# Controlling Crystal Structure and Oxidation State in Molybdenum Nitrides through Epitaxial Stabilization

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## Supporting Information

ABSTRACT: Epitaxial molybdenum nitride films with different crystal structures and chemical compositions were successfully synthesized by a chemical solution deposition technique. Hexagonal MoN was stabilized on c-cut sapphire  $(Al_2O_3)$  but cubic Mo<sub>2</sub>N on (001) SrTiO<sub>3</sub> even though exactly the same Mo-polymer precursor solution and the processing parameters (such as the annealing temperature and environment) were used. Both X-ray diffraction and high-resolution transmission electron microscopy confirmed the growth of epitaxial molybdenum nitride films with an epitaxial relationship between the film and the substrate as  $(0001)_{MoN} || (0001)_{Al2O3}$  and  $[10\overline{1}0]_{MoN} || [11\overline{2}0]_{Al2O3}$  for MoN on c-cut  $Al_2O_3$  and  $(001)_{Mo2N} || (001)_{STO}$  and  $[111]_{Mo2N} || [111]_{STO}$  for  $Mo_2N$ on SrTiO<sub>3</sub>. The formation of epitaxial molybdenum nitride films with different oxidation states resulted in very different electrical properties: a superconducting transition temperature of 12 K for MoN, whereas it was 4.5 K for Mo<sub>2</sub>N.



# **1. INTRODUCTION**

Molybdenum nitrides have attracted much attention because they provide a wide range of functionalities important for applications in catalysts, tribiological coatings, and diffusion barrier layers in microelectronics.<sup>1-9</sup> Furthermore, this class of materials also shows superconducting properties. Molybdenum nitride can form different crystal structures as well as oxidation states. For example, both  $\gamma$ -Mo<sub>2</sub>N and  $\delta$ -MoN coexist.  $\gamma$ -Mo<sub>2</sub>N crystallizes in a facecentered cubic with randomly distributed nitrogen ions in octahedral sites. It has been reported that  $\gamma$ -Mo<sub>2</sub>N has a superconducting transition temperature around 5 K.3 On the other hand, hexagonal  $\delta$ -MoN crystallizes in a slightly distorted NiAs-type ordered structure under high pressure and has been reported to be superconducting at a temperature of 12 K.<sup>2</sup> A variety of techniques have been used to synthesize molybdenum nitride thin films. For example, both Mo<sub>2</sub>N and MoN films have been deposited by thermal evaporation,<sup>10</sup> magnetron sputtering,<sup>11–13</sup> pulsed laser deposition (PLD),<sup>3,14,15</sup> molecular beam epitaxy (MBE),<sup>16</sup> atomic layer deposition,<sup>17</sup> arc physical vapor deposition (PVD),<sup>18,19</sup> and chemical vapor deposition (CVD).<sup>20,21</sup> However, it is still a challenge to grow molybdenum nitride films with controlled oxidation states and desired superconducting properties. In other words, the phase formation and phase transition of molybdenum nitrides strongly depend on the nitrogen pressure during the

synthetic process and other deposition parameters. For instance, processing parameters such as nitrogen pressure, bias voltage, and the substrate temperature need to be well controlled to grow polycrystalline single phase  $Mo_2N$  and MoN films by either arc PVD or CVD techniques.<sup>18–21</sup> In this Article, we, for the first time in the field, report the growth of epitaxial molybdenum nitride films with both controlled crystal structures and oxidation states using a chemical solution method, a polymer-assisted deposition (PAD).<sup>2</sup> The epitaxial molybdenum nitride films exhibit not only desired crystal structures but also expected superconducting properties.

The detailed PAD process for the growth of metal-oxide films has been described elsewhere.<sup>22,23</sup> The main advantage of the PAD process for epitaxial films is that metal ions can bind to polyethyleneimine (PEI) and/or ethylenediaminetetraacetic acid (EDTA) to form very stable and homogeneous precursor solutions. A wide range of high quality metal-oxide films (both simple and complex metal-oxide films) have been prepared using such a technique. Recently, we have demonstrated that epitaxial metal-nitride films can be grown by PAD.<sup>24-26</sup> We successfully deposited hexagonal GaN films on c-cut Al<sub>2</sub>O<sub>3</sub>

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substrates and cubic TiN and NbN films on  $SrTiO_3$  (STO) substrates.<sup>24–26</sup> It is noted that epitaxial cubic  $Mo_2N$  films have been grown on MgO and sapphire substrates.<sup>10,14,16</sup> However, there is no report on the growth of epitaxial hexagonal MoN films.

## 2. EXPERIMENTAL SECTION

The PAD process is mainly comprised of the following two steps to grow molybdenum nitride films: (1) formation of homogeneous metal polymeric liquid precursors by binding polymer with Mo ions; and (2) thermolysis and ammonolysis of the coated precursor Mo film in flowing ammonia gas to yield the Mo-nitride films. To form Mo-polymer solution, 2 g of EDTA was first dissolved in 40 mL of DI water. Following that, 2 g of ammonium molybdenum oxide  $((NH_4)_6Mo_7O_{24} \cdot 4H_2O)$ was added into this solution. Finally, 2 g of polyethyleneimine was added into the solution. The final solution was well mixed until a homogeneous solution was obtained. After Amicon filtration, the final concentration of Mo of 0.376 M was determined by using a Varian Liberty 220 inductively coupled plasmaatomic emission spectrometer (ICP-AES). The solution was spin-coated on both c-cut Al<sub>2</sub>O<sub>3</sub> and (001) STO substrates at 2000 rpm for 30 s. The films were then heated in ammonia gas at 510 °C for 2 h with a ramping rate of 1 °C/min and then annealed in ammonia gas at 950 °C for 2 h with a ramping rate of 10 °C/min. Films with a thickness in the range of 35-45 nm were obtained from one spin-coat. Thicker films could be deposited by multiple spin-coats. X-ray diffraction (XRD) was used to characterize the crystal structure of the films. The microstructure of the films was analyzed by transmission electron microscopy (TEM). The surface morphology and surface roughness of the films were analyzed by atomic force microscopy (AFM). The electrical resistivity ( $\rho$ ) of the films as a function of temperature (2-300 K) was measured using a standard fourprobe technique by a Quantum Design Physical Properties Measurement System (PPMS).

# 3. RESULTS AND DISCUSSION

We have found that heteroepitaxial stabilization can be effectively used to control the oxidation states and crystal structures of Mo-nitride materials. The formation of different crystal structures and oxidation states of molybdenum nitride films is confirmed by the X-ray diffraction (XRD) analysis. Figure 1 shows the XRD  $\theta$ -2 $\theta$  and  $\phi$ -scans of molybdenum nitride films on either c-cut Al<sub>2</sub>O<sub>3</sub> or STO substrates. As can be seen from the  $\theta - 2\theta$  scan shown in Figure 1a (also see Figure S1, XRD  $\theta$ -2 $\theta$  logarithmic scale, Supporting Information), only (0002) and (0004) peaks from hexagonal MoN are detected for the film on  $Al_2O_3$ . On the other hand, only the (002) peak (see Figure 1c) from cubic  $Mo_2N$  is visible for the film on STO. The appearance of only (00l) or (000l) peaks indicates that both Mo<sub>2</sub>N and MoN films are preferentially oriented along the *c*-axis perpendicular to the substrate surface. It is apparent that two different crystal structures have been formed even though exactly the same Mo-precursor solution and the same processing parameters were used. The in-plane orientation between the film and the substrate was determined by XRD  $\phi$ -scans from  $(02\overline{2}2)$  MoN and  $(10\overline{1}4)$  Al<sub>2</sub>O<sub>3</sub> for the MoN on c-cut Al<sub>2</sub>O<sub>3</sub> or (111) Mo<sub>2</sub>N and (111) STO for the Mo<sub>2</sub>N film on STO substrate. As shown in Figure 1b, six peaks from MoN shifted  $30^{\circ}$  relative to the Al<sub>2</sub>O<sub>3</sub> indicate an in-plane rotation between the film and the substrate. This further indicates that the film is of



**Figure 1.** XRD patterns: (a)  $\theta - 2\theta$  scan of hexagonal MoN film on Al<sub>2</sub>O<sub>3</sub> substrate; (b)  $\phi$ -scans from (0222) reflection of MoN and (1014) reflection of Al<sub>2</sub>O<sub>3</sub>; (c)  $\theta - 2\theta$  scan of cubic Mo<sub>2</sub>N film on STO substrate; and (d)  $\phi$ -scans from (111) reflection of Mo<sub>2</sub>N and (111) reflection of STO.

hexagonal structure and well aligned in-plane with respect to the substrate. On the other hand, as shown in Figure 1d, four peaks 90° apart in the  $\phi$ -scans indicate the 4-fold symmetry of the cubic Mo<sub>2</sub>N film on the STO substrate. An average full width at half-maximum (fwhm) value of 1.2° deduced from the six  $\phi$ -scan peaks for hexagonal MoN film and 2.5° for the cubic Mo<sub>2</sub>N film averaged from the four  $\phi$ -scan peaks, in comparison with a value of 0.5° for the single-crystal substrates, indicates both hexagonal MoN and cubic Mo<sub>2</sub>N films having good epitaxial quality.

The heteroepitaxial relationships between cubic Mo<sub>2</sub>N and STO, based on Figure 1c and d, can be described as  $(001)_{Mo2N-}$  $||(001)_{STO}$  and  $[111]_{Mo2N}||[111]_{STO}$ , similar to cubic TiN and NbN films on STO previously reported.<sup>25,26</sup> Such epitaxial relationships can be easily understood by considering the crystal structure and the basal plane lattice parameters of Mo<sub>2</sub>N and STO. From the (002) and (111) diffraction peaks of Mo<sub>2</sub>N, the lattice parameter of the epitaxial cubic  $Mo_2N$  can be determined to be a =4.07 Å. As compared to the lattice parameter of bulk  $Mo_2N$  (*a* = 4.16 Å), a compressive strain (STO: a = 3.9 Å) makes the lattice parameter of the Mo<sub>2</sub>N slightly smaller. On the other hand, the inplane lattice parameter of the epitaxial hexagonal MoN was a =5.715 Å, very close to the bulk MoN of a = 5.72 Å. A 30° rotation with respect to the Al<sub>2</sub>O<sub>3</sub> substrate is anticipated for hexagonal MoN by considering the lattice mismatch between MoN and the substrate. Such an in-plane rotation gives a lattice mismatch of around 4% ( $a_{\text{film}} = 5.715 \text{ Å}$ ,  $a_{\text{sub}} = 4.76 \text{ Å}$ , and the lattice mismatch =  $(3a_{\rm film} - 2\sqrt{3}a_{\rm sub})/2\sqrt{3}a_{\rm sub})$ . The heteroepitaxial relationships between hexagonal MoN and Al<sub>2</sub>O<sub>3</sub> can be described as  $(0001)_{MoN} || (0001)_{Al2O3}$  and  $[10\overline{1}0]_{MoN} || [11\overline{2}0]_{Al2O3}$  based on Figure 1a and b.

Both films are dense and smooth with no detectable microcracks (Figure S2, Supporting Information). The root-meansquare (rms) surface roughness was about 3 and 5 nm for MoN and  $Mo_2N$  films, respectively. Figure 2a and b shows the crosssectional high-resolution TEM (HRTEM) images of a hexagonal MoN film on  $Al_2O_3$  and a cubic  $Mo_2N$  film on STO. The epitaxial relationship between the film and the substrate deduced



Figure 2. Cross-sectional high-resolution transmission electron microscopy (HRTEM) images and fast Fourier transferred (FFT) diffraction patterns from the interface between the hexagonal MoN and the  $Al_2O_3$ and between the cubic  $Mo_2N$  and the STO.

from the corresponding fast Fourier transferred (FFT) diffraction patterns (shown in the inset of Figure 2a and b) is consistent with the XRD analysis. It is noted that the FFT patterns from both films show epitaxial growth of single phase material without any diffraction dots from other phases. However, the interface between the MoN and  $Al_2O_3$  is much sharper than that of the  $Mo_2N$  on STO. There is a large amount of local defects and strain contours in the  $Mo_2N$  film on STO. On the other hand, the MoN film on  $Al_2O_3$  shows much clearer epitaxial lattice without obvious lattice distortion and strain contours.

Figure 3 shows the resistivity versus temperature characteristics of both epitaxial MoN on Al<sub>2</sub>O<sub>3</sub> and Mo<sub>2</sub>N on STO measured by a standard four-probe technique. The superconducting transition temperature  $(T_c)$  is 12 K for hexagonal MoN and 4.5 K for cubic Mo<sub>2</sub>N (see inset in Figure 3). In general, the superconducting transition temperature of metal-nitrides is sensitive to the crystallinity, nitrogen stoichiometry, and oxygen contamination. A transition temperature of 12 K for our epitaxial hexagonal MoN is consistent with the bulk MoN,<sup>2</sup> lower than that (14 K) of MoN prepared or treated under high pressure.<sup>4</sup> A transition temperature of 4.5 K for our epitaxial cubic Mo<sub>2</sub>N is higher than that (2.8-3 K) of epitaxial cubic Mo<sub>2</sub>N film prepared by MBE<sup>16</sup> and slightly lower than that (5.1 K) of the polycrystalline Mo<sub>2</sub>N films prepared by PLD.<sup>3</sup> Our films show metallic resistivity versus temperature behaviors in the normal state with a room temperature resistivity of 10  $\mu\Omega$  cm for MoN and 20  $\mu\Omega$  cm for Mo<sub>2</sub>N. Both the desired superconducting transition temperature and the residual resistivity ratio  $(\rho_{300K}/\rho_{13K} =$ 3.3 for MoN and  $\rho_{300K}/\rho_{10K}$  = 43 for Mo<sub>2</sub>N) indicate the high epitaxial quality of our films prepared by a polymer-assisted deposition with small scattering from intragrain and intergrain.



Figure 3. Temperature dependence of resistivity of (a) hexagonal MoN on  $Al_2O_3$  and (b) cubic  $Mo_2N$  on STO. Inset is the plot of resistivity at low temperature.

We would like to point out that heteroepitaxial stabilization has also been used to control crystal structures and oxidation states of metal oxides.<sup>22,27,28</sup> For example, epitaxial anatase and rutile TiO<sub>2</sub> films can be grown on LaAlO<sub>3</sub> and r-cut Al<sub>2</sub>O<sub>3</sub> substrates, respectively, by either pulsed-laser deposition or polymer-assisted deposition.<sup>22,27</sup> Different oxidation states such as  $UO_2$  and  $U_3O_8$  films have also been grown on LaAlO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> substrates, respectively.<sup>28</sup> Here, for the first time, we demonstrate that the crystal structure and oxidation states of metal nitrides can be stabilized by single crystal substrates as well. It is reasonable to understand that the Mo<sub>2</sub>N films cube-on-cube epitaxially grow on the STO substrates, similar to the cubic TiN and NbN on STO substrates prepared by PAD,<sup>25,26</sup> which is also consistent with the cubic Mo<sub>2</sub>N on the similar structural MgO substrates prepared by MBE.<sup>16</sup> However, it is interesting to find out that hexagonal MoN films were obtained on the c-cut Al<sub>2</sub>O<sub>3</sub> by our chemical solution approach of PAD, instead of the epitaxial cubic  $Mo_2N$  grown on c-cut  $Al_2O_3$  with its (111) planes parallel to the substrate surface by MBE, 16 or cubic NaCl type B1-MoN phase grown on c-cut Al<sub>2</sub>O<sub>3</sub> with its (111) planes parallel to the substrate surface by PLD.<sup>14</sup> By considering the lattice mismatch between the films and the substrates, the cubic Mo<sub>2</sub>N on the c-cut Al<sub>2</sub>O<sub>3</sub> has lattice mismatch of 1.3% ( $a_{\text{film}} =$ 4.07 Å,  $a_{\rm sub}$  = 4.76 Å, and the lattice mismatch =  $(2a_{\rm film}$  –  $\sqrt{3a_{sub}}/\sqrt{3a_{sub}}$ , the B1-MoN on the c-cut Al<sub>2</sub>O<sub>3</sub> has lattice mismatch of 2.1% ( $a_{\text{film}} = 4.21$  Å,  $a_{\text{sub}} = 4.76$  Å, and the lattice mismatch =  $(2a_{\text{film}} - \sqrt{3}a_{\text{sub}})/\sqrt{3}a_{\text{sub}})$ , and the hexagonal MoN on c-cut Al<sub>2</sub>O<sub>3</sub> has lattice mismatch of nearly 4% (see the above XRD discussion), therefore all three phases of molybdenum nitride actually could grow epitaxially on the c-cut Al<sub>2</sub>O<sub>3</sub> substrates. As both the thermodynamics equilibrium and the kinetic diffusion during the process can control the film growth, the solution approach offers unique bottom-up growth to obtain

hexagonal-on-hexagonal epitaxial growth in our case, but the PLD or MBE offers top-down cubic-on-hexagonal epitaxial growth.

#### 4. CONCLUSIONS

In summary, we have successfully prepared both hexagonal MoN and cubic  $Mo_2N$  by a simple chemical solution deposition technique. We have demonstrated that heteroepitaxial stabilization can be used to control the oxidation states and crystal structures of Mo-nitride materials, which lead to excellent superconducting properties of the films.

# ASSOCIATED CONTENT

**Supporting Information.** XRD  $\theta - 2\theta$  logarithmic scale and AFM images for the MoN and Mo<sub>2</sub>N films. This material is available free of charge via the Internet at http://pubs.acs.org.

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