Ultraviolet detection from energetically deposited titania films

Field, Matthew; Murdoch, Billy; McCulloch, Dougal; Partridge, James

https://researchrepository.rmit.edu.au/esploro/outputs/9921859413001341/filesAndLinks?institution=61RMIT_INST&index=null

Field, M., Murdoch, B., McCulloch, D., & Partridge, J. (2014). Ultraviolet detection from energetically deposited titania films. *Applied Physics Letters*, 104(13), 1–4. <https://doi.org/10.1063/1.4870069>
Document Version: Published Version

Published Version: <https://doi.org/10.1063/1.4870069>

Thank you for downloading this document from the RMIT Research Repository.

The RMIT Research Repository is an open access database showcasing the research outputs of RMIT University researchers.

RMIT Research Repository: <http://researchbank.rmit.edu.au/>

Citation:

Field, M, Murdoch, B, McCulloch, D and Partridge, J 2014, 'Ultraviolet detection from energetically deposited titania films', Applied Physics Letters, vol. 104, no. 13, pp. 1-4.

See this record in the RMIT Research Repository at:

<http://researchbank.rmit.edu.au/view/rmit:24501>

Version: Published Version

Copyright Statement: © 2014 AIP Publishing LLC.

Link to Published Version:

<http://dx.doi.org/10.1063/1.4870069>

PLEASE DO NOT REMOVE THIS PAGE

Ultraviolet detection from energetically deposited titania films

M. R. Field, B. J. Murdoch, D. G. McCulloch, and J. G. Partridge

Citation: [Applied Physics Letters](#) **104**, 131905 (2014); doi: 10.1063/1.4870069

View online: <http://dx.doi.org/10.1063/1.4870069>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/104/13?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Structural, morphological, FTIR and photoluminescence properties of gallium oxide thin films](#)

J. Vac. Sci. Technol. B **32**, 03D119 (2014); 10.1116/1.4868523

[Resistive switching properties of amorphous Pr_{0.7}Ca_{0.3}MnO₃ films grown on indium tin oxide/glass substrate using pulsed laser deposition method](#)

Appl. Phys. Lett. **100**, 212111 (2012); 10.1063/1.4722797

[Synthesis, characterization, and photoactivity of In Ta O₄ and In_{0.9}Ni_{0.1}Ta O₄ thin films prepared by electron evaporation](#)

J. Vac. Sci. Technol. A **28**, 127 (2010); 10.1116/1.3273597

[Structural and electrical properties of metal contacts on n-type ZnO thin film deposited by vacuum coating technique](#)

J. Vac. Sci. Technol. B **27**, 2124 (2009); 10.1116/1.3196786

[Synthesis and characterization of ZnO thin film grown by electron beam evaporation](#)

J. Appl. Phys. **99**, 123105 (2006); 10.1063/1.2204333

AIP | Journal of
Applied Physics

Journal of Applied Physics is pleased to
announce **André Anders** as its new Editor-in-Chief

Ultraviolet detection from energetically deposited titania films

M. R. Field, B. J. Murdoch,^{a)} D. G. McCulloch, and J. G. Partridge

School of Applied Sciences, RMIT University, GPO Box 2476 V, Melbourne, VIC 3001, Australia

(Received 24 October 2013; accepted 20 March 2014; published online 2 April 2014)

Thin films of unintentionally doped n-type titania have been energetically deposited from a filtered cathodic vacuum arc. All films were dense, smooth, and transparent with crystallinity depending on the deposition/annealing temperature. At a growth temperature of 600 °C, the preferred phase could be changed from rutile to anatase by increasing the oxygen process pressure thereby reducing dynamic annealing. Pt/TiO_x/Pt ultraviolet detectors exhibiting rectifying current-voltage characteristics and ultraviolet-visible rejection ratios exceeding 10⁴:1 were formed on selected films. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4870069>]

Titanium oxide (or titania) is a polymorphous, wide bandgap semiconducting material with electrical and optical properties that vary with its microstructure.¹ The lower temperature anatase structure has an indirect optical bandgap of ~3.2 eV,² whilst rutile titania has a direct optical bandgap of ~3.0 eV. Anatase and rutile titania both exhibit high refractive index, good chemical stability, biocompatibility, high transmission in the visible region, and electrical conduction that can be readily tuned through doping and/or native defects.³ Existing applications include bio-coatings,⁴ biosensors,⁵ ultraviolet (UV) light detectors,⁶ solar cell layers,⁷ and transparent electronic devices.⁸ Thin films of titania are normally grown using low-energy physical vapour or chemical vapour deposition techniques.^{9–11} Energetic physical vapour deposition can produce high quality thin films over large areas and provides a means to access a greater variety of microstructures at lower growth temperatures.¹²

In this Letter, titania coatings were energetically deposited (up to ~20 eV) using a filtered cathodic vacuum arc (FCVA).¹³ This method is capable of producing dense, well adhered metal oxide coatings over large areas with optical and electrical properties suitable for device applications.^{14–17} The microstructures, optical, and electrical properties of films dynamically annealed during growth were compared with those deposited at room temperature (RT) and subsequently annealed. In addition to studying the crystallography and local bonding, the titania films were evaluated as active layers in UV light detectors.

All the titania films were deposited at floating potential onto quartz and sapphire substrates using a Nanofilm FCVA system¹⁸ equipped with a 68 mm diameter 99.99% purity Ti cathode. The arc current was 115 A and other operating conditions were as shown in Table I. The sheet resistances of the TiO_x films (also shown in Table I) were measured at room temperature using an Ecopia HMS-3000 system and lithographically defined Van der Pauw Ti/Au Ohmic contacts. Atomic force microscopy, performed using tapping mode, revealed uniform morphologies with surface roughness less than 1% of the film thickness. The composition of the films was analysed using X-ray photoelectron spectroscopy and

found to be within 1% of stoichiometric TiO₂. As shown in Fig. 1, X-ray diffraction (XRD) (obtained using a Bruker D8 Discover GADDS micro-diffractometer with monochromatic Cu K α source) revealed an amorphous microstructure in the film prepared at room temperature. Powder standards (Deguss P25 with anatase:rutile:amorphous ratio of 78:14:8 as-received and largely rutile after annealing at 800 °C) show clear peaks associated with the anatase and rutile phases.

The local bonding in the RT film was investigated using X-ray absorption spectroscopy (using the soft X-ray beam-line at the Australian synchrotron). The X-ray absorption near edge structure (XANES) of the Ti L₂ and L₃ edges (collected using the Auger electron yield) is shown in Fig. 2. The figure also shows the corresponding edges from the P25 and An-P25 powder standards and from a Ti foil (Ti). Peaks a and b arise from interactions between the newly formed core-hole and poorly screened 3d electrons.¹⁹ The L₂ and L₃ edges each consist of a doublet caused by crystal field splitting of the L energy bands into e_g and t_{2g} sub bands, seen clearly in the spectrum from the Ti foil. Changes in the long range order of the sample can cause further splitting of each e_g peak into d₁ and e₁ peaks.²⁰ This splitting is evident in the L₃ peak from the P25 and An-P25 standards but, due to lifetime broadening, is not clear in the L₂ peak. The L₃-e_g peak is sensitive to the bonding environment and is frequently used to identify the phase of the material. Changes in the phase (from a mixed phase to rutile) after annealing the P25 powder standard become clear with the increase in intensity of the e₁ peak relative to the d₁ peak. The XANES from the RT film is similar to that from the largely anatase (as-received) P25, indicating that anatase bonding is prevalent in this film. However, the broader e_g peaks from RT are consistent with its highly disordered microstructure.

A typical UV-visible transmission plot with accompanying Tauc plot²¹ is shown in Fig. 3 with the extracted optical bandgaps from all films shown in Table I. The low resistivity and optical bandgap exhibited by the RT film are consistent with a disordered anatase material. The defects most likely to cause the low resistivity of this film are those related to oxygen deficiency. Pt contacts, consisting of 20 inter-digital strips each of thickness 10 nm, length 280 μ m, and width 6 μ m, were lithographically patterned on all films and their current-voltage (*I*-*V*) characteristics were measured in light

^{a)} Author to whom correspondence should be addressed. Electronic mail: billy.murdoch@rmit.edu.au

TABLE I. Film synthesis conditions and key properties of the TiO_x coatings prepared using FCVA.

Film ID	Deposition temp.	Oxygen pressure (mTorr)	Annealing temp.	Optical bandgap (eV)	Sheet resistance (MΩ/□)	Dark:UV current ratio (at 1 V)	Structure
RT	Room temp.	1.5	...	3.3	2.4	1:1	Amorphous anatase
An-650	Room temp.	1.5	650 °C	3.2	31	1:20	Polycryst. rutile and anatase
An-750	Room temp.	1.5	750 °C	3.2	480	1:1000	Polycryst. rutile
600	600 °C	1.5	...	3.1	22	1:2	Polycryst. rutile
600-HO	600 °C	3.0	...	3.2	2.9 × 10 ⁶	1:400	Polycryst. anatase

and dark conditions. The active area of each device was assumed to be 500 × 500 μm². Illumination through the substrate was achieved using light emitting diodes (calibrated to provide equal optical power density and with <20 nm FWHM) with different centre wavelengths (λ_c) mounted beneath the detectors on a purpose made probe station. The RT film exhibited Ohmic characteristics and little sensitivity to light.

Samples of the RT film were annealed in vacuum for 1 h at temperatures straddling the commonly accepted anatase-rutile bulk transition temperature.²² The XRD from the film annealed at 650 °C (An-650) was consistent with a mixed microstructure with peaks attributable to both anatase and rutile phases. According to Scherrer's equation,²³ the difference in the widths of the anatase and rutile peaks indicates that the anatase crystallites in the film are largest, apparently with rutile crystallites in the early stages of nucleation. The XANES from this film contradicts the XRD

indicating that the local bonding is largely rutile. The disagreement is attributed to the presence large numbers of rutile nano-crystallites in the film and a relative lack of sensitivity to these nano-crystallites compared to the XANES.²⁴ As noted by Limpijumnong *et al.*,²⁴ XANES accurately reveals the phases present in the films (determining the photoelectronic properties) regardless of the size of the constituent crystallites. The film annealed at 750 °C exhibits a more ordered, principally rutile, microstructure. The optical bandgaps of An-650 and An-750 are both 0.1 eV lower than the as-deposited film and the electrical resistivity increases with annealing temperature. These measurements are consistent with a reduction in defects associated with oxygen deficiency, resulting from the increased order in the annealed films.

FIG. 1. X-ray diffraction from the FCVA deposited titania thin films, a TiO₂ powder standard as-received (Deguss P25 with anatase:rutile:amorphous ratio of 78:14:8) and after transformation to rutile by annealing at 800 °C. Arrows marked "A" and "R" mark the positions of the anatase and rutile peaks, respectively.

FIG. 2. XANES from the titania films (black) compared with a Ti metal foil, a powder standard as-received (Deguss P25 with anatase:rutile:amorphous ratio of 78:14:8) and after transformation to rutile by annealing at 800 °C.

FIG. 3. UV-visible transmission from the 600-HO TiO_x film with accompanying Tauc plot as inset.

Detectors formed on the annealed films exhibited rectifying I - V characteristics and improved sensitivity to UV light (see Table I). Fig. 4(a) shows the I - V characteristics of a Pt- TiO_x -Pt inter-digital contact structure (shown in inset) formed on An-750 measured in dark and illuminated conditions. The non-linearity of the I - V characteristics results from the rectifying Schottky junctions at the Pt- TiO_x interfaces. The UV:dark current ratio measured at +500 mV is $>1000:1$ (for $\lambda_c = 285$ nm and 365 nm). The photo-responsivity (R) of the device at the different wavelengths is shown as an inset. Comparing R at $\lambda_c = 285$ nm with R at $\lambda_c = 470$ nm, provides an ultraviolet-visible rejection ratio of $\sim 22\,000:1$. Response and recovery times for this device were measured during and after 120 s periods of UV light exposure. The response time, defined here as the time at which the current at 500 mV is $>90\%$ of its maximum value during UV exposure, was ~ 30 s. The recovery time, defined as the time taken for the current at 500 mV to reach $<200\%$ of its minimum (dark) value, was ~ 600 s. The relatively slow response/recovery times are attributed in part to the presence of oxygen vacancies that are known to trap holes in TiO_x , preventing recombination with electrons after UV exposure.^{25,26} Molecular oxygen, bound to the defective TiO_x surface is also expected to contribute to the extended response/recovery times. Adsorption of molecular oxygen on the surface of TiO_2 is well characterised and central to applications in photo-catalysis.²⁷ Whilst O_2 does not adsorb on a perfect neutral TiO_2 surface,²⁸ it does adsorb and form O-Ti bonds when excess negative charges (photo-excited electrons and/or subsurface oxygen vacancies) are available. The O_2 adsorbed on the surface of TiO_2 captures photo-induced electrons as well as the free electrons located on oxygen vacancy states. This effect, coupled with the subsequent desorption of O_2 and release of captured electrons, would cause prolonged response and recovery times in the TiO_x UV detectors.

FIG. 4. Current-voltage characteristics of Pt- TiO_x -Pt inter-digital detectors formed on (a) An-750 and (b) 600-HO titania films in dark and illuminated conditions. Insets show the contact arrangement and the photo-responsivities (R) of the devices.

The effects of dynamic annealing were explored with a titania film grown at 600°C but with otherwise identical conditions to those used for the RT film. The XRD (Fig. 1) and XANES (Fig. 2) from this “600” film show it to be dominated by the rutile phase. The XRD has prominent $\{101\}$ and $\{200\}$ rutile peaks. Whilst the preferred crystallographic orientation is different to that observed in the annealed films, the XANES shows the local bonding is similar. The 3.1 eV optical bandgap is consistent with a largely rutile microstructure, whilst its low electrical resistance suggests the presence of a large number of active defects. This manifests itself in relatively poor UV detection (see Table I).

The aforementioned deposition was repeated but with higher oxygen pressure to reduce the effects of oxygen deficiency. This film, labelled 600-HO, produced XRD and XANES, consistent with a largely anatase ordered microstructure. Increased oxygen pressure therefore resulted in different growth to that occurring during the deposition of the 600 film. Since both deposition rate and average energy in the depositing flux are reduced with increased process pressure (due to increased collisions with the process gas), the change in growth/microstructure at higher pressure is attributed to reduced dynamic annealing. The optical bandgap of

600-HO (3.2 eV) is consistent with its predominantly anatase microstructure. Importantly, the electrical resistivity exceeds that in all other films and the Pt-TiO_x-Pt detector on this film is sensitive to UV light, as shown in Fig. 4(b). The inset in Fig. 4(b) shows the photo-responsivity, R , plotted as a function of the centre wavelength of illuminating light. Comparing R at $\lambda_c = 285$ nm with R at $\lambda_c = 470$ nm, provides an ultraviolet-visible rejection ratio of $\sim 200:1$. The detectors formed on An-750 (Fig. 3(a)) and 600-HO (Fig. 3(b)) respond differently to light with $\lambda_c = 365$ nm. Due to the differing dominant phases in the films and their differing optical bandgaps, the cut-off of the detector on the An-750 film appears as expected, at a longer wavelength.

In summary, titania films energetically deposited from a filtered cathodic arc have been structurally, optically, and electronically characterised before being implemented in UV detection devices. An oxygen pressure dependent transition from anatase to rutile occurred at a growth temperature of 600 °C. All films exhibited low surface roughness and optical bandgaps between 3.1 and 3.3 eV. Higher growth and annealing temperatures resulted in higher resistivity, consistent with more efficient oxygen incorporation. Pt/TiO_x/Pt inter-digital (back-to-back) rectifying junctions formed on the high-temperature grown and annealed films exhibited nonlinear I - V characteristics and sensitivity to UV light. The most sensitive UV detector exhibited an ultraviolet-visible rejection ratio of $\sim 22\,000:1$ (for $\lambda_c = 285$ nm and 365 nm).

The authors gratefully acknowledge support from the Australian Research Council (ARC), the Australian Synchrotron and the RMIT microscopy and microanalysis facility (RMMF).

¹U. Diebold, *Surf. Sci. Rep.* **48**(5–8), 53 (2003).

²R. Asahi, Y. Taga, W. Mannstadt, and A. J. Freeman, *Phys. Rev. B* **61**(11), 7459 (2000).

³M. C. K. Sellers and E. G. Seebauer, *J. Vac. Sci. Technol., A* **29**(6), 061503 (2011).

⁴J. Liu, D. Yang, F. Shi, and Y. Cai, *Thin Solid Films* **429**(1–2), 225 (2003).

⁵A. D. Barros, K. F. Albertin, J. Miyoshi, I. Doi, and J. A. Diniz, *Microelectron. Eng.* **87**(3), 443 (2010).

⁶X. Kong, C. Liu, W. Dong, X. Zhang, C. Tao, L. Shen, J. Zhou, Y. Fei, and S. Ruan, *Appl. Phys. Lett.* **94**(12), 123502 (2009).

⁷M. Thelakkat, C. Schmitz, and H. W. Schmidt, *Adv. Mater.* **14**(8), 577 (2002).

⁸N. Zhong, J. J. Cao, H. Shima, and H. Akinaga, *IEEE Electron Device Lett.* **33**(7), 1009 (2012).

⁹C. H. Heo, S. B. Lee, and J. H. Boo, *Thin Solid Films* **475**(1–2), 183 (2005).

¹⁰E. György, G. Socol, E. Axente, I. N. Mihailescu, C. Ducu, and S. Ciuca, *Appl. Surf. Sci.* **247**(1–4), 429 (2005).

¹¹G. A. Battiston, R. Gerbasi, A. Gregori, M. Porchia, S. Cattarin, and G. A. Rizzi, *Thin Solid Films* **371**(1), 126 (2000).

¹²A. Anders, *Thin Solid Films* **518**(15), 4087 (2010).

¹³A. Anders, *Cathodic Arcs: From Fractal Spots to Energetic Condensation* (Springer-Verlag, New York, 2008).

¹⁴S. Elzwawi, H. S. Kim, M. Lynam, E. L. H. Mayes, D. G. McCulloch, M. W. Allen, and J. G. Partridge, *Appl. Phys. Lett.* **101**(24), 243508 (2012).

¹⁵N. Biluš Abaffy, D. G. McCulloch, and J. G. Partridge, *Surf. Coat. Technol.* **207**(0), 529 (2012).

¹⁶M. R. Field, J. G. Partridge, E. H. Mayes, K. Latham, and D. G. McCulloch, *J. Appl. Phys.* **110**(1), 014108 (2011).

¹⁷E. L. H. Mayes, D. G. McCulloch, and J. G. Partridge, *Appl. Phys. Lett.* **103**(18), 182101 (2013).

¹⁸N. Biluš Abaffy, J. G. Partridge, J. du Plessis, and D. G. McCulloch, *Phys. Status Solidi A* **205**(6), 1439 (2008).

¹⁹F. M. F. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky, and H. Petersen, *Phys. Rev. B* **40**(8), 5715 (1989).

²⁰S. O. Kucheyev, T. van Buuren, T. F. Baumann, J. H. Satcher, Jr., T. M. Willey, R. W. Meulenbergh, T. E. Felner, J. F. Poco, S. A. Gammon, and L. J. Terminello, *Phys. Rev. B* **69**(24), 245102 (2004).

²¹J. Tauc, R. Grigorovici, and A. Vancu, *Phys. Status Solidi B* **15**(2), 627 (1966).

²²D. J. Won, C. H. Wang, H. K. Jang, and D. J. Choi, *Appl. Phys. A* **73**(5), 595 (2001).

²³P. Scherrer, *Nachrichten von der Königl. Gesellschaft der Wissenschaften zu Göttingen* **1**, 96 (1918).

²⁴S. Limpitjumnong, J. Jutimoosik, N. Palakawong, W. Klysubun, J. Nukeaw, M. Du, and S. Rujirawat, *Appl. Phys. Lett.* **99**(26), 261901 (2011).

²⁵B. J. Morgan and G. W. Watson, *Phys. Rev. B* **80**(23), 233102 (2009).

²⁶D. P. Colombo and R. M. Bowman, *J. Phys. Chem.* **99**(30), 11752 (1995).

²⁷X. Pan, M.-Q. Yang, X. Fu, N. Zhang, and Y.-J. Xu, *Nanoscale* **5**, 3601 (2013).

²⁸E. Lira, S. Wendt, P. Huo, J. Ø. Hansen, R. Streber, S. Porsgaard, Y. Wei, R. Bechstein, E. Lægsgaard, and F. Besenbacher, *J. Am. Chem. Soc.* **133**, 6529 (2011).