

# Influence of the ion energy on the growth of $WS_x$ films prepared by reactive magnetron sputtering

S. Seeger, R. Mientus<sup>1</sup> and K. Ellmer

Hahn-Meitner-Institut, dept. solar energetics, Glienicker Str. 100, 14109 Berlin, Germany

<sup>1</sup>Optotransmitter-Umweltschutz-Technologie e.V., Köpenicker Str. 325b, 12555 Berlin, Germany

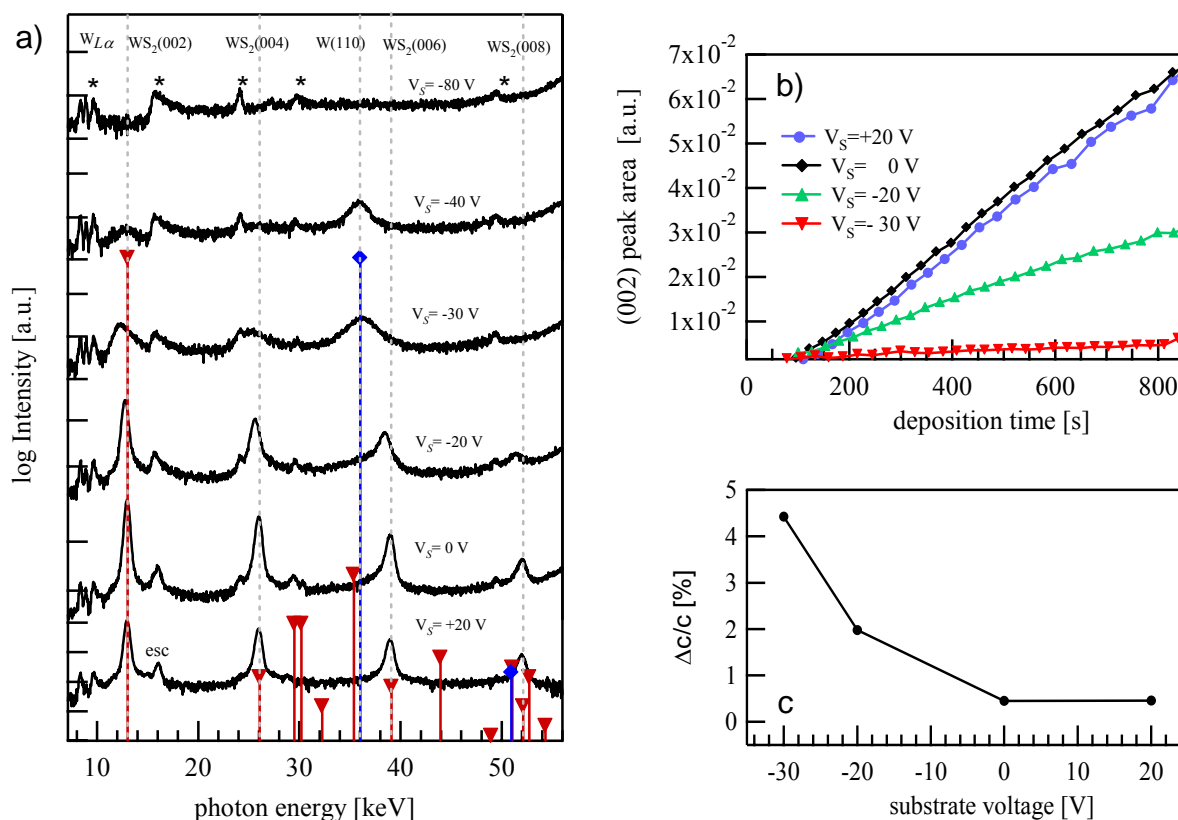
Tungsten disulfide belongs to the transition dichalcogenides which were proposed as absorber materials in thin film solar cells by Tributsch [1] because of the high photo conversion efficiency and good stability in electrochemical solar cells. Among the transition dichalcogenides, the stability and nontoxicity of tungsten disulfide ( $WS_2$ ) makes this layered semiconductor interesting as absorber material in photovoltaic energy conversion. Tungsten disulfide is a layered material consisting of stacked S-W-S slabs. The bonding between the hexagonally arranged sulfur and tungsten atoms in the slabs is very strong whereas the stacked S-W-S slabs are weakly connected by intermolecular or van der Waals forces. The binding energy between the S-W-S slabs in c-direction is about 0.14 eV [2]. The van der Waals type bonding between the sulfur atoms in c-direction leads to planes which exhibit no dangling bonds. The van der Waals type surfaces of the layered semiconductors are ideal for forming p-n heterojunctions because of the absence of inherent surface states arising from unsaturated bonds [3]. However, to be used as photosensitive films, it is required to grow tungsten disulfide films with large crystallites oriented with their c-axis perpendicular to the substrate plane, i.e. a (001) texture.

In this work polycrystalline  $WS_x$  films with the required crystallographic quality were prepared by reactive magnetron with radio frequency at 27.12 MHz from a tungsten target in a gas mixture of argon and  $H_2S$  with a  $H_2S/Ar$  ratio of 3. A magnetron sputtering chamber, designed for *in situ* energy dispersive X-ray diffraction (EDXRD) experiments during the deposition described elsewhere [4], was used to study the growth of the films. The  $WS_x$  films were deposited onto oxidized silicon at a substrate temperature of about 620°C and a total gas pressure of about 2 Pa. The systematic variation of the substrate voltage  $V_S$  from floating potential  $V_S = +20$  V to a negative voltage of about  $V_S = -80$  V increases the energy of positive ions impinging on the growing film. The EDXRD spectra which were continuously measured during the deposition in time intervals of 20 to 30 s contain information on the deposition rate and the crystallographic quality of the films. The crystallographic structure of the films is probed in the symmetric Bragg geometry at a fixed diffraction angle of about 4.4°. The deposition rate (in W-atoms/cm<sup>2</sup>) can be extracted from the intensity of the tungsten fluorescence lines ( $W_{L\alpha,\beta}$ ).

Fig. 1a shows the EDXRD spectra of the sputtered  $WS_2$  films for different substrate voltages. The EDXRD spectra include the tungsten X-ray fluorescence lines ( $W_{L\alpha,\beta}$ ) below 10 keV and the diffraction peaks, which can be assigned to the structure of 2H- $WS_2$  (JCPDS 8-237). From the intensity of the tungsten fluorescence peaks in the spectra it can be seen that the thickness of the films is comparable hence the deposition rates are nearly independent on the substrate bias. The spectrum of the  $WS_x$  film deposited at floating substrate potential  $V_S = +20$  V shows a pronounced (001) texture. The good crystallographic quality can also be seen from the occurrence of the diffraction lines belonging to the (002l) group, up to  $l = 4$ . Fig. 1b depicts the normalized peak area of the (002) diffraction lines versus the deposition time. It can be seen that the (002) peak area increases continuously. The  $WS_x$  film prepared at grounded substrate potential ( $V_S = 0$  V) grows also with the preferred (001) orientation (Fig. 1a), but due to the increased ion bombardment the (006) peak shows already a weak shoulder to lower photon energy, which indicates that additionally the diffraction line of metallic tungsten ( $W(110)$ ) appears. With increasing negative substrate voltage the tungsten diffraction line at a photon energy of about 36 keV can be seen more clearly. At higher applied negative substrate voltages the (001) texture of the  $WS_x$  films is reduced while the tungsten diffraction line dominates. At  $V_S = -80$  V the spectrum of the grown  $WS_x$  films shows neither the tungsten disulfide diffraction lines nor the line of crystalline tungsten. Obviously, the energy of the positive ions impinging onto the growing films is sufficient to prevent the crystallization of the films completely. Furthermore, the shift of the (002) peak position in the spectra indicates that with increasing negative bias the distance of the c-lattice planes is extended.

Fig. 1c depicts the relative c-lattice expansion  $\Delta c/c$  calculated from the spectra (Fig. 1a) as a function of the applied substrate voltage. At  $V_S = -30$  V the relative lattice expansion  $\Delta c/c$  has a value of about 4.4 %. This large effect is attributed to the formation of lattice defects [5].

In conclusion we have found that due to the weak binding between the S-W-S slabs in c-direction a low energy of argon ions impinging the films is sufficient to disturb the growth of the  $WS_x$  films during the deposition by magnetron sputtering. Even at grounded substrate potential an increased ion bombardment influences the crystallographic structure of the films. To avoid changes of composition and defect formation in the growing  $WS_x$  films it is necessary to adjust the ion bombardment during the deposition carefully.



**Figure 1:** a) *In situ* EDXRD spectra of  $WS_x$  films prepared by reactive magnetron sputtering (RF 27.12 MHz) at different substrate potentials  $V_S$ . The spectra show the tungsten fluorescence peaks ( $W_{L\alpha,\beta}$ ) and the  $WS_2$  diffraction peaks (002l), with  $l = 1-4$ . With increasing negative substrate potential an additional peak appears, which can be attributed to metallic tungsten W(110). The bars with symbols show the positions and intensities of the powder diffraction files of  $WS_2$  (JCPDS 8-237) and W (JCPDS 01-1204). The peaks, marked by stars (\*) are caused by electronic effects of the counting system. b) Normalized peak areas of the (002) diffraction lines versus the deposition time. c) Relative c-lattice expansion  $\Delta c/c$  calculated from the spectra of Fig. 1a as a function of the applied substrate voltage.

## References

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