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# Epitaxial Ternary Nitride Thin Films Prepared by a Chemical Solution Method

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Nitrides have been known to exhibit a number of important properties such as superconductivity, catalytic activity, unusual magnetic properties, and high hardness and mechanical strength.[1-7] Many studies have been focused on binary nitrides. Binary nitride and some mixed nitride films such as (Ti,Zr)N, (Ti,Nb)N, and (Zr,Nb)N have been prepared by physical or chemical vapor deposition.[8,9] Since the 1990s, ternary nitrides have attracted more attention. One of the commonly studied ternary nitride systems is $AMN_2$ (A = alkali metal, alkaline earth metal, or transition metal, and M = transition metal or lanthanide).[10-15] Two methods have been used to prepare these materials in bulk: a standard high temperature "ceramic method" by ammonolysis of oxides or binary nitrides, and the growth of submillimeter crystals from reactions containing molten metals as flux.[3,4] The development of a versatile technique for thin film deposition of ternary nitrides enables a wider range of technological applications. To the best of our knowledge, there is no report on the growth of epitaxial ternary nitride $AMN_2$ thin films. In this communication, we report the growth of epitaxial $SrTiN_2$ (STN) films using a chemical solution approach, polymer-assisted deposition (PAD).[16-18] Chemical solution deposition, where a precursor solution is deposited by spin- or dip-coating onto a single-crystal substrate, has shown many advantages to grow thin films including low costs and simplicity in processing.[19] In the PAD process, the commercially available water soluble polymer not only controls the desired viscosity, but also binds the metal ions to prevent premature precipitation and to form a homogeneous solution.[18]

To form epitaxial nitride films, we started with a homogeneous metal polymeric liquid precursor by binding polymer with metal ions. The precursor films were then thermally treated in ammonia gas to yield the metal nitride films. Briefly, the precursor for epitaxial STN films was a mixture of two separate Sr and Ti-polymer solutions. Sr binds to polyethyleneimine (PEI) polymer as an ethylenediaminetetraacetic acid (EDTA) complex. Ti binds to carboxylated- polyethyleneimine (PEIC).[17] (see Supporting Information for details). The precursor solution was spin-coated onto (001) $LaAlO_3$ (LAO) substrates at 2000 rpm for 30 s. The annealing was done in flowing ammonia gas at 1000 °C for 1 h.

As compared to LAO (pseudo cubic with a lattice constant a = 0.379 nm), STN crystallizes in the tetragonal structure with space group of P4/nmm (a = 0.388 nm, c = 0.77 nm).[12] Such a relatively small lattice mismatch makes it possible for STN films to grow epitaxially on LAO substrates. Figure 1 shows the X-ray diffraction (XRD) results from the θ-2θ scan and ϕ–scans for a STN film on LAO substrate. The presence of only the (004) peak from tetragonal STN indicates that the film is preferentially

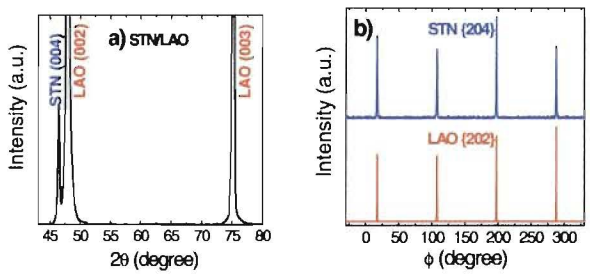


***Figure 1.*** XRD patterns: (a) θ-2θ scan of a STN film on LAO; (b) ϕ-scans from (204) reflection of STN and (202) reflection of LAO.

oriented along the *c*-axis perpendicular to the substrate surface. It is noted that no detectable peaks from binary nitrides were observed in the XRD patterns. The in-plane orientation between the film and substrate was determined by XRD ϕ-scans from the (204) of STN and (202) of LAO (see Figure 1b). The epitaxial relationships between the film and substrate can be deduced as $(001)_{film}\|(001)_{sub}$ and $[102]_{film}\|[101]_{sub}$ based on XRD θ-2θ and ϕ–scans. An average full width at half-maximum (FWHM) value of 1.1° for STN, as compared to 0.7° of the single crystal substrate, indicates the film to be of good epitaxial quality.

It will be interesting to understand the growth mechanism of nitrides by treating the metal-polymer precursor in ammonia at high temperature. The conversion of the metal-polymer precursor to nitrides is proposed to be controlled by the transamination process.[20] It is known that PEI can be completely depolymerized at high temperature when the precursors are treated in different environments.[19] Ammonia can be thermally decomposed to release various gaseous species ($NH_2$, NH, $N_2$, N, $H_2$ and H) at temperatures higher than 600 °C.[20,21] In our PAD process, it is likely that the amine groups from ammonia decomposition replace the polymer to bind metals at high temperature through the transamination process.

The surface morphology and surface roughness of the films were investigated by both scanning electron microscopy (SEM) and atomic force microscopy (AFM). All the films are dense and smooth with no detectable micro-cracks (Figure S1). An AFM phase image of an STN film grown on LAO (Figure S2) indicates that the film has a root mean square (rms) surface roughness of about 6 nm. Figure 2 shows the cross-section high resolution transmission electron microscopy (HRTEM) images of a STN film on a LAO substrate. The STN film thickness is about 35 nm. It is clear that the interface between the nitride film and the substrate is clean. The corresponding selected area electron

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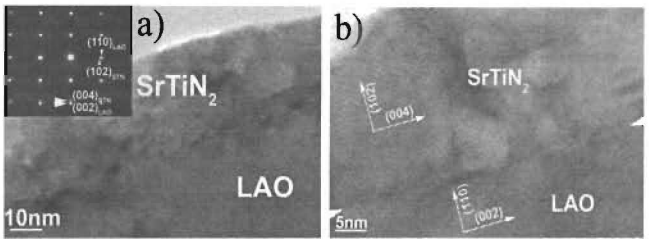


***Figure 2.*** (a) A bright-field cross-section TEM image of a STN film on a LAO substrate. The inset shows the corresponding SAED pattern; (b) HRTEM image taken from the interface between STN and LAO.

diffraction (SAED) pattern taken from the interface (see insert in Figure 2a) confirms the epitaxial growth of tetragonal STN film on LAO, evidenced by the distinct diffraction dots from the film and the substrate. The epitaxial relationships between the film and the substrate deduced from the SAED pattern are consistent with the XRD results.

First principle calculations predict that STN would show metallic and paramagnetic behavior.[12] Our ability to fabricate epitaxial STN films allowed us to investigate their physical properties. As shown in Figure 3, the STN film is conductive with a room temperature resistivity of around $4.7\times10^{-4}$ Ω·cm measured by a four-probe technique. Different from the first principle calculations, our epitaxial films show semiconductive resistivity vs temperature behavior, although the resistivity shows very weak temperature dependence in the range of 300 K to 50 K. Scattering from grain boundaries and carbon or oxygen contamination at the grain boundaries in the STN films can all contribute to such effect, even though the XRD analysis has not revealed any detectable other phases. It should be noted that the STN powder prepared by the solid-state reaction did show the metallic behavior from 77 K to 300 K; however, the STN powder contained 30 wt% Sr and SrO as impurities.[12]

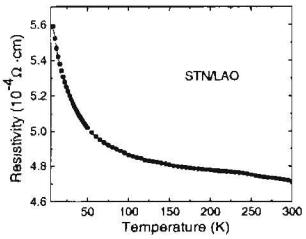


***Figure 3.*** Temperature dependence of resistivity of a STN film on LAO.

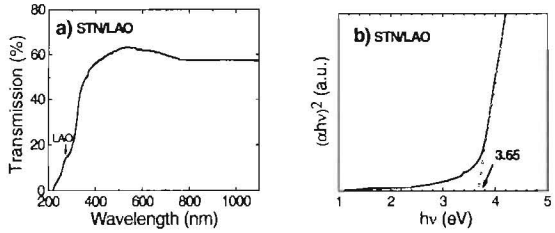


***Figure 4.*** (a) Optical transmission spectrum of STN film on LAO; (b) $(\alpha h\nu)^2$ versus $h\nu$ plot for the determination of optical gaps of STN film on LAO, where α is the absorption coefficient and $h\nu$ is the photon energy.

Figure 4a shows the optical transmission characteristics of a 35 nm thick STN film on LAO. The film is transparent, having an optical transmission of around 60 % in the 400-1100 nm wavelengths range. If we consider STN as a semiconductor based on the resistivity vs temperature behavior (see Fig.3), we can determine its optical band gap from the fundamental absorption, which corresponds to the electron excitation from the valence band to the conduction band. A sharp absorption edge was observed around 360 nm from STN, where the absorption around 270 nm was from LAO substrate (Figure S3). Following Tauc's equation,[22] the optical band gap of a transparent semiconductor can be deduced from a plot of $(\alpha h\nu)^m$ versus $h\nu$, where α is the optical absorption coefficient, $h\nu$ is the photon energy, and m depends on the type of transition: m = 2 for a direct band transition and m = ½ for a indirect band transition. A linear relationship between $(\alpha h\nu)^2$ and $h\nu$ (Figure 3b) indicates that the STN film has a direct energy band with a band gap of 3.65 eV by extrapolating the straight portion of the curve to $(\alpha h\nu)^2 = 0$. The band gap value indicates that the STN film behaves like a wide-band-gap semiconductor.

In summary, we report the first growth of smooth epitaxial tetragonal ternary $SrTiN_2$ thin films by a chemical solution approach of polymer-assisted deposition. The PAD technique offers considerable promise for making complex nitride thin films by simply mixing the different metal polymer solutions. The epitaxial relationships between the film and the substrate are $(001)_{film}\|(001)_{sub}$ and $[102]_{film}\|[101]_{sub}$. The films are conductive with a room temperature resistivity of $4.7\times10^{-4}$ Ω·cm. At the wavelength in the range of 400-1100 nm, the optical transmittance of the film is 60 %. The energy band gap of semiconductive $SrTiN_2$ film is estimated to be 3.65 eV.

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**Supporting Information Available**: Solution, film preparation, and characterization of nitride films are available free of charge via the Internet at http://pubs.acs.org.

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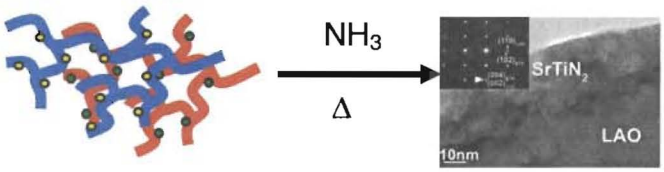


It is indispensable to use thin films for many technological applications. This is the first report of epitaxial growth of ternary nitride $AMN_2$ films. Epitaxial tetragonal $SrTiN_2$ films have been successfully prepared by a chemical solution approach, polymer-assisted deposition. The structural, electrical and optical properties of the films are also investigated.

# Supporting Information

# Epitaxial Ternary Nitride Thin Films Prepared by a Chemical Solution Method

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*1. Sample Preparation*

The precursor for the growth of $SrTiN_2$ (STN) films was a mixture of aqueous solutions of Sr and Ti bound to polymers. Both polyethyleneimine (PEI) and ethylenediaminetetraacetic acid (EDTA) were purchased from BASF Corporation of Clifton, NJ and were used without further purification. The two solutions were separately purified by repeated Amicon filtration that retains the high molecular weight polymer with bound metal atoms, while allows any low molecular weight (<10,000 g/mol) species to pass through. Metal analysis was conducted using a Varian Liberty 220 inductively coupled plasma–atomic emission spectrometer (ICP-AES), following the standard SW846 EPA (Environmental Protection Agency) Method 6010 procedure.

For the Sr solution, 1 g of EDTA and 1 g of PEI were dissolved in 30 mL of water, followed by addition of 1 g of $Sr(NO_3)_2$. For the Ti solution, small amounts of the titanium solution (2.5 g titanium tetrachloride was added slowly to a mixture of 2.5 g of 30% peroxide in 30 mL of water) were added to a solution containing 1 g PEI, 1g EDTA and 30 mL water until precipitation occurred (the pH was maintained at 7.5). After filtration, the final Sr and Ti concentration were 157 and 408 mM, respectively. The precursor solutions with the desired stoichiometric molar ratio of Sr/Ti = 1 from Sr and Ti solutions were spin-coated on (001) $LaAlO_3$ (LAO) substrates at 2000 rpm for 30 s. The films were annealed in ammonia gas at 1000 °C for 1 h (or 900 °C for 3 h). Films with a thickness in the range of 30-40 nm were obtained from one spin-coat. Thicker films could be deposited by multiple spin-coats.

*2. Sample Characterization*

X-ray diffraction (XRD) was used to characterize the crystallographic orientation of the films. The surface morphology and surface roughness of the films were analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The microstructure of the films was analyzed by transmission electron microscopy (TEM). The optical properties of the films were examined by ultraviolet-visible (UV-Vis) transmittance and absorption at room temperature. The electrical resistivity ($\rho$) was measured from 5-300 K using a standard four-probe technique by a Quantum Design Physical Properties Measurement System (PPMS).

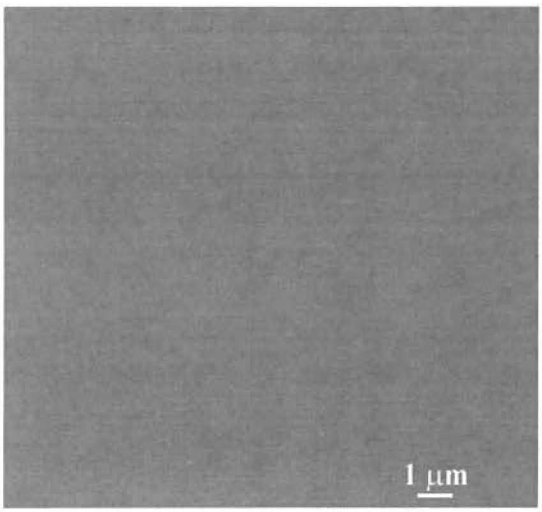


***Figure S1.*** SEM image of a STN film on LAO.

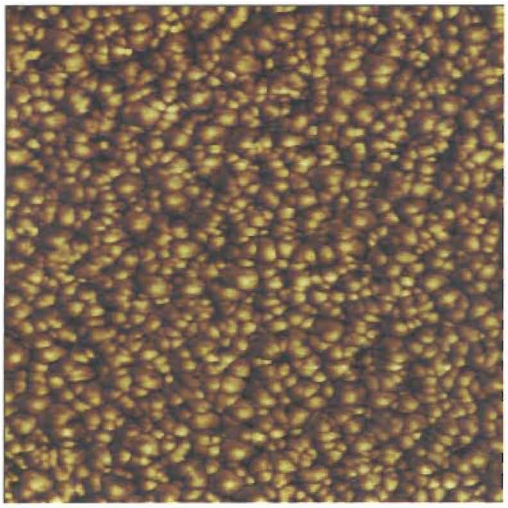

***Figure S2***. AFM phase image of a STN film on LAO (1 μm × 1 μm).

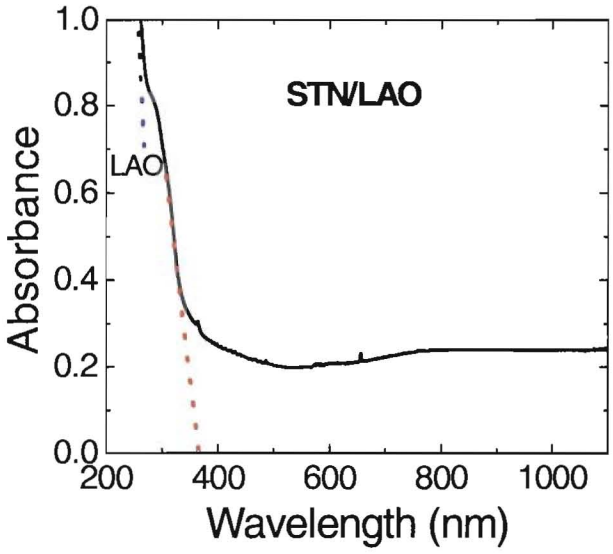


***Figure S3.*** Absorption spectrum of a STN film on LAO.