ChemComm

Low temperature electrochemical synthesis of titanium nitride

Lucy E. Griffiths,[a] Martin R. Lee,[b] Andrew R. Mount,[a] Hiroshi Kondoh,[c] Toshiaki Ohta[c] and Colin R. Pulham*[a]

[a] *Department of Chemistry, The University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh, Scotland, UK EH9 3JJ. E-mail: C.R.Pulham@ed.ac.uk*
[b] *Department of Geology and Geophysics, The University of Edinburgh, Grant Institute, West Mains Road, Edinburgh, Scotland, UK EH9 3JW*
[c] *Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Received (in Cambridge, UK) 19th January 2001, Accepted 20th February 2001
First published as an Advance Article on the web 7th March 2001

Electrochemical oxidation of a titanium electrode in a solution of potassium amide in liquid ammonia resulted in the deposition of titanium nitride either as a thin film or as nanoparticles.

Titanium nitride is a technologically important material that exhibits excellent chemical stability, good wear resistance, and high electrical conductivity. As a thin film, titanium nitride finds uses as a hard coating for cutting tools,[1] as a diffusion barrier for microelectronic devices,[2] as an optical coating,[3] and as a gold-coloured surface for jewellery.[4] Conventional routes to thin films of TiN include heating titanium metal in a stream of ammonia,[5] reactive sputtering,[6] and chemical vapour deposition.[7] Many of these techniques require high temperatures and/or expensive equipment or precursors. Electrochemical synthesis is therefore an alternative route that has attracted significant interest. Previous studies have included anodisation of titanium in acetonitrile at an applied cell voltage of up to 1500–3000 V,[8] and nitridation of a titanium anode in an acetonitrile solution containing a primary amine and tetrabutylammonium bromide followed by heating at high temperatures.[9] Each of these routes produces TiN films, but incorporation of carbon-containing impurities is significant. A reduction in the level of carbon incorporation has been achieved by the use of NH_4Br–NH_3 electrolyte solutions. This resulted in an uncharacterised powder which on calcining at 1100 °C under flowing ammonia produced either small particles of TiN or could be used to coat substrates with TiN after calcining.[10] Electrochemical surface nitriding of titanium in a molten LiCl–KCl eutectic melt has been shown to produce TiN films, but the operating temperature of this process is 450 °C.[11] Titanium nitride powders have also attracted interest in the field of powder technology as precursors for the fabrication of sintered compact or thin films. A route describing the production of TiN particles by galvanostatic electrolysis using a titanium plate in a solution of *n*-butylamine in acetonitrile has recently been reported, but post-processing by heating to 200–1000 °C in the presence of ammonia was invariably required in order to generate TiN.[12]

In this work we describe an electrochemical process that operates at or below ambient temperatures to give, in one step, thin films or particles of TiN. Furthermore, the nature of the process favours nitride formation, with no incorporation of carbon, oxygen or halogen. This is because it involves liquid ammonia solutions containing the basic electrolyte KNH_2 rather than organic solvents containing the acidic NH_4Cl or NH_4Br electrolytes used previously.[9,10,12]

The apparatus for the electrochemical experiments is described below.† Sweeping the titanium electrode potential at sweep rates of 50–100 mV s^{-1} between 0.00 V and a negative potential limit, in excess of -1.50 V, produced a reduction current of several mA. During the reverse sweep to 0.00 V in the cyclic voltammogram (CV), an associated oxidation peak was observed at *ca.* -750 mV. On continued cycling, this oxidation peak was observed to diminish as the reduction wave shifted to more negative potentials. The CV recorded after 30 min showed little decrease in the negative sweep and no oxidation peak in the positive sweep at these potentials. It seems likely that this reduction reaction involves the reduction of the native titanium(IV) oxide with the loss of oxide from the titanium surface. The oxidation peak then corresponds to the reformation of the oxide surface. On repeated cycling, a fraction of the reduced oxide is lost to the bulk solution by diffusion. Thus the cycling eventually results in the production of an oxide-free titanium surface.

On stepping the potential of the cleaned titanium electrode from 0.00 to +3.00 V, a large positive current of several mA was initially observed, indicative of electrode oxidation, which fell slowly with time. Increasing the electrode potential (first to +4.00 V, then to +5.00 V) resulted in increases in the oxidation current, as did increasing the temperature of the solution from -78 to -33 °C, with no sign of gas evolution at the electrode. Stirring of the solution did not increase the current, indicating that the current is not limited by mass transport of solution species to the electrode. These results are consistent with the growth of a surface nitride film on the electrode surface by an oxidation that involves liquid ammonia and/or amide. Removal of the titanium electrode and washing with water revealed a golden coloured film.

CV sweeps to oxidising potential for clean titanium also showed an oxidation current due to nitride film growth. Each cycle resulted in the progressive shift of this oxidation current to more positive potentials. The increase by >1.00 V in the oxidative potential limit of this electrode, whilst retaining a similar pseudocapacitance, indicates that the deposited film is relatively inert and is conducting; this is a strong indication that the film is titanium nitride. The observed increase in current on raising the temperature of the ammonia solution from -78 to -33 °C allows one to calculate an activation energy for the process in the order of +20 kJ mol^{-1}. Extrapolation to 25 °C would predict an approximately 50-fold increase in the current compared with the current passed at -78 °C. For this reason, a pressure cell was constructed such that liquid ammonia at 25 °C could be safely contained. The predicted increase in current was indeed observed, but in this case small particles of a yellow–brown material grew on the surface of the titanium electrode. Evidence that these particles were electrically conducting was provided by the observations that (i) the particles grew as 'tendrils' towards the counter electrode, and (ii) when dislodged from the electrode surface by gentle tapping the current *decreased*, indicating a reduction of electrically conducting surface area. The small size of the particles caused them to be readily oxidised to TiO_2 in the presence of air and aqueous base. Hence it was essential to remove excess KNH_2 by washing the particles with portions of liquid ammonia, followed by removal of the last traces of ammonia *in vacuo* before handling in air. Glancing angle X-ray powder diffraction of the film and particles showed no peaks, but did show significant background scattering indicative of an amorphous or nano-crystalline phase.

DOI: 10.1039/b100713k

Attempts to anneal the film at 800 °C under argon resulted in some degree of sharpening, but were not conclusive. Subsequent characterisation involved a range of techniques that required as little processing of the film as possible.

The electrodeposited film showed a transition from metallic to superconducting behaviour at *ca.* 4.5 K in a field of 100 G; the magnitude of the transition, when correlated with the charge passed during synthesis, further indicated that titanium nitride was the major product of reaction. The temperature of the transition also suggested that the stoichiometry of the TiN_x film is such that x is very close to 1.[13]

The SEM-EDX spectrum also pointed to a nitride-containing film. Not surprisingly given the nature of the sample (TiN on bulk Ti) the spectrum was dominated by the strong Ti Kα line, but clearly discernible was the N 2p line (adjacent to the Ti Lα line). Quantitative assessment of the stoichiometry was not possible owing to the considerable contribution to the intensity from the titanium substrate. It is significant, however, that no peaks corresponding to either oxygen or potassium contaminants were observed.

Conclusive evidence for the identification of both the film and powder as TiN was provided by the Raman spectra. These display three broad bands, the positions of which were in extremely good agreement both with spectra described in the literature,[14] and with spectra obtained from authentic stoichiometric TiN powder. Previous Raman studies have shown that the relative intensities of the Raman bands at 550 and 235 cm^{-1} depend upon the stoichiometry of the titanium nitride.[14] The band at lower energy is ascribed to nitrogen vacancies in the lattice and its intensity relative to the band at 550 cm^{-1} increases rapidly with increasing nitrogen deficiency. When compared with published spectra, the Raman spectra of both film and powder suggest a value of x for the TiN_x that is close to unity.

Analysis of the films by X-ray photoelectron spectroscopy (XPS) was dominated by strong peaks for titanium (2p) and oxygen (1s) characteristic of TiO_2. This was not entirely unexpected given that several months elapsed between preparation and examination by XPS and points to aerial oxidation of the TiN film at its surface. After argon ion sputtering to an approximate depth of 50 nm, the Ti 2p peak shifted to a lower binding energy and a N 1s peak appeared at 397.2 eV, indicative of stoichiometric TiN.[15] The N 1s peak persisted to a depth of ~600 nm into the sample consistent with the expected film thickness based on the amount of charge passed. Transmission electron microscopy showed aggregates of approximately spherical particles of diameter *ca.* 5–10 nm (Fig. 1).

Electron diffraction from these particles produced distinct rings with the occasional appearance of spots. The separation of these rings corresponds to *d*-spacings in good agreement with those reported for the osbornite phase of TiN.[16]

We have demonstrated in this work that electrochemical oxidation of a titanium electrode in liquid ammonia/KNH_2 at temperatures between −78 and 25 °C, results in the deposition of TiN either as a thin film or as nanoparticles depending on the current density. A key step in the production of coherent thin films has been found to be repeated cycling of the titanium electrode to negative potentials such that a substantial negative current is observed. In this way, the native oxide layer is removed, thereby facilitating growth of chemically pure TiN when the electrode is subsequently held at positive potential. Furthermore, there is no requirement for post-processing of the films or particles at elevated temperatures. Preliminary results using other metal electrodes (*e.g.* Ta, Mo and W) suggest that this process is a general low-temperature route to metal nitrides.

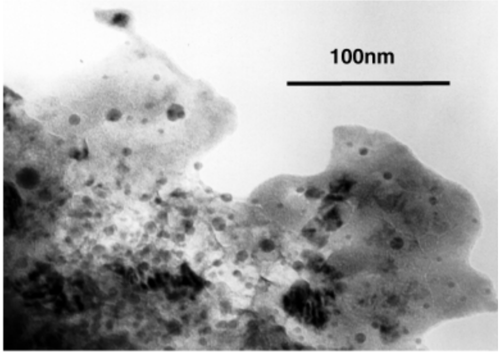

Fig. 1 TEM image of TiN particles mounted in epoxy resin.

We thank the EPSRC for a studentship (L. E. G.) and the British Council for a Monbusho Research Fellowship (L. E. G.). We dedicate this communication to the memory of the late Dr Marten Barker—a major contributor to the field of metal nitride chemistry.

Notes and references

† All operations were performed under dry, oxygen-free nitrogen. Saturated solutions of KNH_2 in liquid NH_3 at −78 °C were prepared by the addition of oxide-free potassium metal to dry liquid NH_3. Electrochemical experiments were performed using a three-electrode system; working electrode Ti foil (area ≈ 1 cm^2), counter electrode Pt coil (area >> 1 cm^2), pseudo-reference electrode (PRE) bright Pt wire. All potentials are reported with respect to this PRE. Electrochemical experiments at 25 °C involved a pressurised Pyrex vessel.

1 R. Bühl, H. K. Pulker and E. Moll, *Thin Solid Films*, 1981, **80**, 265.
2 G. I. Grigorov, K. G. Grigorov, M. Stayanova, J. L. Vignes, J. P. Langeron and P. Denjean, *Appl. Phys. A*, 1993, **57**, 195.
3 E. Velkonen, T. Karlsson, B. Karlsson and B. O. Johansson, *Proc. SPIE 1983 Int. Conf.*, 1983, **401**, 41.
4 B. Zega, M. Kornmann and J. Amiquet, *Thin Solid Films*, 1977, **54**, 577.
5 L. E. Toth, *Refractory Materials Vol. 7: Transition Metal Carbides and Nitrides*, Academic Press, New York, 1971.
6 O. Auciello, T. Barnes, S. Chevacharoenkul, A. F. Schreiner and G. E. McGuire, *Thin Solid Films*, 1989, **181**, 65.
7 T. Gerfin and K.-H. Dahmen, in *CVD of Non-Metals*, ed. W. S. Rees Jr., VCH, Weinheim, 1996, pp. 155–170.
8 J. Schrekenback, F. Schlottig, D. Dietrich, A. Hofman and G. Marx, *Appl. Surf. Sci.*, 1995, **90**, 129.
9 C. Rüssel, *Chem. Mater.*, 1990, **2**, 1941.
10 C. B. Ross, T. Wade and R. M. Crooks, *Chem. Mater.*, 1991, **3**, 768; T. Wade and R. M. Crooks, *Chem. Mater.*, 1996, **8**, 832.
11 T. Goto, M. Tada and Y. Ito, *Electrochim. Acta*, 1994, **8**, 1107; T. Nishikiori, T. Nohira, T. Goto and Y. Ito, *Electrochem. Solid State Lett.*, 1999, **2**, 278.
12 K. Nakajima and S. Shimada, *J. Mater. Chem.*, 1998, **8**, 955.
13 F. Lefloch, C. Hoffmann and O. Demolliens, *Physica C*, 1999, **319**, 258.
14 W. Spengler, R. Kaiser, A. N. Christensen and G. Müller-Vogt, *Phys. Rev. B*, 1978, 1095; R. D. Vispute, J. Narayan and Jagannadham, *J. Electron. Mater.*, 1996, **25**, 151.
15 M. J. Vasile, A. B. Emerson and F. A. Baiocchi, *J. Vac. Sci. Technol. A.*, 1990, **8**, 99.
16 N. Schönberg, *Acta Chem. Scand.*,1954, **8**, 213.