In situ reflection electron microscopy for investigation of surface processes on Bi₂Se₃(0001)

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Abstract. The sublimation and van der Waals (vdW) epitaxy on Bi₂Se₃(0001) surface have been first visualized using in situ reflection electron microscopy. When Bi₂Se₃(0001) surface was exposed to a Se molecular beam (up to 0.1 nm/s) and heated to ~400°C, we observed ascending motion of atomic steps corresponding to congruent Bi₂Se₃ sublimation. During the sublimation, grooves made by probe lithography act as sources of atomic steps: groove depth increases and generates atomic steps that move in the ascending direction away from the source. We used this phenomenon to create self-organized regularly-spaced zigzag atomic steps having 1 nm height on the Bi₂Se₃(0001) surface. The deposition of Bi (up to ~0.01 nm/s) onto the Bi₂Se₃(0001) surface at constant Se flux (up to ~0.1 nm/s) reversed the direction of the step flow, and vdW epitaxy was observed. The deposition of In and Se onto the Bi₂Se₃(0001) surface at ~400°C led to the epitaxial growth of layered In₃Se₂. This vdW heteroepitaxy started with 2D island nucleation and, after 3–5 nm growth, continued with a screw-dislocation-driven formation of 3D islands. Ex situ Raman scattering measurements have shown that the grown 20-nm-thick In₃Se₂ film exhibits vibrational modes that originate from the β-In₃Se₂ crystal phase.

1. Introduction
Since the beginning of the XXI century layered two-dimensional (2D) materials have been promising candidates for use in microelectronics, photonics, and photovoltaics [1], and nanostructures based on 2D metal chalcogenides have proved their outstanding performance as infrared photodetectors [2]. Being bendable, 2D materials are suitable for the creation of flexible heterostructures [3]. To grow high-quality heterostructures and superlattices, molecular beam epitaxy is used [4], but various defects are generated during the growth: point defects [5], twin domain boundaries [6], antiphase boundaries caused substrate’s atomic steps [7]. Therefore, the growth of wafer-scale high-quality films is a fundamental issue of van der Waals (vdW) epitaxy that requires profound investigation of growth mechanism using in situ experimental techniques. In this work, we first show that in situ reflection electron microscopy (REM) can be applied to study the processes on the surface of 2D metal chalcogenides.

2. Experimental details
We used in situ reflection electron microscope (REM, 100 kV accelerating voltage) equipped with two separate evaporators for Se and metal (Bi or In). The purity of commercial Se, Bi, and In was 99.9996%, 99.999%, and 99.9%, respectively. Samples were prepared from Bi₂Se₃ single crystal by cleavage along
(0001) plane into ~0.2 mm slabs using a sharp razor; then the slabs were cut into 8×3 mm pieces. *In situ* REM technique allows observation of reflection high-energy electron diffraction (RHEED) patterns to control surface structure and align electron beam incidence with (1120)-type direction for maximum REM image intensity. The small angle of electron beam incidence makes REM images contracted in a vertical direction by ~50 times. During *in situ* REM experiment, samples were heated resistively by passing a direct electric current. Above 100°C, the samples were exposed to a Se molecular beam (up to ~0.1 nm/s) to avoid noncongruent Bi₂Se₃ sublimation.

Ex *situ* analysis of surface morphology was carried out by atomic force microscopy (AFM, Multimode 8, Bruker). The same equipment was used for the creation of 15–30-nm-deep grooves by probe lithography (figures 1a,b). The crystal phase of obtained In₂Se₃ films was analyzed by ex *situ* Raman scattering measurements (XploRa Plus, Horiba, 532 nm laser).

**Figure 1.** AFM image of Bi₂Se₃ surface: (a) after cleavage, (b) after groove formation by probe lithography, (c) after sublimation. (d) Zoom-in image of the area bordered by a dashed rectangular.

**Figure 2.** REM images of Bi₂Se₃(0001) surface transformations: (a–c) ascending motion of atomic steps during sublimation with 0.022 nm/s rate, (d–f) groove annealing, (g–i) descending step flow during Bi₂Se₃ growth with 3×10⁻⁴ nm/s rate. 1-nm-high atomic steps are marked with black arrows.

3. **Results and discussion**

3.1. **Bi₂Se₃ sublimation**

When exposed to a Se molecular beam, Bi₂Se₃ can be heated above 300°C without degradation of surface composition. Under these conditions, *in situ* REM image shows bright-contrast singular (0001) terraces separated by dark-contrast atomic steps (figure 2a). Figures 2b,c obtained at ~400°C show that the atomic steps move in ascending direction (to the left), which is first observed on Bi₂Se₃ surface by *in situ* REM. We have observed neither change of terrace contrast nor three-dimensional (3D) Bi island nucleation after 30 nm sublimation and conclude thus that Bi₂Se₃ surface does not decompose, and the sublimation is congruent. After *in situ* experiments, the samples were cooled to room temperature while Se deposition stopped around ~200°C. Ex *situ* AFM investigation shows that wide contrast of the atomic steps is caused by their zigzag shape (figure 3a). One can see also 1-nm-deep 2D vacancy islands nucleated on wide terraces that have dimensions greater than Bi adatom diffusion length.

Figure 2d shows a REM image of a groove (vertical line) formed by probe lithography and a dark-contrast impurity particle serving as an immovable reference point. During Bi₂Se₃ sublimation at
~400°C, the groove widens and many 2D vacancy islands nucleate, grow, and coalesce on the terraces (speckled black-and-white contrast marked with a white arrow in figure 2e) analogously to periodic island nucleation observed on a silicon surface during epitaxial growth [8] and etching [9]. After sublimation of 10 Bi₂Se₃ layers, one can see that the groove annealing has formed atomic steps and step bunches aligned along the groove (dark-contrast zigzag lines in figure 2f). The center of the groove is visible in both AFM (figure 1c) and REM (figure 2f) images and acts as a source of atomic steps: groove depth increases, generates new atomic steps that move in the ascending direction away from the source and attach to the step bunches. The ascending motion of the step bunches is accompanied by their decomposition into regularly-spaced 1-nm-high atomic steps at the distance ~50–100 µm from the groove center (figure 1d). We used this phenomenon to create self-organized regular zigzag atomic steps on the Bi₂Se₃(0001) surface.

![Figure 3.](image)

**Figure 3.** (a,b) AFM images of Bi₂Se₃(0001) surface after: (a) sublimation and (b) In₅Se₃ growth. (c) Raman spectra of a 20-nm-thick In₅Se₃ film excited with 532 nm laser.

3.2. Bi₂Se₃ growth

To study vdW epitaxy by *in situ* REM, a patterned Bi₂Se₃(0001) surface was exposed to Se molecular beam (≤0.1 nm/s) and heated to ~400°C. During annealing, lithographically preformed grooves generated atomic steps that moved in ascending direction with a velocity corresponding to ~0.001 nm/s sublimation. After Bi deposition onset (10⁻²–10⁻⁴ nm/s in different experiments), the steps moved in descending direction (to the right in figures 2g–i). During this growth on the Bi₂Se₃(0001) surface, we observed no change in REM contrast of terraces and steps; RHEED pattern remained the same. This authenticates that the layer-by-layer Bi₂Se₃ growth visualized first by *in situ* REM is epitaxial.

3.3. In₅Se₃ growth on Bi₂Se₃

In₅Se₃ can be used for the development of solar cells, broadband photodetectors, and storage devices [10]. Despite recent successful implementation of wafer-scale growth of few-nm-thick β-In₅Se₃ films on sapphire, vdW heteroepitaxy of thicker In₅Se₃ films and other layered 2D materials on different substrates suffers from transition to spiral growth induced by screw dislocations that strongly affect films’ optical [11] and electronic properties [12].

To study vdW heteroepitaxy, we carried out *in situ* REM experiments similar to the one described in Section 3.2 but used In evaporator instead of the Bi one. When In was deposited onto Se-exposed (≤0.1 nm/s) Bi₂Se₃(0001) surface sublimating with ~0.0015 nm/s rate, film growth started with 2D island nucleation. The 2D islands grew and coalesced after 40 s film growth, which was accompanied by a significant decrease in the intensity of streaky RHEED reflections and corresponded to layer-by-layer In₅Se₃ growth with a ~0.025 nm/s rate. However, after 3–5 nm growth, 3D island nucleation was observed in REM images and RHEED patterns. *Ex situ* surface morphology investigation of a 20-nm-thick film revealed that the growth of each 3D island is induced by one or several screw dislocations (figure 3b). *Ex situ* Raman spectra of the grown In₅Se₃ film reveal a set of vibrational modes which are typical for the β-In₅Se₃ crystal phase. These *in situ* REM observations agree with Ref. [10], in which authors concluded that β-In₅Se₃ film “growth occurs mainly in a layer-by-layer mode from the first layers, evolving to spiral growth for thicker layers.”
4. Conclusions
We have first visualized morphological transformations of the Bi$_2$Se$_3$(0001) surface by in situ REM during sublimation and vdW epitaxy. When Bi$_2$Se$_3$(0001) surface is exposed to Se molecular beam and heated to ~400°C, congruent sublimation triggers ascending motion of atomic steps. During the sublimation, 15–30 nm deep grooves preformed by probe lithography increase in depth and lateral dimensions and act as sources of atomic steps having 1 nm height on the Bi$_2$Se$_3$(0001) surface. Simultaneous deposition of Se and metal (Bi or In) at ~400°C induces vdW growth, and in situ REM shows that the Bi$_2$Se$_3$ homoepitaxy with rates up to ~0.01 nm/s proceeds via descending step flow. The growth of layered β-In$_2$Se$_3$ on the Bi$_2$Se$_3$(0001) surface with a 0.025 nm/s rate started with 2D island nucleation and, after ~5 nm growth, continued with the formation of 3D islands. These results show that in situ REM technique can be applied to study real-time surface dynamics of the layered 2D materials during sublimation, adsorption, and vdW epitaxy.

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