Correlated Nitride Thin Films - Synthesis, Structural Characterization, and Spectroscopy of Rare-Earth Nitride Thin Films

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We report our study on the synthesis of epitaxial rare-earth nitride thin films by molecular beam epitaxy using ultra-high vacuum base pressures and moderate growth conditions. By systematically tuning the substrate temperature and molecular nitrogen pressures, we are able to prepare high-quality HoN and SmN films with controlled stoichiometry and well-ordered crystalline structure. We investigate the influence of the growth conditions on the composition and on the structural, electronic, and magnetic properties by in-situ electron diffraction and x-ray spectroscopies as well as ex-situ x-ray diffraction and magnetometry. Our results provide new insights into the magnetic properties of HoN films and the Sm valence / 4*f* configuration in nitrogen-deficient SmN films.

The remarkable combination of electronic and magnetic properties of rare-earth mononitrides (RENs) makes them attractive candidates for spintronic applications and has renewed interest in this class of materials, especially in thin film form. However, progress and developments in the field have been hindered by their poor stoichiometry and high reactivity under ambient conditions. It was not until recently that studies on thin films under vacuum conditions have started to unveil some of their unique characteristics and resolve long-standing controversies. Nevertheless, there are still significant challenges that remain to be addressed. The typically high growth rates and nitrogen pressures, the use of activated nitrogen sources or reactive nitrogen precursors, and the lack of suitable substrates for epitaxial growth may contribute to the generally high defect concentration and overall poor control of stoichiometry in thin film samples.

The rare-earth nitrides crystallize in the *fcc* rocksalt structure with lattice constants varying from 5.31-4.76 Å across the rare-earth series. Modern calculations predict a semiconducting nature, which has been confirmed experimentally by resistivity and optical measurements. The resistivity has been found to be strongly dependent on the stoichiometry, and it has been shown that the conductivity can be tuned over many orders of magnitude by variation of the nitrogen content. Most rare-earth nitrides are ferromagnetic. In contrast to the resistivity, the magnetic properties are mainly determined by the rare-earth ions. For example, while GdN has a large magnetic moment of about 7 μ_B/Gd^{3+} ion, SmN has been found to be a near-zero moment ferromagnet. An overview of the properties and challenges of rare-earth nitrides thin film research can be found in reference [1].

In our work, we prepare rare-earth nitride thin films by molecular beam epitaxy (MBE) under ultra-high vacuum base conditions. By using slow deposition rates, moderate temperatures and pressures, maintaining a high degree of cleanliness, we aim for a maximum control of the stoichiometry.

We start our study with HoN and SmN. Holmium and samarium evaporate at moderately high temperatures (<1000 °C), which allows for the use of standard effusion cells, thus avoiding heavily outgassing, high-temperature e-beam evaporators. Like most rare-earths, holmium and samarium have a catalytic effect that allows them to react with molecular nitrogen to form the rare-earth nitride layer, bypassing the need for activated nitrogen sources. Holmium has only one stable valence state of 3+, whereas samarium can adopt two valence states: 3+ and 2+. This additional valence degree of freedom for samarium can complicate the growth process and the understanding of the properties. Nevertheless, an investigation of the $4f$ configuration of samarium in SmN is expected to provide important information about the electronic structure of rare-earth nitrides, especially when considering the nitrogen-deficient case.

Using in-situ reflection high-energy electron diffraction, x-ray photoelectron and x-ray absorption spectroscopies, as well as ex-situ SQUID magnetometry and x-ray diffraction measurements, we investigate how the growth conditions affect the crystallinity, the nitrogen content, the electronic structure, and the properties of the rare-earth nitride films. We would like to note that spectroscopic data of high-quality samples are in particular important as theory relies on the experimentally determined energy positions of the $4f$ states.

Growth of epitaxial HoN films [2]

We first examine the growth of HoN, which has the very stable rare-earth 3+ valence state. To optimize the MBE growth conditions and to explore the growth window, three sets of HoN samples were prepared at molecular nitrogen pressures of 1×10^{-7} mbar, 1×10^{-6} mbar, and

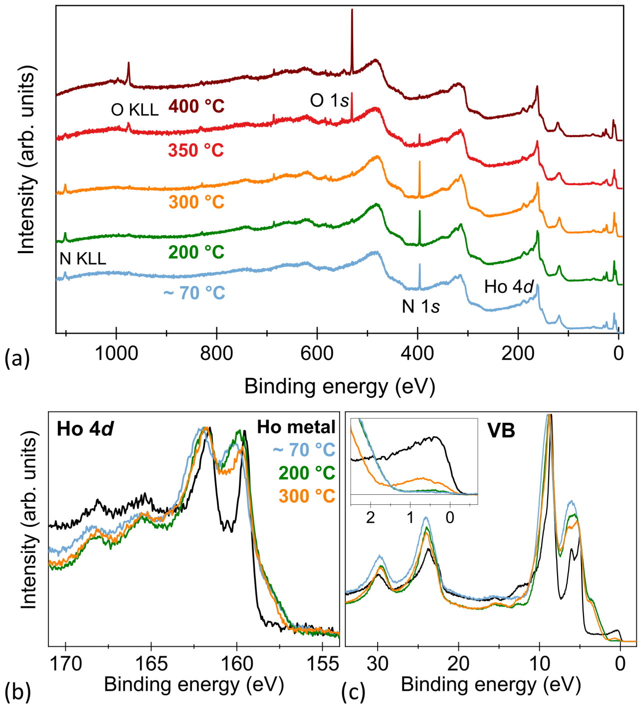

Fig. 1: HoN growth study. (a) XPS wide scans, (b) Ho 4d core levels, and (c) valence band spectra of HoN films grown on MgO (100) at P_{N_2}=1 × 10^{-6} mbar and at the indicated substrate temperatures. Ho metal spectra are shown in black for reference.

1 × 10^{-5} mbar, with the Ho flux rate set to 1 Å/min, and the substrate temperature used as a variable parameter. By systematically varying the deposition conditions for two different substrates, MgO (100) and $LaAlO_3$ (100), we established how these parameters affect the crystalline growth, stoichiometry, and electronic structure.

Figure 1 shows exemplary x-ray photoelectron spectroscopy (XPS) results for HoN films grown at P_{N_2}= 1 × 10^{-6} mbar on MgO (100) for different substrate temperatures. One immediately notices that the Ho 4d and valence band (VB) features are significantly broader for HoN compared to the Ho metal (black). The valence band spectra are composed of the Ho 4f states at ~5-10 eV and the Ho 5p states at ~23-32 eV. The peak at 2.7 eV in the HoN spectra has no counterpart in the metal spectrum, suggesting that it is related to the nitrogen. The features become closer to the shape of the metal for the higher temperatures indicating that the stoichiometry is changing dependent on the substrate temperature. This is confirmed by the wide scans which show a systematic variation in the nitrogen to holmium core level intensities. Furthermore, it is observed that oxygen is incorporated into the films at high substrate temperatures. The composition of all films is derived from the integrated intensities of the XPS core levels and summarized in Figure 2. The stoichiometry generally improves at higher nitrogen pressures and elevated substrate temperatures during deposition. However, above a certain temperature threshold, which depends on the nitrogen pressure and the substrate, the nitrogen content decreases and eventually oxygen is incorporated into the film. We found strong evidence that the formation of the HoO_x phase is related to the oxide substrates, which provide oxygen at high temperatures with which the Ho reacts at the detriment of nitrogen. The temperature range for growing stoichiometric HoN films is larger at higher nitrogen pressures, and the overall growth window is wider for the $LaAlO_3$ (100) substrate. Reflection high-energy electron diffraction shows that HoN grows epitaxially on MgO (100) and $LaAlO_3$ (100) substrates at elevated but not too high substrate temperatures, with a significantly improved crystallinity on $LaAlO_3$, which has a better lattice match assuming a 45° rotation of the pseudocubic lattice. X-ray diffraction measurements of an optimized HoN film on $LaAlO_3$ (100), capped with Cr to prevent degradation in air, confirm phase-pure (100)-epitaxial growth with a lattice constant in agreement with the bulk value.

With the growth recipe established and a well-controlled stoichiometry achieved, we can now proceed with the characterization of the intrinsic properties of HoN.

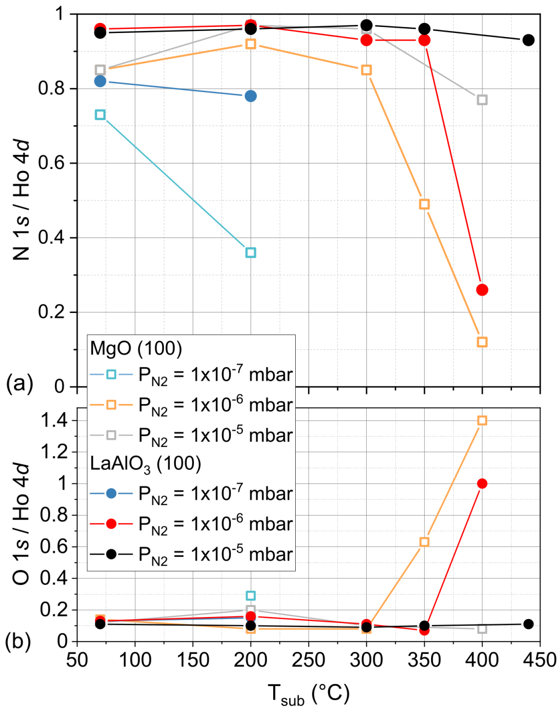

Fig. 2: Determination of the composition of the HoN films. (a) N 1s/ Ho 4d and (b) O 1s/ Ho 4d ratios calculated from the integrated intensities of the XPS core levels and considering photoionization cross sections of the corresponding elemental subshells.

Magnetic properties of HoN [2]

The saturation magnetic moment associated with the Ho^{3+} ion is large, with $gJ = 10\ \mu_B$. However, experimental studies on HoN bulk samples and thin films have reported values lower than theoretically expected for a simple ferromagnetic behavior. The reduction has been explained with a partial quenching of the orbital moment or a complex spin structure due to crystal field effects. Although the detailed mechanism is not fully understood yet, it is generally concluded that HoN has a spontaneous magnetization with a Curie temperature of about 13-18 K.

We investigate the magnetic properties of our high-quality HoN films by SQUID magnetometry (Fig. 3). The film grown under optimized conditions shows a nicely shaped temperature-dependent magnetization curve and also a clear field-dependent hysteresis with a coercive field of 250 mT, confirming the expected predominantly ferromagnetic behavior of HoN. We find a Curie temperature of about 27 K which is around 50% higher than observed in earlier studies. The measured magnetic moment of 6 μ_B/Ho^{3+} at 7 T is significantly larger than in other thin film reports. It is comparable to previous bulk measurements, but still lower than expected for the free Ho^{3+} ion. If nitrogen vacancies are present, the saturation moment as well as the hysteresis do not change considerably, cf. the results of HoN films with 2% (red) and 4% (blue) less nitrogen, indicating that these properties are mainly determined by the holmium ions. However, the Curie temperature shows a clear trend, with the transition blurring and moving to lower values for nitrogen-deficient films. We observe a reduction of the magnetic ordering temperature by about 3 K for a HoN film with ≈ 4% less nitrogen. This suggests that the Curie temperature can be used as a measure of sample quality and that samples with lower transition temperatures suffer from off-stoichiometry.

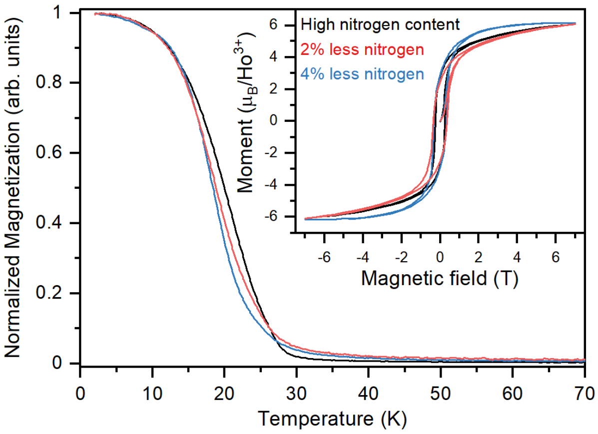

Fig. 3: Temperature-dependent magnetization of HoN films grown on $LaAlO_3$ (100) under optimized conditions (black), with 2% less (red), and 4% less nitrogen (blue) at 0.001 T. Inset: Field dependence at 2 K.

The role of the Sm 5*d* states in SmN [3]

With the knowledge about the growth of HoN, we continue with the intriguing case of SmN with the additional valence-state degree of freedom. Epitaxial SmN films were prepared on $LaAlO_3$ (100) substrates and the composition was controlled by carefully tuning the growth parameters. In-situ photoelectron spectroscopy and x-ray absorption spectroscopy (XAS) were used to study the influence of the composition on the Sm valence. We would like to note that in the rare-earth community, the valence is usually referred to the $4f$ occupation, i.e. Sm^{3+} has the $4f^5$ configuration and Sm^{2+} has the $4f^6$ configuration.

Figure 4 shows the XPS Sm $3d$ and XAS Sm $M_{4,5}$-edges and N K-edge spectra of three SmN films with different nitrogen contents from optimized to highly off-stoichiometric. To identify the 3+/2+ multiplets energy positions, we compare our spectra to a Sm metal reference which has a mixed valence surface. The high nitrogen content (optimized) sample shows as expected only the features of the 3+ multiplets. Also the SmN film with 19% less nitrogen exhibits only 3+ character. This is surprising since nitrogen vacancies are known to act as electron donors. One might expect a reduced samarium valence or more precisely a contribution of a $4f^6$ configuration near a vacancy. The 2+ multiplets should be detectable in our spectra even for only a few percent of nitrogen deficiency. However, such a contribution is only observed for the highly nitrogen-deficient film with 30% less nitrogen. The high vacancy concentration needed to observe a $4f^6$ signature may indicate that it is actually not related directly to the vacancies but rather to the formation of metallic clusters. This raises now the question of where the extra electrons are in SmN with moderate nitrogen vacancy concentrations. One can speculate that the empty Sm $5d$ states play a role as charge reservoir stabilizing the $4f^5$ configuration as has been observed for SmB_6. In the N K-edge absorption spectra we see a reduced intensity of the spectral features for the nitrogen-deficient films. As the main peaks have been assigned to rare-earth $5d$ states, the low intensity may suggest that there are fewer holes in the $5d$ shell, which may indeed support the picture that a $4f^5 5d^1$ configuration is formed in a samarium ion surrounding the vacancy site. This scenario may be not unrealistic as also samarium metal, which has no nitrogen ions to absorb the electrons, adopts the $4f^5 5d^1$ configuration in the bulk and only at the surface Sm^{2+} $4f^6$ multiplets are observed.

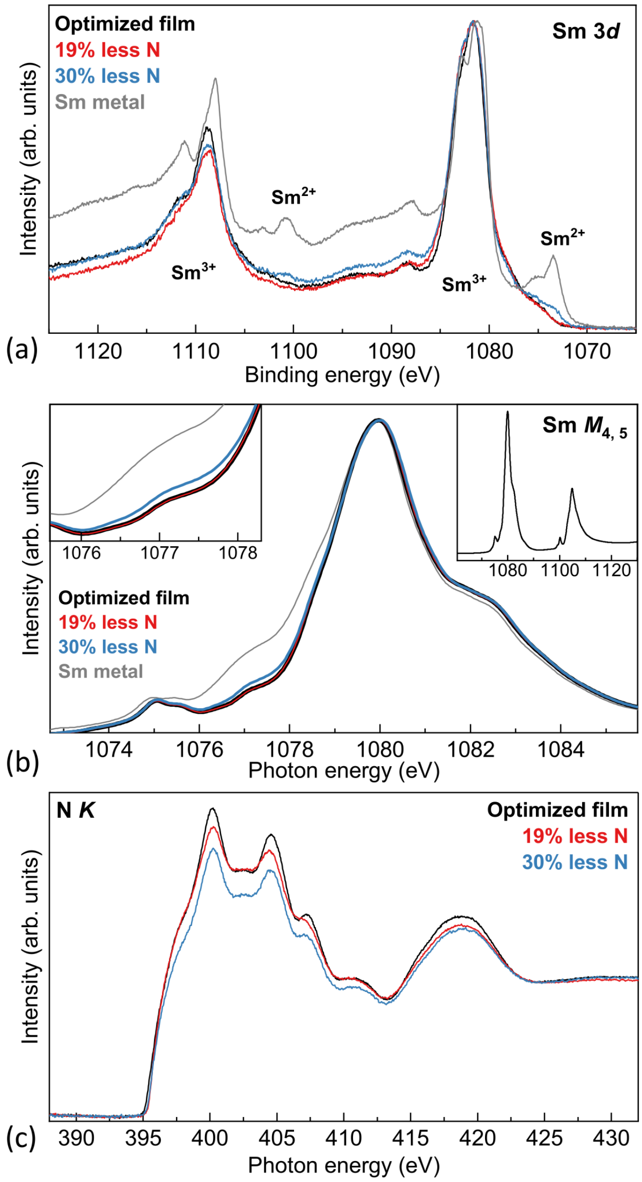

Fig. 4: Sm valence: (a) Sm 3d XPS spectra, (b) Sm XAS $M_{4,5}$ edges, and (c) N XAS K-edges of an optimized SmN film grown on $LaAlO_3$ (100) (black), a film with 19% less nitrogen (red) and a film with 30% less nitrogen (blue). A metal reference is shown for the Sm spectra.

Conclusions

We have successfully developed growth recipes for epitaxial HoN and SmN films using molecular nitrogen and moderate growth conditions. In a field where precise composition and cleanliness of the environment are of the utmost importance, a controlled fabrication under ultra-high vacuum base conditions forms the basis for investigating and understanding of the intrinsic properties of the materials. Using in-situ reflection high-energy electron diffraction, x-ray photoelectron spectroscopy, x-ray absorption spectroscopy and ex-situ SQUID magnetometry and x-ray diffraction, we study the influence of the growth parameters on the composition, the crystalline and electronic structures, and the properties of the films.

For HoN, we find nicely shaped, Brillouin-like magnetization curves for the optimized sample with a Curie temperature of about 27 K, i.e. 50% higher than previously reported. We observe that the presence of nitrogen vacancies reduces the Curie temperature and broadens the transition, suggesting that the Curie temperature may serve as an indicator for the sample quality. Saturation magnetization values of about 6 μ_B/Ho^{3+} were measured for both the optimized and the moderately nitrogen-deficient films.

In SmN we study the influence of the nitrogen stoichiometry on the Sm valence / $4f$ configuration. As the $4f^5$ configuration was found to be stable for nitrogen deficiencies of up to 20%, our results suggest that the extra electrons present in the nitrogen-deficient system occupy the empty $5d$ states rather than the $4f$ states, forming a $4f^55d^1$ configuration. Thus, the $5d$ states may play an important role in SmN as charge reservoir, which stabilizes the $4f^5$ configuration.

This work marks the beginning of a new research project for our thin film group. With the knowledge gained, we will now be able to investigate many other members of the rare-earth nitride series and solve further long-standing open questions.

External Cooperation Partners

Chien-Te Chen (NSRRC, Hsinchu, Taiwan)

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