

Epitaxial growth of samarium nitride on yttria stabilized zirconia

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1 Introduction

The rare earth elements form the section of the periodic table over which the $4f$ electron shell is filled. This gives them interesting magnetic properties which vary widely over the series. Sm and Gd are of express interest due to their electronic configurations. Both take the form $4f_x5d_26s_1$ where Sm has 5 $4f$ electrons and Gd has 7. When grown as rare earth nitrides both of these elements form the $NaCl$ rock-salt structure giving up their $5d$ and $6s$ electrons to nitrogen atoms. Leaving the electronic configuration in the case of samarium nitride of $4f_5$ and gadolinium nitride as $4f_7$.

By applying Hund's rules to these configurations we see that GdN will have a magnetization of $7\mu_B$ per Gd and SmN will have a vanishingly small net magnetization due to cancellation between orbital and spin magnetic moments. In perfectly stoichiometric samples both GdN and SmN are insulators with all conduction electrons used to create nitrogen bonds, however any nitrogen vacancy (N_v) in the lattice can contribute up to three conduction electrons to the material, thus the carrier concentration may be doped by altering the amount of N_v . These properties include SmN and GdN to the small class of magnetic semiconductors, making them of interest to the area of spintronics. Of even more interest is that doping either material with N_v will not influence its magnetic properties, making these materials somewhat unique. Not only is SmN the only known near net zero ferromagnetic semiconductor [reference] but it has also displayed superconductivity when heavily doped with N_v while in its ferromagnetic phase.

The electronic structure of GdN has been the subject of several studies [reference] and its band structure is mostly understood [check this]. The band structure of SmN however is much less understood, particularly the band gap in the ferromagnetic phase [check this] and the location of the lowest $4f$ level in the conduction band. If a clearer picture of the band structure of SmN were provided some of its more interesting and unique properties may be able to be understood.

One measurement technique that may pro-

vide information on the band structure of SmN is angle resolved photo-electron spectroscopy (ARPES). ARPES measures both the speed and scattering of electrons excited out of a sample by soft x-rays. This enables the determination of both the energy and momentum enabling the band structure to be reconstructed. As only electrons excited from a sample are measured ARPES only yields information regarding the density of states in the valence band of a given material. ARPES measurements on SmN may provide new information into the band structure and although only the conduction band would be probed these measurements are of obvious value. For ARPES measurements to be successful a sample must be single crystal and as close as possible to atomically flat, this is as the angle of emission of excited electrons from the sample must be determined. The manufacture of these samples was the primary goal of this project.

Previous work has been completed regarding the epitaxial growth of SmN [big one and jay]. Chan et al. report on the occurrence of multiple rotational domains in epitaxial SmN grown on a hexagonal AlN net, while Natalie et. al. report on the lattice mismatches between possible substrates and the REN series. It is desirable to grow a single crystal sample with a minimal lattice mismatch to reduce strain. This requires a cubic net with a similar lattice parameter to SmN , such requirements can be found in Yttria stabilized zirconia (YSZ) which on its [100] face

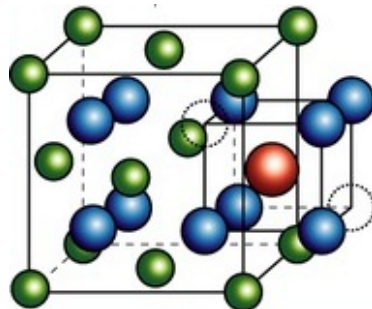


Figure 1: YSZ displays a cubic face on [100] and a lattice parameter that matches very well with RENs, however mobile O^- ions due to vacancies can cause an oxide layer to form at the sample substrate interface.

has a cubic net with and a lattice parameter of 5.12\AA a 98 match to SmN which has a lattice parameter of 5.02\AA .

The cubic net of $[100]$ YSZ along with the small lattice mismatch with SmN may make it look very appealing for single crystal epitaxial growth, however a diligent experimentalist will soon notice a caveat. The crystal structure of YSZ pictured in figure [??] displays an O^- vacancy, this makes YSZ an efficient O^- ionic conductor which finds important application in fuel cell technology, however causes problems in the fabrication of RENs. RENs have a proficiency to degrade to their oxide form Re_2O_3 when exposed to oxygen [source]. This is normally mitigated by the use of a capping layer, typically AlN , GaN or metallic Sm or Gd . This capping layer can not however protect a sample from its own substrate. Thus it is expected an oxide layer would form at the interface between a sample and its substrate, this was observed by Ludbrook et al. [ref] in similar growths involving GdN . Thus for the creation of a successful sample the mobile O^- ions must be removed from the YSZ substrate. The thermal emission characteristics of O^- ions from YSZ is shown by Fujiwara et. al. [ref] to follow an exponential relationship as would be naively expected from the Boltzmann equation.

2 Experimental Methods

Before samples were grown experiments were carried out on bare YSZ substrates to determine if it was possible to deplete the levels of O^- ions enough to avoid the creation of an oxide layer at the sample-substrate interface. This involved baking the substrate at temperatures well above the growth temperature while monitoring the gas composition inside the chamber using a mass spectrometer. Initial tests indicated mixed results. Figure [] shows the partial pressure of various ions in the chamber as a function of time. All ions tracked can be clearly seen to increase with temperature and drop once a stable temperature has been reached, as expected. It is difficult to determine how effective this treatment was as levels of any given ion rarely fall below

base pressure, however the significantly elevated levels at high temperature do indicate that the baking process was at least somewhat successful. Some ions of specific interest are O_2 , H_2O and N_2 . The partial pressure of O_2 can be seen to decrease well below the base pressure once the substrate had been cooled, indicating that the levels of mobile O^- ions in the substrate may well have been depleted. However H_2O and N_2 show much more interesting behaviour, the levels of H_2O continue to rise even after a stable substrate temperature is reached, this is matched by the levels of H_2 in the chamber. A possible explanation may be due to the much slower heating of the chamber walls which will outgas hydrogen, leading to increasing levels of H_2 and H_2O as the experiment progresses. What is more interesting is the increase in level of both H_2O and N_2 when the substrate heater was turned off, no explanation is offered at the present for this behaviour.

Samples were grown on $10\text{mm} \times 10\text{mm} \times 0.5\text{mm}$ YSZ $[100]$ substrates, which were backed for various times before growth from 2 to 8 hours. Growth temperatures were 600°C under an atmosphere of $1e^{-4}\text{mb}$ of 99.999% pure nitrogen with a Sm flux of $1 - 5\text{\AA}/\text{s}$. Nitrogen was not ionised, instead the catalytic cracking of N_2 molecules on contact with rare earth was used (reference). During growth the sample surface was monitored using reflection high energy electron diffraction (RHEED) this enabled the *insitu* measurement of the evolution of the lattice parameter. As the exact geometry of the RHEED set-up was not available the assumed lattice parameter of the YSZ substrate (5.12\AA) was used to calibrate the device for measurements.

Once sample growth was completed the affect of purging the chamber of nitrogen on the sample surface was investigated using RHEED. Sample were also annealed while RHEED images were taken to observe any effect on the sample surface.

To prevent oxidation of the surface layer sample were capped with either Sm metal or AlN . Following growth X-ray diffraction (XRD) measurements were taken to confirm the composition and orientation of the samples.

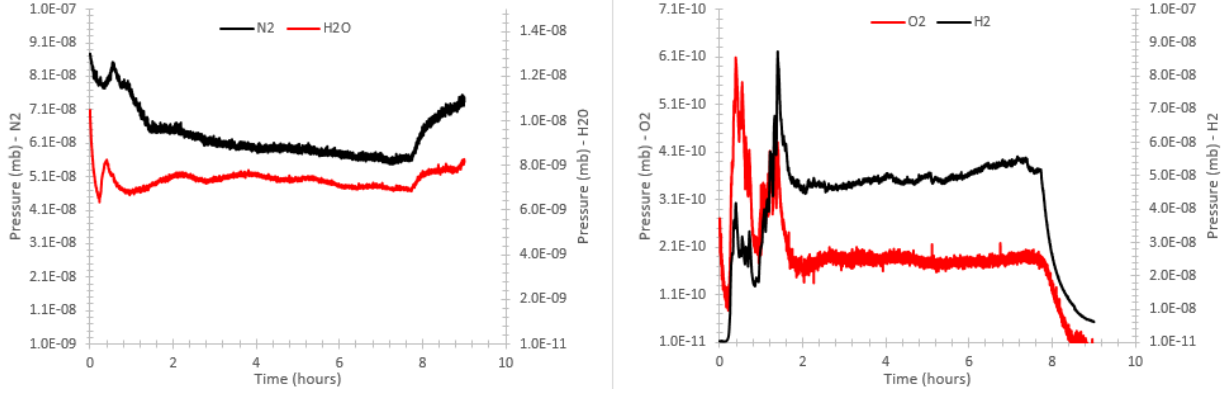


Figure 2: YSZ displays a cubic face on $[100]$ and a lattice parameter that matches very well with RENs, however mobile O^- ions due to vacancies can cause an oxide layer to form at the sample substrate interface.

3 Results

As samples were grown RHEED images were taken and later analysed to determine the evolution of the lattice parameter as a function of substrate thickness during the growth. Figure [] shows this evolution for sample A375. If figure [] is examined the lattice parameter can be seen to begin at the known value for the YSZ substrate of 5.12\AA , it can then be seen to increase to 5.45\AA , close to the known value for Sm_2O_3 indicating the formation of an oxide layer. Af-

ter 20nm of growth the lattice parameter can be seen to decrease to 4.8nm closer to the expected lattice parameter of SmN . These lattice can be compared to the XRD scans taken shown in figure [].

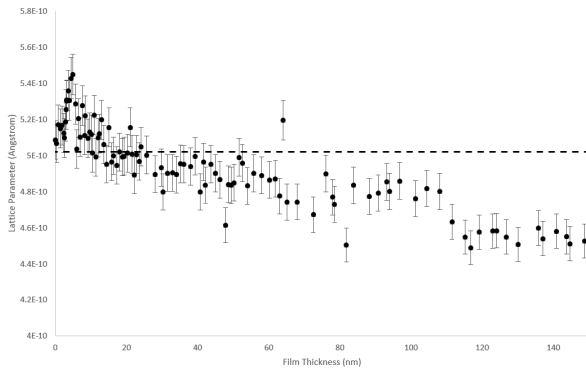


Figure 3: YSZ displays a cubic face on $[100]$ and a lattice parameter that matches very well with RENs, however mobile O^- ions due to vacancies can cause an oxide layer to form at the sample substrate interface.