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# Low temperature deposition of cerium dioxide film by chemical reaction

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**A cerium dioxide ($CeO_2$) film with characteristic cubic lattice and optical band gap energy has been deposited chemically onto a non-conductive glass substrate at 333 K by simple immersion into an aqueous solution containing hydrous cerium(III) nitrate and dimethylamineborane (DMAB).**

Cerium dioxide ($CeO_2$) films find use in numerous applications such as in electrodes in solid oxide fuel cells (SOFC), as a photocatalyst, and as a corrosion protection coating alternative to chromate film. The $CeO_2$ film is prepared by several techniques such as evaporation of Ce followed by oxidation, sputtering, dip-coating, and sol–gel methods. The preparation of oxide films from aqueous solutions has several advantages over the above-mentioned techniques. Several authors have reported the preparation of $CeO_2$ films by electrodeposition onto conductive substrates from an aqueous cerium chloride solution saturated with dissolved oxygen.[1,2]

The authors have already proposed a chemical process for the preparation of oxide films using a reduction reaction of nitrate ions in an aqueous solution containing the nitrate salt and dimethylamineborane (DMAB), and have demonstrated preparations of zinc oxide (ZnO),[3–5] indium oxide ($In_2O_3$),[6] and magnetite ($Fe_3O_4$) films.[7] In this chemical process, DMAB acts as the reducing agent for the nitrate ion. The cell used for the process has an uncomplicated design, and the films can be obtained by simple immersion of the substrate into the solution. Also, materials including metals, ceramics, and polymers can be used as the substrate, regardless of their conductivity and melting point. The chemical preparation could be exploited very easily in industrial fields, because it has a low cost and is suited to mass production.

In this paper, we present the preparation of $CeO_2$ films onto a non-conductive substrate at 333 K by simple immersion of the substrate into an aqueous solution containing hydrous cerium nitrate ($Ce(NO_3)_3 \cdot 5.7H_2O$) and DMAB. Aqueous solutions containing 0.01 mol $L^{-1}$ hydrous cerium(III) nitrate and 0.005–0.1 mol $L^{-1}$ DMAB were prepared using distilled water and reagent grade chemicals and showed a pH value of 4.3. Corning no. 1737 glass was used as the substrate. Prior to deposition, the glass substrates (20 mm × 20 mm × 1.1 mm) were rinsed in acetone and then catalyzed using an industrially employed, two-step Pd/Sn activation process.[8]

Depending upon the DMAB concentration, transparent or white colored films were deposited onto the substrate. The film thickness was evaluated by averaging five measurements obtained from the SEM (JEOL JSM-5800) micrographs of film cross sections; the thickness increased with an increase in deposition time up to 4 h. The deposition rates were 280, 350, and 460 nm $h^{-1}$ for 0.005, 0.05, and 0.1 mol $L^{-1}$ DMAB solutions, respectively. The deposition rates were reproduced even for the solutions kept at 333 K for 24 h.

Electron spectra recorded from 0 to 1000 eV showed that the films contained the elements Ce, B, and O. Fig. 1 shows Ce 3d, B 1s, and O 1s electron spectra for a $CeO_2$ film prepared from the 0.01 mol $L^{-1}$ DMAB solution. The spectra were almost the same in profile and peak energies as for the films prepared from the 0.005–0.1 mol $L^{-1}$ DMAB solutions.

The Ce 3d spectrum obtained in this work was different in profile, compared with those already reported for $CeO_2$ samples.[9] Burroughs *et al.* indicated that the Ce 3d spectrum excited from their $CeO_2$ sample showed a complex shape

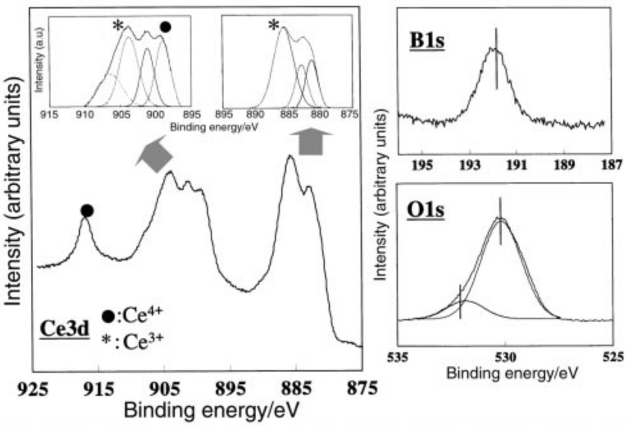

**Fig. 1** Ce 3d, B 1s, and O 1s electron spectra for $CeO_2$ films prepared from the 0.01 mol $L^{-1}$ DMAB solution. Electron spectrum measurements were performed using ULVAC-PHI ESCA-5700MC operated in vacuum at *ca.* $1.2 \times 10^{-10}$ Torr with MgKα radiation. Binding energies were corrected from the charge effect by referencing the C 1s signal of adventitious contamination hydrocarbon to 284.8 eV. The electron pass energy in the analyzer was set at 11.75 eV, corresponding to 0.776 eV of full-width at half-maximum (FWHM) of the Ag $3d_{5/2}$ peak at 368.35 eV.

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composed of eight components, attributed to Ce $3d_{5/2}$, $3d_{3/2}$ photoelectrons and satellite peaks of 'shake-down' type, and that the $CeO_2$ contained two states of $Ce^{3+}$ and $Ce^{4+}$ on the basis of the Ce 3d spectra measured for $Ce^{4+}$ and $Ce^{3+}$ in tetramethylheptanedionato cerium complexes.[10]

The Ce 3d spectra could be deconvoluted to eight peaks using a least-square curve fitting method with a mixture of Gaussian and Lorentzian functions on a Shirley-type background,[11] as shown in Fig. 1. Two peaks at 916.6 and 899.6 eV, and two peaks at 903.8 and 885.8 eV were assigned to Ce $3d_{5/2}$ and $3d_{3/2}$ photoelectrons attributed to $Ce^{4+}$ and $Ce^{3+}$ states, respectively. The peaks, except for the photoelectron peaks, were identified as satellite peaks of 'shake-down' type. The chemically prepared $CeO_2$ film showed strong $Ce^{3+}$ peaks and weak $Ce^{4+}$ peaks, compared with those already reported.[10] This suggested that the chemically prepared $CeO_2$ film will contain a relatively large amount of $Ce^{3+}$ ions, and this resulted in the difference in profile. Quantitative analysis for the ratio of $Ce^{3+}$ to $Ce^{4+}$ states could not be performed on the Ce 3d spectra, because of the complex shapes.

The B $1s_{1/2}$ spectrum showed a peak energy of 192.0 eV, which is close to that for the $B^{3+}$ state in $B_2O_3$.[12] The boron atoms contained within the film originate from DMAB contained within the solution.

The O $1s_{1/2}$ spectrum showed a peak energy of *ca.* 530 eV with a large FWHM value of 2.7 eV and clearly broadened on the high binding energy side. The O 1s spectrum could be deconvoluted to two peaks using the same curve fitting method as described above. The low binding energy peak at 530 eV represented the $O^{2-}$ contribution in both Ce–O bonds, since the $O^{2-}$ contributions of $Ce^{3+}$–O and $Ce^{4+}$–O bonds represented peak energies of 529.8 and 530.3 eV, respectively.[9] Also, the high binding energy peak at 533 eV contributes to the $O^{2-}$ in $B_2O_3$.

Fig. 2 shows the X-ray diffraction spectrum for the film prepared from the 0.01 mol $L^{-1}$ DMAB solution – X-ray diffraction spectra were almost the same in profile and peak angles, regardless of DMAB concentration. The four peaks observed in the amorphous type X-ray diffraction pattern originated from the glass substrate and were assigned to those for $CeO_2$ with a cubic structure.[13] The unit-cell parameter calculated from the peak angles was 0.5422 nm, which was greater than the value (0.5411 nm) tabulated in the ICDD card.[13]

Any peaks assigned to $Ce^{3+}$ compounds including $Ce_2O_3$, and to boron compounds including $B_2O_3$, could not be seen on the X-ray diffraction spectrum. It has already been reported that the $Ce^{3+}$ ion has an ionic radius larger than that for the $Ce^{4+}$ ion,[14] and that the $B^{3+}$ ion gives a lattice expansion in chemically prepared ZnO films.[4] The expansion of the $CeO_2$ lattice can be attributed to the incorporated $Ce^{3+}$ and $B^{3+}$ ions.

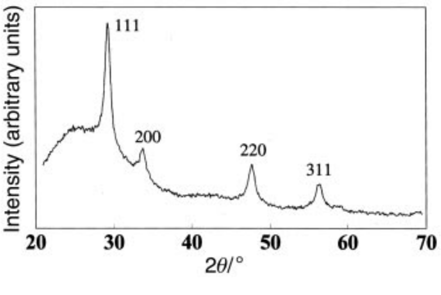

**Fig. 2** X-Ray diffraction spectrum for a film prepared from 0.01 mol $L^{-1}$ DMAB solution. Spectra were recorded using a MAC Science MXP18 diffractometer system with monochromated CuKα radiation operated at 40 kV and 200 mA. The diffraction angles were referenced to those for high purity Si powder.

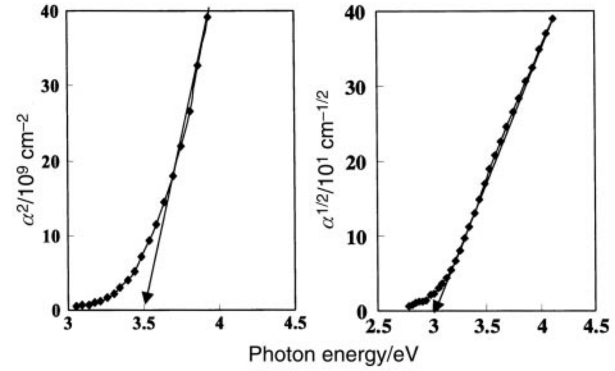

**Fig. 3** Dependence of $\alpha^2$ and $\alpha^{1/2}$ on photon energy for $CeO_2$ films prepared from the 0.01 mol $L^{-1}$ DMAB solution. Optical absorption spectra were recorded with a reference glass substrate.

The $CeO_2$ films showed random orientation, since the relative intensities almost resembled those tabulated in the ICDD card. The (111) diffracted X-ray peak showed a large full-width at half-maximum (FWHM) value of around 0.56° in $2\theta$. Peak broadening of the diffracted X-ray lines is caused by several factors, such as grain size and non-uniform strain.[15] This suggested that the $CeO_2$ film had either a small grain size or large non-uniform strain.

The films prepared from 0.005–0.01 mol $L^{-1}$ DMAB solutions were composed of aggregates of granular particles of 15.2 nm in size, and showed a smooth surface of 3.7 nm in the root-mean-square roughness (RMS) calculated from the atomic force microscopy (AFM) (Digital Instruments, NanoScope IIIa, Dimension 3000) image. $CeO_2$ films prepared from the 0.1 mol $L^{-1}$ DMAB solutions showed large surface irregularity.

The smooth $CeO_2$ films prepared from the 0.005–0.01 mol $L^{-1}$ DMAB solutions showed a high optical transmission, from 60 to 80% at wavelengths in the visible light region. The rough $CeO_2$ films prepared from the 0.1 mol $L^{-1}$ DMAB solution, however, showed poor transmissions of below 10%.

The optical band gap energy ($E_g$) was evaluated using the following dependence of the absorption coefficient (α) on the photon energy ($E_{pt}$): $(E_{pt}-E_g)\propto\alpha^2$ for direct transition, and $(E_{pt}-E_g)\propto\alpha^{1/2}$ for indirect transition. The absorption coefficient (α) was calculated from the absorbance obtained from the absorption spectra and film thickness measurements.

Fig. 3 shows the plots of $\alpha^2$ and $\alpha^{1/2}$ *versus* photon energy on the transparent $CeO_2$ film prepared from the 0.01 mol $L^{-1}$ DMAB solution. The band gap energy obtained by extrapolating to $\alpha = 0$ was *ca.* 3.5 eV for direct and 3.0 eV for indirect transitions, which were in agreement with those already reported.[16] The band gap energy for the film prepared from the 0.1 mol $L^{-1}$ DMAB solution could not be evaluated because of the poor optical transmission.

In conclusion, $CeO_2$ films were deposited directly onto a non-conductive substrate at 333 K from an aqueous solution containing hydrous cerium(III) nitrate and dimethylamine-borane (DMAB). The $CeO_2$ films had a slightly expanded cubic lattice due to incorporation of boron and $Ce^{3+}$ ions, and showed optical band gap energies of 3.5 eV for direct and 3.0 eV for indirect transitions.

## Notes and references

1 F. B. Li and G. E. Thompson, *J. Electrochem. Soc.*, 1999, **146**, 1809.
2 A. J. Aldykiewicz, A. J. Davenport and H. S. Isacca, *J. Electrochem. Soc.*, 1996, **143**, 147.
3 M. Izaki and T. Omi, *Appl. Phys. Lett.*, 1996, **68**, 2439.
4 M. Izaki, *J. Electrochem. Soc.*, 1999, **146**, 4517.
5 M. Izaki and J. Katayama, *J. Electrochem. Soc.*, 2000, **147**, 210.
6 M. Izaki, *Electrochem. Solid State Lett.*, 1998, **1**, 215.

7 M. Izaki and O. Shinoura, *Adv. Mater.*, 2001, **13**, 142.

8 M. Schlesinger, in *Modern Electroplating, 4th Edition*, ed. M. Schlesinger and M. Paunovic, Wiley-Interscience, New York, 2000, p. 668.

9 G. Praline, B. E. Koel, R. L. Hance, H.-I. Lee and J. M. White, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **21**, 17.

10 P. Burroughs, A. Hamnett, A. F. Orchard and G. Thornton, *J. Chem. Soc., Dalton Trans.*, 1976, 1686.

11 D. Briggs and M. P. Seah, in *Practical Surface Analysis, Vol. 1, Auger and X-Ray Photoelectron Spectroscopy*, Wiley, West Sussex, 1992, p. 555.

12 J. Chastain, in *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Minnesota, 1992, p. 215.

13 Joint Committee of Powder Diffraction Standard, Powder Diffraction File, No. 34-0394, International Centre for Diffraction Data, Pennsylvania, 1992.

14 R. Jenkins and R. L. Snyder, in *Introduction to X-Ray Powder Diffractometry*, Wiley-InterScience, New York, 1996, p. 89.

15 G. Adachi, in *Science of Rare Earths*, Kagaku Dojin, Tokyo, 1999, p. 871.

16 Z. C. Orel and B. Orel, *Phys. Status Solidi B*, 1994, **186**, K33.