Phys. Status Solidi C **9**, No. 3–4, 605–608 (2012) / **DOI** 10.1002/pssc.201100363

physica status solidi pss c
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current topics in solid state physics

Epitaxial growth and properties of GdN, EuN and SmN thin films

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Received 8 July 2011, revised 24 August 2011, accepted 5 September 2011
Published online 7 December 2011

Keywords rare-earth nitrides, epitaxial growth, ferromagnetic, semiconductor

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This paper contains a summary of selected aspects of the epitaxial growth of rare-earth nitride thin films and the recent progress achieved in this field. The discussion is focussed on GdN, SmN, EuN compounds grown by both pulsed laser deposition and molecular beam epitaxy on different substrates including YSZ (001), c-plane (0001) AlN and GaN. While a N_2 plasma cell is used as a nitrogen source for growing EuN, we take advantage of the catalytic breakdown of molecular nitrogen by rare-earth atoms to grow GdN and SmN in the absence of activated N_2. The structural, magnetic and transport properties of the thin films are assessed by reflection high-energy electron diffraction, x-ray diffraction, Hall Effect, temperature-dependent magnetization and resistivity.

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1 Introduction

The rare-earth (RE) series, across which the 4*f* atomic shell is filled, have been recognised for some time as exploitable for their strongest magnetic moments among the stable elements. Until recent studies their potential for spintronics was discouraged by the fact that they are metallic in their elemental form. However their 3^+ ions react with the pnictides to form simple face centred cubic (NaCl) structure with obvious potential to integrate with the cubic lattice of silicon. Most of those pnictides are antiferromagnets, making them unsuitable for spintronics, but the ferromagnetic exception, the nitrides, have recently gained attention [1-4]. Many and perhaps most of the rare-earth nitrides (REN) are semiconductors [5-8], though there are likely semimetals also among their number. The RE 5*d* conduction bands and N 2*p* valence bands experience opposing exchange splitting, so that both electrons and holes carry the same majority spin in the ferromagnetic state [7]. That character also ensures that when the bands overlap the resulting semimetals all have the majority spin; they form half-semimetals. However their properties are poorly explored, in large part because they have a strong propensity to forming nitrogen vacancies (V_N) and to form oxides when exposed to air. Additionally, most of the films studied in the literature are polycrystalline and there are still controversial discussions with respect to the electrical properties even with the most thoroughly studied nitrides, GdN, SmN and EuN. Therefore, the epitaxial growth of high-quality crystalline REN samples is needed to establish unambiguously their properties. In this paper we report on the epitaxial growth of RENs thin films pointing out the issues encountered and the solutions we propose to overcome these difficulties. The structural, magnetic and transport properties of the REN thin films were investigated through combined measurements of reflection high-energy electron diffraction (RHEED), X-ray diffraction (XRD), Rutherford Backscattering Spectroscopy (RBS), Hall effect, temperature-dependent magnetization and resistivity.

2 Growth procedures and discussions

The RENs adopt an fcc structure with a lattice parameter from 5.295 Å to 4.766 Å for lanthanum and lutetium, respectively [9]. The most preferable substrate for REN epitaxy is YSZ (001) as it takes an fcc structure, similar to

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the RENs, with a lattice parameter of 5.125 Å [10], nearly matching all the REN series. Our first attempts were focused on growing GdN and SmN thin films on YSZ substrates using pulsed laser deposition (PLD) technique. A 99.9% purity elemental Gd and Sm sputtering target was employed for the GdN and SmN growth respectively, and an YSZ substrate was used as a target for the film capped. The nitrogen species are provided by an Oxford Applied Research HD25 rf N_2 plasma source operating at 400 W. The nitrogen partial pressure during the growth is 10^{-4} Torr. The REN layers were grown under N-rich conditions with a growth rate of about 60 nm/h. Substrates were outgassed at 800 °C for a minimum of 1 hour before starting the REN growth in a temperature range of 600-850 °C. The growth stages were monitored using RHEED as showed for SmN films in Fig. 1. After a diffuse and weak intensity during the first 2 nm (cf Fig. 1a), the RHEED pattern becomes streaky and more intense, as displayed on Fig. 1b for a 30 nm thick SmN layer. The thickness has been deduced from ex-situ RBS experiments and by in-situ evaporation rate measurements using a quartz crystal thickness monitor. The in-plane lattice parameter was also monitored during growth as presented on Fig. 1c. From the initial substrate lattice constant of 5.125 Å there is a sharp increase to ~5.5 Å before the lattice begins to contract towards the bulk value of SmN, 5.035 Å [9]. With the strong affinity of RE for oxygen and the mobility of oxygen in YSZ [11] it is likely that samarium oxide (Sm_2O_3) is forming at the interface at high temperature. The lattice constant of approximately 5.5 Å agrees with this conclusion: Sm_2O_3 in its cubic form takes the 'bixbyite' crystal structure with a lattice constant of 10.932 Å [12]. We have observed the same behaviour for GdN thin film grown on YSZ using PLD technique as displayed on Fig. 1c [13]. In the meantime, a small amount of EuO in the EuN thin films grown by molecular beam epitaxy (MBE) is observed when performing XRD 2θ-scans. Once again, we associate the formation of the thin oxide layer at the EuN/substrate interface with the mobile oxygen in the YSZ [14]. As a ferromagnetic semimetal material, EuO may affect strongly the magnetic and electrical properties of EuN thin films. While it would have been a real advantage to demonstrate the growth of high-quality of REN films on YSZ, we pointed out that traces of oxygen are present in the thin films which may lead to some controversy about the intrinsic properties of the RENs studied. It should be mentioned that historically the first epitaxial growth of a REN, GdN, has been performed on MgO(100) substrates [15]; but at this time it has been observed that thick films lead to very rough surfaces.

To surmount the drawbacks described previously, 2 groups took advantages of the hexagonal symmetry of the {111} plane of the REN rock salt structure, to investigate their growth on c-plane (0001) wurtzite GaN [16] and latter on AlN [17]. Figure 2 shows the lattice mismatch between (111) REN lattice and c-plane (0001) wurtzite AlN, GaN and InN lattices as a function the RE atomic number.

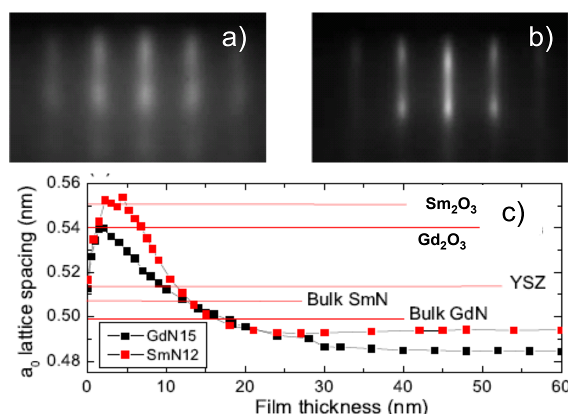

Figure 1 RHEED pattern evolution of SmN surface along the [100] azimuth after (a) ~2 nm and (b) 30 nm at 650 °C. (c) Evolution of in-plane lattice parameter of SmN and GdN as a function of the film thickness during the early growth stages.

This graph shows that RENs can be grown nearly lattice-matched on InN substrate, but its non commercial availability makes GaN and AlN more attractive for the moment. The 7.5-15% lattice mismatch between the RENs and AlN and GaN, though relatively severe, should not be an insurmountable problem. We can legitimately consider the group-III nitrides as a potential template for the epitaxial growth of REN films. Additionally, this may open the way to develop new functionalities combining nitride semiconductors and REN materials.

We have focussed on the growth by MBE of GdN, SmN and EuN on Ga-polar GaN and Al-polar AlN templates grown on both sapphire and silicon (111) substrates. The AlN and GaN templates on sapphire substrates have been grown by HVPE (MTI corporation) while the AlN templates on Si(111) substrates have been grown by MBE [17]. Gd and Sm metals were evaporated by using an electron beam and from a tungsten wire basket, respectively. The SmN and GdN growth were at a rate of 60-80nm/h, under a pressure of pure N_2 ranging from 4×10^{-5} to 4×10^{-4} Torr with the substrates held at temperatures from room temperature (RT) to 750 °C. Under these conditions the N_2 flux on the growth surface is 10^2-10^3 times larger than the Gd and Sm flux; for substantially lower N_2 pressure the films were severely Gd or Sm rich. A polycrystalline AlN capping layer was grown at RT by evaporating Al in the presence of activated nitrogen. Figure 3 shows XRD 2θ-scans for a polycrystalline and epitaxial GdN films grown at RT and at 650 °C, respectively. In the inset is displayed both the RHEED patterns of the epitaxial and polycrystalline films taken at RT. A single phase polycrystalline GdN and the epitaxial character of the GdN film grown at high

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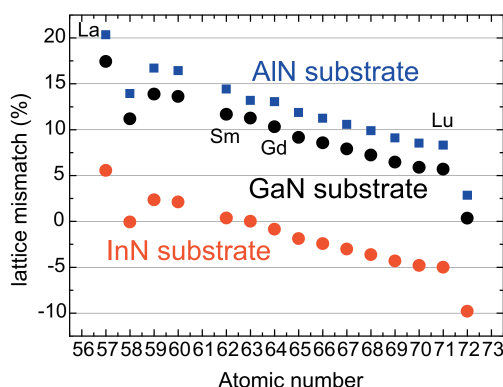

Figure 2 Calculated lattice mismatch between (111) REN and c-plane (0001) wurtzite AlN, GaN and InN lattices as a function of the RE atomic number. The lattice parameters used for AlN, GaN and InN are 3.112, 3.189 and 3.548 Å, respectively.

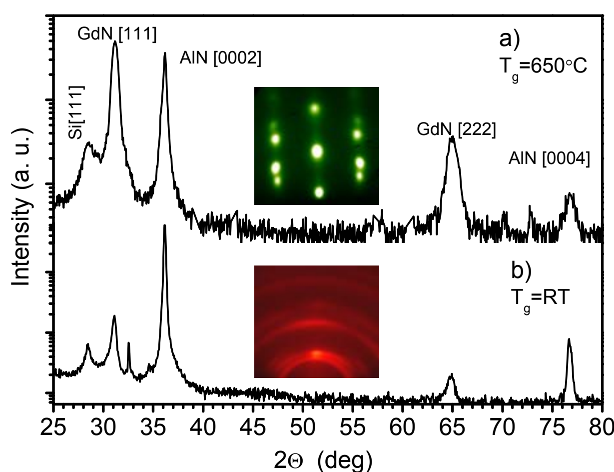

Figure 3 2Θ-scan XRD scans of epitaxial (a) and polycrystalline (b) GdN films a grown at 650 °C and room temperature, respectively. The RHEED patterns of the epitaxial and polycrystalline films along the Si [110] azimuth taken at room temperature are also displayed.

temperature are observed on the XRD 2θ-scans. In addition to the peaks of AlN and Si we observe only the (111) and (222) reflections of GdN. Clearly the hexagonal face of AlN favours a fully (111)-oriented GdN film. It is worth mentioning that the RHEED pattern of the epitaxial film shows the presence of twin islands which have been explained by Scarpulla *et al.*, using symmetry considerations [16]. A full discussion of this phenomenon is beyond the scope of this paper, but vicinal surfaces and surfactant addition during the growth may be the way to follow to suppress the twins. The reaction of Gd with N_2 takes place at the surface to form an epitaxial GdN layer, even in the absence of activated N_2. Such growth has previously been demonstrated for polycrystalline films of GdN, SmN, DyN, ErN, and LuN. When growing SmN in the same conditions as GdN under pure N_2, XRD 2θ-scans showed films are strongly textured in the (111) direction. However a (200) scattering peak is observed meaning that the epitaxial growth of SmN is not as straightforward as the epitaxial growth of GdN.

We have recently focused on the growth of EuN using a Kaufman type ion source to supply 125 eV ion nitrogen species at a beam current of 0.24 mA. The EuN epitaxial thin films are obtained when the growth occurs in an adsorption-controlled growth regime. In this regime, the Eu flux is set to be much higher than the N_2 flux and a high substrate temperature (~800 °C) is maintained to re-evaporate any excess of Eu. Only Eu atoms that have paired with a nitrogen atom remain on the sample. Grown on c-plane (0001) wurtzite AlN and GaN, the EuN thin films have similar characteristics as GdN thin films from a RHEED and X-ray point of views. The RHEED patterns suggest that the growth occurred by the nucleation of two rotational variants of EuN which coalesce when increasing the thickness. XRD 2θ-scans demonstrate that only (111)-oriented EuN is present in the films.

3 Properties and discussions

We now turn to the electrical properties by showing the temperature dependent resistivity for polycrystalline GdN films prepared by MBE as pure N_2 gas pressure was decreased (Fig. 4). An epitaxial GdN thin film grown by PLD is displayed for comparison. In each case the peak in the resistivity coincides with the ferromagnetic ordering temperature (T_c) as previously reported [8, 13, 16-18]. The film with the highest resistivity was grown in a nitrogen partial pressure of about 4×10^{-4} mbar compared to 2×10^{-5} mbar for the film with the lowest resistivity. The sample with the highest resistance is quite clearly semiconducting, while the sample with the lowest resistance, the PLD sample, almost appears to be metallic in that they have a resistivity of roughly 2×10^{-4} Ω.cm, positive temperature coefficient down to T_c and no sign of the upturn in resistance is seen at low temperature. It is important to mention that we see evidence of droplets using high magnification optical microscope for most of all the PLD samples. The behaviour of the differential conductivity with N_2 partial pressure indicates that a lower pressure results in layer growth with a higher concentration of carriers, and the observed doping is likely due to N vacancies, as both we and others have concluded previously. Although Fig. 4 deals with polycrystalline thin films, we also observed semiconductor-like resistivity behaviour above and below T_c for epitaxial thin films grown by MBE under pure N_2 [17]. Our data differ in this respect from those reported by Scarpulla *et al.* [16] and Ludbrook *et al.* [13] since they observed metallic conductivity behaviour. It is worth mentioning that the resistivity of epitaxial thin films grown by MBE can be tuned by varying the N_2 pressure [17]. Our magnetic measurements (not shown) reveal that near stoichiometry GdN epitaxial thin films show the familiar

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ferromagnetic response below a Curie temperature (T_C) of 70 K. In the ferromagnetic state, at 10 K, the moment of epitaxial thin films is more easily saturated to 7 μB/Gd ion in low fields applied in plane than are the polycrystalline films. This might be explained by the larger crystallite volume in epitaxial films than in polycrystalline films. The coercive field scales as the inverse of the crystallite volume [13]. Larger crystallites correspond to a lower coercive field; typical value about 150 Oe are measured at 10 K for epitaxial films while it reaches about 380 Oe for polycrystalline films which gives some clues as to the origin of the coercive field [19].

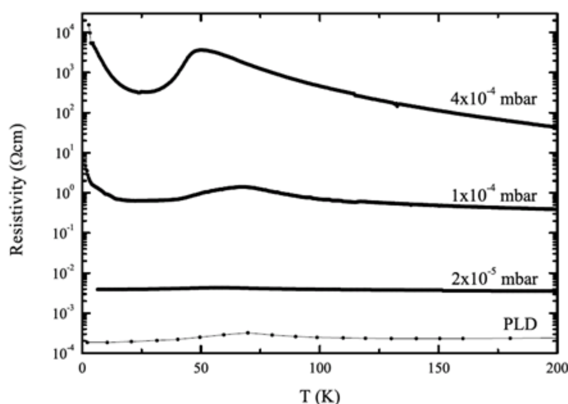

Figure 4 Temperature dependent resistivity for samples prepared under different pure nitrogen pressures. In each case the peak in the resistivity coincides with the ferromagnetic ordering temperature. The plot labelled PLD refers to the sample grown by PLD technique.

Acknowledgements The research was supported by the New Zealand New Economy Research Fund, Grant No. VICX0808, and the Marsden Fund, Grant No. 08-VUW-030. The MacDiarmid Institute is supported by the New Zealand Centres of Research Excellence Fund.

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