MoS$_2$ growth by ion implantation and subsequent heating

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The SIMPLANT project aims at the synthesis of thin transition metal dichalcogenide films by ion implantation. A prominent example is MoS$_2$. Since MoS$_2$ films have a tunable band gap with respect to the thickness of the film, our new approach may provide an excellent control over the film growth which enables one to fully exploit the band gap for the potential applications in ultrathin electronics. Furthermore, it avoids the potentially hazardous synthesis conditions of the conventional H$_2$S CVD approach.

In the first phase of the project, several implantation profiles of Mo and S in thin Au films were tested. Examples are given in Figure 1. Our contribution comprises of in situ X-Ray Photoelectron Spectroscopy (XPS) probing the state of the substrate as well as the precipitating Mo and S species during heating at different heating rates and their depth distribution in the vicinity of the sample surface.

So far, the best results are achieved for samples with a broad implantation profile and a heating rate $\leq 10°C/min$. Figure 2 gives an overview of the typical evolution of the Mo 3d, S 2p and C 1s intensities (Fig. 2A) as well as the fitted Mo 3d and S 2p spectra directly after the growth (Figs. B and C, respectively).
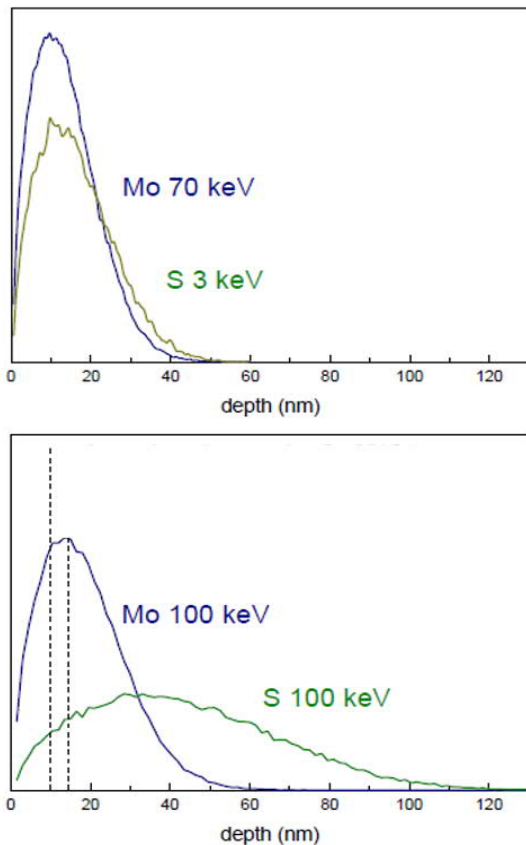

Fig. 1: Example of two different implantation profiles of Mo and S in Au with their respective acceleration voltages. Top: Narrow implantation profile with 1.2 MLE Mo and 1.5 MLE S. Bottom: Broad implantation profile with 1.5 MLE Mo and 2 MLE S.

Mo and S reach the surface already around 300 - 400°C (Fig. 2A). However, as long as larger amounts of C are present, the diffusion is limited. In a temperature window between 500°C and 650°C the amount of C on the surface is strongly reduced while the Mo and S diffusion rates simultaneously increase. If the sample temperature exceeds 650°C, Mo and S are no longer thermally stable on the surface and their intensities are diminished because of a competition between growth and decay of Mo-S bonds. When reaching the surface the Mo and S atoms firstly pass through a precursor state and subsequently form Mo-S bonds at T ≈ 500°C. The Mo 3d and S 2p fits shown in Figs. 2B and C reveal the formation of MoS mainly, while only a

small fraction of MoS_2 is detected.[1] The MoS growth proceeds in a two-dimensional fashion as evidenced by spectral depth profiling, TEM and Raman spectroscopy. Interestingly, while the MoS_2 peaks comprise of one Mo $3d$ and two S $2p$ components, as expected, the situation for MoS is reversed with two Mo $3d$ and only one S $2p$ component(-s). Theoretical calculations of the formation enthalpy and core level shifts not only confirm the stability of MoS but also suggest that the stacking sequence and local geometry of MoS causes the splitting of Mo $3d$ peaks. Moreover, our calculations on triangular MoS_2 flakes with different edge terminations and S coverages at the edge exhibited a wide range of Mo $3d$ and S $2p$ core level shifts, indicating the possibility of co-existence of MoS_2 flakes with MoS during the growth process.
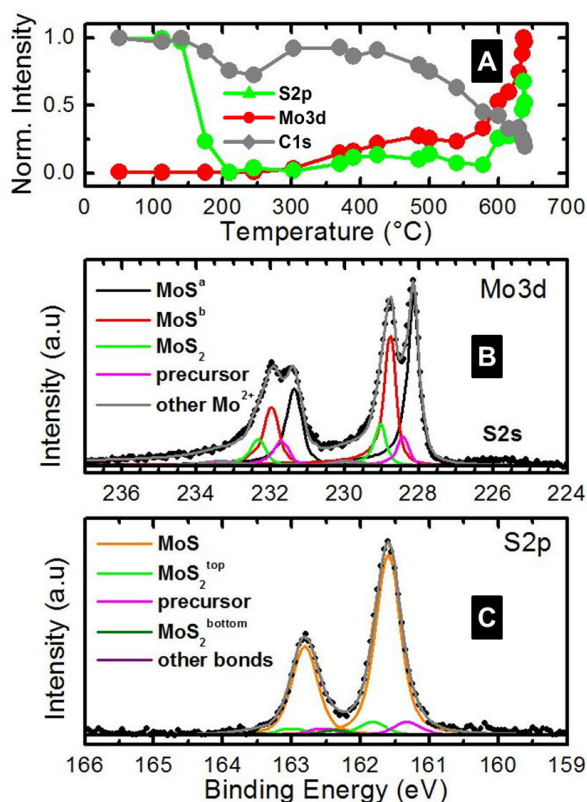

Fig. 2: Example of MoS growth on a sample with a broad implantation profile heated with 10°C/min to 645°C. A: Normalized intensity evolution of C1s, S2p and Mo3d in dependence of annealing temperature. B: Fit of Mo3d region after growth. C: Fit of S2p region after growth.

As to the comparatively slow growth of MoS_2 two obstacles have to be considered: 1. The residual surface carbon contamination, which cannot be removed by simple Ar^+ sputtering because of Mo and S preferential sputtering,[2] seems to block the Mo and S diffusion until a sufficiently high temperature ($\approx$ 500°C) is reached. 2. While Mo is immiscible with Au, calculations of bulk Au-S structures suggest the formation of Au-S bonds for large amounts of S. Both obstacles will be addressed in the ongoing project by a) an alternative routes to remove surface carbon by ozone and b) by changing the implantation procedure. For the latter, the order of implantation, Mo before S, may help to prevent Au-S bond formation. Furthermore, more S will be implanted to increase the probability of S reaching the surface. Finally, a different substrate, Ag instead of Au, will be tested.

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2. M.A. Baker, R. Gilmore, C. Lenardi, W. Gissler; Applied Surface Science, 1999, 150, pp 255.