

Rapid Crystallization of WS₂ Films Assisted by a Thin Nickel Layer: An *in situ* Energy-Dispersive X-Ray Diffraction Study

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Abstract

By rapid thermal crystallization of an amorphous WS_{3+x} film, deposited by reactive magnetron sputtering at temperatures below 150 °C, layer-type semiconducting tungsten disulfide films (WS₂) were grown. The rapid crystallization was monitored in real-time by *in situ* energy-dispersive X-ray diffraction. The films crystallize very fast (>40 nm/s), provided that a thin nickel film acts as nucleation seeds. Experiments on different substrates and the onset of the crystallization only at a temperature between 600 and 700 °C points to the decisive role of seeds for the textured growth of WS₂, most probably liquid NiS_x drops. The rapidly crystallized WS₂ films exhibit a pronounced (001) texture with the van der Waals planes oriented parallel to the surface, leading to photoactive layers with a high hole mobility of about 80 cm²/Vs making such films suitable as absorbers for thin film solar cells.

1. Introduction

Transition metal dichalcogenides are layer-type semiconductors with energy band gaps and absorption coefficients which make them candidates for absorber layers in thin film solar cells. Already in 1977, molybdenum and tungsten disulfide were proposed as absorber materials [1]. In order to use the advantageous (weak) van der Waals bonding of the sulfur-terminated (001) lattice planes in these materials thin films have to be prepared with a strong (001) texture, i.e. with the c-axis perpendicular on the substrate. Different methods have been used to deposit tungsten disulfide (WS₂) films: reactive and nonreactive magnetron sputtering [2,3], sulfurization of WO₃ films with assistance of nickel [4,5] or crystallization of amorphous WS_{3+x} films with the assistance of thin films of Ni, Co, Fe, Mn [6]. Recently, we have shown that direct reactive magnetron sputtering of WS_{2-x} films at substrate temperatures of more than 600 °C leads to (001) textured films [7], provided the deposition is performed onto substrates at floating potential. Decreasing the substrate potential by only 30 V leads to a disturbed film growth, pointing to low defect formation energies in WS₂ caused by the weak van der Waals bonding between the stacked S-W-S layers. However, even these films deposited under energetically advantageous conditions (floating potential), exhibit a low mobility and were not photoactive.

In this article a thin film preparation route was investigated which avoids ion-bombardment-induced defects by crystallizing an amorphous sulfur-rich WS_{3+x} (0 ≤ x ≤ 1) film. We performed for the first time a time-resolved monitoring of the crystallization process of the WS₂ films by *in situ* X-ray diffraction analysis with a time resolution down to 2 s. From these investigations a refined model for the metal-promoted crystallization of WS₂ is derived.

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2. Experimental

In our experiments the sulfur-rich WS_{3+x} films were prepared by reactive magnetron sputtering from a pure tungsten target in an argon- H_2S atmosphere with 75 % H_2S at a working pressure of 4 Pa. The oxidized silicon substrates were not intentionally heated during the deposition and reached only temperatures up to 150 °C. The magnetron plasma was excited by RF (27.12 MHz) at a power of 100 W. The thin nickel films were deposited by an electron beam evaporator onto the oxidized silicon wafers with (100) orientation. The thickness (5 nm) was controlled by a quartz crystal monitor.

The film growth was monitored by *in situ* energy-dispersive X-ray diffraction (EDXRD) at the beamline F3 of the HASYLAB synchrotron radiation source (DESY-Hamburg). The deposition and *in situ* EDXRD setup was described recently [8,9]. The films grew X-ray amorphous at these low substrate temperatures with a rate of about 20 nm/min (thickness 350 nm). Immediately after the deposition the films were heated in the deposition chamber in the argon- H_2S atmosphere with 75 % H_2S with a fast ramp (about 7 K/s) up to temperatures of 1000 °C. The morphology of the films was analyzed by a field-emission scanning electron microscope (Hitachi S-4100). Energy-dispersive X-ray fluorescence (EDX) was used to analyze the composition of selected crystallites in the films. The conductivity and the Hall coefficient were measured with the samples contacted in the van der Pauw geometry by evaporated gold pads (≈ 200 nm). The magnetic flux for Hall measurement was 0.9 T. Time-resolved microwave conductivity (TRMC) measurements ($f=10$ GHz) with a laser excitation wavelength of 532 nm (pulse duration 10 ns) were used to check the photoactivity of the crystallized WS_2 films [10]. The composition and the elemental depth profiles of the layers were calculated from elastic recoil detection analysis spectra, measured with 350 MeV Au^+ ions [11].

2. Results and discussion

The X-ray diffraction patterns of two WS_2 films grown on Ni-coated (a) and uncoated (b) SiO_2/Si (100) substrates after the rapid annealing process are shown in Fig.1. The EDXRD spectra also exhibit the X-ray fluorescence peaks $WL_{\alpha,\beta}$ below 10 keV which are a measure of the film thickness. The other peaks are X-ray diffraction peaks which can be assigned to the hexagonal modification of tungsten disulfide 2H- WS_2 (JCPDS 8-237). While the film annealed with the nickel underlayer shows a very pronounced (001) texture, the film grown directly on the SiO_2 layer exhibits only very weak (002 l , $l=1-4$) diffraction peaks (note the logarithmic intensity scale). The spectrum of the badly crystallized film displays also a broad combined peak of WS_2 (100/110), which represents crystallites grown with their c-axes parallel to the substrate surface. The SEM pictures given in Fig.1 too, complement the above observation of the formation of well crystallized films only with nickel assistance. Besides the large WS_2 crystallites the SEM micrograph of the Ni-promoted film shows also smaller crystallites (see the arrow in Fig.1) extending above the WS_2 crystallites. Fig. 2 shows another rapidly crystallized WS_2 sample with two hexagonal crystallites. By EDX it was found that it consist of nickel sulfide (see the EDX spectra in Fig.2). This means during the rapid crystallization a laterally inhomogeneous phase mixture of WS_2 and NiS_x is formed. This result is supported by the compositional analysis by ERDA. The overall stoichiometry of this film is: 29.1 at% W, 62.5 at% S and 4.1 at% Ni, 2.9 at% H and 1.2 at% C. Taking these values a phase mixture of 88% WS_2 and 12% NiS can be calculated. The homogeneous nickel depth distributions, derived also from the ERDA spectra, shows that the thin nickel film at the interface between SiO_2 and WS_{3+x} has vanished and transformed into NiS_x crystallites. Interestingly, depositing a WS_{2-x} film on a nickel-coated SiO_2/Si substrate at 700 °C leads to films with a significantly worse crystallinity, compared to the rapidly crystallized films [9].

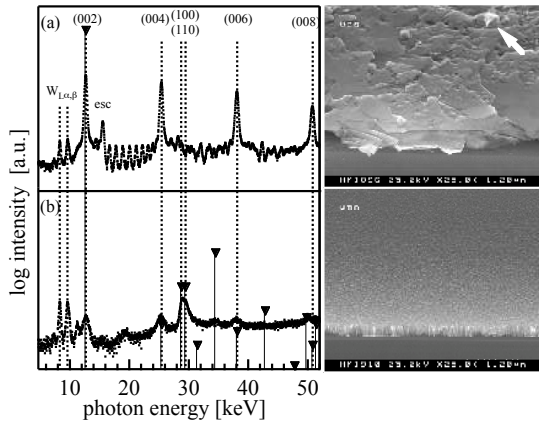


Figure 1 *In situ*-EDXRD spectra of WS₂ films prepared by rapid crystallization of an amorphous WS_{3+x} film deposited by RF (27.12 MHz) reactive magnetron sputtering at a substrate temperature below 150 °C. The two spectra correspond to films, which were crystallized (a) on top of a thin nickel layer (5 nm) on SiO₂ and (b) directly on the SiO₂ (without a Ni film). The bars with triangles mark the positions and intensities of the powder diffraction file of 2H-WS₂ (JCPDS 8-237), the most prominent reflexes are marked with their indices (dotted lines). The (004) escape peak from the Ge detector is signed by „esc“. The regular pattern between the escape and the (004) peak in (a) is caused by a signal overflow, due to the excellent crystalline quality of this film. The white arrow in the upper SEM picture points to a NiS_x crystallite.

Obviously, the nickel (sulfide) serves as nucleation seeds for the WS₂ crystallites, which was earlier reported by Regula et al. [12]. When the nickel films, promoting the crystallization, were deposited directly on the oxidized silicon substrates it mostly happened that the WS₂ films did not adhere on the substrate, flaking off already during the heating ramp, as revealed by a sudden decrease of the tungsten fluorescence signals before the crystallization started, i.e. at temperatures below about 500 °C. This could be avoided by using a thin adhesion layer between SiO₂ and the nickel film.

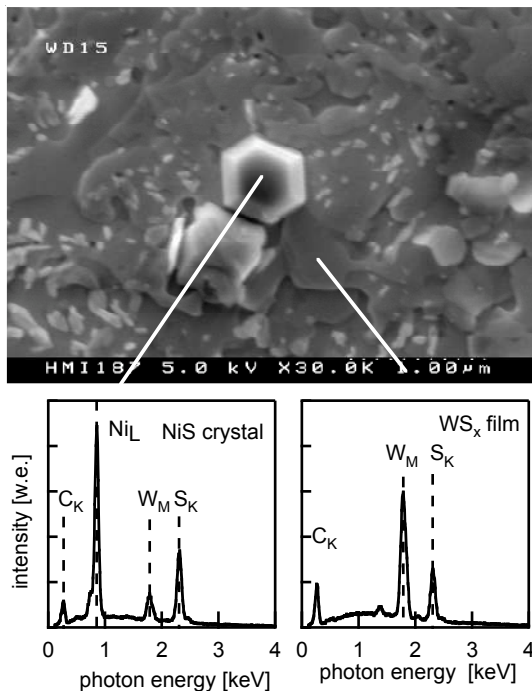


Figure 2 SEM micrograph of another rapidly crystallized WS₂ sample with nickel assistance and EDX spectra from one of the hexagonal crystallites in the center and from the surrounding film area proving that the hexagonal grain consist of NiS_x.

Fig.3 shows the time-evolution of the (002)-diffraction peak area together with the actual substrate temperature. It can be seen that the crystallization starts at substrate temperatures above 600 °C and proceeds very fast. Within 10 s the (002) signal rises from nearly zero to the saturation value (note the logarithmic y axis). From the final thickness of the crystallized film of about 400 nm one can derive a crystallization velocity of 40 nm/s. In lateral direction the crystallization velocity is comparable, since the lateral size of the crystallites is about 1 μm . These values can be compared, for instance, with recrystallization velocities of laser- or ion-amorphized silicon by halogen-lamp annealing, which are in the range of 20-40 nm/s at 650 °C [13].

In order to use WS_2 films as absorber layers in thin film solar cells, the films have to be grown on a metallic back contact. Therefore, we tried to perform this rapid crystallization also on thicker nickel films (40 nm). However, the complete sandwich of Ni/ WS_{3+x} flaked off the substrate shortly after heating up. In a second experiment to crystallize WS_{3+x} films on a back contact, we deposited 5 nm Ni on top of a tungsten film (300 nm). In this case the films adhered well on the substrate, however, only very weak WS_2 diffraction peaks were observed, with an intensity more than an order of magnitude smaller compared to a nickel-promoted WS_2 film.

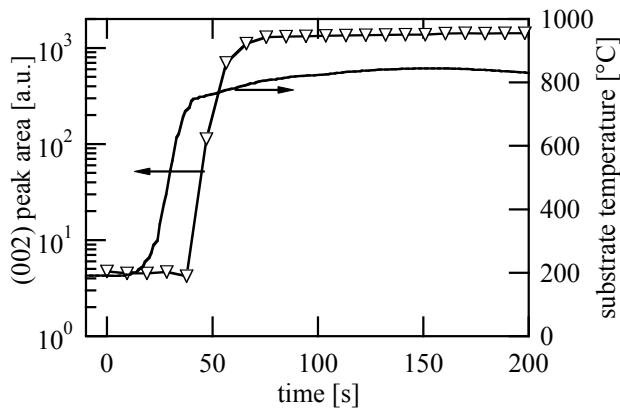


Figure 3 Time evolution of the intensity of the (002) WS_2 diffraction line during the rapid crystallization process by heating the substrates up to 850 °C. The substrate temperature is displayed by the continuous line.

From these observations the following conditions for the rapid WS_2 crystallization process can be derived. The rapid crystallization occurs only:

- (i) If the WS_{3+x} layer is amorphous, i.e. it does not yet exhibit WS_2 seed crystallites. This means, the WS_{3+x} layer has to be deposited at temperatures below about 150 °C.
- (ii) If the nickel layer forms small clusters due to surface tension, which are sulfurized to liquid drops (NiS_x) at the eutectic temperature of the Ni-S system ($T_{\text{eu}} = 635$ °C), which most probably constitute the nucleation seeds (see the SEM pictures in Fig.1 and 2).
- (iii) If a sufficient adherence of the nickel film/droplets to the substrate exists.

Obviously, the surface-tension-driven formation of nickel droplets does not occur for thicker Ni films and for nickel on tungsten since the surface-tension is either no longer sufficient to form droplets (thick nickel) or the adherence to the tungsten film is too high. This is in agreement with the formation process of carbon nanotubes out of small nickel droplets on SiO_2 [14], which is reported also to occur only up to a Ni thickness of 10 nm. The whole crystallization process is comparable to the formation of single crystalline silicon whiskers via the vapor-liquid-solid mechanism reported by Wagner and Ellis already in 1964 [15], where a liquid metal (in their case gold) drop acts as reservoir and seed for the silicon whisker growth. Different to Wagner and Ellis, in our experiment the vapor source (SiCl_4 in case of silicon growth) is replaced by the amorphous WS_{3+x} layer, i.e. we have a solid-liquid-solid process where the sulfur surplus evaporates during the crystallization. Recently, also the aluminium-

induced crystallization of amorphous silicon was reported [16,17]. This process is a true solid-phase crystallization since it occurs well below the eutectic temperature of the Al-Si system ($T_{\text{eu}}=577\text{ °C}$). The crystallization velocity is as high as 7 nm/s at an annealing temperature of 500 °C [18]. Also in this case the seed density is very important for the size of the final silicon grains, which depends on the thickness of the aluminium oxide film at the interface between Al and a-Si.

With contacts in the van der Pauw geometry the electrical properties were measured, displayed in Fig.4. The rapidly crystallized film is p-type and exhibits a room temperature mobility of about $80\text{ cm}^2/\text{Vs}$, better or at least comparable to values reported for rapidly crystallized WS_2 films in literature [5,19,20]. For comparison, WS_2 films sputtered at high pressure, high substrate temperature and low energy ion bombardment [21] exhibit mobilities of only about $1\text{ cm}^2/\text{Vs}$.

The mobility of the rapidly crystallized film decreases with decreasing temperature, which is caused by thermally activated emission of holes over the grain barriers. Applying the model of Werner [22], a grain barrier height of 35 to 40 meV can be derived (see the fit of the mobility curve in Fig.3). These films were also photoactive, measured by time resolved microwave conductivity and should be well suited for absorber layers in thin film solar cells.

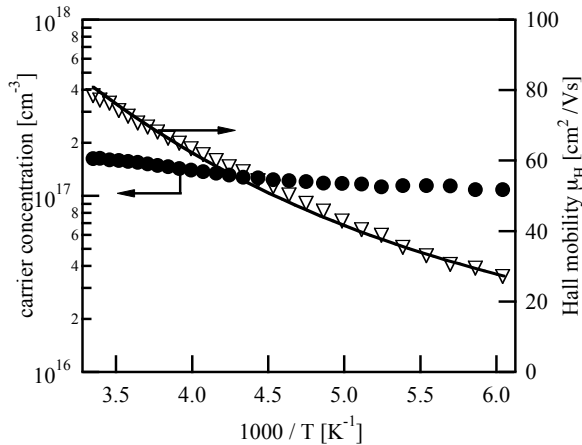


Figure 3 Temperature-dependent carrier concentration and Hall mobility of a rapidly crystallized WS_2 film (400 nm) on a quartz substrate.

4. Conclusions

We have monitored in real-time the rapid crystallization of amorphous WS_{3+x} to WS_2 films with *in situ* energy-dispersive X-ray diffraction. The films crystallize very fast ($>40\text{ nm/s}$), exhibit a pronounced (001) texture and a high carrier mobility of about $80\text{ cm}^2/\text{Vs}$, making it suitable as absorber films in thin film solar cells. Our experiments prove the decisive role of seeds for the growth of WS_2 , most probably liquid NiS_x drops, which can be formed only for sufficiently thin nickel films ($\approx 5\text{ nm}$). Further investigations are necessary to reveal the details of the formation of the WS_2 crystallites from the NiS_x seeds.

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5. References

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