Low-temperature CVD of $\eta$-Mn$_3$N$_2$ from bis[di(tert-butyl)amido]manganese(II) and ammonia

Teresa S. Spicer  
Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 201 Materials Science and Engineering Building, 1304 W. Green St., Urbana, Illinois 61801

Charles W. Spicer  
School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 S. Mathews Ave., Urbana, Illinois 61801

Andrew N. Cloud  
Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 201 Materials Science and Engineering Building, 1304 W. Green St., Urbana, Illinois 61801

Luke M. Davis and Gregory S. Girolami  
School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 S. Mathews Ave., Urbana, Illinois 61801

John R. Abelson  
Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 201 Materials Science and Engineering Building, 1304 W. Green St., Urbana, Illinois 61801

(Received 1 February 2013; accepted 15 March 2013; published 8 April 2013)

Manganese nitride films are grown by low-pressure chemical vapor deposition from the novel precursor bis[di(tert-buty1)amido]manganese(II) and ammonia. Mixed-phase films containing crystalline manganese nitride can be grown on substrates at temperatures as low as 80 °C. Above 200 °C, the films consist entirely of crystalline manganese nitride. The crystalline material has the same tetragonal unit cell as $\eta$-Mn$_3$N$_2$, but composition analysis of the Mn:N suggests that the material is best denoted as $\eta$-Mn$_{3-x}$N$_{2-x}$ with $x \sim 0.7$. Both oxygen and carbon contamination in the bulk of the films are <1 at. %. Deposition rates of up to 10 nm/min are observed. The growth of crystalline films of a ceramic material at such low temperatures and high rates is highly unusual. The authors attribute this outcome to the presence of high-moment manganese atoms in mixed valence states and to vacancies in the nitrogen sublattice; both features lower the energies needed to break and reform metal-nitrogen bonds and thus allow the deposited atoms to settle more easily into a low-energy ordered arrangement. © 2013 American Vacuum Society. [http://dx.doi.org/10.1116/1.4799036]

I. INTRODUCTION

Manganese nitride exhibits a variety of crystalline structures with distinct magnetic and electrical properties. The phase has the highest known nitrogen content (Mn$_6$N$_5$); closely related is the $\eta$ phase, Mn$_3$N$_2$. Both adopt tetragonally distorted NaCl structures with vacancies in the nitrogen sublattice, and both are antiferromagnets. Among the lower nitrides, the hexagonal $\zeta$ phase is compositionally broad and encompasses stoichiometries such as Mn$_3$N$_2$, Mn$_2$N, and Mn$_2$N$_{0.86}$; it has a NiAs-type structure in which the nitrogen sites are partially occupied and is an antiferromagnet. The cubic $\varepsilon$-Mn$_4$N phase adopts an antiperovskite structure and is ferrimagnetic. Finally, manganese-doped gallium nitride, Ga$_{1-x}$Mn$_x$N, is a magnetic semiconductor at room temperature with potential applications in spintronic, microelectronic, and optoelectronic devices.

Manganese nitride thin films have not been extensively studied because they are relatively difficult to synthesize. Films of various manganese nitride phases have been deposited by molecular beam epitaxy, ion-assisted deposition, reactive sputtering, and recently by chemical vapor deposition. CVD has been used to deposit thin films of manganese-doped gallium nitride by adding a Mn-containing precursor such as manganocene, Mn(C$_{5}$H$_{5}$)$_{2}$, to a CVD process for depositing GaN between 800 and 1100 °C. Elemental manganese films have been deposited from the volatile bis[tri( trimethylsilyl) amido]manganese(II) dimer, Mn$_2$[N(SiMe$_3$)$_2$]$_2$. Gordon et al. have recently synthesized Mn$_3$N films from bis(N,N'-disopropylpentylamidinato)manganese(II) and ammonia, but no CVD routes to thin films of other manganese nitride phases are known.

CVD of transition metal nitride films is routinely accomplished from a mixture of ammonia and a transition metal dialkylamide precursor, e.g., TiN from tetrakis (dimethylamido)tin(titaniunm(IV)) (TDMAT) and related precursors. When grown in the absence of ammonia, the deposited films are severely carbon-contaminated owing to reactions that generate M-N-C rings. When NH$_3$ is provided as a co-reactant, however, a transamination reaction occurs in which the metal-dialkylamide groups react with ammonia in the gas phase to form dialkylamine and species with M-NH$_x$ functional groups. The latter transform into largely carbon-free metal nitride films.
We have recently investigated the transition metal chemistry of the sterically bulky ligand di(t-Butyl)amide. Here, we report the CVD of manganese nitride films grown from the two-coordinate manganese(II) amide bis[di(t-Butyl)amido]manganese(II), Mn[N(t-Bu)₂]₂, as a function of the ammonia partial pressure and the substrate temperature. A remarkable finding is the growth of completely crystalline films of manganese nitride at the unusually low temperature of 200 °C.

II. EXPERIMENT

Thin films are deposited in a previously described chamber of ultrahigh vacuum construction with a base pressure of 5 × 10⁻⁹ Torr. Quadrupole mass spectrometry of the residual gases indicates that the majority of the background is dihydrogen, which is inefficiently pumped by the turbopump. Substrate temperatures less than 300 °C are measured using a k-type thermocouple; for higher temperatures an infrared pyrometer is used. Substrates are heated up to 200 °C by radiant heating from a tungsten filament and to higher temperatures by Joule heating of the silicon substrates. The Mn[N(t-Bu)₂]₂ precursor, prepared as described previously, is kept in a heated stainless steel reservoir (40 °C ≤ T ≤ 85 °C) and delivered to the substrate with the assistance of a carrier gas (N₂ or Ar, 10–40 sccm); the delivery lines are not heated. Control experiments show that the carrier gases are unreactive toward the precursor. Growth is monitored by in situ spectroscopic ellipsometry.

Most of the films are grown on degenerately doped n-type Si(100); a few films are also grown on plasma-deposited amorphous carbon on Si(100), and holey carbon transmission electron microscope (TEM) grids. All substrates except the TEM grids are cleaned ultrasonically by successive immersions in trichloroethane, acetone, isopropanol, and deionized water. The silicon substrates are given a final rinse in 10% HF solution to remove the native oxide; this procedure affords hydrogen-terminated, Si(100)-H, surfaces. The Mn:N ratio determined by Auger electron spectroscopy is roughly 2.5:1 and independent of flux and temperature within this range. When the films are grown at 200 °C and below, the carbon content is below the detection limit (<1 at. %). The N 1s XPS binding energy of 396.5 eV and the Mn 2p 3/2 binding energy of 641.5 eV are both consistent with the presence of a manganese nitride phase. The reported Mn 2p 3/2 binding energies for “MnN” and Mn metal are 641.5 and 639.0 eV, respectively.

Remarkably, the films are partly or fully crystalline even when grown at 80 °C with no annealing (Fig. 1). The XRD patterns show that the crystalline phase grown between 80 and 200 °C has cell parameters, a = 2.98(6) and c = 12.02(4) Å, which are consistent with literature values for η-Mn₃N₂ (a = 2.97(4), c = 12.128(5) Å). In all of the films, the crystalline grains are textured (i.e., preferentially oriented), with the (110) plane nearly parallel to the film surface.

The formal oxidation state of the manganese in the precursor Mn[N(t-Bu)₂]₂ is +2, which should give rise to stoichiometric Mn₃N₂ films if no nitrogen loss takes place. Because the films have a Mn:N ratio that is close to 2.5:1, the overall stoichiometry of the films can be represented as Mn₃N₂₋ₓ with x ~ 0.7. The reported homogeneity range of η-Mn₃N₂ extends at least from Mn₃N₁.84 to Mn₃N₂.08; our stoichiometry is outside this range, but the films are grown at relatively low temperature, which may lend this phase kinetic stability.

The grain size, calculated from the Scherrer equation, increases from 10 nm at 80 °C to 23 nm at 200 °C. At a constant deposition temperature of 200 °C, the η-Mn₃N₂₋ₓ grain size increases from 10 to 20 nm as the ammonia flux increases from 1.0 to 4.3 sccm; at higher fluxes, the grain size decreases slightly.

![Figure 1](https://example.com/figure1.png)
Bright-field TEM micrographs and STEM nanodiffraction patterns show that films grown on holey carbon grids at 100°C with an ammonia flux of 5 sccm consist of crystalline grains of $\eta$-Mn$_3$N$_2$-$x$ embedded in an amorphous matrix (Fig. 2). A geometric estimate based on the STEM micrographs suggests that ~25 vol. % of the film is crystalline. In contrast, bright-field TEM micrographs show that the films grown at 200°C and the same ammonia flux are completely crystalline: the crystalline grains abut one another in a dense structure, apparently with no intervening amorphous material (Fig. 3). The TEM diffraction patterns are consistent with those found by XRD; indexing of the patterns confirms that the films are composed of crystalline $\eta$-Mn$_3$N$_2$-$x$ (Fig. 3, inset). Nanodiffraction patterns taken from different nanometer-sized areas of the film exhibit diffraction spots from one or several crystalline grains. The grain sizes calculated directly from the TEM diffraction patterns agree with those calculated from the XRD data.

When the deposition from Mn[N(t-Bu)$_2$]$_2$ and ammonia is conducted at 300°C, the films contain nearly equal amounts nitrogen and carbon, with the Mn:N:C ratio from AES being approximately 4:1:1. The XRD results show that films deposited at this higher temperature consist of three crystalline components: tetragonal $\eta$-Mn$_3$N$_2$-$x$, hexagonal $\zeta$-Mn$_2$N$_{1.08}$, and cubic Mn$_2$C$_6$. The grain size of the multiphase material, calculated from the Scherrer equation, is 10 nm.

Depositions carried out in the absence of ammonia afford relatively little film at growth temperatures below 300°C, and above this temperature the films are heavily contaminated with carbon (15%–42% as determined by AES). Nitrogen is not present in detectable amounts in the films grown without ammonia at these higher temperatures. This behavior is similar to the chemistry seen for other transition metal amides. For example, in the absence of ammonia, the titanium precursor TDMAT deposits a mixed titanium carbide/nitride phase. Interestingly, the films grown without ammonia sometimes exhibit XRD peaks due to elemental manganese. The behavior of Mn[N(t-Bu)$_2$]$_2$ thus resembles that of transition metal complexes of the bis(trimethylsilyl)amido ligand, which is the silicon analog of the di(tert-butyl)amido group. Such complexes have been shown to react with ammonia in solution, but give elemental metal (sometimes contaminated with carbon) when used as CVD precursors in the absence of ammonia.

B. Roughness and microstructure

Scanning electron microscopy (SEM) shows that the smoothest films, with an RMS roughness of 1.9 nm, are obtained at 200°C and an ammonia flux of 10 sccm. The roughest films, with a RMS roughness of 12 nm, are the mixed-phase films grown at 300°C with an ammonia flux of 4.3 sccm. Films grown at 80°C and an NH$_3$ flow of 4.3 sccm have a RMS roughness of 8.6 nm.

SEM also shows that the films grown at 80 and 100°C at an ammonia flux of 4.3 sccm consist of very well-defined and separated columns [Fig. 4(a)]. Such columnar microstructures are often observed in films grown by physical vapor deposition techniques or by CVD when the sticking coefficient of the precursor is high and surface mobility is low. When the films are deposited at 200°C, the columns are clearly visible, but touch to form a more compact microstructure [Fig. 4(b)]. At this growth temperature, the microstructure is independent of the ammonia flux between 1 and 10 sccm. The mixed-phase film deposited at 300°C exhibits a rod-like microstructure [Fig. 4(d)].

A film grown at 200°C with an ammonia flux of 5 sccm was annealed for 120 min at 500°C. This annealing protocol eliminates the (100) diffraction peak and increases the texture coefficient of the (110) peak. Annealing also increases the RMS roughness of the films nearly tenfold to 21 nm and nearly doubles the grain size to 40 ± 4 nm. The correlation between the increase in roughness, grain size, and texture...
suggested that considerable grain growth occurs during annealing and that grains oriented with the (110) plane parallel to the surface grow faster than other grain orientations. This behavior is consistent with the van der Drift theory of texture formation.\textsuperscript{42}

\section*{C. Growth kinetics}

The film growth rate is weakly dependent on substrate temperature from onset to 200°C; this finding suggests that even at the lowest temperature the growth is in the flux-limited regime. Even at the lowest ammonia flow rates we investigated, the flux of ammonia is much higher than that of the precursor, and growth rates are nearly invariant to ammonia flow rate between 1 and 10 sccm. When the ammonia rate is increased to 40 sccm, the growth rate drops to near zero, indicating that ammonia serves as a growth suppressant when it is present at high partial pressures, probably by site blocking effects (discussed below). The growth rate can be increased significantly by increasing transport of precursor out of the container, either by heating to 75°C (i.e., above the precursor melting point of \( \sim 72°C \))\textsuperscript{30} or by increasing the carrier gas flow rate. Growth rates of up to 10 nm/min can be achieved with liquid precursor.

\section*{IV. DISCUSSION}

Our results are consistent with a growth mechanism for \( \eta\text{-}\text{Mn}_3\text{N}_2\text{-}_x \) in which \( \text{Mn}[\text{N}(\text{t-But})_2]_2 \) reacts with ammonia by means of a transamination reaction to give \( \text{Mn-NH}_2 \) groups and di(\text{tert-butyl})amine; the former species reacts to form the film whereas the latter leaves the growth surface. Subsequent reactions eliminate hydrogen and some nitrogen, most likely as \( \text{NH}_3 \) and \( \text{N}_2 \), to generate \( \eta\text{-}\text{Mn}_3\text{N}_2\text{-}_x \). A similar mechanism dominated by gas-phase transamination operates in titanium nitride deposition from TDMAT and ammonia.\textsuperscript{25,43} The complete lack of growth below 300°C observed for \( \text{Mn}[\text{N}(\text{t-But})_2]_2 \) in the absence of ammonia supports the idea that the low-temperature growth of \( \eta\text{-}\text{Mn}_3\text{N}_2\text{-}_x \) involves transamination of \( \text{Mn}[\text{N}(\text{t-But})_2]_2 \) with ammonia, and that ammonia is the source of the nitrogen present in the films.

The columnar film structure seen at all temperatures indicates that the gas phase species from which the film is formed have high sticking coefficients, and that the surface-bound adsorbates have low mobilities (the shadowing effects which cause columnar growth are negated if film-generating surface species can relocate easily, either by re-emission from the surface or by diffusion).\textsuperscript{41} These observations are most consistent with the hypothesis that the film-generating species contain \( \text{Mn-NH}_2 \) groups generated by irreversible transamination reactions. This hypothesis is also consistent with the temperature independence but precursor flux dependence of the growth rate between 80 and 200°C.

The chamber design (the distance between precursor dosing tube outlet and substrate is ca. 4 cm) and mean chamber pressure during growth (ca. 5 mTorr) ensure that gas-phase collisions between the precursor and ammonia will occur before the precursor arrives at the substrate. The incorporation of carbon at temperatures above 300°C could mean that the transamination is incomplete in the gas phase, and that \( \gamma\text{-} \text{hydrogen abstraction from residual dis(\text{tert-butyl})amide groups generates metallacycles containing Mn-C bonds. If this mechanism is correct, then manganese nitride films free of carbon should be obtainable at 300°C by using higher ammonia fluxes than we examined, such that the transamination rate exceeds the \( \gamma\text{-} \text{hydrogen abstraction rate. Alternatively, the carbon could arise because the dis(\text{tert-butyl})amine byproduct is reactive at these higher temperatures, and decomposes on the surface to generate Mn}_3\text{C}_6 \). In this case, reducing the residence time of the byproducts in the hot zone could reduce the carbon content.}

The complete suppression of growth by high pressures of ammonia is not likely to be a result of volatilization of surface manganese amido fragments as ammonia adducts, \( \text{Mn(NH}_2)_2\text{(NH}_3)_4 \); such species are not expected to be stable or volatile enough. It is more likely that large ammonia fluxes block reactive sites on the surface, preventing the gas-phase manganese-containing species from adsorbing and reacting.\textsuperscript{44,45} While ammonia dissociates on bare \text{Si}(100) surfaces and thus has a high sticking coefficient (for example, it is 0.9 at 80°C and 0.5 at 300°C), as the surface coverage of adsorbates approaches unity this coefficient drops to less than 0.1 at all temperatures.\textsuperscript{46} On the \text{Si}(100)-H surfaces used in our experiments, ammonia does not dissociate and thus does not adsorb strongly.\textsuperscript{47}

Although we did not carry out any experiments on \text{SiO}_2, it is known that ammonia can suppress CVD growth on this surface despite the fact that ammonia adsorbs only weakly.\textsuperscript{48} For example, inhibition of film growth by ammonia has been reported for \text{TaN} deposition from TDMAT on \text{SiO}_2,\textsuperscript{49} and complete suppression reported for carbon deposition from acetylene on amorphous \text{SiO}_2.\textsuperscript{50} We have reported complete

\begin{figure}[htb]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{(Color online) (a) 89 nm-thick film of \( \eta\text{-}\text{Mn}_3\text{N}_2 \) grown at 80°C. (b) 73 nm-thick film of \( \eta\text{-}\text{Mn}_3\text{N}_2\text{-}_x \) grown at 200°C. (c) AFM micrographs of a 95 nm-thick \( \eta\text{-}\text{Mn}_3\text{N}_2\text{-}_x \) film grown at 200°C and 5.0 sccm ammonia flow, as deposited. The RMS roughness is 2.3 nm. (d) 185 nm-thick mixed-phase film of \( \eta\text{-}\text{Mn}_3\text{N}_2 \), \( \gamma\text{-} \text{phase Mn}_2\text{N}_1.08 \), and cubic Mn$_3$C$_6$ grown at 300°C.}
\end{figure}
suppression of the growth of HfB₂ from Hf(BH₄)₄ on SiO₂ at 250 °C with 1 mTorr of ammonia,⁵¹ and recently determined that nucleation proceeds unabated but steady-state growth is suppressed by ammonia adsorption to HfB₂ surfaces.⁵² Thus, it seems reasonable to conclude that inhibition of growth by high pressures of ammonia in our experiments also entails site-blocking by ammonia, which either suppresses nucleation on Si(100)-H or suppresses steady-state growth on the nucleated manganese nitride surface.

We were surprised that crystalline films of the ceramic phase η-MnₓN₂₋ₓ can be grown at growth temperatures as low as 80°C. Recently, Mn₃N films with at least some crystallinity have been grown by CVD at 130 °C;¹⁶ in contrast, temperatures of 290 °C or higher are required to obtain crystalline manganese nitrides by other techniques such as solvothermal synthesis from MnCl₂ and sodium azide.⁵³ Both the low growth temperature and the crystallinity of the CVD-grown manganese nitride films may reflect the high chemical reactivity of the high-spin, two-coordinate manganese(II) center in Mn[N(t-Bu)$_2$]$_2$.³²,³³ Two-coordinate complexes are often very reactive owing to coordinative unsaturation,⁵⁴ and complexes with high-spin transition metal centers are kinetically labile and undergo rapid ligand substitution reactions.⁵⁵

In addition, the high-spin Mn⁵⁺ center in the precursor is likely to remain high-spin throughout a significant fraction of the reaction sequence that leads to film growth. Notably, the more nitrogen-rich manganese nitrides, including Mn₃N₂, have magnetic properties and Mn-N distances that are consistent with the presence of high-moment manganese atoms in mixed valence states.¹³,¹⁴ Because the different valence states of manganese have different preferred coordination geometries, we suggest that change in the charge state of a manganese atom can promote local atomic rearrangement, similar to the Bourgoin-Corbett diffusion mechanism.⁵⁶ In addition, the presence of vacancies in the nitrogen sublattice can provide mechanisms for atom movement and lower the annealing temperatures. Together, these factors lower the energies needed to break and reform metal-nitrogen bonds and thus allow the deposited atoms to settle more easily into a low-energy ordered arrangement. As a result, crystalline films are formed even at what are extraordinarily low growth temperatures for a ceramic phase.

V. SUMMARY AND CONCLUSIONS

We have demonstrated the growth of crystalline η-MnₓN₂₋ₓ films at low temperatures between 80 and 200°C. The growth likely proceeds via rapid transamination of the precursor with ammonia to afford manganese amido fragments with high sticking coefficients and low surface mobilities. These fragments decompose to the manganese nitride film, and crystallization during this process may be facilitated by the kinetic lability of the high-spin manganese atoms along with the presence of manganese centers in mixed valence states and vacancies in the nitrogen sublattices. A general strategy to obtain ceramic films with good crystallinity at low CVD growth temperatures may be to employ precursors with high-spin metal centers able to adopt two or more valence states. Finally, the present results indicate that it may be possible to grow epitaxial films of MnₓNᵧ phases at low temperatures on suitable substrates.

ACKNOWLEDGMENTS

This research was supported by NSF Grant Nos. CHE11-12360 and DMR 10-05715. A. N. Cloud was supported by a National Science Foundation Graduate Research Fellowship. The film characterization was carried out in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois.

²⁶ L. H. Dubois, Polyhedron 13, 1329 (1994).