Atomically thin transition metal halides grown on metal substrates

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1. Introduction

Atomically thin 2D materials are characterized by a strong covalent bonding in the layers and a weak interlayer interaction. By limiting the symmetry, the electrical, optical and magnetic properties of the 2D materials differ from their 3D counterpart. There has been a great interest in 2D materials beyond graphene. Two dimensional compounds (MXenes, oxides, nitrides and chalcogenides) have been reported in succession. A novel class of 2D materials, transition metal halides, have recently been synthesised **[1]**. These are characterised by a magnetic ground state even in the monolayer limit and thus provide a fertile platform for exploring low-dimensional magnetism and developing novel spintronic devices. Therefore an understanding of the epitaxial growth of this class of materials is advantageous. Here, using frequency-modulated scanning force microscopy in non-contact mode combined with Kelvin probe microscopy, we investigate different phases and layer thicknesses down to the one monolayer thickness. All experiments were performed in a home-built low-temperature AFM (EMPA, Dübendorf). For more details see REF **[2]**.

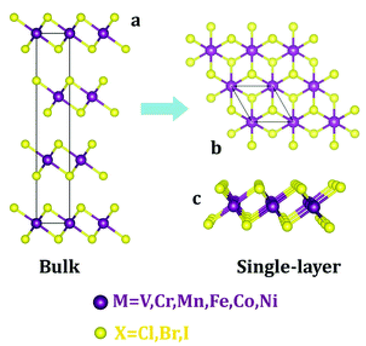

Fig.1: Illustration of the trigonal structure of MX_2 at 300 K **[3]**

2. Growth of $NiBr_2$ on Au(111)

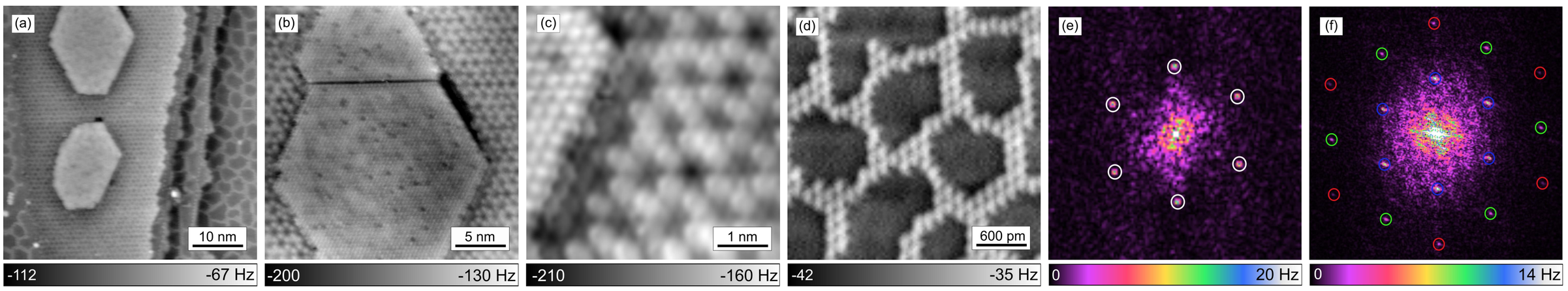

Fig.2: First flexural mode resonance frequency shift data recorded at constant tunnelling current. (a) I_t = 10 pA, V_{bias} = 1000 mV (b) I_t = 120 pA, V_{bias} = 300 mV (c) I_t = 450 pA, V_{bias} = 260 mV (e) 2D FFT of $NiBr_2$ (f) 2D FFT of buffer layer.(a)-(f): Pt coated Si cantilever, A_{1st} = 3 nm, f_{res} = 294.46 kHz, Q = 30000, c = 40 N/m, T = 6.3 K

- co-existence of different phases
- 1 ML $NiBr_2$ growing on a buffer layer
- ML height. 195 ± 10 pm

- Buffer layer: (**Fig. 1 (b) and (c)**)
  - unknown stoichiometry ($NiBr_{2-x}$)
  - lattice constant: 1.2 nm

- Br-Mesh: (**Fig. 1 (d)**)
  - pattern with hexagonal-like symmetry
  - quasi periodicity of 3.5 nm

- 2D FFT: (**Fig. 1 (e)-(f)**)
  - (e) $NiBr_2$
  - (f) $NiBr_{2-x}$

3. Atomic Structure of $NiBr_2$

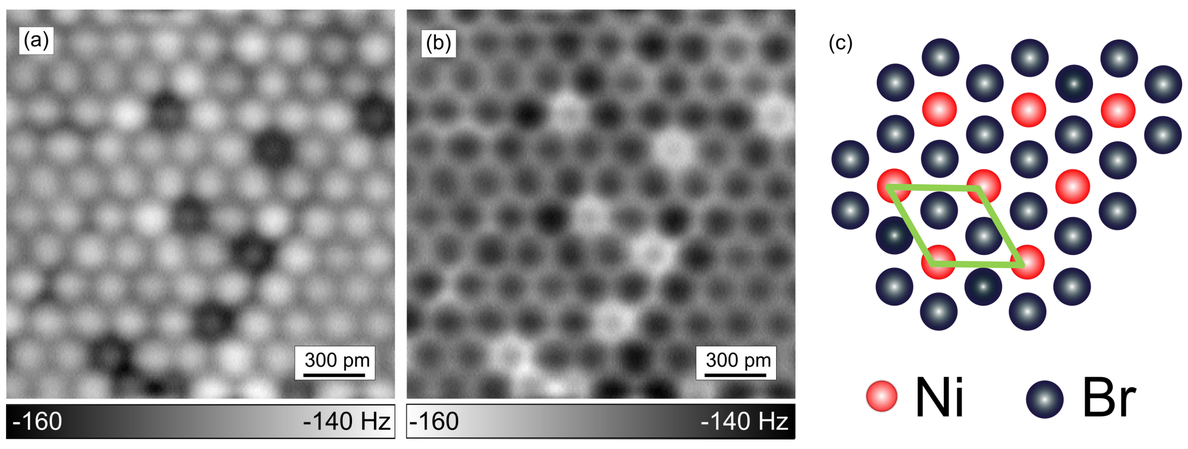

Fig.3: First flexural mode resonance frequency shift data recorded at constant tunnelling current.(a) and (b): Pt coated Si cantilever, I_t = 50 pA, V_{bias} = 200 mV, A_{1st} = 3 nm, f_{res} = 283.9 kHz, c = 40 N/m Q = 30000, T = 6.3 K. The green parallelogram in (c) indicates the unit cell. Fig. 3 (b) is the inverted image of Fig. 3 (a).

- Mesured lattice constants $|\overrightarrow{a_1}| = |\overrightarrow{a_2}| = 3.8 \pm 0.05$ Å
  - Slightly larger then the prediction from theory $|\vec{a}_{DFT}|$ = 3.61 Å [2]
- Lattice shows triangular symmetry (compare **Fig. 2 (e)**)
- Ni atoms are seen as protrusion in (a) and as depression in (b)

4. Kelvin Probe Force Microscopy

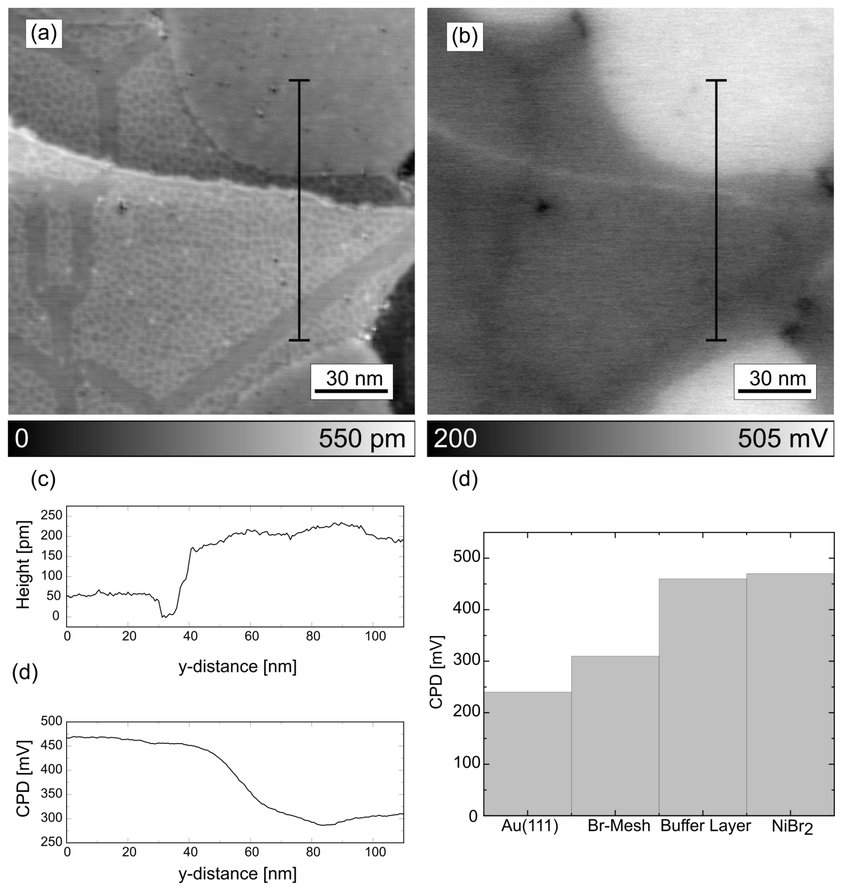

Fig.4: Data measured with a Pt coated Si cantilever in FM-AFM mode on the first flexural resonance. (a) topography image and (b) FM-KPFM signal (first side band detection). Δf = -10 Hz, A_{1st} = 6 nm, f_{ac} = 450 Hz, V_{ac} = 250 mV f_{res} = 283.9 kHz, Q = 30000, c = 40 N/m, T = 6.3 K

- $NiBr_2$ shows a layer-dependent work function
  → charge transfer between $NiBr_2$ and Au(111)

5. Conclusion

- Two structures are formed: $NiBr_2$, $NiBr_{2-x}$
- 1st $NiBr_2$ layer grows on a buffer layer
- CPD between the buffer layer and $NiBr_2$ of 10 mV suggest a similar stoichiometry, i.e. $NiBr_{2-x}$
- Residual Br atoms forming hexagonal-like network

References: **[1]** Bikaljević, D., *et al.* , ACS Nano **15**, 14985 (2021) **[2]** Liu, H., *et al., Beilstein Journal of Nanotechnology* **13**, 1120 (2022) **[3]** Kulish, V. V., *et al.*, J. Mater. Chem. C. **5**, 8734 (2017)