ABSTRACT

The textured film growth of polycrystalline MoS$_x$ and WS$_x$ thin films deposited on Si substrates by reactive magnetron sputtering with H$_2$S from molybdenum and tungsten targets was investigated in situ for the first time by energy dispersive x-ray diffraction (EDXRD) using synchrotron radiation. MoS$_2$ and WS$_2$ are materials that are of interest as potential absorbers in thin film solar cells. They are layer type semiconductors that crystallise into a characteristic sequence of S-M-S stacks (M = Mo, W) in an hexagonal structure. The stacks are only linked to each other weakly by van-der-Waals forces, whereas the bonds within the stacks are of a covalent nature. This is the cause of the strong anisotropic electrical properties of these quasi two-dimensional materials. Reactive magnetron sputtering is a well known method of thin film deposition and has the advantage that potentially lower substrate temperatures can be used than in other deposition methods because it involves an ion bombardment of the film from the plasma. Analysing the stoichiometry of the films using elastic recoil detection analysis (ERDA) and Rutherford backscattering (RBS) revealed sulphur-to-metal ratios of $x \leq 2.3$, dependent on the amount of H$_2$S in the sputtering gas. Stoichiometric MS$_2$ is however only formed at substrate temperatures below 200°C, at which the films are practically x-ray amorphous. It was possible to prepare well crystallised films at substrate temperatures of 450°C and above; the S/M ratio then equalled approximately $x = 1.7 - 1.8$.

From in situ-EDXRD spectra which were measured with a time resolution of 20 – 30 s structural properties of the films were obtained in dependence on the deposition parameters H$_2$S partial pressure, sputtering power, sputtering pressure (0.005 to 0.09 mbar), substrate temperature (190 - 620°C) and film thickness. Low deposition rates led to the formation of a strong (001) texture, in which the van-der-Waals planes were parallel to the substrate, which is a prerequisite for high photoactivity of MS$_x$ films. At high deposition rates, the initial (001) preferential orientation of the crystallites turns into a (100) texture, i.e. the van-der-Waals planes are then perpendicular to the substrate. The development of the lattice strain $\varepsilon$ of the c-axis relative to the lattice parameter of the powder material and the relative volume of the coherently scattering crystallites which have their c-axes perpendicular to the substrate could be derived during sputtering from the energetic position and the intensity of the (002) peak. It was observed from SEM and TEM images that the (001)-oriented basal layer had a thickness of about 20 nm to a maximum of 100 nm. X-ray reflection measurements revealed a density of the basal layer which is near to the bulk density of MS$_2$. Films deposited with increasing deposition rates showed densities that were up to
70% smaller were grown and analysed by ERD which is a additional proof of the extremely porous structure of the films.

It it proposed that the texture cross-over be interpreted on the basis of the model of competing contributions of surface energy and microstrain energy to the total energy of the crystallites. The cross-over of the texture is irreversible what can be explained by different growth velocities of the crystallites in the directions perpendicular and parallel to their c-axes.

The strain $\varepsilon$ of the c-axis of the unit cell of MoS$_2$ and WS$_2$ exhibited a characteristic evolution with increasing film thickness which was proved not to result from mechanical stress in the films. A steep increase in the strain up to a maximum value was observed at the beginning of the deposition followed by a relaxation towards a slightly smaller saturation value. The maximum value of $\varepsilon$ was up to 4% and depended on the deposition rate. The saturation values of the c lattice strain of MoS$_x$ and WS$_x$ films revealed contradicting dependencies on the deposition rate. While the saturation value was about 1% (MoS$_x$) and 2.5% (WS$_x$) at high rates it increased for WS$_x$ but decreased for MoS$_x$ if the deposition rate was reduced. It is assumed that crystal defects such as dislocations, self intercalation or by analogy to graphite, turbostratic growth, i.e. a random stacking deviation from the perfectly parallel stacking order of the 2H or 3R polytypes, is responsible for the c lattice strain. This is plausible because of the weak bonds between the S-M-S stacks. In combination with the metal surplus of many films in comparison to stoichiometric MS$_2$ the strain of the crystallographic unit cell can also be explained by the intercalation of additional metal atoms between the van-der-Waals planes.

The analysis of the full width at half maximum (FWHM) of the (0 0 2l) reflections ($l = 1, 2, 3$) resulted in a grain size of up to a maximum of 60 nm (MoS$_x$) or 14 nm (WS$_x$). The grain growth reached a plateau with increasing film thickness. The very small grains can be explained by a high defect density. The intrinsinc films show high electrical resistivities of up to several hundred $\Omega$ cm. Measurements of the Seebeck coefficient showed low p-type conductivity of both reactively sputtered MoS$_x$ and WS$_x$ thin films. Dislocation densities of up to $3 \times 10^{12}$ cm$^{-2}$ were estimated from high resolution TEM images.

It is proposed that higher substrate temperatures or an additional annealing process should be used in order to reduce the defect density and to obtain an enlargement of the crystallite size, so that highly photoconductive MoS$_x$ and WS$_x$ films can be achieved which are required for thin film solar cells.