Breaking Molecular Nitrogen under Mild Conditions with an Atomically Clean Lanthanide Surface

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ABSTRACT: A route to break molecular nitrogen (N₂) under mild conditions is demonstrated by N₂ gas cracking on, and incorporation into, lanthanide films. Successful growth of lanthanide nitride thin films, made by evaporation of lanthanides in a partial N₂ atmosphere at room temperature and pressure as low as 10⁻⁸ Torr, is confirmed using X-ray diffraction. In situ conductance measurements of pure lanthanide thin films exposed to N₂ gas show an immediate surface reaction and a slower bulk reaction. Finally, we report partial reversal of the nitrogen incorporation in a lanthanide nitride by cycling vacuum and nitrogen conditions in the sample chamber.

INTRODUCTION

Ammonia (NH₃) is among the most important chemicals in today’s economy and an irreplaceable precursor in the fertilizer production supporting the world’s population. However, the industrial synthesis of NH₃ from molecular nitrogen (N₂) and hydrogen (H₂), the Haber–Bosch process, is one of the most severe processes in the chemical industry. The cleavage of the N₂ bond, the main challenge in the industrial NH₃ synthesis, is only feasible under extreme conditions of high temperatures and pressures, consuming a few percent of the world’s energy production. As a consequence, breaking the immensely strong triple bond of molecular nitrogen has attracted an enormous research effort. Catalysts that could allow a facile breaking of N₂ and a potential energy-efficient NH₃ synthesis include typically enzymatic and organometallic approaches as well as electro and photocatalytic materials, with a strong interest in mimicking biological systems such as nitrogen fixation.

The focus has concentrated on these relatively complex approaches suffering from a number of drawbacks, for example, large atomic cluster-based catalysts that do not lend themselves to theoretical treatments and the lack of in situ and real-time characterization on an atomic level. In stark contrast, here, we report on a radically different approach: the facility to use an atomically clean surface of lanthanide (L) metal to break molecular nitrogen at room temperature and under pressure much lower than one atmosphere, typically seven to eight orders of magnitude smaller, through both in situ and ex situ measurements.

The primary evidence points for N₂ reacting efficiently with the lanthanide presented in this paper are fourfold. First, we show the formation of lanthanide nitrides (LN) during lanthanide evaporation in a partial nitrogen atmosphere at room temperature. Second, we demonstrate a change in electrical conductivity in LN thin films, samarium nitride (SmN) and gadolinium nitride (GdN), when the L:N ratio during deposition is changed. Third, the electrical conductance and crystallographic properties are significantly altered in lanthanide thin films when exposed to N₂. Last, the conductance in SmN films when cycling N₂ pressure and ultrahigh vacuum conditions shows the possibility of removing nitrogen from the SmN lattice.

RESULTS AND DISCUSSION

The deposition and subsequent N₂ exposure of the lanthanide (L) thin layers are carried out in an ultrahigh vacuum system, with a base pressure of <10⁻⁸ Torr. It is worth pointing out that the lanthanide elements, sometimes referred to as rare-earth elements, are by no means rare, with the exception of promethium, which has no stable nuclear isotope. They are found in the earth’s crust at concentrations exceeding those of Ag, Cd, and Hg and similar to Ge and As. The purity of the as-received L charges is typically 3 or 4 N (5$5$–10/g), and the purity of N₂ is at least 4 N and is introduced through a Ni sponge. Several L elements are evaporated on the surface of an amorphous substrate (fused silica) in the presence of N₂ (Figure 1). The substrate is kept at ambient temperature (~30 °C), the partial pressure of N₂ is ∼10⁻⁴ Torr, and the deposition rate is typically 200–300 nm/h, resulting in thin films with thickness of a few hundred nanometers. Surprisingly, most lanthanide mononitrrides are successfully formed by simply depositing L elements in the presence of N₂ as displayed in Figure 1, where the X-ray diffraction (XRD)
patterns are shown. The lanthanides that are most rigidly trivalent (Sm, Gd, Dy, Er, and Tb) \(^{14}\) react with \(N_2\) and form a rock-salt-structured mononitride (L\(^{3+}\)−N\(^3\)), showing characteristic (111)-dominated polycrystalline patterns as expected for room-temperature-grown LN thin layers. \(^{15}\) As illustrated below, it is necessary that the \(N_2\) flux on the substrate is two or more orders of magnitude larger than the flux of lanthanide atoms to form a stoichiometric LN film, clearly indicating a significant reaction coefficient for \(N_2\). As a contrast, the more readily divalent lanthanides (Eu and Yb) \(^{14}\) do not react with \(N_2\) to form a mononitride but instead form a pure lanthanide thin film. It is possible to grow the divalent lanthanide nitrides, but this requires activated nitrogen. \(^{15}\) The results seem to suggest that the valency of the lanthanides influences their reaction with \(N_2\), and it is also interesting to point out that nonreacting L elements, Eu and Yb, possess the largest atomic volume. \(^{16}\)

To further investigate the reaction coefficient during the L:N\(_2\) reaction, we perform in situ electric conductance of GdN and SmN thin films for varying \(N_2\) pressures (and hence different L:N ratios) during ambient temperature growth (Figure 2). The films are grown between predeposited electric contacts on a SiO\(_2\)/Si substrate, and the electrical resistance is recorded as the films grow. As the nitrogen pressure (\(P_{N_2}\)) in the chamber is lowered, the conductivity of the LN film increases. This increase is expected as lower nitrogen pressure introduces more nitrogen vacancies (\(V_{N}\)) acting as n-type dopants in the lattice, which donate one to three electrons each. \(^{17,18}\) The conductivity, supported by Hall measurements, signals a carrier concentration of \(\approx 1 \times 10^{20} \text{ cm}^{-3}\) in films grown in about \(10^{-4}\) Torr \(N_2\). The \(V_{N}\) concentration in LN films is only of the order of \(1\%\). At \(N_2\) pressures smaller than \(10^{-4}\) Torr (i.e., lower \(N_2\) flux), the \(V_{N}\) concentration rises as \(P_{N_2}\)\(^{-1}\), immediately suggesting an enhanced reaction probability when the molecules strike a N-poor surface. The \(P_{N_2}\)\(^{-1}\) dependence can be modeled by assuming that the probability of dissociation is zero for molecules striking a fully nitrided site and a finite value (\(s_0\)) at an unnitrided lanthanide ion. Within this simple description, the number of nitrogen molecules that stick to the surface per second is \(n_{\text{stick}} = 2s_0x_{\text{LN}}\) where \(x\) and \(n_{\text{N}}\) are the \(V_{N}\) concentration and the \(N_2\) flux at the surface, respectively. The nitrogen/lanthanide ratio in the film is then

\[
1 - x = n_{\text{stick}}/n_{\text{N}} = 2s_0(n_{\text{N}}/n_{\text{L}})\tag{1}
\]

and

\[
x/(1 - x) = [2s_0(n_{\text{N}}/n_{\text{L}})]^{-1}\tag{2}
\]

where \(n_{\text{N}}\) is the lanthanide atom flux. Thus, for small \(V_{N}\) levels (e.g., \(x < 10\%\)), \(x\) and the conductivity follow an inverse dependence on the \(N_2\) pressure during growth, as is observed. Further measurements of the carrier concentration in our films, coupled with assumptions that each \(V_{N}\) introduces one electron into the conduction band, suggest that of order half of the molecules striking a free L ion on the surface introduces two N atoms into the network, that is, \(s_0 \approx 0.5\). The reaction cross section is indeed very large.

Our ability to grow LN thin layers at different \(N_2\) pressures suggests a catalytic reaction at the surface that breaks the \(N_2\) bond to allow the L + \(N_2\) → LN reaction to take place at room temperature and pressure as low as \(10^{-4}\) Torr. To glean some information about this reaction, we grew a thin (25 nm) film of pure Gd and then exposed it to \(N_2\) within the same UHV system. The exposure was carried out at room temperature for 10 min and under a partial \(N_2\) pressure of \(2 \times 10^{-4}\) Torr. To confirm the Gd + \(N_2\) → GdN reaction, XRD measurements are performed ex situ after removing the \(N_2\)-exposed Gd layer from the UHV system. In order to prevent modification in air, the \(N_2\)-exposed Gd layer was capped with a passivation layer. Figure 3 shows the X-ray diffraction 2\(\theta\) scan for a 25 nm-thick Gd layer after \(N_2\) exposure (black). We can see only a peak associated to GdN(111). No trace of pure Gd is detected. For comparison, an XRD 2\(\theta\)-\(\omega\) scan of a pure 25 nm-thick Gd lanthanide layer is shown (gray).

We have also monitored the in situ conductance of some pure lanthanide films (Sm, Gd, and Dy) as they were exposed at ambient temperature to \(N_2\) (Figure 4). The data show the conductance of the films relative to the pure lanthanide films before \(N_2\) exposure. The dose is the total \(N_2\) gas dose that the

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**Figure 1.** XRD 2\(\theta\) scans of thin films of lanthanides deposited at ambient temperature in a \(N_2\) atmosphere. Trivalent lanthanides form a rock-salt-structured mononitride, whereas divalent lanthanides do not react with \(N_2\).

**Figure 2.** Electrical conductivities of GdN and SmN thin films at ambient temperature as a function of the \(N_2\) pressure during lanthanide evaporation. GdN data is from the study of Granville et al.\(^{16}\) Note that the conductivities of pure Sm and Gd are four orders of magnitude larger.
steady-state value. We attribute the initial drop to the plateau, with varying steepness and lengths for L elements, and conductance. This di

Figure 3. XRD 2θ scans of a 25 nm-thick Gd layer after N2 exposure (black) at ambient temperature and a pure 25 nm-thick Gd lanthanide layer (gray).

films are exposed to in the chamber. It is worth noting that there is more than four orders of magnitude difference in conductivity between the lanthanide and its lanthanide nitride. This difference in magnitude means that if we view each unit layer of the lanthanide (nitride) thin film as a parallel resistor, we can set the conductance contribution of the lanthanide nitride in such a network to zero.

We observe, (Figure 4), an initial immediate drop in conductance as soon as the film is exposed to N2, then a plateau, with varying steepness and lengths for L elements, and finally another decrease in conductance before leveling off to a steady-state value. We attribute the initial drop to the nitridation of the top 5–10% of the lanthanide film. Remembering the more than four orders of magnitude difference in conductivity of the LN compared to L, we can assume that the layers that nitrided no longer contribute to the conductance. This difference means that the 5–10% initial drop corresponds to the top 2 nm of the lanthanide being nitrided. As more N2 hits the now-nitrided surface, there are fewer unbound L sites to crack N2. This necessitates a transition to either (i) atomic nitrogen diffusion from the LN to the L or (ii) molecular N2 diffusing through the LN to react with L. If nitrogen diffuses through SmN as N ions, then this would suggest that there are free Sm sites on the surface to crack N2. On the other hand, nitrogen diffusing through SmN as N2 would suggest that availability of catalytically active Sm sites on the surface is reduced. In both scenarios, it is important to point out that the diffusion of N2 or N ions through the SmN layer is a diffusion-limited process; only a fraction of the Sm layer is converted into SmN. It is also worth pointing out that nitrogen vacancies are known to play a critical role in transition-metal nitrides, enhancing the catalysis for N2 dissociative chemisorption and desorption.18,19 A similar reaction pathway may be central in the L–N adsorption and desorption due to the propensity of LN to be nitrogen-deficient. Given the polycrystalline nature of our LN films, as seen in Figure 1, it is likely that nitrogen diffuses through grain boundaries either in an atomic or molecular format. Our first attempt to model the nitridation process after the initial drop suggests a process similar to silicon oxidation based on the Deal–Grove model.20 As more of the L turns into LN, the conductance continues to drop, but the conductance change slows down further, as the diffusion through the LN layer (or the cracking efficiency at an almost fully nitrided surface) is now the rate-limiting step. After 40 min of N2 exposure, the conductance has reached a steady state for most films.

Since we have described the top 5–10 monolayers as more reactive, we assume that these would release nitrogen and/or N2 easier from a LN film. To study this, we made a polycrystalline SmN thin film with a high concentration of V_N. The conductance of this SmN film is monitored as the sample environment is cycled between N2 growth pressure (10−4 Torr) and UHV (10−9 Torr) at room temperature, as seen in Figure 5a. As the sample gas environment changes, the conductance also changes. When N2 is introduced at pressure levels used in typical growths in the UHV chamber, the SmN conductance decreases, which indicates filling of V_N in the lattice. When the chamber is under UHV conditions, the conductance of the sample increases, indicating the creation of more V_N. The increase in the conductance of ~10% correlates well with the experiments described in Figure 4, indicating that the top 10% of the film is easily accessible for reactions. The creation of V_N under UHV conditions could be explained by 10−9 Torr being below the equilibrium nitrogen pressure for SmN, so nitrogen is released from the SmN lattice, although no measurements of the equilibrium pressure for N in SmN exist. The relative conductance change of the SmN film is comparable to the initial nitridation of the pure Sm film, which is surprising as the SmN film is already mostly nitrided. It is also interesting to note that the SmN in these experiments is denitrided at room temperature, and the amount of nitrogen that can be extracted from the lattice may increase significantly if the temperature is increased.

**CONCLUSIONS**

In conclusion, we have demonstrated cracking and incorporation of molecular nitrogen in a variety of lanthanides by successful growth of lanthanide nitrides and conductance and XRD measurements highlighting the conversion of atomically clean surfaces of lanthanides into their nitrides. Surprisingly, this L + N2 → LN reaction can take place under mild conditions, room temperature, and N2 pressure as low as 10−5 Torr. It is also worth mentioning that our observations suggest

Figure 4. Relative conductance of three lanthanide thin films at ambient temperature as they react with N2.
that this reaction can only happen in a very clean environment and that any surface contamination, for example, with oxygen, will not allow the N₂ breaking. We have also observed that the more polycrystalline the L layers are, the deeper the nitridation is, suggesting that grain boundaries contribute in the nitridation of lanthanides as the boundaries provide an accessible diffusion path to unreacted lanthanide. We have also provided evidence of nitrogen desorption from SmN thin films by conductance measurements in a cycling nitrogen—vacuum atmosphere. We believe our results pave the way to further increase the interest on the reaction between lanthanide and N₂ not only from a fundamental point of view but also for its potential in the nitrogen cracking industry.

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Notes
The authors declare no competing financial interest.

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