Available online at www.sciencedirect.com
SCIENCE DIRECT®
Current Applied Physics 6 (2006) 407–410
Current Applied Physics
An official journal of the KPS
www.elsevier.com/locate/cap
www.kps.or.kr

TEM characterisation of GdN thin films

W.R. McKenzie [a,*], P.R. Munroe [a], F. Budde [b], B.J. Ruck [b], S. Granville [b], H.J. Trodahl [b]

[a] School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia
[b] MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

Available online 27 December 2005

Abstract

The rare-earth metal nitrides have been predicted to possess a wide range of electronic structures, ranging from ferromagnetic to half-metallic to semiconducting, which makes these materials attractive for a range of applications. In this study, GdN thin films were grown at room temperature on silicon and glass quartz substrates by thermally evaporating gadolinium metal in nitrogen atmospheres. A detailed microstructural characterisation of these films was carried out using a variety of techniques such as transmission electron microscopy (TEM), Rutherford backscattering spectroscopy (RBS) and energy dispersive X-ray spectrometry. TEM analysis indicated the films are nano-crystalline, with crystallite sizes being affected by the ionisation state of the nitrogen atmosphere used. Sources of the films' internal stress were discussed with a significant amount of oxygen absorption, identified by RBS, being a probable cause. Electron diffraction and energy dispersive X-ray studies found that GdN was the only phase present with oxygen uniformly distributed throughout the film.

PACS: 68.55.a

Keywords: GdN; Gadolinium nitride; Thin film; TEM; FIB

1. Introduction

The rare-earth metal nitrides, which all crystallise in the FCC rock-salt structure, have been predicted to show a wide range of electronic properties, ranging from ferromagnetic to half-metallic to semiconducting [1]. These materials have been paid relatively little attention in the literature, in part due to difficulties that are encountered in their production. Most notably, rare-earth metal nitrides react quickly upon exposure to air, although the details of this reaction and the resulting material have not been fully explored.

This work forms part of a larger study into the production and properties of thin films of one such rare earth nitride, GdN, in light of the possibility that it may possess novel electronic or magnetic properties. One potential application is its use as a replacement for rare-earth chalcogenides as spin filtering devices [1]. This paper presents a microstructural characterisation, based on transmission electron microscopy (TEM) and Rutherford backscattering spectroscopy (RBS), of two thin films of GdN that were first grown in an ultra-high vacuum system and subsequently exposed to the atmosphere. The results highlight the changes induced in the material by exposure to air, and provide an insight into the structure of the as-grown material.

2. Experimental method

GdN thin films were grown in an ultra-high vacuum deposition chamber (base pressure below 10^{-8} mbar) by the thermal evaporation of Gd metal in the presence of 10^{-4} mbar of high-purity nitrogen gas. Two separate GdN films were prepared on substrates mounted on a water-cooled substrate holder held at room temperature. In the first instance the nitrogen was fed into the chamber

* Corresponding author. Fax: +61 2 9385 6400.
E-mail address: warren@materials.unsw.edu.au (W.R. McKenzie).

1567-1739/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cap.2005.11.029

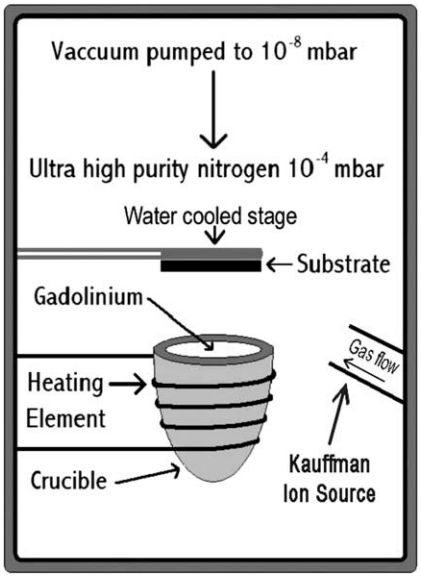

Fig. 1. Schematic diagram of the deposition apparatus.

via a Kauffman type ion source, which ionised roughly 10% of the nitrogen molecules and accelerated them through a 500 V potential. This film was deposited onto a single crystal silicon substrate cut with the surface parallel to the (1 0 0) crystal plane. The second film, prepared on quartz glass, was grown under flowing nitrogen gas at a pressure of 10^{-4} mbar without the use of the ion source. It was found that this technique was sufficient to cause nitrogen to be incorporated into the film, and it was noted that the process reduces the nitrogen pressure in the chamber by a factor of 10 upon commencement of the Gd metal evaporation. A schematic of the apparatus used is given in Fig. 1.

A quartz crystal microbalance was used during growth to monitor the film thickness. It was noted that the microbalance registered approximately 25% increase in the films' mass within minutes of the chamber being vented to atmosphere. During this time the films changed from a semi-transparent brownish colour to highly transparent. It is worth noting that the mass increase is considerably larger than the increase that would be expected if the films simply converted to Gd_2O_3 after reaction with atmospheric oxygen.

For both samples, TEM specimens were prepared using an FEI Nova 200 Nanolab Focused Ion Beam miller (FIB). This was done using the "Lift-out" technique, details of which are given by Giannuzzi and Stevie [2]. This process involves milling and then detaching a TEM foil from the bulk material with the FIB then transferring the electron transparent region to a carbon coated copper TEM grid using a micro-manipulator. Coatings of platinum were first deposited on to the films, in situ in the FIB, to protect the film during processing. The cross-sectional TEM samples were analysed in a 200 kV Philips CM-200 TEM to which an EDAX energy dispersive X-ray spectrometer (EDS) was interfaced.

3. Results and discussion

The cross-sectional structures of each film are presented in the bright field TEM images shown in Fig. 2. The GdN film on the silicon substrate (Fig. 2A), deposited in an atmosphere of nitrogen ions, has a thickness ≅100 nm, and exhibits a polycrystalline structure of nominally equiaxed grains typically about 30 nm in diameter, although the grain size is seen to vary considerably. A number of voids, up to ≅20 nm in diameter, are also present in this film. In contrast, Fig. 2B shows a bright field TEM image of the specimen deposited on the glass quartz substrate in an atmosphere of nitrogen gas. This film is considerably thicker (≅400 nm), but the average grain size is much

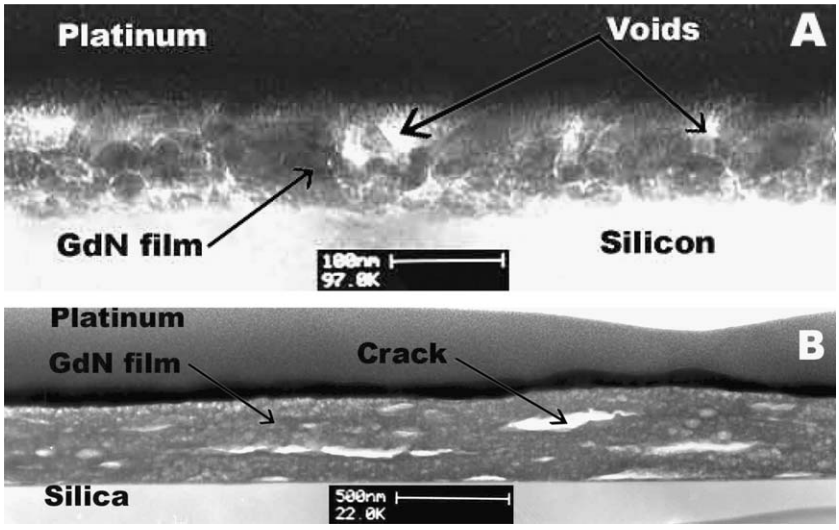

Fig. 2. Bright field TEM images of the GdN film grown on (A) the silicon substrate with partially ionised nitrogen and (B) the glass quartz substrate with non-ionised nitrogen.

smaller (≅20 nm). This film also contains a number of cracks running parallel to the interface, although fewer pores are visible.

The difference in film thickness is a direct result of varying deposition times for each film as both grew at approximately 1 Å s^{-1}. That is, the deposition time for the film deposited on quartz in an atmosphere of nitrogen gas was longer. The difference in grain size appears to be a direct result of the ionisation state of the nitrogen atmosphere in the chamber. It is believed that this difference in grain size is a result of either; faster grain growth from an increased surface diffusion rate of the nitride across the grains, in the sample grown using nitrogen ions, or, thermodynamic conditions favouring an increased number of grain nucleation sites for the sample grown using nitrogen gas.

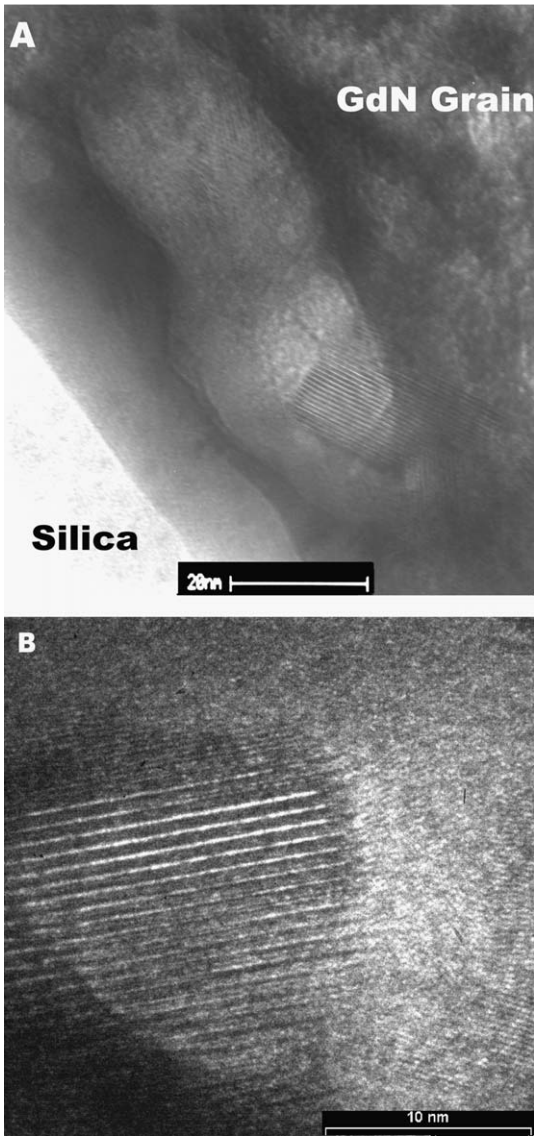

Fig. 3. (A) A high magnification bright field TEM image of GdN grains grown from nitrogen gas onto the glass quartz substrate. The grains appear to have been elongated parallel to the interface. (B) High resolution TEM image of the lattice fringes are seen (A).

A closer look at the grain structure for the GdN growth with nitrogen gas on the glass quartz substrate is given in Fig. 3. This shows grains that are slightly larger than average in size, but appear to be elongated parallel to the quartz substrate. This elongation is likely to be a result of grain growth or grain boundary movement being affected by the slower growth rate in the film. The absence of similar elongated grains in the film grown with nitrogen ions on a silicon substrate supports this view. One final finding in relation to the grain structure is the existence of lattice fringes in the film grown with nitrogen gas (Fig. 3B). These fringes indicate that there are low angle grain boundaries between the grains, which suggests the grains grow with similar orientation.

Cracking in the GdN film, grown on the glass quartz substrate with nitrogen gas, is observed in Fig. 2. This is expected to have an adverse effect on the magnetic or electronic properties of the films. As the cracks, which exhibit

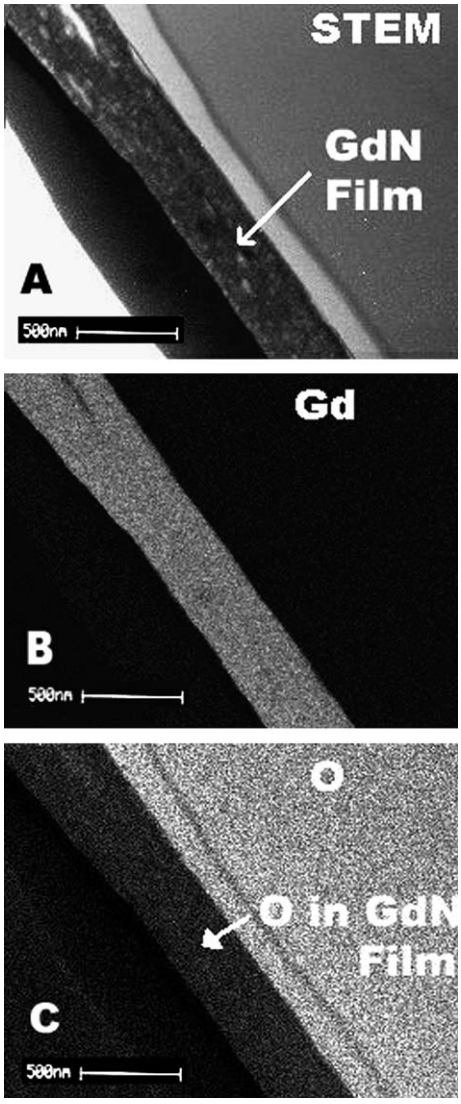

Fig. 4. (A) STEM image, (B) Gd map and (C) O map of the GdN on the glass quartz substrate.

variations in width, run parallel to the interface, and there are corresponding fluctuations in the overall film thickness, it can be presumed they are caused by compressive stresses generated in the film. The absence of cracking in the GdN on silicon sample is thought to be from the thinner films increased ability to deform to accommodate stress, rather than a reduced stress in this sample.

The most likely source of the residual compressive stress is the expansion of the film from the absorption of mass after the deposition. RBS analysis revealed that film contained approximately equal concentrations of oxygen, nitrogen and gadolinium, suggesting that the film may have converted to either an oxide, oxy-nitride, or hydrated nitride after atmospheric exposure. We note that the RBS analysis is not sensitive to the presence of hydrogen, for example in the form of water. To clarify this, electron diffraction measurements obtained from both films generated patterns that were, in each case, consistent with rock-salt structure GdN, showing that the atmospheric exposure does not substantially modify the crystal structure of the GdN.

The presence of oxygen was investigated further using energy dispersive spectroscopy (EDS) analysis. Two elemental maps, with the corresponding scanning TEM image, were generated for the GdN thin film on the glass quartz substrate, these are shown in Fig. 4. Similar results were obtained from the GdN on silicon sample. The Gd map, Fig. 4B, clearly shows the location and thickness of the GdN film. The oxygen map shows not only the relatively high intensity of oxygen, as expected from the glass quartz substrate, but also a detectable and uniform distribution of oxygen in the GdN thin film. The presence of oxygen is consistent with RBS analysis, and the homogeneous distribution of this element, counters any suggestion that the oxygen may exist between the grains or preferentially at the surface of the film. Unfortunately, EDS does not allow meaningful quantification of spectra for elements such as oxygen and nitrogen, but RBS data, as noted above, suggests a significant concentration of oxygen in the GdN.

More recently attempts have been made at capping the films with a material, such as aluminium or magnesium fluoride, to limit the exposure of the GdN with air. To date, it has been possible to slow, but not stop, the absorption of oxygen into the film. Such attempts at capping are the subject of ongoing investigations.

4. Conclusions

The current work involves a TEM analyses, supported by RBS data, of the microstructure of GdN films grown by vapour assisted deposition. It forms part of a larger study into the properties and potential applications of the film.

Gadolinium nitride in the rock-salt structure was successfully grown by thermally evaporating gadolinium metal in atmospheres of both nitrogen gas and nitrogen, partially ionised by a Kauffman type ion source, onto glass quartz and silicon substrates respectively. The major features of the deposition onto silicon utilising nitrogen ions included; a film thickness $\cong$100 nm, equiaxed grains with an average size of $\cong$30 nm and occasional voids in the microstructure. The major features of the deposition onto the glass quartz substrate utilising nitrogen gas included; a film thickness $\cong$400 nm, an average grain size $\cong$20 nm with some larger grains elongated parallel to the interface. The presence of lattice fringes in one of these grains in this sample indicated that low angle grain boundaries existed between crystallites. This thicker sample contained many large cracks indicating the presence of a residual compressive stress produced in the film after the deposition. This is believed to be caused by oxygen absorption of the film on its exposure to the atmosphere.

The absence of cracking in the sample grown onto silicon is thought to be from the thinner films enhanced ability to accommodate stress, relative to a thicker film, rather than a reduced stress in this sample.

References

[1] C.M. Aerts, P. Strange, M. Horne, W.M. Temmerman, Z. Szotek, A. Svane, Phys. Rev. B 69 (2004) 045115.
[2] L.A. Giannuzzi, F.A. Stevie, Micron 30 (1999) 197.