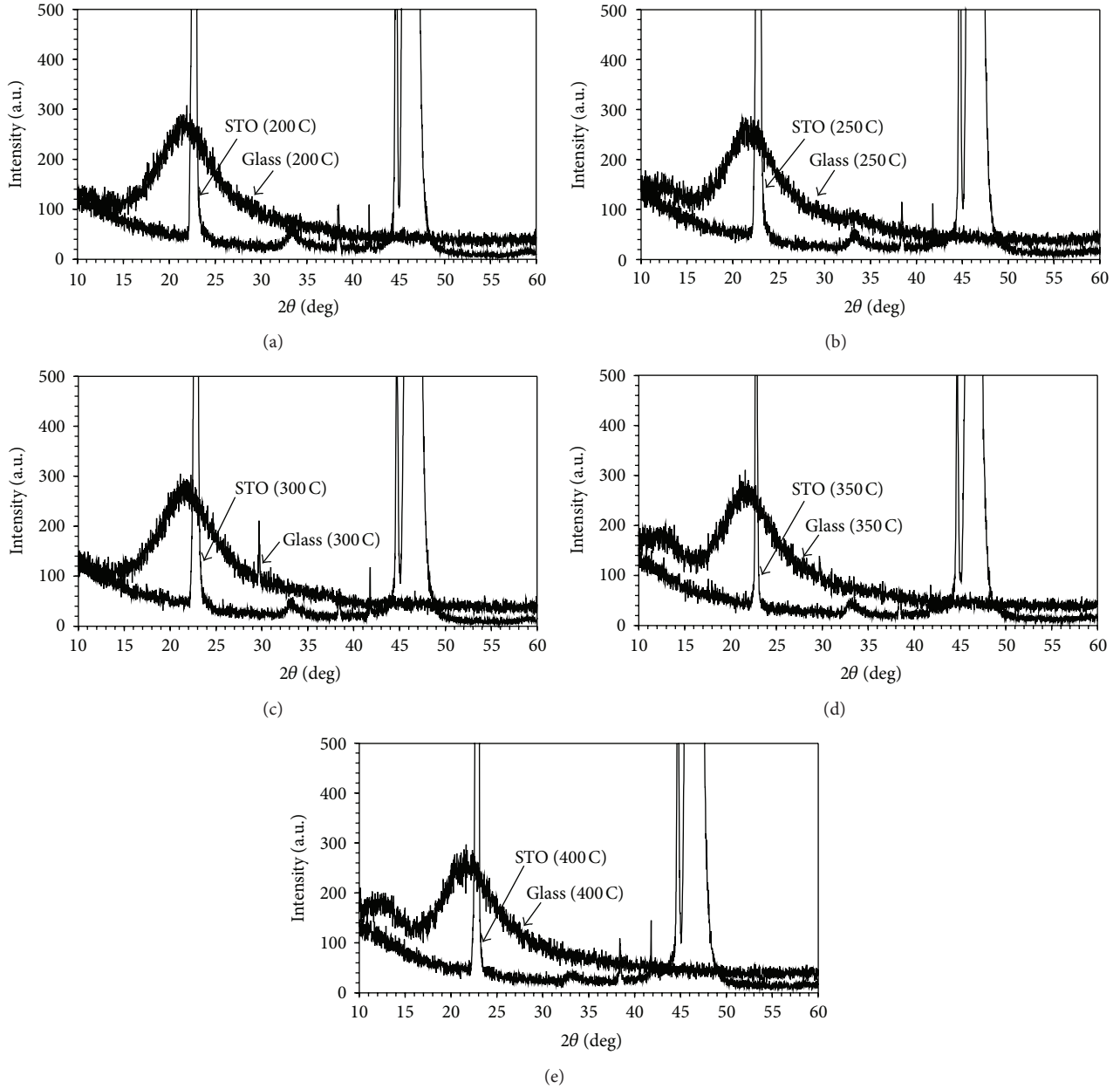


FIGURE 1: XRD patterns of WS_2 films on STO and soda-lime glass substrates at different temperatures ranged between 200°C and 400°C at 50°C increment.

2. Experimental

All the thin films of WS_2 that were studied for this paper were deposited on soda-lime glass, quartz, STO, and sapphire substrates at different temperature using the PLD/MBE-2300 system from PVD Products, Inc. KrF (248 nm) excimer laser (Compex Pro 205) with pulse duration of 20 ns and a repetition with rate of 10 Hz was used for ablation of the target, which was held in a rotating carousel to enable uniform ablation of the target surface. The incident angle of the laser with respect to the target was $\sim 45^\circ$ with laser energy of 300 mJ; the partial pressure was sustained at 2×10^{-6} mTorr during the growth process. A WS_2 target of 99.9%

purity from American Elements Co. is used. The as deposited films were characterized using X-ray diffraction (XRD) and ellipsometer for structural and optical data.

3. Results and Discussions

3.1. XRD Analysis. Figure 1 shows the diffraction patterns of WS_2 films deposited on STO and soda-lime glass substrates with the diffraction angle 2θ varied between 10° and 60° at different growth temperatures ranging between 200°C and 400°C. No peaks are obtained from the films grown on top of glass substrates and films turned to be amorphous.

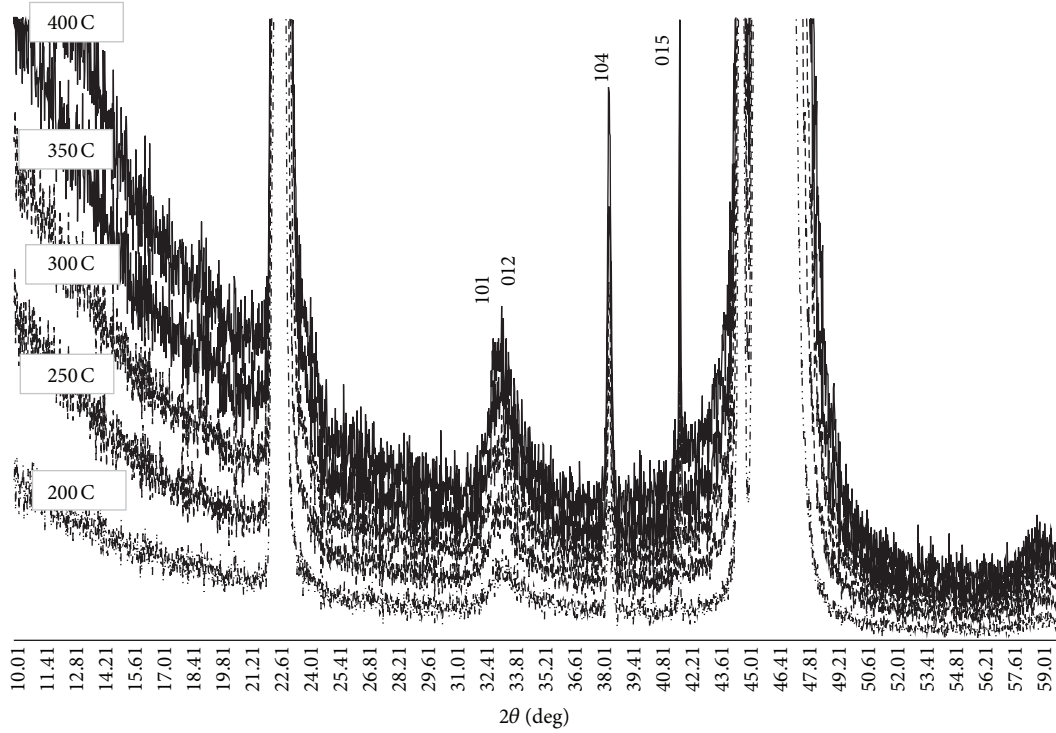


FIGURE 2: XRD patterns of polycrystalline WS_2 films on STO substrates at different temperatures ranged between 200°C and 400°C at 50°C increment.

This amorphous phase is also obtained for the films grown on quartz and sapphire due to the high lattice mismatch between the deposited films and substrate [22–27].

Yet, there are sharp peaks for the WS_2 grown on STO substrates. The large peaks at 2θ equal to 22.8° and 46.5° are due to the STO substrates. All the other peaks are associated with WS_2 films. This illustrates that WS_2 films crystal orientation can be controlled by a proper selection of substrates, and this feasible possibility is shown in the next paragraph through growing preferred orientation.

Figure 2 combines all XRD data of the films grown on STO substrates. The peaks are associated with (101), (012), (104), and (015) orientations, which corresponds to the rhombohedral WS_2 (JCPDS 35-0651) with the aforementioned peaks being intense among others. Due to the small lattice mismatch of about 3%, it was possible to realize a polycrystalline growth WS_2 films on STO [22].

3.2. Optical Characterization. The optical characterization of the as grown samples was carried out using an ellipsometer. Figure 3 shows the measured extinction coefficient (k) values for the films deposited at the various temperatures. It can be observed at the higher temperature ($>350^\circ\text{C}$) that k is not vanishing for low energies. The formation of metallic tungsten droplets at these comparatively high temperatures is the main reason for this effect. Beside this, the high value of refractive index ($n > 2$) (Figure 4) is obtained for all the WS_2/STO films, which is certainly desirable for PVs [1, 2, 28].

Figure 5 shows the absorption coefficients for the as deposited films. It is fractionally smaller than what has been

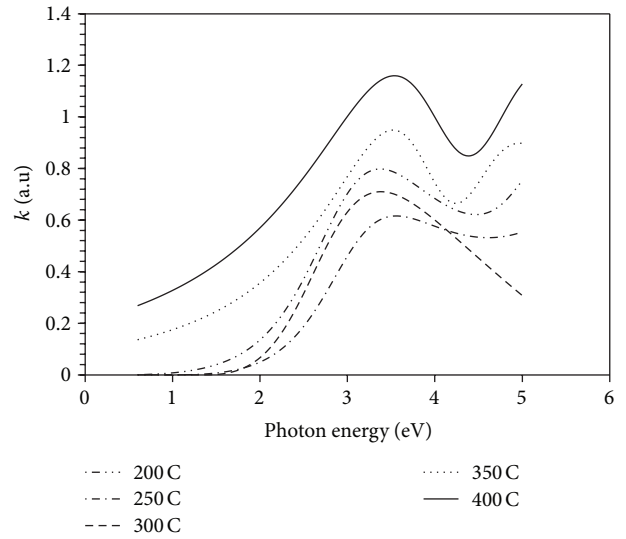


FIGURE 3: k values of the grown WS_2 films.

reported before [1, 15, 16]. Yet, the obtained values are still very promising for PVs.

3.3. Thickness and Roughness Analysis. The thicknesses and roughnesses are also estimated from ellipsometry measurements. Figures 6 and 7 show the thickness and the ratio between the roughness and thickness variations, respectively, with temperature. Clearly, the thickness has a decreasing trend with the temperature. This behavior is common for the sulfides where the sulfur deficiency increases with the

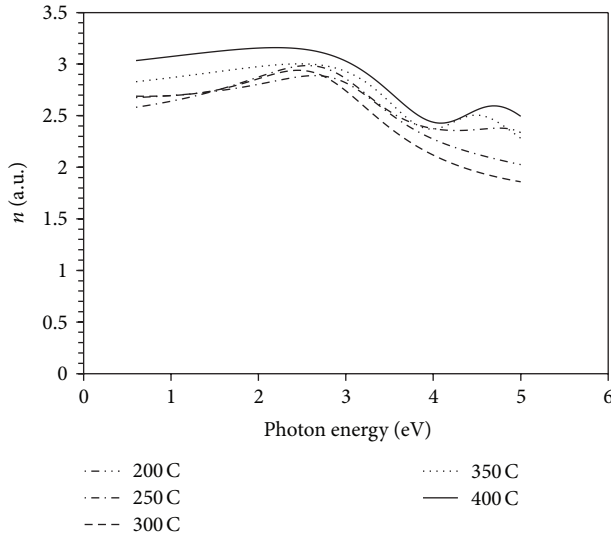


FIGURE 4: n values of the grown WS_2 films.

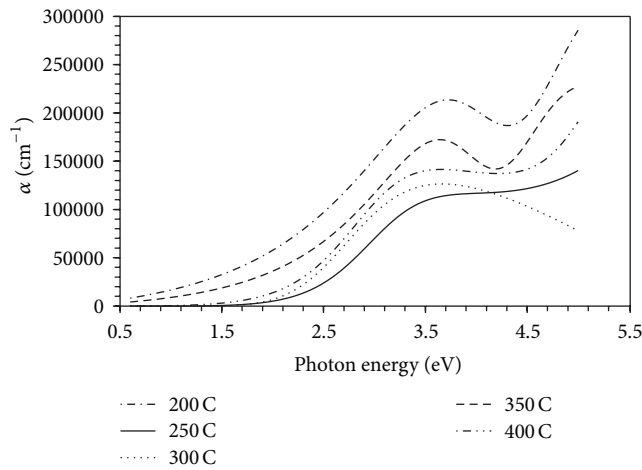


FIGURE 5: The absorption coefficients of the grown WS_2 films.

temperature. For the roughness, the ratio values between it and thickness are obviously increasing with the temperature due to the formation of droplets and also the reduction of the thickness.

4. Conclusion

Polycrystalline WS_2 films were grown by PLD at relatively low temperature. This is part of the initial work to use WS_2 for PVs. The main objective of this initial study is to optimize the growth conditions for polycrystalline WS_2 films at relatively low-temperature. As known, the low-temperature growth of polycrystalline is desirable as PVs are largely multilayer. Different growth conditions and substrates are used and examined systematically. It is found out that films grown on STO substrate resulted in the best structural properties when compared to other substrates examined in this work. This is mainly due to the small lattice mismatch of 3%. X-ray diffraction and optical characterizations of these films reveal crystallographic growth and very promising optical

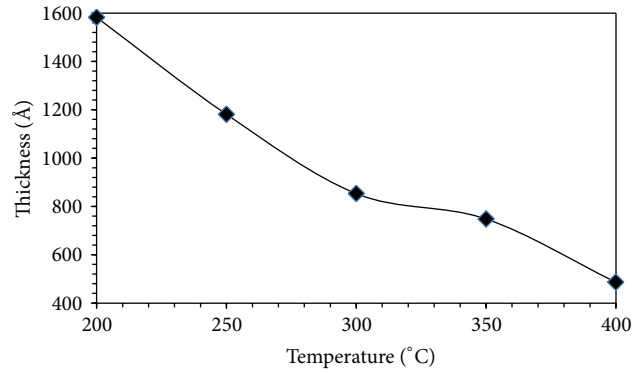


FIGURE 6: Thickness variation of WS_2 films for the temperature 200°C–400°C.

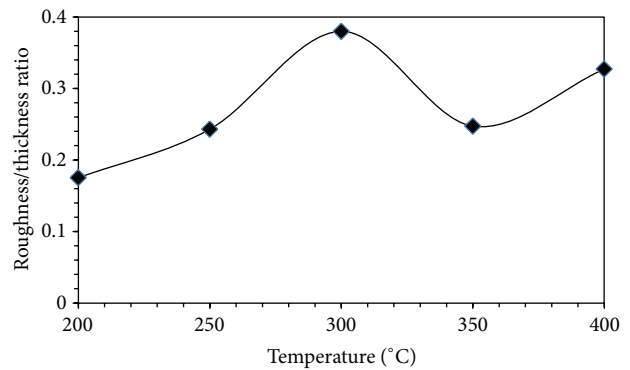


FIGURE 7: The ratio values between the roughness and thickness of WS_2 films (200°C–400°C).

properties for PVs. Furthermore, it was observed that higher growth temperature ($>300^\circ\text{C}$) has an unfavorable effect on the layers by creating some tungsten metallic droplets.

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