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Epitaxial Superconducting δ-MoN Films Grown by a Chemical Solution Method

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ABSTRACT: The synthesis of pure δ-MoN with desired superconducting properties usually requires extreme conditions, such as high temperature and high pressure, which hinders its fundamental studies and applications. Herein, by using a chemical solution method, epitaxial δ-MoN thin films have been grown on *c*-cut Al_2O_3 substrates at a temperature lower than 900 °C and an ambient pressure. The films are phase pure and show a T_c of 13.0 K with a sharp transition. In addition, the films show a high critical field and excellent current carrying capabilities, which further prove the superior quality of these chemically prepared epitaxial thin films.

The superior mechanical strength and durability[1] as well as the great catalytic activity[2] of transition-metal nitrides over many traditionally used metallic elements and/or metal oxides have made metal nitrides very attractive for a wide range of technological applications. Furthermore, the diverse transport properties (such as semiconducting, magnetic, metallic, and superconducting properties)[3,4] of this class of materials also make metal nitrides the choice for the fundamental understanding of multifunctionalities in extreme conditions, such as low temperature and high pressure. For instance, molybdenum nitrides have attracted broad interests due to their superconductivity.[3,5,6] Molybdenum nitrides can crystallize in different crystal structures including γ-Mo_2N (cubic),[7] β-Mo_2N (tetragonal),[8] and δ-MoN (hexagonal).[9,10] Among those phases, hexagonal δ-MoN shows the highest superconducting transition temperature (T_c), which is reported to be around 12 K, even though a higher T_c has been theoretically predicted for the cubic B_1-MoN.[11] To synthesize pure δ-MoN with desired superconducting properties, extreme conditions, such as high pressure (up to several GPa) and high temperature (above 1000 °C), are usually required.[5,10] Such processing conditions hinder the studies and applications of δ-MoN materials. Up to now, very few studies reported the synthesis of a pure δ-MoN phase with T_c above 12 K, especially in the thin film format. Accordingly, its important superconducting properties have been rarely studied. A versatile technique to synthesize high-quality δ-MoN thin films with desired superconducting properties is in great demand for exploring the fundamental properties and the potential applications of superconducting MoN.

Here, we report the deposition of epitaxial δ-MoN thin films with excellent superconducting properties by a chemical solution approach, polymer-assisted deposition (PAD),[12] at a temperature lower than 900 °C and under an ambient pressure. To the best of our knowledge, this is the first report on the epitaxial growth of superconducting δ-MoN films by a chemical solution technique. The successful growth of epitaxial MoN thin films by a controllable and reproducible route enables us to investigate the intrinsic superconducting properties of epitaxial MoN films, which is a significant step toward the applications of superconducting MoN films.

Epitaxial δ-MoN films were grown on *c*-cut sapphire (Al_2O_3) substrates by a chemical solution deposition or PAD. The Mo precursor solution used in this work was prepared by dissolving 2.6 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 15.0 mL of H_2O, then mixing with 4.0 g of ethylenediaminetetraacetic acid (EDTA) and 3.5 g of poly-ethyleneimine (PEI) followed by ultrafiltration. The precursor was spun coated on *c*-cut sapphire substrate at 3000 rpm for 30 s. Then the film was annealed at 890 °C for 2 h in flowing NH_3 gas at an ambient pressure to get the superconducting δ-MoN films. The film thickness is 40 nm, which can be tuned by varying the spin speed and the number of coatings. In comparison, a much higher processing temperature has to be used to prepare superconducting δ-MoN in other methods. For example, δ-MoN films were synthesized at a pressure of 6 GPa and a temperature of 1500 °C[5] or at 10 GPa and 1027 °C.[10]

The water-soluble polymer, PEI, used in the PAD process plays crucial roles for getting high-quality films. It controls the viscosity of the solution and, more importantly, binds the metal ions to form a homogeneous solution and to prevent premature precipitation of metal ions. Besides, the use of a single crystal substrate with crystalline structure similar to the structure of the film allows the heteroepitaxial stabilization of desired phases without the utilization of extreme conditions.

The epitaxial growth of δ-MoN on *c*-cut Al_2O_3 has been confirmed by X-ray diffraction (XRD) analysis. As shown in

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Figure 1a, the presence of only (000*l*) peaks from δ-MoN indicates that the film is preferentially oriented along the *c*-axis perpendicular to the substrate surface. No detectable diffraction from other molybdenum nitrides suggests the formation of highly pure δ-MoN. A value of 0.23° for the full width at half-maximum (fwhm) of the (0002) rocking curve (inset of Figure 1a) indicates the high crystalline quality of the thin film. The in-plane alignment of the MoN on Al_2O_3 is confirmed by the scans of (20−22) MoN and (11−26) Al_2O_3. As shown in Figure 1b, six peaks with 60° apart confirm the formation of hexagonal δ-MoN. The epitaxial relationships between the δ-MoN and the substrate are determined to be (0001)MoN||(0001)Al_2O_3 and [20−22]MoN||[11−26]Al_2O_3. The lattice parameters of δ-MoN film, calculated from the (0004) and (20−22) diffraction peaks, are a = 0.5716 nm and c = 0.5617 nm. Compared with those of bulk δ-MoN (a = 0.5725 nm and c = 5.6080 nm), the in-plane lattice parameters of the film are slightly smaller, which is consistent with the fact that the δ-MoN film is under compressive strain in-plane.

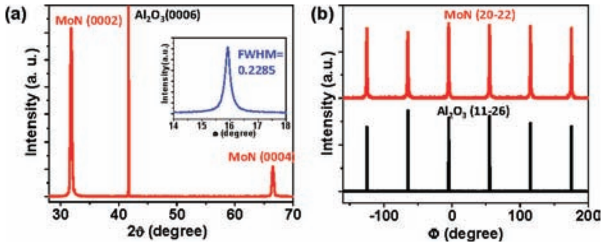

Figure 1. XRD patterns of δ-MoN film on *c*-cut sapphire (Al_2O_3). (a) θ-2θ scan. The inset in (a) is the rocking curve of (0002) MoN. (b) ϕ scans of (20−22) MoN and (11−26) Al_2O_3.

The microstructure of the δ-MoN film on Al_2O_3 was investigated by cross-sectional transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). As shown in Figure 2, the interface between the film and the substrate is well-defined. The distinct lattice demonstrates the high epitaxial quality of the δ-MoN on Al_2O_3. The corresponding selected area electron diffraction (SAED) pattern confirms the epitaxial growth of δ-MoN on the substrate. The epitaxial relationships between δ-MoN and the Al_2O_3 determined from the SAED patterns and the HRTEM are consistent with the above XRD results, i.e., (0001)MoN||(0001)Al_2O_3 and (22−40)MoN||(30−30)Al_2O_3. Besides, we have also investigated the surface morphology and the surface roughness of the epitaxial MoN film by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The δ-MoN film is dense and smooth with no detectable microcracks. The root-mean-square (rms) surface roughness for a 40 nm thick film, measured from a 4 μm × 4 μm area, is 3.8 nm.

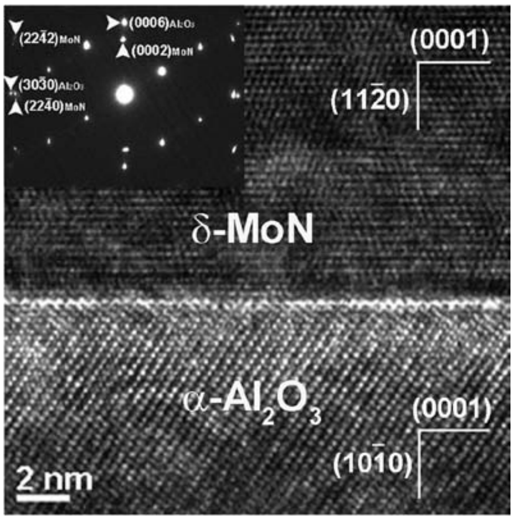

Figure 2. HRTEM taken from the interface between the δ-MoN film and the substrate. Inset shows the corresponding SAED pattern.

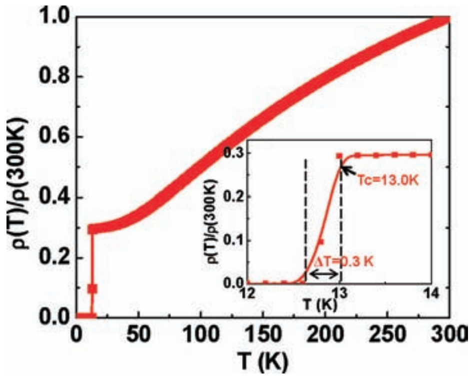

Figure 3. Normalized resistivity as a function of temperature for an epitaxial δ-MoN film on a sapphire substrate. Inset shows the corresponding magnified plot near the transition with a transition width (ΔT) of 0.3 K.

The epitaxial δ-MoN thin films exhibit excellent superconducting properties. Figure 3 shows the temperature dependence of normalized resistivity of a typical MoN film on Al_2O_3 substrate. The epitaxial MoN film shows a characteristic metallic-like resistivity vs temperature above the superconducting transition. As shown in the inset of Figure 3, the onset of the superconductivity takes place at a transition temperature (T_c) of 13.0 K (at which the resistance decreases by 10%). The midpoint of the superconducting transition (at which the resistance decreases by 50%) is 12.85 K, and the transition width, ΔT_c, is less than 0.3 K (between 10 and 90% of the transition). To the best of our knowledge, the highest reported T_c of bulk δ-MoN is 15.1 K with a transition width of 1.9 K,[5] which was measured for samples prepared under high-temperature and high-pressure conditions (about 1500 °C, 6 GPa). Such a sharp transition of our epitaxial film indicates the high purity and high epitaxial quality of the δ-MoN phase, as the existence of other phases, such as β-Mo_2N and γ-Mo_2N, and low angle grain boundaries could broaden the transitions.[13] It has been suggested that high-pressure annealing can promote the formation of ordered δ-MoN structure which leads to improved T_c. Our results suggest that single phase δ-MoN can be stabilized through heteroepitaxial growth. It should be noted that β-Mo_2N, γ-Mo_2N and B_1-MoN phases have been synthesized on single-crystal substrates by physical vapor deposition.[7,8,14] Single phase δ-MoN films have also been prepared through a three-step process, which includes deposition, purification, and nitridizing of Mo films.[15] However, there is no report on epitaxial δ-MoN films based on a chemical solution deposition technique, especially with a processing temperature under 900 °C. In our study, the combination of the novel chemical solution method and the use of single crystal substrate contribute to the formation of high-quality epitaxial δ-MoN films with desired superconducting properties.

The upper critical field (H_{c2}, the field at which a superconductor becomes normal) and the irreversibility field (H_{irr}, the field at which a superconductor ceases to carry supercurrent) are important parameters for high-field applications of superconductors. The superconducting transition of the δ-MoN film was measured as a function of magnetic fields (Figure 4a). H_{c2} and H_{irr} were determined by the following criteria: H_{c2} and H_{irr} are the fields at which resistance (R) is 90 and 10% of the normal state resistance (R_0) right above the transition temperature, respectively. The inset of Figure 4a shows the temperature (T) dependence of H_{c2} and H_{irr}. The values of the H_{c2} and H_{irr} are 6.0 and 5.0 T, respectively, at liquid helium temperature (4.2 K). The H_{c2} of our as-grown epitaxial MoN film is higher than a value of around 4 T for the film prepared by a three-step process.[15]

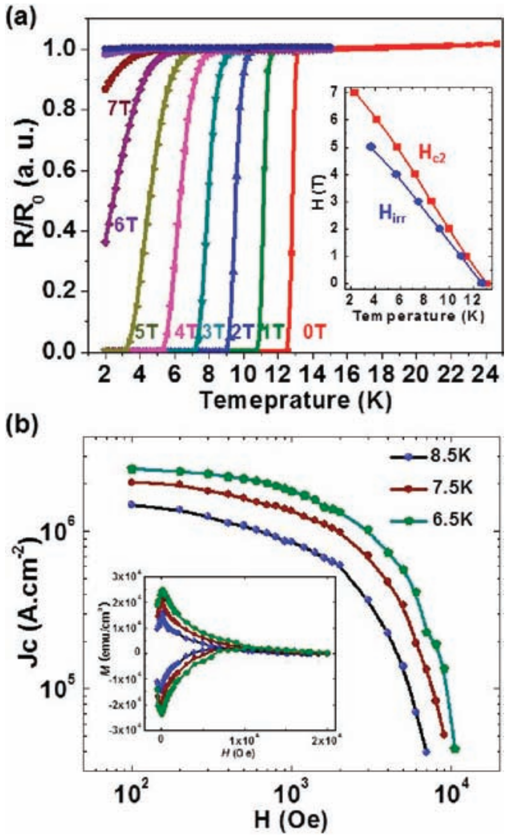

Figure 4. (a) Temperature dependence of normalized resistance under magnetic fields from 0 to 9 T applied perpendicular to the substrate of an epitaxial δ-MoN film on a sapphire substrate. Inset shows upper critical field (H_{c2}) and irreversibility field (H_{irr}) vs temperature curves. (b) Log−log plots of critical current density (J_c) vs applied magnetic field (H) of the film measured by a magnetization method at 6.5, 7.5, and 8.5 K. Inset shows isothermal M vs H curves at 6.5, 7.5, and 8.5 K.

The δ-MoN thin film also shows excellent current carrying capabilities. The irreversible magnetization $M(H)$ was measured in a commercial superconducting quantum interference device (SQUID) magnetometer and used to calculate $J_c(H,T)$ according the Bean critical state model.[16] Figure 4b is a log−log plot of the critical current density (J_c) vs applied magnetic field (H) measured at 6.5, 7.5, and 8.5 K, where the J_c is deduced from the isothermal magnetization vs applied magnetic field (M vs H) curves (inset of Figure 4b). As can be seen from the plots, the film has a J_c value of 2.5, 2.1, and 1.5 × 10^6 A/cm^2 at 6.5, 7.5, and 8.5 K, respectively, under a field of 100 Oe. There are very limited reports on the J_c of δ-MoN. Early work reported a J_c value of 10^5 A/cm^2 at 4.2 K from a δ-MoN-rich film under zero magnetic field.[17]

In summary, high-quality epitaxial δ-MoN thin films have been synthesized for the first time by a polymer-assisted deposition process. The formation of epitaxial and single phase δ-MoN on c-cut Al_2O_3 has been confirmed by both XRD and TEM. The δ-MoN film shows excellent superconducting properties. including a transition temperature of 13.0 K, a transition width of 0.3 K, a H_{c2} of 6.0 T, a H_{irr} of 5.0 T at 4.2 K, and a J_c of 2.5 × 10^6 A/cm^2 at 6.5 K under a field of 100 Oe. Further studies on the fundamental physical properties of δ-MoN film are underway. The reported simple and low-cost chemical solution method enables widely fundamental investigation and industrial applications of superconducting MoN films.

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