Low temperature chemical vapor deposition of superconducting vanadium nitride thin films

Elham Mohimi, Zhejun V. Zhang, Justin L. Mallet, Sumeng Liu, Brian B. Trinh, Pralav P. Shetty, Gregory S. Girolami, and John R. Abelson

1Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304 W. Green St., Urbana, Illinois 61801
2Lincoln Laboratory, Massachusetts Institute of Technology, 244 Wood Street, Lexington, Massachusetts 02421-6426
3Department of Chemistry, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

(Received 7 January 2019; accepted 3 April 2019; published 19 April 2019)

Superconducting thin films of vanadium nitride have been grown by low temperature (250–300 °C) chemical vapor deposition from tetrakis(dimethylamido)vanadium (TDMAV) and ammonia. For example, films grown from TDMAV (1 sccm Ar as carrier gas) and 7 mTorr ammonia at 300 °C are nanocrystalline (cubic δ-phase) with an average crystal size of 20 nm, have relatively low room temperature resistivities of 250 μΩ cm, and are superconducting with critical temperatures as high as 7.6 K (versus a bulk value of 9 K). The films have a V:N ratio of 1:1, with a carbon content of <5 at. % and an oxygen content of <3 at. % (as determined by high resolution XPS). The V 2p3/2 and N 1 s XPS binding energies of 513.5 and 397.3 eV, respectively, are consistent with the presence of a nitride phase. In contrast, films grown at lower temperatures <200 °C show carbon incorporation, have a much higher resistivity of ∼3000 μΩ cm, and are not superconducting. The results suggest that, at low temperatures, the thermally activated transamination reaction with ammonia becomes too slow to remove dimethylamido groups from the surface, resulting in carbon-rich films (10–15 at. % carbon). The conformal step coverage of the VN films depends on the growth conditions. For thermal growth of nonsuperconducting films at 150 °C, the step coverage is >95% in trenches of an aspect ratio of 4:1; for superconducting films grown at 250 °C, the step coverage is 65% for an aspect ratio of 3:1. At 150 °C, near-stoichiometric films with <2 at. % carbon and <3 at. % oxygen can be deposited if the gaseous ammonia is prerecracked by a remote plasma source; the resulting films have low resistivities of 320 μΩ cm but are not superconducting down to 4 K.

Published by the AVS. https://doi.org/10.1116/1.5088050

I. INTRODUCTION

There is considerable interest in the possibility of using superconducting materials in future generation integrated circuits because the resulting devices should be ultrafast and highly energy efficient. Among the superconducting phases of interest for this application is the cubic δ-phase of vanadium nitride (VN), which has a bulk critical temperature of ≈9 K.1–3 It is a strong candidate for the fabrication of Josephson junction devices, superconducting interconnect lines, and single photon detectors;4 in addition, it is highly conductive at room temperature, chemically and thermally stable, and has a bulk hardness of 18 GPa.

An excellent way to deposit transition nitride films at low temperatures is the reaction of transition metal dialkylamido precursors, M(NR2)2, and ammonia.5,6 Such depositions generally occur by means of a transamination reaction in which the NR2 ligands (where R is an alkyl group) are replaced with NHx groups (x = 1 or 2), which subsequently react to form the nitride phase.7–9 In this reaction, the NR2 ligands are converted by H transfer from ammonia to molecules of the corresponding dialkylamine, which desorb from the growth surface. Previously, Fix, Gordon, and Hoffman showed that VN thin films can be grown from tetrakis(dimethylamido)vanadium (TDMAV) and ammonia under atmospheric pressure chemical vapor deposition (CVD) conditions.5 When grown at 200 °C, the films are slightly nitrogen rich and have room temperature electrical resistivities of ∼1000 μΩ cm that are considerably above the bulk value of ca. 85 μΩ cm.10 No low temperature resistivity measurements were carried out in this previous study, so it was not known whether the VN films were superconducting. Superconducting VN films have also been obtained from molecular precursors by bulk ammonolysis (i.e., non-CVD) methods, but only at significantly higher growth temperatures of 450–700 °C.11,12

Here, we report that CVD at 300 °C from TDMAV and ammonia at total pressures in the mTorr range (rather than at atmospheric pressure as in Fix et al.) affords near-stoichiometric VN thin films with physical densities approaching the bulk value, electrical resistivities of 250 μΩ cm, and superconducting critical temperatures as high as 7.6 K. When grown under otherwise identical conditions at temperatures below 200 °C, the films have poor crystallinity, contain significant amounts of carbon, are more resistive, and are not superconducting. We find that near-stoichiometric carbon-free VN films with low electrical resistivities can be grown at 150 °C by employing a remote ammonia plasma as a source of activated NHx groups for the surface transamination reaction.
These films, however, are not superconducting. Nevertheless, the demonstration in the current paper that superconducting VN films can be grown at 250–300°C is an important advance, and further improvements in the deposition protocol (for example, a larger flux of plasma-activated species) may enable similar results even at lower growth temperatures.

II. EXPERIMENT

The growth of vanadium nitride films is performed in a turbo-pumped chamber of high vacuum construction as described elsewhere. The TDMAV precursor is kept in a reservoir maintained at room temperature, where it sublimes and is carried by an Ar carrier gas that flows through the source container to deliver the sublimed precursor to the chamber. The carrier flow rates are 1–10 sccm. The ammonia coreactant is purified by distillation from sodium to remove water and decrease the adventitious incorporation of oxygen into the films. The ammonia is delivered to the chamber through an independent gas line; the flow is regulated by a needle valve to afford partial pressures of 1–30 mTorr. All tubes are aimed at the substrate; hence, the local fluxes are higher than those indicated by the isotropic background pressure.

The growth chamber is equipped with a remote microwave plasma source that can generate active NH species from ammonia. The source consists of a 9.5 mm i.d. Pyrex tube with a 2.45 GHz Evenson cavity located outside of the chamber. The net plasma power (forward minus reverse) is varied between 40 and 60 W. Owing to the small diameter tube (6 mm i.d.) that connects the source to the chamber, the outward gas flow velocity is large and precursor species cannot diffuse upstream into the active plasma area. Thus, it is possible to create an active species in the plasma and deliver it to the growth surface while simultaneously delivering undissociated precursor to the surface through a separate gas line. Previous work in our group using an earlier version of this apparatus has shown that, at a net plasma power of 45 W and a hydrogen flow rate that affords 1–5 mTorr in the chamber (which corresponds to >100 mTorr in the plasma apparatus due to flow restriction), the atomic hydrogen flux at the substrate surface is between 2 × 10^{14} and 8 × 10^{15} cm^{-2} s^{-1} depending on the prior treatment of the plasma tube wall. The flux of ammonia fragments at the substrate is likely of the same magnitude.

Si(100) with native oxide and 300 nm thermal SiO_2/Si are used as substrates. Microtrenches of SiN_x with multiple aspect ratios are used to study the conformality of VN growth under various growth conditions. Conformality is evaluated via the step coverage (SC), which is defined as the film thickness on the lower sidewall divided by the thickness on the upper sidewall. The growth temperature, as measured by a K-type thermocouple attached to the radiatively heated sample holder, is varied between 150 and 300°C.

Film thickness and microstructure are determined from cross-sectional SEM images. Compositional depth profiles are obtained by AES; atomic composition and elemental binding energies are measured by XPS. Because there is an overlap of the oxygen KLL_{23}L_{23} and vanadium L_{3}M_{45}M_{45} lines in the Auger spectra, the bulk oxygen content is analyzed by high resolution XPS after 2 min of Ar⁺ sputtering to remove surface contamination due to air exposure. Selected films are capped, before being removed from the growth chamber, with 30 nm of HfB_2 to block any possible diffusion of oxygen into the film upon exposure to atmosphere. (Samples for superconductivity test are not capped.) Film crystallinity is measured by glancing incidence x-ray diffraction (GIXRD). Cross-sectional transmission electron micrographs and electron diffraction patterns are obtained on a JEOL 2100. The resistivity of VN films grown on SiO_2 substrates is measured by the four-point probe method; room temperature measurements are conducted on Illinois, and measurements down to 4 K are conducted at the MIT-Lincoln Laboratories.

III. RESULTS AND DISCUSSION

A. Thermal CVD of vanadium nitride from TDMAV and ammonia

The current study involves the low temperature CVD growth of superconducting vanadium nitride thin films from the precursor TDMAV and ammonia. We have focused our experiments in the low-pressure regime in which the total chamber pressure is typically about 10 mTorr.

In the absence of the ammonia coreactant, no deposition occurs when TDMAV (delivered with 1 sccm of Ar carrier gas) is passed over a surface at 150°C; above 175 in the absence of ammonia, thermolysis of the TDMAV precursor commences but the films contain significant amounts of carbon; for example, when grown at 250°C in the absence of ammonia, the films contain 42 at. % carbon and have a V/N ratio of 1.5. These results are consistent with previous reports under atmospheric pressure CVD conditions, for which no growth occurs from TDMAV in the absence of ammonia at 150°C.

Addition of 0.5 mTorr of ammonia to the TDMAV flux at 150°C causes film growth to occur slowly at ~0.5 nm/min; the flux increases only slightly with increasing ammonia pressure and saturates at 0.7 nm/min for ≥7 mTorr of ammonia. The films are relatively smooth [Fig. 1(a)], and after air exposure, the room temperature resistivity is relatively large, 3000 μΩ cm. An AES depth profile shows that the air-exposed films have a V/N ratio of ~1.5 and also contain 10 at. % carbon and 25 at. % oxygen. When the film is capped in situ using 20 nm of HfB_2 to prevent oxidation upon exposure to air, the V/N ratio is 1.1, and the C and O contents are 15 and 5 at. %, respectively. Films grown in this way at 150°C are not superconducting down to 4 K.

These results indicate that, at 150°C, the reaction of TDMAV with 0.5 mTorr of ammonia does not completely remove the dimethylamido groups from the precursor. The resulting film extensively oxidizes (or hydrolyzes) when exposed to air, which suggests that the films are under-dense, as expected for the growth of a refractory material at low temperatures. Increasing the ammonia pressure during growth from 0.5 to 7 mTorr (while keeping the precursor carrier flow rate at 1 sccm Ar) does not change the film microstructure, but the carbon content (for HfB_2-capped films) decreases slightly from 30 to 23 at. %.
At higher growth temperatures of 250–300 °C, the removal of dimethylamido ligands by reaction with ammonia becomes efficient under our low-pressure conditions. Thus, for a film grown at 250 °C from 7 mTorr ammonia and 1 sccm of Ar carrier gas, the AES depth profile analysis shows a V:N ratio of 1:1, with a carbon content of <5 at. % and an oxygen content of <3 at. % (as determined by high resolution XPS). The V 2p3/2 and N 1s XPS binding energies of 513.5 and 397.3 eV, respectively, are consistent with the presence of a nitride phase. An SEM cross section shows that the film has a columnar and dense microstructure. An SEM cross section shows that the film has a columnar and dense microstructure [Fig. 1(b)]. The film resistivity for a 45 nm thick film is quite low, 180 μΩ cm; this value compares favorably to the bulk resistivity of 85–100 μΩ cm.

The films grown at 250 °C undergo a transition to a superconducting phase at a critical temperature (Tc) of 6.2 K (Fig. 2), compared to ≈9 K for bulk vanadium nitride. When the deposition is repeated under the same gas pressures at 300 °C, the carbon contamination decreases to 2 at. %. The resulting film is dense and columnar as indicated by cross-sectional SEM and exhibits a superconducting critical temperature of 7.6 K (Fig. 2).

Films grown at 250 °C from 1 sccm Ar carrier gas and 8 mTorr ammonia show small broad diffraction peaks representative of the cubic δ-phase of vanadium nitride with small crystal size. At a substrate temperature of 300 °C and a high ammonia/precursor ratio (7 sccm NH3 and 1 sccm Ar carrier gas), the films are crystalline with grain sizes of ~15–20 nm, as calculated from the Scherrer equation. Cross-sectional TEM images of these films confirm the presence of ~20 nm crystalline grains, which are elongated in the growth direction [Fig. 3(a)]. Selected area diffraction patterns consist of spotty rings, indicating that the films are polycrystalline [Fig. 3(b)]; the continuous rings are due in part to overlap of the beam with the fine-grained Pt layer, which was measured in a separate diffraction pattern (not shown). The spotty rings index as δ-VN with a cubic lattice parameter a = 4.20, 4.19, and 4.16 Å for hkl = 111, 200, and 220, respectively; the lattice parameter for bulk δ-VN is slightly smaller at 4.13 Å.

For these latter experiments, the growth rate at constant temperature increases with increasing TDMAV precursor pressure (carrier gas flow rate), indicating that deposition is in the flux-limited regime. As judged from in situ ellipsometry data, there is no nucleation delay for vanadium nitride growth on Si(100) or SiO2, for all temperatures investigated in this study. Facile nucleation is typically associated with a high areal density of nuclei; thus, it may be possible to grow very thin VN films that are smooth and pinhole free.

B. Film conformality for thermal CVD of vanadium nitride

We investigated depositions of VN from TDMAV and ammonia in trenches of depth:width (aspect) ratios between 3:1 and 4:1. For films grown at 250 °C from 1 sccm Ar precursor carrier and 8 mTorr ammonia, the SC is only ~10% [Fig. 4(a)]. Conformal film growth in a recessed feature requires that the growth species have small reactive sticking coefficients (< 1) so that they can survive many wall encounters as they diffuse under molecular flow down a feature. The results suggest that under these conditions the growth intermediates (TDMAV precursor and its initial reaction products with ammonia) have relatively large sticking coefficients.

One approach to reduce the effective sticking coefficient and improve conformality is to employ higher precursor pressures in an effort to saturate the surface. Thus, we find that increasing the TDMAV carrier flow rate from 1 to 10
sccm Ar, while keeping the ammonia pressure at 8 mTorr, improves the SC to \(\sim 65\%\) in a trench with an aspect ratio of 3:1 [Fig. 4(b)]. The growth rate under these conditions is still relatively high, \(\sim 10.5\) nm/min. This film has a resistivity of 650 \(\mu\)\(\Omega\) cm, is x-ray amorphous, and contains 10 at.\% oxygen and 20 at.\% carbon. Thus, it is possible to achieve reasonable conformality, but at the expense of greater film resistivity. When the ammonia pressure is increased to 30 mTorr, the film conformality decreases, which is similar to the result for a low precursor flux. Unfortunately, the film grown under these conditions is not superconducting.

Conformality can sometimes be improved in a different way: by reducing the growth temperature. In the current system, reducing the growth temperature from 250 to 150 °C under conventional CVD conditions results in poor quality films, but we can decrease the normal resistivity greatly by employing a cyclic CVD process involving a remote ammonia plasma (below). Notably, we find that highly conformal films can be grown in a trench of an aspect ratio 4:1 at 150 °C using 1 sccm carrier gas for the TDMAV precursor and 8 mTorr ammonia [Fig. 4(c)].

C. Remote plasma enhanced CVD of vanadium nitride from TDMAV

As described above, the film quality is poor when grown from TDMAV and ammonia at 150 °C, owing in part to incomplete removal of the dimethylamido ligands. Therefore, we investigated the effect of a coflow of precracked \(\text{NH}_x\) groups from a remote plasma source. The results are quite dramatic. At a substrate temperature of 150 °C, a net plasma power of 40 W, and an ammonia pressure of 7 mTorr, the room temperature resistivity of a 25 nm thick air-exposed film is 320 \(\mu\)\(\Omega\) cm, as opposed to 3000 \(\mu\)\(\Omega\) cm in the absence of the plasma. The film is, however, not superconducting down to 4 K. The Auger depth profile of an uncapped film after air exposure indicates \(\text{V}/\text{N}\approx 1:1\), \(<2\) at.\% carbon and \(<12\) at.\% oxygen. When the film is capped with \(\text{HfB}_2\), the oxygen content decreases to \(<3\) at.\%. Thus, a supply of precracked \(\text{NH}_x\) groups greatly improves the quality of the films deposited at low temperatures. The oxidation of the uncapped film upon exposure to air indicates that the film is under-dense. Increasing the plasma power to 60 W or increasing the \(\text{NH}_3\) flow through the plasma source results in a similar film resistivity, 350 \(\mu\)\(\Omega\) cm.

In contrast, at a film growth temperature of 150 °C with 6 mTorr \(\text{H}_2\) plasma at the same plasma power with no ammonia added, the film resistivity is more than 4000 \(\mu\)\(\Omega\) cm, the \(\text{V}/\text{N}\) ratio is \(\approx 2:3\), and the carbon and oxygen contents are 20 and 25 at.\%, respectively (without \(\text{HfB}_2\) capping). Therefore, atomic hydrogen alone is not capable of removing the dimethylamido ligands and instead of a film with both carbon and oxygen impurities results. At 4 mTorr of hydrogen and a plasma power of 60 W, with molecular ammonia injected separately into the chamber, the film resistivity is 500 \(\mu\)\(\Omega\) cm. Repeating the growth with mixed \(\text{NH}_3\) and \(\text{H}_2\) in the plasma results in a film resistivity of 400 \(\mu\)\(\Omega\) cm. However, the film is not superconducting down to 4 K.

Interestingly, we find that we can obtain low-carbon VN films at 150 °C by a cyclic CVD process in which the

Fig. 3. Vanadium nitride film grown on SiO\(_2\) substrates at 300 °C using 1 sccm carrier gas for precursor and 7 mTorr ammonia: (a) cross-sectional TEM image; (b) selected area electron diffraction pattern. See text for details.

Fig. 4. Cross-sectional SEM images of vanadium nitride films grown at (a) 250 °C using 1 sccm carrier gas for precursor and 8 mTorr NH\(_3\); (b) 250 °C using 10 sccm Ar carrier gas for precursor and 8 mTorr NH\(_3\); (c) 150 °C using 1 sccm carrier gas for precursor and 8 mTorr NH\(_3\); the latter is the most conformal result and also has the highest trench aspect ratio.
following two steps are alternated: (1) brief exposure of the surface to the TDMAV precursor and ammonia and (2) brief exposure to the remote NH$_3$ plasma. Each cycle consists of 1 min thermal CVD using the precursor and molecular ammonia at 150 °C, followed by 2 min of “cleaning” using 8 mTorr of remote ammonia plasma at a power of 60 W. After 20 cycles are performed, giving a total film thickness of 20 nm, the carbon content is less than 2 at. % and the film resistivity is 800 μΩ cm. The films, however, are not superconducting down to 4 K, probably due to poor crystallinity: there is no crystalline structure in GIXRD scans. Annealing may recover superconductivity, but in that approach, plasma processing affords no advantages over thermal CVD at higher temperatures.

Replacing step (2) with exposure to a remote H$_2$ plasma results in a degradation of film quality. In a cyclic CVD approach for 16 cycles, consisting of 2 min growth using precursor and ammonia and 3 min cleaning with an H$_2$ plasma, the film resistivity is 1200 μΩ cm.

In all cases, the addition of an ammonia exposure step to the deposition protocol, especially in the remote plasma, leads to greatly improved film stoichiometries and much lower film resistivities at low substrate temperatures.

**D. Discussion**

In the present work, at low (mTorr) deposition pressures, films grown by thermal CVD at temperatures below 200 °C contain substantial amounts of carbon. The transamination reaction must be inefficient at low temperatures. As a result, some of the dimethylamido groups remain on the surface; these groups lead eventually to the incorporation of carbon into the films, thereby accounting for the higher resistivities. By keeping the pressures low but increasing the deposition temperature to 250–300 °C, we can obtain near-stoichiometric, nearly carbon-free films with resistivities as low as 180 μΩ cm. Films grown under these conditions are superconducting with a critical temperature as high as 7.6 K; a previous study using the same precursor did not examine this property.

Films grown at 300 °C have lower resistivities and improved superconductivity compared with those grown at ≤250 °C. It is known that the residual hydrogen content in the films decreases with temperature; residual hydrogen atoms will alter the band structure of the material or may segregate to grain boundaries and form an insulating phase. In addition, the higher temperatures promote better crystallinity and, presumably, better intergranular electrical contacts. Finally, the higher temperatures also promote the efficient activation of N–H bonds in ammonia by VN (the same is true for VC if the surface is partially substituted by C); the resulting surface-bound hydrogen atoms may assist in removal of carbon-containing intermediates from the growth surface. Such N–H activation processes are known from surface science studies, which show that the apparent activation energy for ammonia decomposition on vanadium nitride is relatively low, 20 kcal/mol (0.87 eV), at temperatures <420 °C.

**IV. SUMMARY AND CONCLUSIONS**

We investigate the CVD growth of vanadium nitride films from tetrakis(dimethylamido)titanium and ammonia. At low temperatures (150 °C), the rate of transamination on the growth surface is small (the process is inefficient), resulting in carbon-rich and highly conformal films, showing high resistivities and no superconductivity. When grown at temperatures between 250 and 300 °C, however, the films show a V:N stoichiometry near 1:1, contain little carbon, are nanocrystalline (cubic δ-phase), and are superconducting. However, the films show poor conductivity due to high sticking coefficients of the growth intermediates. By reaction of TDMAV with predissociated NH$_3$ species from a remote plasma, near-stoichiometric VN films can be grown at temperatures as low as 150 °C but these films are not superconducting down to 4 K under the present experimental conditions.

**ACKNOWLEDGMENTS**

The financial support from MIT-Lincoln Laboratory is gratefully acknowledged. G.S.G. acknowledges support from the National Science Foundation (NSF) under Grant Nos. CHE 1362931 and CHE 1665191. J.R.A. acknowledges support from the NSF under Grant No. 1410209.

---