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Gamma and X-ray sensitivity of Gd_2O_3 heterojunctions

Juan A. Colon Santana
University of Nebraska-Lincoln, juan.colon.santana@gmail.com

C M. Young
Air Force Institute of Technology

J W. McClory
Air Force Institute of Technology, john.mcclory@afit.edu

J C. Petrosky
Air Force Institute of Technology, James.Petrosky@afit.edu

X Wang
University of Wyoming, xianjiewanghit@yahoo.com.cn

See next page for additional authors

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Juan A. Colón Santana [a], C.M. Young [b], J.W. McClory [b], J.C. Petrosky [b], X. Wang [c], P. Liu [c], Jinke Tang [c], V.T. Adamiv [d], Ya.V. Burak [d], Keisuke Fukutani [e], P.A. Dowben [e,*]

[a] College of Engineering and Technology, The Nebraska Center for Materials and Nanoscience, Walter Scott Engineering Center, 17th & Vine Streets, University of Nebraska-Lincoln, Lincoln, NE 68588-0511, USA
[b] Air Force Institute of Technology, Department of Engineering Physics, 2950 Hobson Way, Wright Patterson Air Force Base, OH 45433-7765, USA
[c] Department of Physics and Astronomy, University of Wyoming, Laramie, WY 82071, USA
[d] Institute of Physical Optics, 23 Dragomanov St., Lviv 79005, Ukraine
[e] Department of Physics and Astronomy, The Nebraska Center for Materials and Nanoscience, Theodore Jorgensen Hall, 855 North 16th Street, University of Nebraska-Lincoln, P.O. Box 8800299, Lincoln, NE 68588-0299, USA

HIGHLIGHTS

- Gadolinium oxide solid state detectors are not gamma blind.
- Gd_2O_3 devices appear sensitive to the X-ray photoemission events.
- Thin layer Gd_2O_3 heterojunction devices are not very sensitive to neutrons.
- Pulsed laser deposition (PLD) Gd_2O_3 favors a (−402) texture growth direction.

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ABSTRACT

We find that Gd_2O_3 thin films strongly favor a (−402) texture growth on a variety of substrates and will form heterojunction diodes with silicon, especially when doped with oxygen vacancies. Even in the thin film limit, these heterojunction diodes appear to be sensitive to gamma radiation, likely from the X-rays created by scattering events, adding to the numerous hurdles that must be overcome if Gd based semiconductor devices are to be used for solid state neutron detection applications.

1. Introduction

The ^{157}Gd neutron capture cross section is over 60 times larger than the cross section of the $^{10}B(n,\alpha)^7Li$ reaction (Garber and Kinsey, 1976, Gebauer et al., 1997, KAERI 2000, McLane et al., 1988, Mireshghi et al., 1994). The Gd cross section remains significantly higher than the thermal neutron capture cross section of ^{10}B out to neutron energies of ~200 meV. Because of the large natural Gd thermal neutron capture cross section of 46,000 b, including a 15.65% natural abundance of the ^{157}Gd isotope with a thermal neutron capture cross section of 255,000 b (Cerullo et al., 2009, Garber and Kinsey, 1976, Gebauer et al., 1997, KAERI 2000, McLane et al., 1988, Mireshghi et al., 1994), Gd has often been touted as the primary conversion component of a neutron detector (Ali et al., 1994, Becvar et al., 2000, Groshev et al., 1958, Kandlakunta et al., 2013, Kinsey and Bartholomew, 1953, 7–12, Sakurai and Kobayashi, 2002, Schultz et al., 2010). The ^{157}Gd isotope neutron absorption of the neutron leaves the ^{158}Gd in an excited state that releases energy through emission of high and low energy gamma rays, X-rays, and internal conversion (IC) and Auger Coster-Kronig (ACK) conversion electrons as:

$$^{157}Gd(n,\gamma) \rightarrow {}^{158}Gd + \gamma + X - rays + IC\ e^- + ACK\ e^- \quad (1)$$

with details of the decay processes (Ali et al., 1994, Becvar et al., 2000, Cerullo et al., 2009, Groshev et al., 1958, Kandlakunta

* Corresponding author. Tel.: +1 402 472 9838.
E-mail addresses: juan.colon.santana@gmail.com (J.A. Colón Santana), John.McClory@afit.edu (J.W. McClory), james.petrosky@afit.edu (J.C. Petrosky), xianjiewanghit@yahoo.com.cn (X. Wang), jtang2@uwyo.edu (J. Tang), adamiv@ifo.lviv.ua (V.T. Adamiv), burak@ifo.lviv.ua (Ya.V. Burak), nekocat@unl.edu (K. Fukutani), pdowben1@unl.edu (P.A. Dowben).

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et al., 2013, Kinsey and Bartholomew, 1953, 7–12, Sakurai and Kobayashi, 2002, Schultz et al., 2010) now nicely summarized in (Schultz et al., 2010). A similar result occurs with the neutron capture process $^{155}Gd(n,\gamma)^{156}Gd$. A gadolinium doped HfO_2 to silicon based semiconductor heterojunction, nonetheless, can produce pulses characteristic of the K-shell Auger electron resonances following neutron capture (Schultz et al., 2010), provided the full energy of the electron can be captured. The resulting Auger electron spectrum is characteristic of the atomic electronic transitions that include a Gd 1s (K-shell) hole, and is therefore not sensitive to the neutron energy, so long as there is neutron capture (Kandlakunta et al., 2013, Schultz et al., 2010). As in Fig. 1, the estimated gamma cross-section is low, so the simple minded idea is that a thin film solid state device would in fact be gamma blind (insensitive to background gamma radiation) in spite of contained elements of large Z. The problem is that with a gadolinium device, gamma rejection (gamma blindness) is not a given because of the large photoemission cross-sections of gadolinium compounds – and the recognition that there is a huge X-ray ambient background caused by gamma radiation scattering (including Compton scattering) with anything in the vicinity of the detector. There are other problems with designing a Gd based semiconductor device for the detection of neutrons. Less than 5% (3.4% + 1.4%) of all ^{157}Gd neutron capture events produce charged particles (internal conversion electrons) capable of generating electron-hole pairs in a Gd-based semiconductor device. The large band gap for Gd_2O_3 (5.4 eV) combined with the low energy of the conversion electron (roughly 79 keV or less) means very few electron hole pairs are created by neutron capture (compared to semiconductors containing boron or lithium) which then compete with the 43 keV **K**-shell and 7 keV **L**-shell and the more outer Gd shell characteristic X-ray photoemission. Even for the **K**-shell conversion electrons, the limited pulse height requires sensitive (1–10 fF) charge-to-voltage amplifiers, a low noise readout system and low device leakage currents, and the device must have a very large depletion region if there is to be any hope of extracting the full pulse height (Bickley et al., 2011). As a point of reference, a 79 keV electron deposits nearly all of its energy in ~40 μm of silicon and in ~25 μm of gadolinium (CASINO 2009), whereas the depletion regions of the devices of interest typically have a depletion width of <10 μm (Bickley et al., 2011). This is much larger that the 5 μm mean free path of the lithium and alpha daughter fragments created with neutron capture by ^{6}Li and ^{10}B.

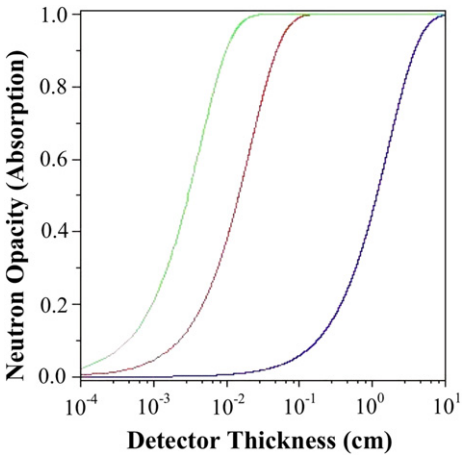

Fig. 1. Calculated attenuation of 30 meV (green line) and 100 meV (red line) neutron and 1 MeV gamma (blue line) radiation in 15% unenriched Gd-doped HfO_2 (or similar oxide) as a function of film thickness.

Thin-layer semiconducting gadolinium oxide diode heterostructures with silicon have, however, been fabricated (Losovyj et al., 2009) with very strong (−402) texture growth of the Gd_2O_3 (Komesu et al., 2009, Losovyj et al., 2009). The pulse collection following Gd neutron capture should produce a pulse height spectrum with features that are attributable to the Gd K-shell Auger electron resonances. Here we show that making such a device gamma blind will be a challenge and we do so by comparing very strong (−402) texture growth of the Gd_2O_3 heterostructures using both silicon and lithium tetraborate, $Li_2B_4O_7$, as substrates. The latter exhibits a very large neutron cross-section because of the lithium and boron isotopes, but with low gamma and hard X-ray cross-sections because of the very low Z of all the constituents of lithium tetraborate.

2. Experiment

The Gd_2O_3 was grown on Si(100) and Mn doped $Li_2B_4O_7$ substrates using a pure Gd_2O_3 target. As in prior studies (Komesu et al., 2009, Losovyj et al., 2009), before the deposition, the Si(100) substrates were cleaned with diluted HF acid, rinsed with acetone, and then immediately put into a vacuum chamber. Before deposition, the surface of the Si wafer and the Mn doped $Li_2B_4O_7$ substrates were sputter cleaned in a plasma of H_2(8%) and Ar (92%) mixture created by a DC sputtering gun operating in the reverse bias mode. The films were deposited at a substrate temperature of 500 °C. The chamber was pumped to a base pressure of 3×10^{-7} Torr and the deposition was carried out in a mixture of H_2 and Ar (8% H_2) to introduce the necessary oxygen vacancies. The vacuum was maintained at 10^{-5} Torr during the deposition. The identification of a monoclinic phase was determined by both X-ray diffractions and extended X-ray absorption spectroscopy (EXAFS), and to some extent by photoemission measurements (Losovyj et al., 2009). The heterojunction of Gd_2O_3 with p-type silicon forms excellent diodes, as described elsewhere (Losovyj et al., 2009). Undoped $Li_2B_4O_7$ (001) is pyroelectric and an excellent dielectric with a wide band gap of 9.8 eV and must be doped to make it semiconducting (Adamiv et al., 2010). Here we used microcrystalline or glassy Mn doped $Li_2B_4O_7$ substrates.

The neutron capture pulse height spectra were taken using n-type Gd_2O_3 film heterostructure diodes formed with either Si (100) or $Li_2B_4O_7$:Mn. The resulting diodes were operating in the reverse biased mode with an applied bias of −2 V; a value well below the breakdown voltage. These experiments were carried out in the Air Force Institute of Technology (AFIT standard graphite pile and the thermal column of the Ohio State University Research Reactor (OSURR). The pile is a graphite moderated subcritical assembly and delivers a softened neutron spectrum as provided by a 7 Ci PuBe source in a low (electronic) noise environment. The neutron spectrum was measured using BF_3 detectors and verified by activation analysis and hand calculations. The devices were loaded into the vertical axial location by removal of a graphite stringer where the thermal flux was the greatest (~22,000 n/cm^2 s. At the OSURR the flux was varied so that the total thermal flux for 450 kW, 250 kW, and 125 kW reactor powers was 2.57×10^{12} cm^{-2} s^{-1}, 1.48×10^{12} cm^{-2} s^{-1}, and 7.14×10^{11} cm^{-2} s^{-1}, respectively. Because of the expected low pulse height from the 79 keV conversion and associated Auger electrons, low noise and good impedance matching were essential. A thermoelectrically cooled charge sensitive preamp (Amptek A250CF CoolFET, 670 eV FWHM (Si)/~76 electrons RMS) was used for its low noise characteristics.

3. Growth of the Gd_2O_3 thin films

The Gd_2O_3 films grown on Si(100) are highly textured, as noted elsewhere (Komesu et al., 2009, Losovyj et al., 2009). The X-ray

diffraction is consistent with highly textured monoclinic Gd_2O_3, and the textured structure is such that the (−402) planes mostly lie along the surface of the film, as shown in Fig. 2. Some (401) and (202) planes are also found to orient parallel to the surface of the film. Only the (h0l) planes (planes parallel to the *b* axis) are grown parallel to the surface. The lattice spacing along the <−402> direction is about 0.2965 nm and the lattice spacing for <401> and <202> is 0.3033 nm and 0.3402 nm, respectively.

Surprisingly, in spite of the fact that the Mn doped $Li_2B_4O_7$ substrates show little crystallinity (Fig. 3), the Gd_2O_3 films grown on these substrates are also highly textured. The X-ray diffraction of textured monoclinic Gd_2O_3 show that these films grow such that the (−402) planes mostly lie along the surface of the film, as seen in Fig. 3. This suggests that at an oxide interface (silicon oxide, lithium tetraborate), the growth along (−402) is highly favored, and does not require a lattice match or even a crystalline interface.

4. Neutron capture detection

As noted in the introduction, in spite of the large Gd gamma absorption cross-section, the neutron capture cross-section is considerably greater, as summarized in Fig. 1. Consequently, there should be a wide range of thicknesses where the Gd-doped film is opaque to neutrons and yet should be almost transparent to typical gamma rays. So in the case of the heterojunction diodes studied here, fabricated with 250 nm thick Gd_2O_3 thin films, the devices should be insensitive to the gamma radiation that is characteristic of fissile materials, as there is a long attenuation length for gamma radiation (at energies of 1 MeV and above) compared to thermal and epithermal neutrons. But there is the distinct possibility that X-rays produced by inelastic scatting processes in ancillary materials between the source and the detector may cause **K**-shell Auger electron excitations in some devices as well (Bickley et al., 2011, Schultz et al., 2010).

We can test whether Gd_2O_3 on p-type Si(100) heterojunction diodes acting as neutron detectors (and similar structures) will reliably discriminate neutrons from gamma radiation emanating from fissile materials from the experimental pulse height spectra, as shown in Fig. 4. What is important from the pulse height spectra is that the generated counts increase when the heterojunction diode is covered by a cadmium (Cd) foil. The Cd foil is a standard route for blocking thermal neutrons, so an increase in counts from the device, when the neutron flux is blocked, clearly indicates that this heterojunction is sensitive to radiation other than neutrons. The likely source is scattering gamma radiation, but neutron capture by cadmium also generates a plethora of prompt gammas

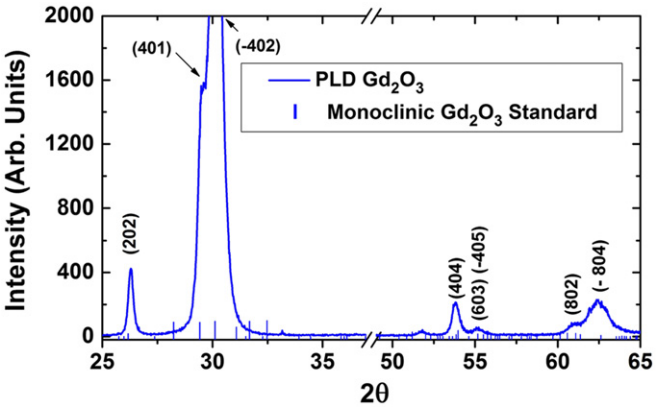

Fig. 2. The X-ray diffraction patterns of PLD grown Gd_2O_3 on p-type Si(100). The bar diagram included in the panel are the standards of monoclinic Gd_2O_3.

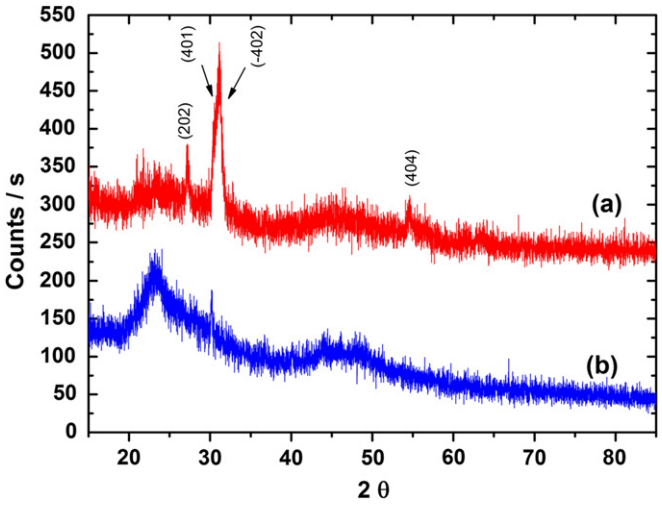

Fig. 3. The X-ray diffraction patterns of PLD grown Gd_2O_3 on (a) glassy Mn doped $Li_2B_4O_7$ (red). The X-ray diffraction of the (b) Mn doped $Li_2B_4O_7$ alone (blue) is clearly characteristic of a microcrystalline or non crystalline material, and the X-ray diffraction scattering features are largely obscured with the deposition of 250 nm of Gd_2O_3. The significant monoclinic Gd_2O_3 X-ray diffraction planes have been labeled. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Pringle et al., 1952, Wisshak et al., 2002). This could be the origin as to why a thinner Cd foil cover leads to more counts than a thicker Pb film, as seen in Fig. 4. The scattering gamma radiation is a major source of detected radiation, which is supported by the still substantial increase in count rates even when the Cd foil is replaced by an even larger Z metal, in this case lead, as shown in Fig. 4. Of course this does not exclude the possibility that some signal is due to neutron capture, although the pulse height spectra is not really characteristic of the K-shell conversion and Auger electron spectra that would be expected from such neutron capture (Ali et al., 1994, Greenwood et al., 1978, Reeder 1994, Sakurai and Kobayashi, 2002, Schultz et al., 2010).

To further test the sensitivity of Gd_2O_3 heterojunction devices, we also tested a heterojunction fabricated with $Li_2B_4O_7$, where the

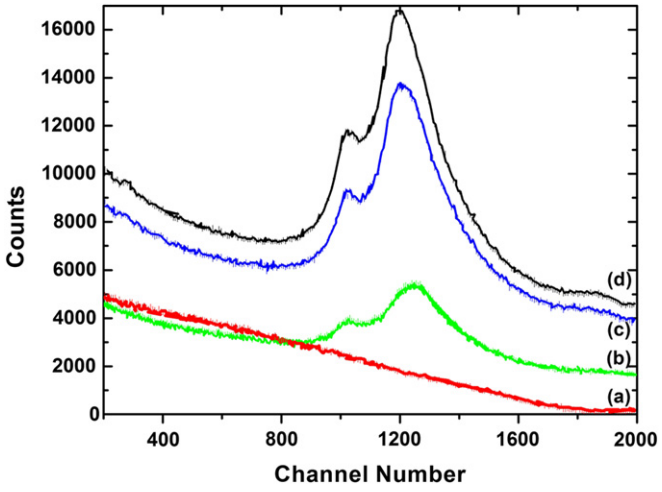

Fig. 4. Pulse height spectra obtained using Gd_2O_3 films on *p*-type single crystal Si(100) substrates heterojunctions, taken at the AFIT standard pile. The dark current response (no radiation fluence (a) and be compared in the presence of the low energy neutron fluence (b). The offset of the baseline from zero volts is not meaningful, and a consequence of the display routine. When the device is obscured with a 3.5 mm of lead foil (c), the counts are seen to increase, and there is a further increase when the Pb foil is replaced with 760 micron Cd foil (d).

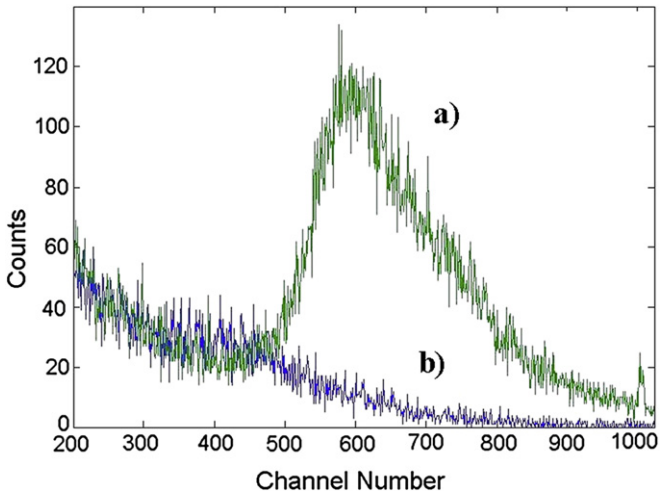

Fig. 5. Pulse height spectra obtained using Gd_2O_3 films on *p*-type single crystal Si(100) substrates heterojunctions, taken at the OSRR reactor. (a) shows the increased pulse height spectra counts following insertion of a 760 micron Cd foil. (b) without the Cd foil.

neutron capture should be hugely increased because of the neutron high capture cross-section of ^{6}Li and ^{10}B. Even with only natural abundances of ^{6}Li and ^{10}B in the Mn doped $Li_2B_4O_7$ substrate, the entire heterojunction will be opaque to thermal neutrons given the 1 mm thickness of the Mn doped $Li_2B_4O_7$ substrate. Here again, the count rates increase significantly when the device is surrounded with a Cd foil instead of exhibiting a suppressed signal, more characteristic of low Z boron rich semiconductor solid state neutron detector devices (Caruso et al., 2006). In fact, the Gd neutron capture generated pulse peaks of Figs. 4 and 5 are not likely to be placed in the same region of the peak observed in the pulse height spectra, as in the feature observed around channel 500–800 of Fig. 5 (Kandlakunta et al., 2013, Sakurai and Kobayashi, 2002, Schultz et al., 2010). The pulse height spectra are more characteristic of a combination of Cd isotopes as would be expected from a natural abundance Cd foil (Wisshak et al., 2002).

5. Conclusions

From these results, it is clear that neutron pulse counting using a gadolinium containing semiconductor device is extremely challenging in spite of the greater Gd neutron cross-sections. Even for the **K**-shell conversion electrons, the limited pulse height requires a sensitive (1–10 fF) charge-to-voltage amplifier, low noise readout system and low device leakage currents because the devices will require a very large depletion region if there is to be any hope of extracting the full pulse height. Most important, such devices will be very difficult to design to ensure that the detection of background gamma radiation is excluded. As a result, it should be noted that boron and lithium based devices, especially if ^{6}Li or ^{10}B enriched, are likely to be a much more robust route to solid state neutron detection. To state what is probably obvious: a solid state device that contains elements of high neutron capture cross-section will not *a priori* lead to a neutron detector. The neutron cross-section is not, by itself, a dominant design factor for solid state neutron detectors.

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