Monitoring the growth of titanium oxide thin films by the liquid-phase deposition method with a quartz crystal microbalance

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The quartz crystal microbalance (QCM) technique has been applied to investigate the formation of titanium oxide thin films by the liquid-phase deposition (LPD) method. A linear relationship was observed between the thickness measured by the QCM technique and that measured by direct observation with a scanning electron microscope, indicating that it is possible to monitor the growth of thin films from aqueous solution systems by the LPD method with the QCM technique. The concentration effects of free F^-, H_3BO_3 and $(NH_4)_2TiF_6$ on the film deposition rate are discussed.

The liquid-phase deposition (LPD) method is a wet process for the formation of metal oxide thin films on substrates.[1,2] By using this method, it is possible to form metal oxide or hydroxide thin films on various kinds of substrates which are immersed only in the treatment solution. Metal oxide or hydroxide thin films form through the ligand-exchange (hydrolysis) equilibrium reaction of metal–fluoro complex ionic species and the F^- consumption reaction of boric acid or aluminium metal as F^- scavengers. In the treatment solution, following ligand-exchange (hydrolysis), an equilibrium reaction of the metal–fluoro complex ion is presumed:

$$MF_x{}^{n-} + nH_2O \rightleftharpoons MO_n + xHF \qquad (1)$$

The equilibrium reaction (1) is shifted to the right-hand side by the addition of boric acid or aluminium metal as F^- scavengers, which readily react with F^- and form more stable complex ions as follows:

$$H_3BO_3 + 4HF \rightleftharpoons BF_4{}^- + H_3O^+ + 2H_2O \qquad (2)$$

$$Al + 6HF \rightleftharpoons H_3AlF_6 + 3/2H_2 \qquad (3)$$

The addition of the F^- scavenger leads to the consumption of F^- ions and accelerates the ligand-exchange reaction (1). This is a very simple process and does not require any special equipment, such as a vacuum system, a high frequency or voltage source. This process can be applied readily to the preparation of thin films on substrates which have complex surface morphologies and large surface areas, and also multicomponent oxide thin films can be formed by the addition of the selected metal ion to the treatment solution, because the LPD method is performed in an aqueous solution which is a typical homogeneous mixing system. So far, we have developed and reported the preparation of titanium oxide thin films from a mixed solution of $(NH_4)_2TiF_6$ and H_3BO_3 by the LPD method.[3]

The quartz crystal microbalance (QCM) is an extremely sensitive sensor capable of measuring small mass changes in the nanogram range, because its oscillating frequency is changed even by a small amount of deposition on the crystal surface.[4] Recently, it has been used widely as a mass-sensitive detector in aqueous solution systems as well as in vacuum and in the gas phase. QCM techniques in solution systems have been applied to the study of electrodeposition,[5–7] ion fluxes in polymer films,[8,9] intercalation phenomena[10] and other interfacial phenomena. The change in oscillating frequency of the quartz crystal (Δf) is proportional to the change in mass (Δm) per unit area (A) of the material deposited on the crystal. The equivalence is expressed as follows:[4,11]

$$\Delta f = -f_0{}^2 \Delta m/(\rho_q NA) \qquad (4)$$

where f_0 is the fundamental frequency of the crystal, N is the frequency constant (1.670×10^5 cm Hz for an AT-cut quartz) and ρ_q is the density of quartz (2.648 g cm^{-3}).

In the present paper, we report the growth of titanium oxide thin films by the LPD method, which was monitored with the QCM technique. We discuss the concentration effects of free F^-, H_3BO_3 and $(NH_4)_2TiF_6$ in the treatment solution on thin film formation by the LPD method.

Experimental

Treatment solutions for the LPD method

As parent solutions for the LPD method, $(NH_4)_2TiF_6$ (Kishida Chemical Co. Ltd.) and H_3BO_3 (Nacalai Tesque Inc.) were dissolved separately in distilled water at concentrations of 0.5 mol dm^{-3}. These solutions were mixed in various compositions and used as the solution for deposition. For the purpose of investigating the concentration effect of free F^- in the treatment solution, an NH_4F aqueous solution (Nacalai Tesque Inc.) was added to the treatment solution at various concentrations.

QCM measurements

The quartz crystal used in the present study was biplanar, circular AT-cut with a diameter of 13 mm. The crystal had a fundamental frequency of 3.58 MHz, and the approximate sensitivity for the frequency change was 35 ng cm^{-2} Hz^{-1} [from eqn. (4)]. The surface of the crystal in contact with the solution was coated with a thin film of metallic gold (*ca.* 100 nm) by vacuum evaporation. The crystal was mounted on a holder using a silicon sealant so as to expose one side of the crystal to the solution.

A schematic diagram of the cell and quartz crystal apparatus is shown in Fig. 1. The cell was made of acrylic resin. The quartz crystal apparatus was immersed in the treatment solution for deposition, and the resonant frequency was measured by a frequency counter (Advantest Inc., TR5823H) at intervals of 15 min at 30 °C.

Results and Discussion

Monitoring the growth of thin films with the QCM

Fig. 2 shows the relationship between the thickness of the film deposited by the LPD method as determined by SEM

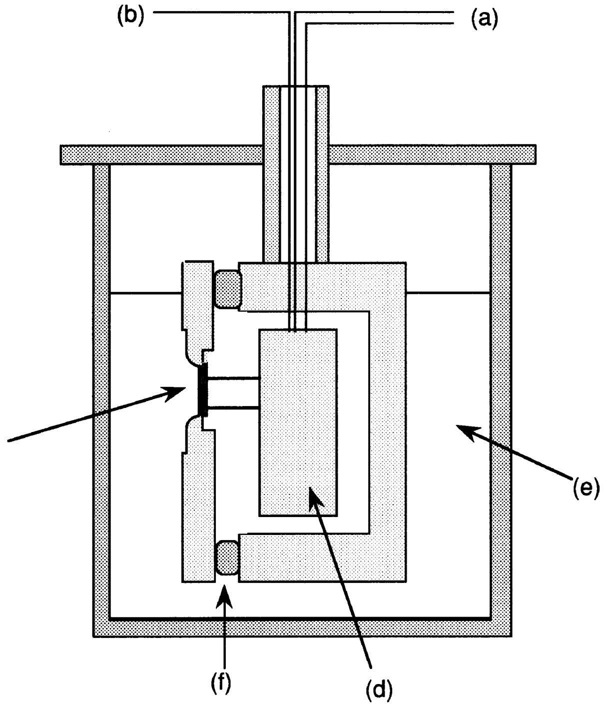

Fig. 1 Schematic diagram of the cell and quartz crystal apparatus. (a) Frequency counter, (b) dc power source, (c) quartz crystal oscillator, (d) oscillating circuit, (e) treatment solution and (f) o-ring. The cell was kept at 30 °C.

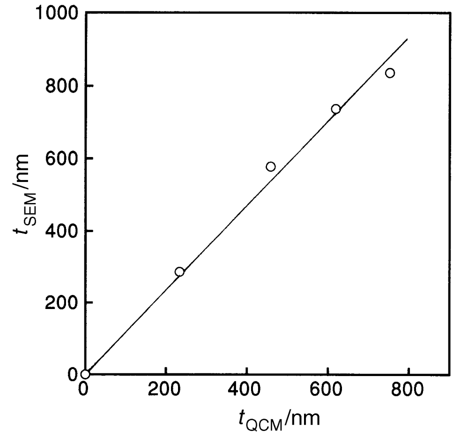

Fig. 2 Relationship between film thickness determined from QCM (t_{QCM}) and SEM (t_{SEM})

observation (t_{SEM}) and that measured by the QCM technique (t_{QCM}). The value of t_{QCM} was determined using the following equation.

$$t_{QCM} = \Delta m \frac{1}{Ad} \qquad (5)$$

where Δm is obtained from eqn. (4), A is the area of the QCM and d is the density of TiO_2 (anatase; 3.90 g cm^{-3}). As shown in Fig. 2, a good linear relationship was observed between t_{SEM} and t_{QCM}. It can be said, therefore, that the QCM technique is suitable for monitoring the growth of thin films by the LPD method. The value of t_{QCM} was expressed as follows:

$$t_{QCM} = 0.85\, t_{SEM} \qquad (6)$$

The value of t_{QCM} was lower than that of t_{SEM} owing to the value of d used in eqn. (5) being larger than the real value, because the crystallinity of the deposited film was low.

Deposition of titanium oxide thin films by the LPD method

The deposition reaction in the LPD method consists of the ligand-exchange (hydrolysis) equilibrium reaction of the metal–fluoro complex ion and the F^- consumption reaction by the addition of boric acid as F^- scavenger. For the ligand exchange (hydrolysis) of $[TiF_6]^{2-}$ ion in aqueous solution, the following equilibrium scheme has been proposed.[12,13]

$$[TiF_6]^{2-} + nH_2O \rightleftharpoons [TiF_{6-n}(OH)_n]^{2-n} + nHF \qquad (7)$$

The value of n is small, and the degree of hydrolysis decreases upon increasing the concentration of $[TiF_6]^{2-}$.[12,13] On the other hand, H_3BO_3 readily reacts with F^- as follows:[14–16]

$$H_3BO_3 + HF \rightleftharpoons HBF(OH)_3 \qquad (8)$$

$$HBF(OH)_3 + HF \rightleftharpoons HBF_2(OH)_2 + H_2O \qquad (9)$$

$$HBF_2(OH)_2 + HF \rightleftharpoons HBF_3OH + H_2O \qquad (10)$$

$$HBF_3OH + HF \rightleftharpoons HBF_4 + H_2O \qquad (11)$$

Reaction steps (8)–(10) are rapid, and step (11) is slow.[14–16] The addition of H_3BO_3 to the $(NH_4)_2TiF_6$ solution accelerates the ligand-exchange (hydrolysis) reaction (7), *i.e.* reaction (7) is shifted to the right, owing to the reaction of H_3BO_3 with F^-. Consequently, titanium oxide thin films form on the substrates upon dehydration of the $[Ti(OH)_6]^{2-}$ species generated by the hydrolysis reaction of $[TiF_6]^{2-}$.

Fig. 3(a) shows the relationship between the deposited film mass (m) and the reaction time. Fig. 3(b) shows the variation of the deposition rate (r) with reaction time. The deposition rate (r) was determined from the gradient of Fig. 3(a). In this case, the deposition rate increased with reaction time up to 6 h, was constant to 9 h, and then decreased gradually. As shown in Fig. 3(b), there are three steps for the deposition rate: (i) increasing with time, (ii) a constant rate region and (iii) decreasing with time. From SEM observation of the

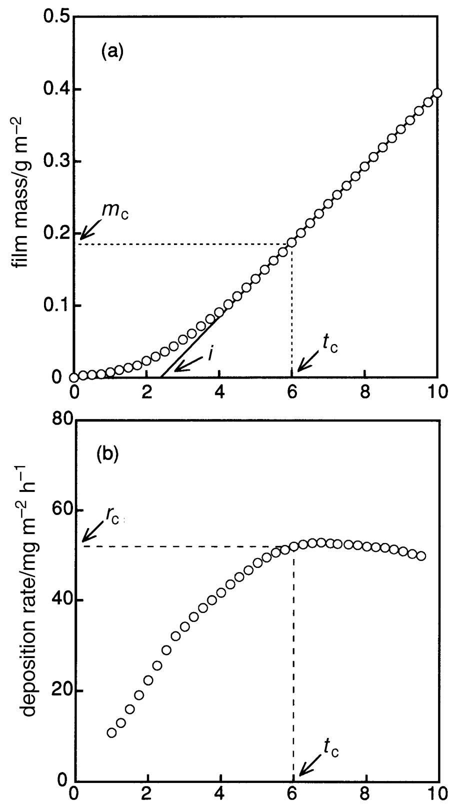

Fig. 3 Dependence of deposited film mass (a) and deposition rate (b) on reaction time. Concentration of $(NH_4)_2TiF_6$ 100 mmol dm^{-3}, and of H_3BO_3 150 mmol dm^{-3}.

deposited film, several nucleation sites were observed on the substrate at step (i), and the number of nucleation sites increased with the reaction time. At steps (ii) and (iii), growth of the nuclei was observed. The decrease in the deposition rate at step (iii) is presumably due to the decrease in the reactant content. Here we introduce some parameters. The reaction time at which the deposition rate was constant is t_c. The deposited film mass at t_c is m_c. The deposition rate at t_c is defined as the film formation rate, r_c. The induction period for deposition (i) is defined as follows:

$$i = t_c - \frac{m_c}{r_c} \qquad (12)$$

These parameters are indicated on Fig. 3.

Effects of the concentration of free F^- in the treatment solution

In the solution, $[TiF_6]^{2-}$ ions partially hydrolyse and release F^-, although the value of n of eqn. (7) is small. Thus free F^- ions may exist in the solution at the initial stage. It is considered that the H_3BO_3, as F^- scavenger, preferentially reacts with such free F^- at the outset of the deposition reaction, therefore the induction period may be strongly correlated with the initial content of free F^-. In order to investigate the effects of the concentration of free F^-, an NH_4F solution was added to the treatment solution. As NH_4F dissociates to NH_4^+ and F^-, the concentration of free F^- in the treatment solution could be controlled by the addition of NH_4F. Fig. 4(a) shows the relationship between the reaction time and the deposited film mass with various concentrations of NH_4F in the treatment solution. The deposited film mass decreased and the induction period increased with increasing concentration of NH_4F, *i.e.* increasing free F^- concentration, whereas the film formation rates were almost constant. The variation of induction period with the concentration of NH_4F is shown in Fig. 4(b). The induction period increased linearly with increasing concentration of NH_4F. Based on these data, we concluded that free F^- ions react with H_3BO_3 in the initial stage of the deposition reaction, *i.e.* the induction period. After that, F^- ions coordinated to $[TiF_{6-n}(OH)_n]^{2-}$ react with H_3BO_3, and then titanium oxide deposition occurs. The film formation rate does not depend on the concentration of free F^-.

Effects of the concentration of H_3BO_3 in the treatment solution

Fig. 5(a) shows the relationship between the deposited film mass and the reaction time. The concentration of $(NH_4)_2TiF_6$ was constant at 100 mmol dm^{-3} and that of H_3BO_3 was varied from 125.0 to 200.0 mmol dm^{-3}. The deposited film mass increased with increasing concentration of H_3BO_3. The film formation rate and the induction period are shown in Fig. 5(b) as a function of the concentration of H_3BO_3. As can be seen, the film formation rate increased and the induction period decreased with increasing H_3BO_3 concentration. Variation of the film formation rate was contrasted with that of the induction period.

As mentioned, free F^- ions exist in the $[TiF_6]^{2-}$ aqueous solution at equilibrium concentration. These free F^- ions react with H_3BO_3 during the induction period, and then F^- ions coordinated to the $[TiF_{6-n}(OH)_n]^{2-}$ complex ion react with H_3BO_3. The concentrations of free F^- are constant for every solution in Fig. 5, and since the concentrations of $(NH_4)_2TiF_6$ are constant, the induction period decreased with increasing H_3BO_3 concentration. The decrease in the induction period slowed when the concentration of H_3BO_3 was more than 162.5 mmol dm^{-3}. As mentioned previously, reaction of F^-

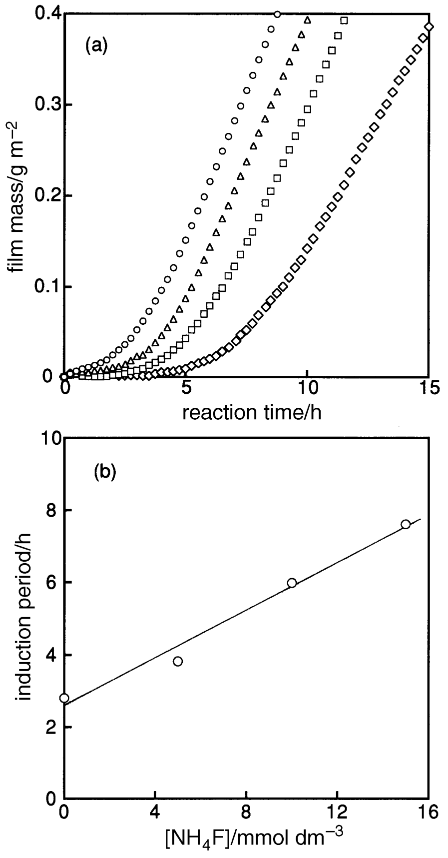

Fig. 4 (a) Relationship between deposited film mass and reaction time. Concentration of NH_4F: ○ 0, △ 5.0, □ 10.0 and ◇ 15.0 mmol dm^{-3}. (b) Variation of induction period with concentration of NH_4F. Concentration of $(NH_4)_2TiF_6$ 100 mmol dm^{-3}, and of H_3BO_3 150 mmol dm^{-3}.

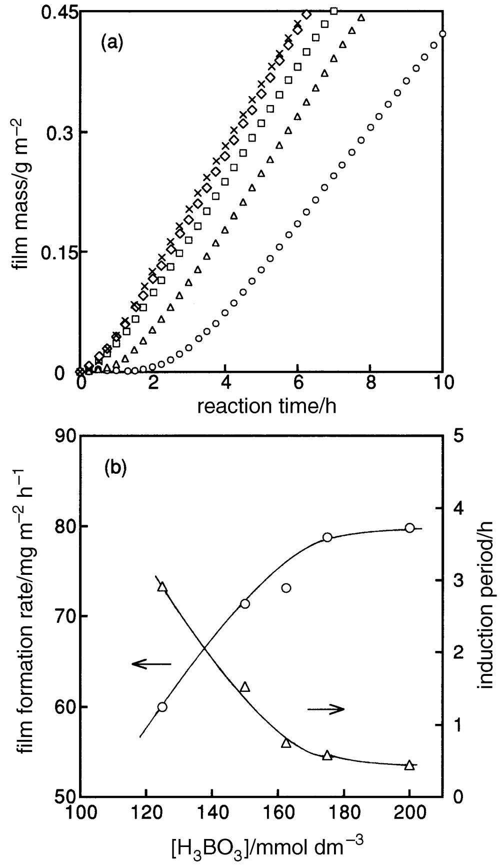

Fig. 5 (a) Relationship between deposited film mass and reaction time. Concentration of $(NH_4)_2TiF_6$ 50.0 mmol dm^{-3}. Concentration of H_3BO_3: ○ 125.0, △ 150.0, □ 162.5, ◇ 175.0 and × 200.0 mmol dm^{-3}. (b) Variations of deposition rate (○) and induction period (△) with concentration of H_3BO_3.

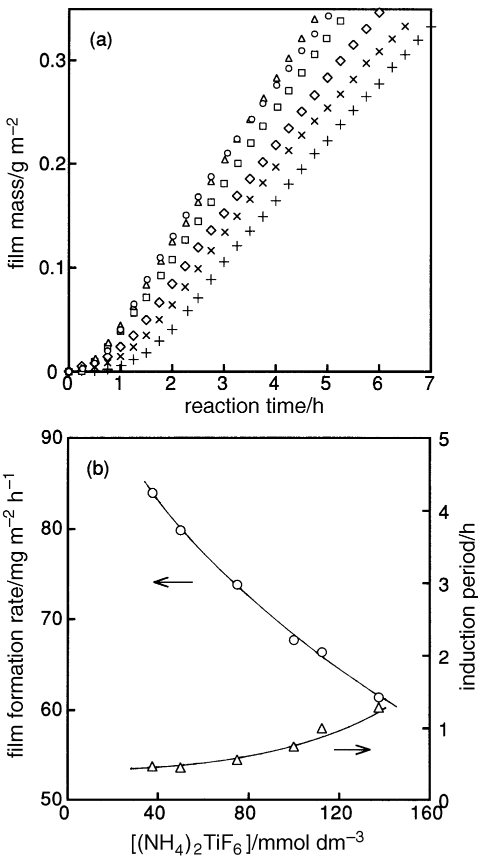

Fig. 6 (a) Relationship between deposited film mass and reaction time. Concentration of H_3BO_3 200 mmol dm^{-3}. Concentration of $(NH_4)_2TiF_6$: ○ 37.5, △ 50.0, □ 75.0, ◇ 100.0, ×112.5 and +137.5 mmol dm^{-3}. (b) Relationship between deposition rate (○) and induction period (△) with concentration of $(NH_4)_2TiF_6$.

ion with H_3BO_3 can be divided into fast steps [eqn. (8)–(10)] and a slow step [eqn. (11)]. It could be considered that when the concentration of H_3BO_3 is higher than 162.5 mmol dm^{-3}, free F$^-$ ions were consumed in the fast steps, therefore the induction period decreased gradually. On the other hand, the film formation rate increased markedly with the H_3BO_3 concentration to 162.5 mmol dm^{-3}, and then increased gradually. The film formation rate is controlled by the reaction of F$^-$ ions coordinated to $[TiF_{6-n}(OH)_n]^{2-}$. We consider that F$^-$ coordinated to $[TiF_{6-n}(OH)_n]^{2-}$ is consumed by H_3BO_3 during the slow step [eqn. (11)] when the concentration of H_3BO_3 is lower than 162.5 mmol dm^{-3}. On the other hand, F$^-$ is consumed in the fast steps [eqn. (8)–(10)] when the concentration of H_3BO_3 is higher than 162.5 mmol dm^{-3}. Therefore the dependence of the film formation rate on the H_3BO_3 concentration varied with the concentration range of H_3BO_3.

Effects of the concentration of $(NH_4)_2TiF_6$ in the treatment solution

Fig. 6(a) shows the relationship between the deposited film mass and the reaction time for various concentrations of $(NH_4)_2TiF_6$. The concentration of H_3BO_3 was constant at 200 mmol dm^{-3}. The deposited film mass decreased with increasing concentration of $(NH_4)_2TiF_6$. The t_c values were almost constant at 3 h. Fig. 6(b) shows the film formation rate and induction period as a function of the concentration of H_3BO_3. The film formation rate decreased monotonically with increasing $(NH_4)_2TiF_6$ concentration. On the other hand, the induction period increased slightly with increasing $(NH_4)_2TiF_6$ concentration. The change of the induction period was smaller than that when the concentration of $(NH_4)_2TiF_6$ was constant [Fig. 5(b)].

As mentioned above, the degree of hydrolysis of $[TiF_6]^{2-}$ decreases with increasing $(NH_4)_2TiF_6$ concentration.[12] The change of concentration of free F$^-$ with the concentration of $(NH_4)_2TiF_6$ may be small. Thus, the dependences of the induction period and t_c on the concentration of $(NH_4)_2TiF_6$ were small. On the other hand, the concentration of partially hydrolysed species of $[TiF_6]^{2-}$ decreased with increasing $(NH_4)_2TiF_6$ concentration, causing the decrease of the film formation rate with increasing $(NH_4)_2TiF_6$ concentration.

Conclusions

The QCM technique has been applied to monitoring the growth of titanium oxide thin films by the LPD method. The concentration effects of free F$^-$, $(NH_4)_2TiF_6$ and H_3BO_3 in the treatment solution on film formation were studied.

In the induction period, the initial stage of the deposition reaction, free F$^-$ ions in the treatment solution preferentially react with H_3BO_3. The induction period increased linearly upon increasing the concentration of added NH_4F, indicating that the induction period depends on the concentration of free F$^-$. The film formation rate, however, is independent of the concentration of free F$^-$. The film formation rate increased and the induction period decreased with increasing H_3BO_3 concentration. When the concentration of H_3BO_3 was greater than 162.5 mol dm^{-3}, the increase in the film formation rate and the decrease in the induction period slowed, suggesting that F$^-$ was consumed by H_3BO_3 in the slow step when the concentration of H_3BO_3 was low; on the other hand, it was consumed in the fast steps when the concentration of H_3BO_3 was high. The film formation rate decreased with increasing $(NH_4)_2TiF_6$ concentration, and the dependence of the induction period on the concentration of $(NH_4)_2TiF_6$ was small.

The QCM technique may be useful in monitoring the formation of thin films by the LPD method for characterizing the kinetics of the growth of the films.

References

1 H. Nagayama, H. Honda and H. Kawahara, *J. Electrochem. Soc.*, 1988, **135**, 2013.
2 A. Hishinuma, T. Goda, M. Kitaoka, S. Hayashi and H. Kawahara, *Appl. Surf. Sci.*, 1991, **48/49**, 405.
3 S. Deki, Y. Aoi, O. Hiroi and A. Kajinami, *Chem. Lett.*, 1996, 433.
4 G. Sauerbrey, *Z. Phys.*, 1959, **155**, 206.
5 M. Seo, K. Yoshida, H. Takahashi and I. Sawamura, *J. Electrochem. Soc.*, 1992, **139**, 3108.
6 R. Beck, U. Pittermann and K. G. Weil, *J. Electrochem. Soc.*, 1992, **139**, 453.
7 M. R. Deakin and O. R. Melroy, *J. Electrochem. Soc.*, 1989, **136**, 349.
8 J. H. Kaufman, K. K. Kanazawa and G. B. Street, *Phys. Rev. Lett.*, 1984, **53**, 2461.
9 D. Orata and D. A. Buttry, *J. Am. Chem. Soc.*, 1987, **109**, 3574.
10 H. K. Park and W. H. Smyrl, *J. Electrochem. Soc.*, 1994, **141**, L25.
11 K. K. Kanazawa and J. G. Gordon II, *Anal. Chim. Acta*, 1985, **175**, 99.
12 R. H. Schmitt, E. L. Grove and R. D. Brown, *J. Am. Chem. Soc.*, 1960, **82**, 5292.
13 Y. A. Buslaev, D. S. Dyer and R. O. Ragsdale, *Inorg. Chem.*, 1967, **6**, 2208.
14 C. A. Wamser, *J. Am. Chem. Soc.*, 1948, **70**, 1209.
15 R. E. Mesmer, K. M. Palen and C. F. Baes Jr., *Inorg. Chem.*, 1973, **12**, 89.
16 C. A. Wamser, *J. Am. Chem. Soc.*, 1951, **73**, 409.

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