Epitaxial growth and surface studies of Bi/ hexagonal ζ- phase Mn_2N/MgO (001) using molecular beam epitaxy and scanning tunneling microscopy

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Manganese nitride (Mn_xN_y) is known to have several different crystallographic phases, including θ, η, ϵ, and ζ [1] which are classified according to the nitrogen content. The growth and structure of the cubic manganese nitrides, namely $\theta - MnN$, $\eta_\perp - Mn_3N_2$, $\eta_\parallel - Mn_3N_2$ and $\epsilon - Mn_4N$, has already been investigated intensively on MgO (001) substrates [2,3]. However, the hexagonal ζ- Mn_2N has remained unexplored. Thin films of hexagonal ζ- Mn_2N were grown successfully on MgO (001) using molecular beam epitaxy (MBE) and used as a substrate to grow a very thin layer of bismuth.

In this presentation, the epitaxial growth of ζ- Mn_2N and multilayer of bismuth will be discussed. The sample growth process was monitored by *in-situ* reflection high energy electron diffraction. RHEED shows a streaky pattern indicating the smooth sample surface throughout the sample growth. During the Mn_2N growth, 1/4th order fractional streaks are observed along $[100]_{MgO}$ + R30$^{\mathbf{0}}$ direction. These fractional streaks indicate the 4× reconstruction on the Mn_2N surface. The presence of a 4× reconstructed surface is also verified by room temperature scanning tunneling microscopy. Moreover, the RT-STM images show the atomically flat terraces, steps, and the atomic resolution of the hexagonal array of the Mn_2N surface. Various *in-situ* and *ex-situ* measurements are performed to calculate the *in-plane* and *out-of-plane* lattice constants. The calculated lattice parameters are in good agreement with the theoretically reported values of ζ- Mn_2N (a=b= 2.83 Å, c= 4.54 Å) [4]. Furthermore, the surface chemistry of the samples was determined by *in-situ* Auger electron spectroscopy at different locations on the sample surface. The stoichiometric ratio of Mn: N on the film is nearly 2:1 which is consistent with ζ- Mn_2N.

After successfully growing ζ- Mn_2N, a very thin film of Bi is deposited, and the surface is studied by RT-STM. Interestingly, the measurements show multiple steps with height of ~1.6 Å which is not matching the step height of bulk Bi (111) (3.94 Å) [5], but this measured step height is consistent with the step height of bismuthene grown on Ag (111) as reported by Sun *et al.* (2022) [6]. Although the step heights suggest multilayer bismuthene, atomic resolution images show a rectangular lattice. The effort to unravel this mystery will be discussed.

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Supplementary Information

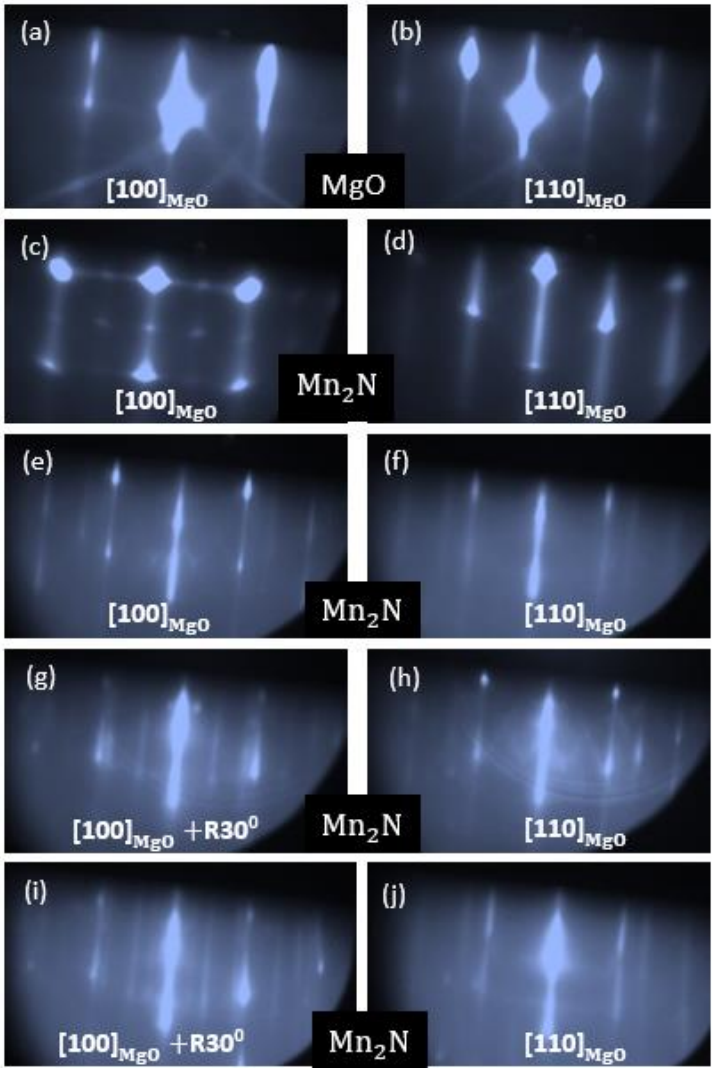

Figure 1: Evolution of RHEED pattern during Mn_2N growth. (a) & (b) MgO (001) after 1 hr. of annealing. (c) & (d) Mn_2N after 1 min. of growth. (e) & (f) Mn_2N after 35 mins. of growth. (g) & (h) After 1 hr. of growth. (i) & (j) Mn_2N at room temperature.

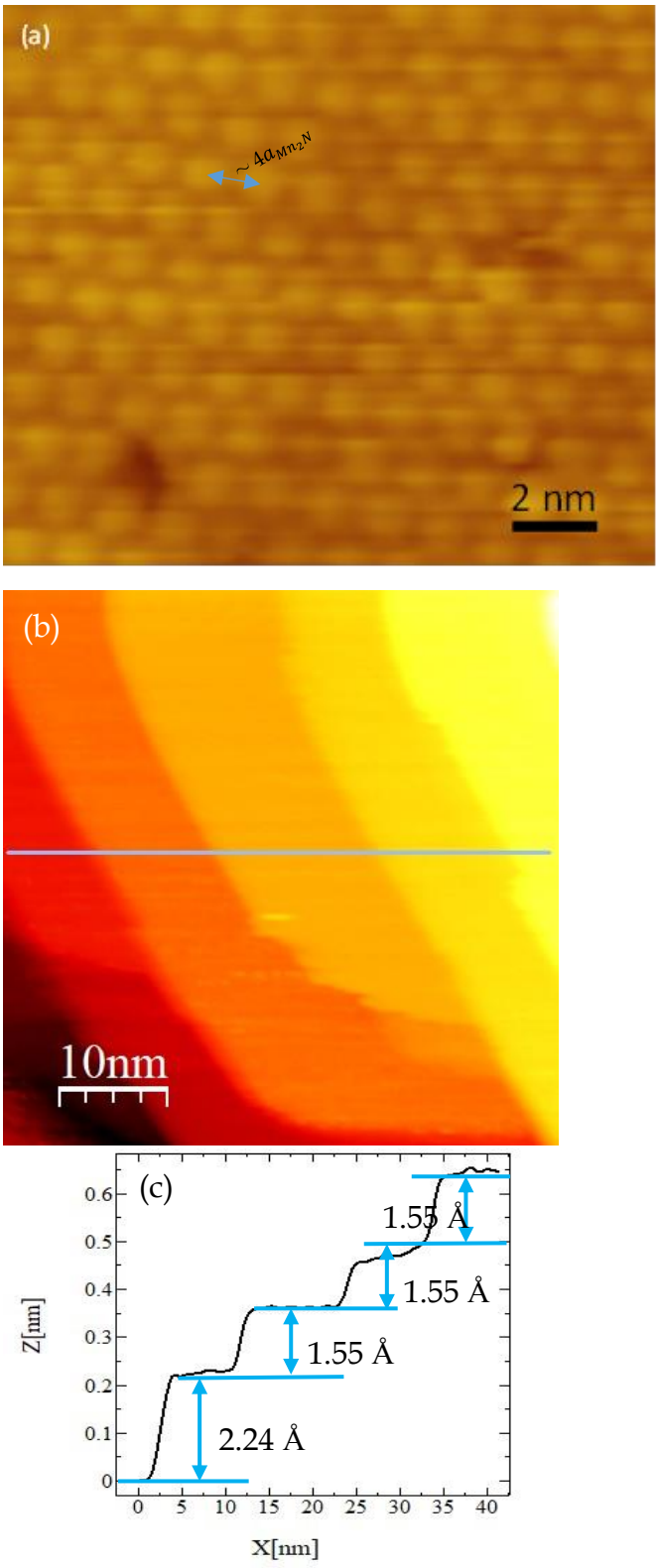

Figure 2: (a) Atomic resolution STM image of Mn_2N showing hexagonal structure. (b) Atomically flat terrace of bismuth on Mn_2N. (c) Line profile along line drawn on (b).