Anisotropy of local anodic oxidation process in thin MoSe₂ films

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Abstract. In this work, various regimes of local anodic oxidation (LAO) of MoSe₂ were studied. Here we show that there is a certain set of oxidation parameters that results in the anisotropic oxidation of MoSe₂. In this mode, LAO leads to the formation of oxidized triangles. The triangles have the same orientation on the surface of the flakes, which indicates that MoSe₂ is oxidized mainly along the crystallographic directions of the zigzag edges. These results can be useful for determining crystallographic directions of zigzag/armchair edges and the degree of single-crystallinity of MoSe₂ flakes.

1. Introduction
Transition metal dichalcogenides (TMD) have been scrupulously studying for the last few years. Such significant interest is associated with the presence of a number of unique properties, such as a widely tunable band gap[1], large exciton binding energy[2], strong light absorption[3] (even in monolayers), and many other properties. All these properties open up the possibility of creating promising electronic and optoelectronic devices[4,5]. The most interesting option for creating such devices seems to be combining of several layered materials in van der Waals (vdW) heterostructures[6,7]. However, it is worth noting that recent studies show that TMDC materials have a strong anisotropy of properties in both in-plane and out-plane directions[8,9]. The layers orientation in such structures results in different structural symmetries and layer-to-layer interactions, which in turn leads to the changing of their electronic properties. This means that different orientation of layers affects the operation of vdW heterostructure devices. For example, the work[10] shows the effect of the layer orientation (zigzag or armchair) on the photoluminescence of the MoSe₂-WSe₂ heterostructure at different polarizations. Thus, crystallographic directions of layers should be taken into account while creating and studying vdW heterostructures. Due to the atomic thickness of these materials, Raman spectroscopy or scanning tunneling microscopy are used to determine crystallographic directions. Here we report that layers orientation (zigzag or armchair), as well as uniformity of orientation along the layer, can also be determined using the local anodic oxidation (LAO) technique. The aim of this work was to study anisotropy of the local anodic oxidation process in thin MoSe₂ films.

2. Samples and methods
Local anodic oxidation is a well-known surface modification method. It has been well studied for classic 3D materials and has already been sufficiently tested for 2D materials such as graphene[11] and transition metal dichalcogenides[12]. The experiment was performed on a Ntegra Aura (NT-MDT) scanning probe microscope using a Si probe (NT-MDT) with a tip diameter of 20 nm in air conditions.
with controlled humidity. The sample consisted of thin films of MoSe$_2$ obtained by micromechanical exfoliation and transferred on a Si substrate covered with gold. The scheme of the structure can be seen in Figure 1.

Figure 1 shows the scheme of local anodic oxidation. The oxidation experiment was carried out at room temperature in ambient with relative humidity of 50%. In these conditions, a surface is covered with a natural water film forming meniscus between a probe and a surface. The experiment was performed in a semi-contact mode. The amplitude was set so that the probe vibrates within 5-10 nm of the surface so as not to rip off the meniscus. The gold-coated surface was grounded, while negative voltage bias was applied to the probe. For oxidation, short (about 0.1 ms) and high (about 25 V) pulses of negative voltage were used. When the negative voltage pulse is applied to the probe, flowing current causes water splitting. Thus, the water meniscus saturates with hydrogen and oxygen. Reactive oxygen is involved in the electrochemical reaction, which leads to oxidation of the sample surface. The oxidation of MoSe$_2$ proceeds as follows:

$$ MoSe_2 + 9H_2O + 14h^+ \rightarrow MoO_3 + 2SeO_3^{2-} + 18H^+ $$

3. Results and discussion
As mentioned in the previous chapter, LAO is a well-studied technique, so results of its application are generally expectable. In a typical case, a single-point LAO results in an oxidized point of a quasi-circular shape. Below we demonstrate it on MoSe$_2$ (Figure 2).
Figure 2 shows a single-point LAO. Each point corresponds to different voltage and exposure time. Voltage was varied from 20 to 25 V, exposure time from 0.5 to 2 ms. Relative humidity was 65%. As can be seen in Figure 2, LAO results in oxidized points of a quasi-circular shape. However, we observed that a certain set of parameters (V ≈ 25 V, t = 0.1 ms, RH ≈ 50%) leads to a change in the shape of the oxidized region. Oxidation ceases to be uniform in all directions. Preferred directions appear, which indicates anisotropy of the process. The results of such oxidation are shown in Figure 3.

Figure 3. Results of single-point LAO in the «anisotropy mode». (a, b) LAO of the same MoSe$_2$ flake; (c) LAO of the another MoSe$_2$ flake.

As can be seen from Figure 3, the shape of the oxidized areas changed from circular to triangular. It should be noted that oxidation experiments presented in Figure 2 and in Figure 3c were performed on the same flake. Thus, the shape of an oxidized area is determined by oxidation parameters, and not by differences in properties of flakes. If we carefully look at the oxidized area (Figure 3b), we will see the structure of a complex shape. In the center of the oxidized area, there is the highest point at which the probe was located during oxidation. This point is surrounded by the oxidized triangle. There might be others inside the first triangle if oxidation has affected the lower layers. The step height of the oxidized area is about 2 nm (as can be seen from the insert in Figure 3b). The depth of the cavity after removal of the oxide is about 0.7 nm, so we believe that a 2 nm step corresponds to a single oxidized layer (which consists of MoO$_3$+Se$_2$O$_3$).

It is also important to note that oxidation parameters are crucial for observing this delicate effect. Relatively low humidity (about 50%) seems to be the most important parameter for the appearance of oxidation anisotropy. High relative humidity leads to the fact that the material right under the probe is immediately oxidized and mixed with water. This creates a high hill of oxides that separates the probe from the flakes, and oxidation is stopped.

Regarding the origin of this oxidation anisotropy, we believe that the kinetics of the oxidation is similar to the kinetics of growth or etching of TMDC materials. It is well known that TMDC materials form triangles during CVD growth[13] and etching[14]. This fact is explained as follows. Comparing to the Mo-based zigzag edge, others are relatively more chemically reactive. According to the classical theory of crystal growth, rapidly growing edges disappear, while slowly growing edges remain. In the case of oxidation, less chemically sustained edges are oxidized, while more chemically sustained edges stop oxidation. Thus, in the LAO process, we have every reason to believe that the triangles are oxidized along zigzag edges. As can be seen from Figures 3 (a) and (b), all oxidized triangles are equally oriented along the same flake. Orientation of triangles remains strictly constant even at a distance of 20 μm between the oxidized areas. Figure 3c shows the different orientation of the triangles because this oxidized area is on another flake. Thus, based on orientation of oxidized triangles, it is possible to determine the direction of zigzag edges (as it is shown in Figure 3b via the insert). Moreover, the degree of single-crystallinity of a layer can be estimated by comparing the orientations of oxidized triangles at different points of a flake.
4. Conclusion
In conclusion, various regimes of local anodic oxidation of MoSe$_2$ were studied. We demonstrated that in addition to the classical oxidation regime, there is a certain set of parameters that results in the anisotropic oxidation of MoSe$_2$. In this mode, LAO leads to the formation of oxidized triangles. We consider relatively low humidity (about 50%) and short (less than 0.5 ms) and high (about 25V) voltage pulses as the most important oxidation parameters for the manifestation of the anisotropic oxidation effect. Based on the theory of crystal growth, we believe that triangles appearing in the «anisotropic regime» are oxidized along zigzag edges. These results can be useful for the investigation of the crystallographic directions of zigzag/armchair edges and the degree of single-crystallinity of MoSe$_2$ flakes. The results obtained also indicate the anisotropy of the inner properties of MoSe$_2$.

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