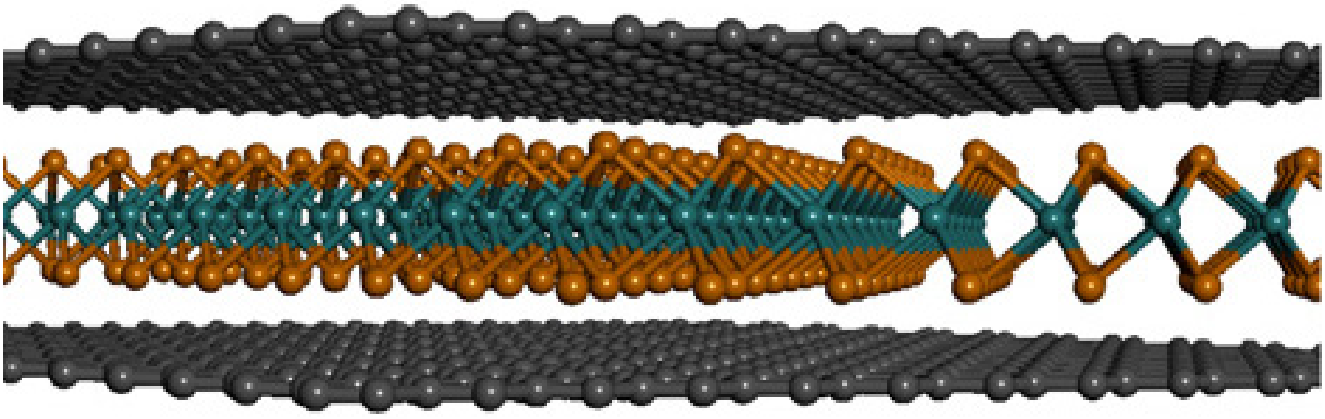

Figure 1. Transition metal dichalcogenide (TMD) / graphene heterostructure. The sandwich configuration protects the soft TMD material.

The behavior of $MoSe_2$ under the electron microscope

Electron radiation damage mechanisms in 2D $MoSe_2$

January 2017 - **Scientists from the Group of Electron Microscopy for Materials Science (EMMS) at Ulm University studied single–layer 2D $MoSe_2$ in an aberration-corrected high-resolution transmission electron microscope operated at 80 kV. By assembling various van der Waals heterostructures of graphene and $MoSe_2$ they estimated the contribution of different damage mechanisms to the total radiation damage. Also by comparing with earlier studies on MoS_2 it was found that the results are not in agreement with the elastic knock-on radiation damage alone. In principle, the radiation damage effect can be explained by a two-step process in which the binding energy of an atom is first reduced by inelastic scattering followed by atom removal by collision with a second electron. Further studies in this new research area are required in order to better understand the different processes leading to radiation damage in materials.**

In recent experiments, scientists of Ulm University,[1] investigated radiation damage occurring in HRTEM experiments for van der Waals heterostructures of $MoSe_2$ and graphene (Gr) [2]. They investigated different radiation damage processes occurring in Gr/$MoSe_2$/Gr and in Gr/$MoSe_2$ [3] (Fig. 2).

The study extends their earlier work on MoS_2 [3] by conducting similar experiments now with another member of the large and new family of the Transition Metal Dichalcogenides (TMD). MoS_2 and $MoSe_2$ have identical crystal structures, and they are isoelectronic,[4-6] while the main difference is the different masses of the chalcogen atoms (32.07 amu for S and 79.0 amu for Se) and the higher amount of electrons (34 for Se and 16 for S), which increase the probability for electron excitations due to the electron beam. As the momentum transfer from the impinging electrons to the target atoms is dependent on the target atom mass, knock-on damage can be expected to be suppressed in the case of $MoSe_2$ with 80 keV electrons (the minimum threshold energy is 6.4 eV for $MoSe_2$ and 6.9 eV for MoS_2 which corresponds, due to the different masses, to a static threshold electron energy of 190 keV and 90 keV, respectively).[7] Surprisingly, $MoSe_2$ has almost identical behavior to MoS_2 in the recent experiment. It was observed that the mass of the chalcogen atom does not influence the damage rates.

As the scientists point out, this result calls for critical assessment of the assumptions about the damage mechanisms, especially the strict separation of elastic and inelastic processes. In order to do so, they applied an experimental scheme which allows for the separation of different contributions to radiation damage. The approach of the study was to construct different graphene-$MoSe_2$ heterostructures, similar to what was done earlier with MoS_2.[1]

The following comparisons were used.[1] (1) The difference between the damage cross section in a sample with the entry surface covered with graphene (G/MoS_2) and a sample with the exit surface covered (MoS_2/G) gives the knock-on contribution. This lays on the assumption that only the knock-on process has a directional dependence, that is, if the entry surface is covered, the sulfur atoms at the bottom can still be displaced into the vacuum (knock-on active), whereas with covering the exit surface the displaced sulfur atoms are stopped by the graphene layer (knock-on disabled). (2) The difference between a free-standing MoS_2 and G/MoS_2 gives the inelastic contribution. This, in turn, is based on the assumption that graphene, which is a supreme electric and thermal conductor, quenches the electronic excitations and dissipates any introduced heat and eliminates sample charging, thus removing the inelastic damage.[8]

Taking the experiments into account it can be concluded that 24% of the damage is produced by knock-on damage, 63% by heat, charge and/or electronic excitations, and 13% of the damage has to be produced by other mechanisms, such as chemical etching and further ionization effects.

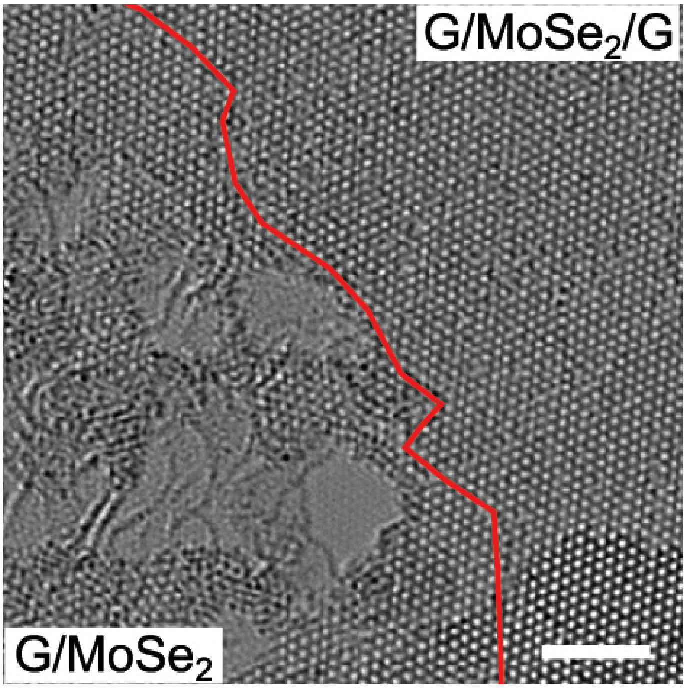

Figure 2: Aberration-corrected high–resolution transmission electron microscopy (AC–HRTEM) at 80 keV image of two different heterostructure configurations. $G/MoSe_2$ (left area) and $G/MoSe_2/G$ (right area) after a total electron dose of 3.1×10^9 e/nm^2. It is striking that the left area with the $G/MoSe_2$ configuration is highly damaged, while the right area is still in a good condition. The right area shows that graphene has the function of a protection layer for soft materials.

The estimated significant contribution of knock-on damage brings the earlier conclusions into question, as the theoretical prediction would indicate no knock-on damage. Here, two possible explanations for this discrepancy can be offered. First, one has to ask whether the methodology employed here is solid. More precisely, does the difference between the $G/MoSe_2$ and $MoSe_2/G$ cases really give the knock-on cross section? As there is no other method available for isolating the knock-on contribution, the correctness of the method cannot be externally evaluated. The alternative interpretation would indicate a marked shortcoming of the damage model, where the damage mechanisms are simply divided into the elastic and inelastic contributions. For example, a process where knock-on thresholds are influenced by inelastic scattering events prior to an electron impact could play a significant role. These results make the need for further studies on the damage mechanisms clear, which will also be carried out in the frame of the SALVE III project.

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