



**Queensland University of Technology**  
Brisbane Australia

This is the author's version of a work that was submitted/accepted for publication in the following source:

Shafiei, M., Shin, K., Yu, J., Han, S.H., Jong, J.W., Motta, N., du Plessis, J., & Wlodarski, W. (2011) Hydrogen gas sensing performance of a Pt/graphene/SiC device. In Xia, Shan hong, Bao, Minhang, & Fan, Long-Sheng (Eds.) *Proceedings of the 16th International Solid-State Sensors, Actuators and Microsystems Conference, TRANSDUCERS'11*, IEEE, China National Convention Center, Beijing, pp. 170-173.

This file was downloaded from: <http://eprints.qut.edu.au/47755/>

**© Copyright 2011 IEEE**

Personal use of this material is permitted. However, permission to reprint/republish this material for advertising or promotional purposes or for creating new collective works for resale or redistribution to servers or lists, or to reuse any copyrighted component of this work in other works must be obtained from the IEEE.

**Notice:** *Changes introduced as a result of publishing processes such as copy-editing and formatting may not be reflected in this document. For a definitive version of this work, please refer to the published source:*

<http://dx.doi.org/10.1109/TRANSDUCERS.2011.5969235>

# HYDROGEN GAS SENSING PERFORMANCE OF A Pt/GRAPHENE/SiC DEVICE

*M. Shafiei*<sup>1,2</sup>, *K. Shin*<sup>3</sup>, *J. Yu*<sup>1</sup>, *S. H. Han*<sup>3</sup>, *J. W. Jong*<sup>4</sup>, *N. Motta*<sup>2</sup>, *J. du Plessis*<sup>5</sup>, *W. Wlodarski*<sup>1</sup>

<sup>1</sup>Sensor Technology Laboratory, RMIT University, Melbourne, Australia

<sup>2</sup>School of Engineering Systems, Queensland University of Technology (QUT), Brisbane, Australia

<sup>3</sup>Department of Chemistry and Graphene Research Institute, Korea

<sup>4</sup>Department of Nano-Science and Technology and Graphene Research Institute, Korea

<sup>5</sup>School of Applied Sciences, RMIT University, Melbourne, Australia

## ABSTRACT

In this work, we present the development of a Pt/graphene/SiC device for hydrogen gas sensing. A single layer of graphene was deposited on 6H-SiC via chemical vapor deposition. The presence of graphene C-C bonds was observed via X-ray photoelectron spectroscopy analysis. Current-voltage characteristics of the device were measured at the presence of hydrogen at different temperatures, from 25°C to 170°C. The dynamic response of the device was recorded towards hydrogen gas at an optimum temperature of 130°C. A voltage shift of 191 mV was recorded towards 1% hydrogen at -1 mA constant current.

## KEYWORDS

Graphene, Hydrogen, Sensor, Chemical Vapor Deposition.

## 1. INTRODUCTION

In recent years, much research effort has been devoted to investigation of graphene as a gas sensing material due to its unique properties. These include room temperature ballistic electronic transport [1, 2], strong hydrogen affinity [3], metal-like characteristics [4-6] and its large surface area, which make graphene incredibly well suited for gas sensing applications [7-13].

Graphene is a two-dimensional material comprising carbon atoms arranged in six-membered rings [2, 4, 14, 15]. It can be classified as: a single-layer graphene (SG), bilayer graphene (BG) and few-layer graphene (FG, number of layers  $\leq 10$ ) [15]. Many techniques have been developed for the deposition of graphene. A micro-mechanical cleavage method was initially used to exfoliate highly oriented pyrolytic graphite using 'scotch-tape' [2]. Other methods include a direct epitaxial growth of graphene from SiC via thermal decomposition [16], chemical vapor deposition (CVD) [17] and the synthesis of graphene via a chemical reduction of graphite oxide [18].

In this work, a Pt/graphene/SiC device for hydrogen gas applications has been developed. SiC is a favourable substrate for the formation of graphene-based sensors due to the fact that graphene can be epitaxially grown on SiC by annealing at elevated temperatures [19]. Pt was chosen as the electrode metal as it forms an electrical contact and also it functions as an excellent hydrogen catalyst. The

work herein investigates a graphene based device as it is applied as a sensor toward hydrogen with different concentrations in a synthetic air. The current-voltage (*I-V*) characteristics are studied as a function of temperature and hydrogen concentration. The electron transport mechanism at the Pt/graphene and graphene/SiC interfaces are also investigated and used to explain the sensing performance.

## 2. EXPERIMENTAL

A Pt/graphene based device was fabricated on *n*-type 6H-SiC substrate (Tankeblue Co. Ltd.). The native oxide on the substrate surface was removed via etching in hydrofluoric acid. A double metal layer of Ti/Pt (40/100 nm) was deposited at the unpolished backside of the substrate using electron beam evaporation. Subsequently, the samples were annealed at 500°C in N<sub>2</sub> for 30 min to form an electrical contact.

A single layer of graphene was grown on Cu foils by CVD technique using methane as a precursor. The as-grown graphene layer was spin-coated with a thin layer of polymethyl methacrylate (PMMA). This film was separated from the Cu foil by dissolving in diluted ferric chloride solution. The graphene/PMMA was then transferred onto a SiC substrate. Subsequently, the PMMA film was removed by heating at 500°C with a stream of hydrogen gas.

Finally, a circular pad of Pt (~25 nm thickness) was deposited onto the graphene layer to form the electrical contact. The fabricated Pt/graphene/SiC device was placed in a multichannel gas testing system to investigate their electrical properties and gas sensing performance. The testing process has been explained in our previous works [8, 9, 20, 21].

## 3. RESULTS AND DISCUSSION

The deposited graphene layers were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Figure 1 shows the TEM micrographs of the graphene layer. The thickness of the synthesized graphene material was measured to be ~0.3 nm.

XPS analysis (Figure 2) revealed a peak at 285.0 eV which identifies the C-C bond and is ascribed to graphene [22]. An attenuated Si-C peak was observed at 283.3eV [23]. Other bonds that were identified include C-OH (285.9eV), C=O (287.1eV) and C-C=O (289.2eV) [22].

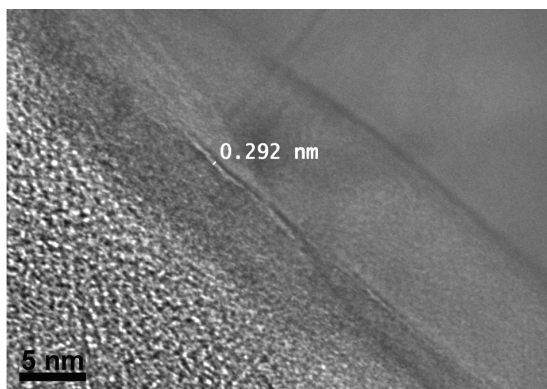


Figure 1: TEM micrograph of the graphene layer.

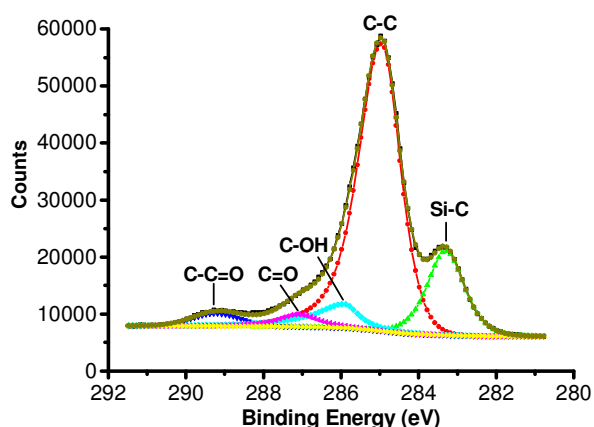


Figure 2: XPS spectra of graphene layer deposited on a SiC substrate.

Raman spectroscopy was used to characterize the quality and thickness of the graphene. The major features of the Raman spectrum are the G band at  $1584\text{ cm}^{-1}$  and the 2D band at  $2690\text{ cm}^{-1}$ . The G band is due to the  $E_{2g}$  vibrational mode, and the 2D band is a second order two phonon mode. The D band at  $1350\text{ cm}^{-1}$  is not Raman active for pristine graphene but can be observed where symmetry is broken by edges or in samples with some defects. The shape, position and intensity of 2D band depend on the number of layers. The strong and symmetrical Lorentzian 2D band and the weak intensity of the D band indicate the CVD-grown graphene was of reasonably good quality.

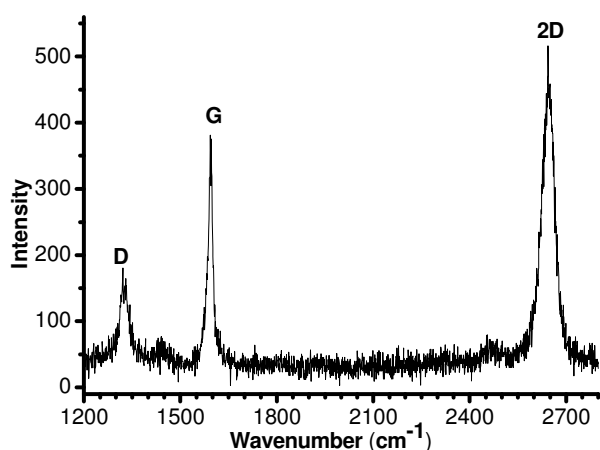


Figure 3: Raman spectrum of the CVD-grown graphene layer.

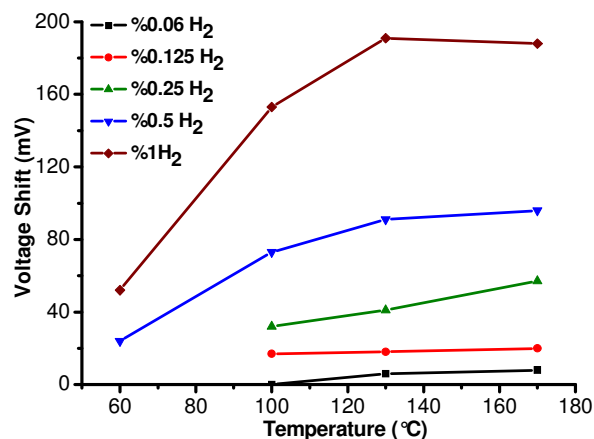


Figure 4: Plot of voltage shift of Pt/graphene/SiC device as a function of temperature towards different hydrogen gas concentrations at a constant reverse bias current of 1 mA.

The  $I$ - $V$  characteristics and dynamic responses of the Pt/graphene/SiC device were measured at the presence of hydrogen gas at temperatures of 25, 35, 60, 100, 130 and  $170^\circ\text{C}$ . The most significant hydrogen response was found at  $130^\circ\text{C}$  and was chosen as the optimal operating temperature. Figure 4 shows the measured voltage shifts of the device as a function of temperature at different hydrogen concentrations.

Figure 5 shows the  $I$ - $V$  characteristics of the Pt/graphene/SiC device at the presence of hydrogen (with different concentrations of 0.06, 0.125, 0.25, 0.5, 1%) at  $130^\circ\text{C}$ . The device was therefore operated in reverse bias as the voltage shift towards hydrogen was significantly larger than in forward bias.

The  $I$ - $V$  characteristics of the Pt/graphene/SiC device can be explained by the electron transport mechanism at two interfaces of Pt/graphene and graphene/SiC [8]. Initially, the electron transfer will encounter a transition from the  $n$ -type SiC to the semi-metallic graphene and then to the metallic Pt. The conduction behaviour will be similar to that between a metal to a metal junction. However, the non-linear  $I$ - $V$  curves (Figure 5) were observed as the graphene behaves semi-metal like.

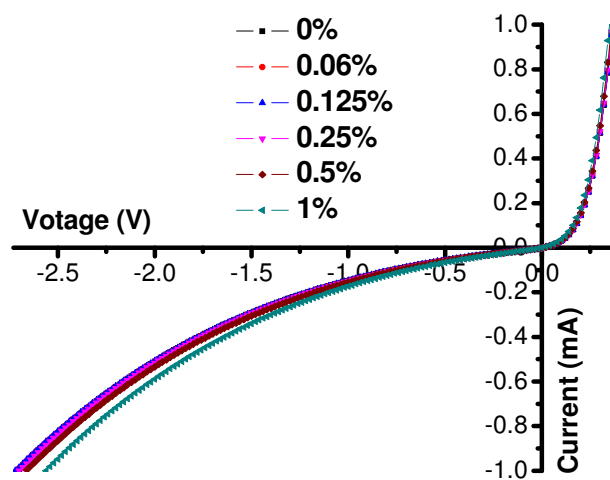


Figure 5:  $I$ - $V$  characteristics of the Pt/graphene/SiC device at the presence of hydrogen gas at  $130^\circ\text{C}$ .

Giovannetti et al. [24] showed that as a thin Pt layer is deposited on the graphene layer, it physisorbs onto the surface and leads to a weak interaction energy (van der Waals) at the Pt/graphene interface and hence preserves the electronic structure of graphene. As the work function of Pt ( $W_M$ ) is larger than work function of graphene ( $W_G$ ), it causes electrons transfer from graphene to Pt and as a result the Fermi levels achieve equilibrium. This electron transfer between the Pt and graphene results in the formation of a dipole layer at the interface and forms a potential step ( $\Delta V$ ) as shown in the energy-band diagram (Figure 6) of Pt on graphene [24].

It is assumed that the graphene layer acts as 'semi-metal' like when deposited on SiC substrate as shown by Tongay et al. [25]; and the main transport mechanism at the graphene/SiC interface is dominated by thermionic emission.

Upon exposure of the device to hydrogen gas, the dissociation of hydrogen molecules occurs on the Pt surface. Then hydrogen atoms diffuse through the Pt catalyst onto graphene. Here, two assumptions are made [8]: (1) the work function of graphene ( $W_G$ ) increases; and/or (2) the separation distance between the Pt and graphene ( $d$ ) increases, which causes an increase in the Fermi-level shift ( $\Delta E_F$ ) [24]. Both increases in  $\Delta E_F$  and  $W_G$  decrease the potential step according to Equation (1):

$$\Delta V = W_{Pt} - W_G - \Delta E_F \quad (1)$$

Therefore, this decrease results in an increase in the current density in the  $I$ - $V$  characteristics.

The dynamic response of the device was measured at 130°C, towards different hydrogen concentrations at a constant reverse bias current of 1 mA (Figure 7). Voltage shifts of 6, 18, 41, 91 and 191 mV were recorded for 0.06, 0.125, 0.25, 0.5 and 1% hydrogen, respectively. The device showed a stable baseline and excellent repeatability over a period of two weeks testing towards hydrogen.

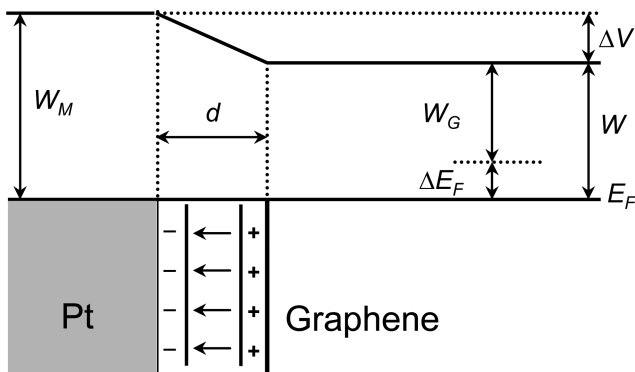


Figure 6: A theoretical energy-band diagram of a Pt/graphene contact, where  $W_M$  is the Pt work function;  $W_G$  is the graphene work function;  $W$  is the Pt-coated graphene work function;  $d$  is the equilibrium separation distance;  $\Delta E_F$  is the Fermi-level shift, and  $\Delta V$  is the potential change generated by the Pt/graphene interaction.

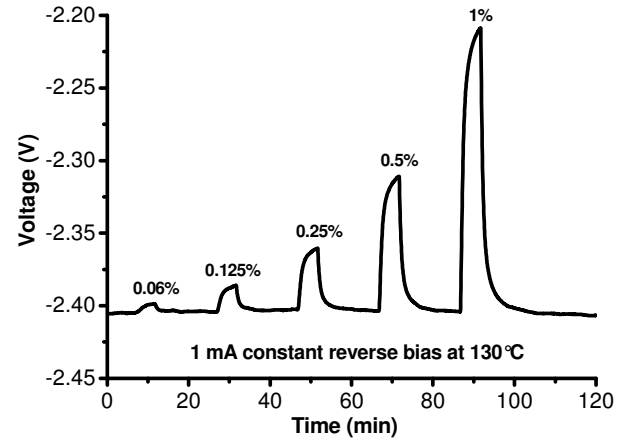


Figure 7: Dynamic response of the Pt/graphene/SiC device towards 0.06, 0.125, 0.25, 0.5 and 1% hydrogen gas in synthetic air at 130°C.

## 4. CONCLUSION

A hydrogen gas sensor based on Pt/graphene/SiC device was successfully fabricated. The TEM showed a single layer of graphene with thickness of  $\sim 0.3$  nm. The developed device operated at an optimal temperature of 130°C. A voltage shift of 191 mV was recorded for 1% hydrogen at 130°C at a reverse constant bias of  $-1$  mA. These results also indicated that hydrogen gas is readily adsorbed and desorbed from the device, which attribute to its repeatability over two weeks of testing.

## ACKNOWLEDGMENT

The authors would like to acknowledge financial support from Queensland Government through NIRAP project, "Solar Powered NanoSensors" and the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education.

## REFERENCES

- [1] EH. Hwang, S. Adam, S. Das Sarma, AK. Geim "Transport in Chemically Doped Graphene in The Presence of Adsorbed Molecules", Physical Review B (Condensed Matter and Materials Physics), Vol. 79, p. 195421, 2007.
- [2] KS. Novoselov, AK. Geim, SV. Morozov, D. Jiang, Y. Zhang, SV. Dubonos, IV. Grigorieva, AA. Firsov, "Electric Field Effect in Atomically Thin Carbon Films", Science, Vol. 306, pp. 666-9, 2004.
- [3] A. Savchenko, "Materials Science: Transforming Graphene", Science, Vol. 323(5914) pp. 589-90, 2009.
- [4] KS. Novoselov, "Graphene: Mind the Gap", Nature Materials, Vol. 6, pp. 720-1, 2007.
- [5] KS. Novoselov, AK. Geim, SV. Morozov, D. Jiang, MI. Katsnelson, IV. Grigorieva, SV. Dubonos, AA. Firsov, "Two-Dimensional Gas of Massless Dirac

- Fermions in Graphene”, *Nature*, Vol. 438 (7065), pp. 197-200, 2005.
- [6] X. Du, I. Skachko, A. Barker, EY. Andrei, “Approaching Ballistic Transport in Suspended Graphene”, *Nat Nanotechnol*, Vol. 3(8), pp. 491-5, 2008.
- [7] R. Arsat, M. Breedon, M. Shafiei, PG. Spizziri, S. Gilje, RB. Kaner, K. Kalantar-zadeh, W. Wlodarski “Graphene-Like Nano-Sheets for Surface Acoustic Wave Gas Sensor Applications”, *Chemical Physics Letters*, Vol. 467(4-6) pp.344-7, 2009.
- [8] M. Shafiei, PG. Spizzirri, R. Arsat, J. Yu, J. du Plessis, S. Dubin, RB. Kaner, K. Kalantar-zadeh, W. Wlodarski, “Platinum/Graphene Nanosheet/SiC Contacts and Their Application for Hydrogen Gas Sensing”, *The Journal of Physical Chemistry C*, Vol. 114(32), pp.13796-801, 2010.
- [9] M. Shafiei, R. Arsat, J. Yu, K. Kalantar-zadeh, S. Dubin, RB. Kaner, W. Wlodarski, “Pt/Graphene Nano-Sheet Based Hydrogen Gas Sensor”, *Proceedings of IEEE Sensors Conference, Christchurch, New Zealand*, 2009.
- [10] JD. Fowler, MJ. Allen, VC. Tung, Y. Yang, RB. Kaner, BH. Weiller, “Practical Chemical Sensors From Chemically Derived Graphene”, *ACS Nano*, Vol. 3(2) pp. 301-6, 2009.
- [11] RK. Joshi, H. Gomez, F. Alvi, A. Kumar, “Graphene Films and Ribbons for Sensing of O<sub>2</sub>, and 100 ppm of CO and NO<sub>2</sub> in Practical Conditions”, *Journal of Physical Chemistry C*, Vol. 114, pp. 6610-3, 2010.
- [12] R. Pearce, T. Iakimov, M. Andersson, L. Hultman, AL. Spetz, R. Yakimova, “Epitaxially Grown Graphene Based Gas Sensors for Ultra Sensitive NO<sub>2</sub> Detection”, *Sensors and Actuators, B: Chemical*, 2011 (DOI: 10.1016/j.snb.2010.12.046).
- [13] L. Al-Mashat, K. Shin, K. Kalantar-Zadeh, JD. Plessis, SH. Han, RW. Kojima, RB. Kaner, D. Li, X. Gou, S. J. Ippolito, W. Wlodarski, “Graphene/Polyaniline Nanocomposite for Hydrogen Sensing”, *Journal of Physical Chemistry C*, Vol. 114(39) pp.16168-73, 2010.
- [14] C. Srinivasan, “Graphene - Mother of All Graphitic Materials”, *Current Science*, Vol. 92 (10) pp. 1338-9, 2007.
- [15] CNR. Rao, AK. Sood, KS. Subrahmanyam, A. Govindaraj, “Graphene: the New Two-Dimensional Nanomaterial”, *Angewandte Chemie International Edition*, Vol. 48(42) pp. 7752-77, 2009.
- [16] E. Rollings, GH. Gweon, SY. Zhou, BS. Mun, JL. McChesney, BS. Hussain, A. Fedorov, PN. First, WA. De Heer, A. Lanzara, “Synthesis and Characterization of Atomically Thin Graphite Films on A Silicon Carbide Substrate”, *Journal of Physics and Chemistry of Solids*, Vol. 67(9-10) pp. 2172-7, 2006.
- [17] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, MS. Dresselhaus, J. Kong, “Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition”, *Nano Letters*, Vol. 9(1) pp. 30-5, 2008.
- [18] S. Gilje, S. Han, M. Wang, RB. Kaner, “A Chemical Route to Graphene for Device Applications”, *Nano Letters*, Vol. 7, p. 3394, 2007.
- [19] WA. de Heer, C. Berger, X. Wu, PN. First, EH. Conrad, X. Li, et al. “Epitaxial Graphene”, *Solid State Communications*, Vol. 143(1-2) pp. 92-100, 2007.
- [20] M. Shafiei, J. Yu, R. Arsat, K. Kalantar-zadeh, E. Comini, M. Ferroni, G. Sberveglieri, W. Wlodarski, “Reversed Bias Pt/Nanostructured ZnO Schottky Diode With Enhanced Electric Field for Hydrogen Sensing”, *Sensors and Actuators B: Chemical*, Vol. 146, pp. 507-12, 2010.
- [21] J. Yu, S. Ippolito, M. Shafiei, D. Dhawan, W. Wlodarski, K. Kalantar-zadeh, “Reverse Biased Pt/Nanostructured MoO<sub>3</sub>/SiC Schottky Diode Based Hydrogen Gas Sensors”, *Applied Physics Letters*, Vol. 94, p.013504, 2009.
- [22] Y. Wang, Y. Shao, DW. Matson, J. Li, Y. Lin, “Nitrogen-Doped Graphene and Its Application in Electrochemical Biosensing”, *ACS Nano*, Vol. 4(4) pp. 1790-8, 2010.
- [23] M. Veres, M. Koo, S. Toth, M. FÜle, I. Pocsik, A. Toth, M. Mohai, I. Bertoti, “Characterisation of a-C:H and Oxygen-Containing Si:C:H Films by Raman Spectroscopy and XPS”, *Diamond and Related Materials*, Vol. 14(3-7) pp. 1051-6, 2005.
- [24] G. Giovannetti, PA. Khomyakov, G. Brocks, VM. Karpan, JVD. Brink, PJ. Kelly, “Doping Graphene with Metal Contacts”, *Physical Review Letters*, Vol. 101(2) p. 026803, 2008.
- [25] S. Tongay, T. Schumann, AF. Hebard, “Graphite Based Schottky Diodes Formed on Si, GaAs, and 4H-SiC Substrates”, *Applied Physics Letters*, Vol. 95(22) p. 3, 2009.

## CONTACT

\*M. Shafiei, Tel: 61-7-3138-5168;  
mahnaz.shafiei@qut.edu.au.