Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 2, 431–434

FABRICATION OF POTASSIUM TANTALATE FILMS BY HYDROTHERMAL ELECTROCHEMICAL METHOD AT LOW TEMPERATURE

T. Hashizume[1*], *A. Yokota*[2], *A. Saiki*[1] *and K. Terayama*[1]

[1]Nano and Functional Material Sciences, Graduate School of Science and Engineering for Research, University of Toyama
3190 Gofuku, Toyama 930-8555, Japan
[2]Material Systems Engineering and Life Science, Graduate School of Science and Engineering for Education, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan

Potassium tantalate was formed to pyrochlore structures on the tantalum substrate by hydrothermal or electrochemical method. In synthesizing process of potassium tantalate, a crystal structure of the substrate surface seemed to be an important factor. Potassium tantalate was synthesized with a simple equipment only, low temperature of 323 K or over, low concentration of 2–4 mol per liter potassium hydroxide aqueous solution and short time.

Keywords: *electric capacitors, hydrothermal electrochemical method, potassium tantalate, thin films*

Introduction

Potassium tantalate thin films have been studied for the development of electric capacitors [1]. The alkali and alkaline earth tantalates such as $KTaO_3$ and $BaTa_2O_6$ have been focused on the photo catalysts for water decomposition [2]. Tantalum double oxide films can be obtained by several methods such as sputter [3, 4], vapor deposition [5], sol–gel [6, 7] and anodization. In recent years, a hydrothermal electrical synthesis method is in the creation technology of the thin film used for electronic material such as a capacitor. This synthesis method belongs to called soft solution processing [8, 9], concerning the fabrication of pure, shaped, sized and oriented ceramic materials in a solution. Synthesis of potassium tantalate film by hydrothermal has been studied in our laboratory. The film has been synthesized easily below 473 K by using this method. Potassium tantalate has perovskite and pyrochlore structures. Pyrochlore type potassium tantalate ($K_2Ta_2O_6$) was fabricated with 3–4 mol per liter KOH aqueous solutions at about 373–473 K [9]. On the other hand, perovskite type ($KTaO_3$) was formed after annealing at about 1100 K [10], or synthesizing at 300 K with hydrothermal method [11]. Several studies of the synthesizing film with hydrothermal method were reported. The development mechanism of a film fabricated on substrate directly was little studied with hydrothermal synthesis. In the present work, we have used hydrothermal electrochemical method to obtain films of potassium tantalate on Ta substrate. Mechanical polishing of Ta substrate was reported [12], however, the orientation of polishing substrate and surface conditions were unclear. The surface condition of tantalum sheet was also studied with XRD.

Experimental

Tantalum metal substrate used as the starting materials was 99.95% purity and dimensions of 15×10×0.4 mm. Two samples were prepared for substrate. Tantalum sheet was annealed at 873 K for 43.2 ks in helium atmosphere. To prevent oxidation of the surface, tantalum sheet was placed into titanium powder. These sheets were electroplated for 30 s at an anodic current density of 200 mA cm^{-2} in an electroplating bath solution composed of 10 vol.% H_2SO_4, 20 vol.% HF and 70 vol.% ethylene glycol [13].

A Teflon beaker containing the KOH aqueous solution was placed in an autoclave cell equipped with electrodes. The autoclave was packed and heated up to 373 K, and an inner pressure in the autoclave was kept about 0.1 MPa. KOH aqueous solution prepared to 2, 3, 4 mol L^{-1} concentrations. A constant current source is used to maintain the current density of 10 A cm^{-2}. The autoclave made of stainless was used. The autoclave was sealed and maintained at 427 K for 14.4 ks without stirring and allowed to cool to room temperature. The sample was washed in water and ethanol using an ultrasonic bath.

XRD (model X`Pert MRD, PANalytical, Japan) has been used to identify the phases. The surface mor-

---

[*] Author for correspondence: hasizume@eng.u-toyama.ac.jp

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

phology and qualitative analysis of the film were investigated by microscope (BHSM-313MB, Olimpus, Japan), SEM (model JEM-6700M, JEOL, Japan), and EPMA (model EPMA-1500, Shimadzu, Japan).

Results and discussion

Substrate

The crystalline of two samples were measured by XRD. Pole figures of (101) plane for tantalum substrates were shown in Fig. 1. In Fig. 1a, the face of tantalum sheet purchased from commercial supplier was arranged in one direction moderately by rolling. In Fig. 1b, the tantalum sheet has orientation of (100) by annealing. For the polished surface of tantalum with emery papers, (110), (200) and (211) Ta were observed. The crystalline of polished tantalum sheet was disturbed on a surface by mechanical polishing in Fig. 1c and d. Then, the annealing sample without mechanical polishing was used in this experiment.

Formation of potassium tantalate

As the formation of a potassium tantalate was proceeded, the peaks of (110) and (211) of a tantalum substrate were decreased preferentially [14].

Potassium tantalate of pyrochlore ($K_2Ta_2O_6$) was formed in potassium hydroxide with hydrothermal electrochemical method at several temperature and concentration of solution (Fig. 2). Phase diagram for the formation of the potassium tantalate films by several temperature and concentration of solution is shown in Fig. 3. Cracks were observed on the surface of $K_2Ta_2O_6$ film synthesized at 3 mol^{-1} or over at 373 K. The film thickness was 4–5 μm. As tantalum substrate was chemically less reactive below 323 K, metal color and smooth surface were observed and tantalum peaks was detected by XRD. $K_2Ta_2O_6$ was formed at 348 K or over for using 2 mol L^{-1} KOH aqueous solution. To research a step of forming $K_2Ta_2O_6$, which was synthesized with 2 mol L^{-1} KOH aqueous solution and DC 10 A m^{-2} for 8 h at several temperatures. Figure 4 shows X-ray diffraction pattern of the film. $K_2Ta_2O_6$ was synthesized at 323 K or over

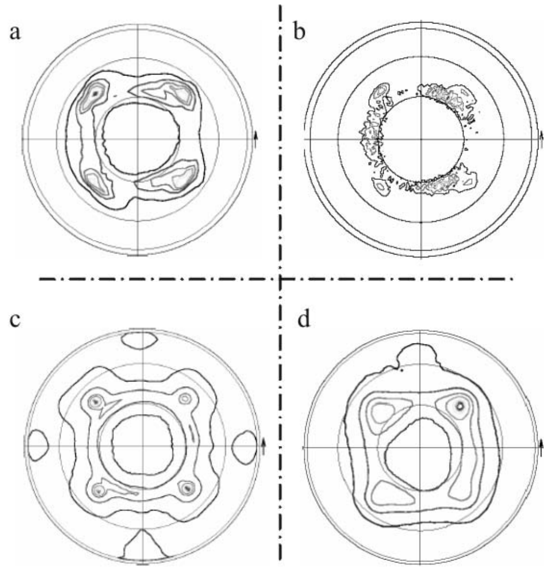

Fig. 1 Pole figure of (101) planes a – as a tantalum sheet, b – annealed, c – polished, d – polished and annealed

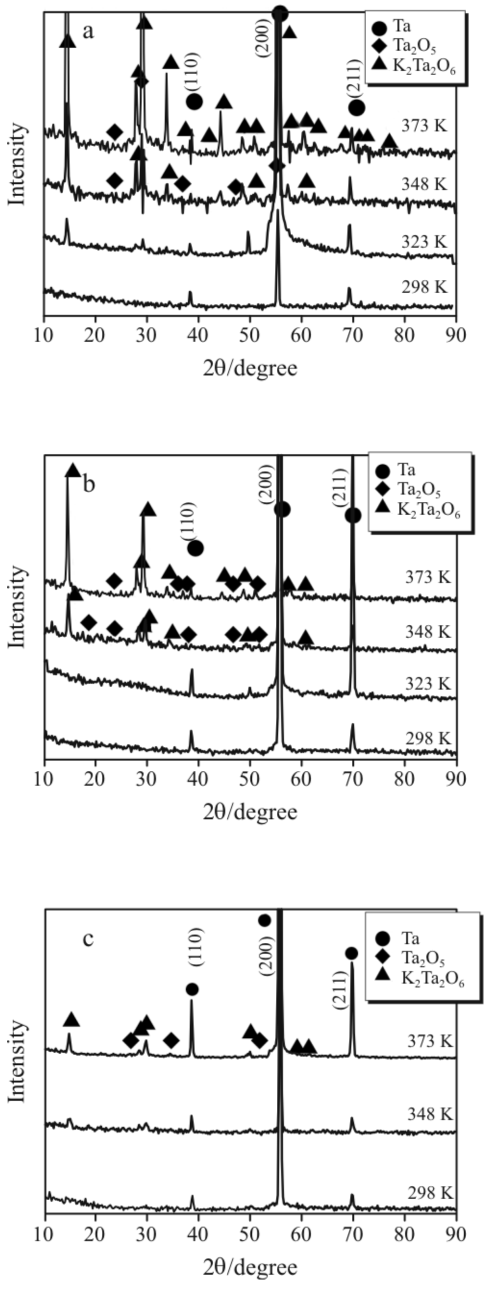

Fig. 2 XRD patterns of samples synthesized for 3.6 ks at 2, 3 and 4 mol L^{-1} KOH aqueous solution at several temperatures; a – 4 M KOH, 1 h, b – 3 M KOH, 1 h, c – 2 M KOH, 1 h

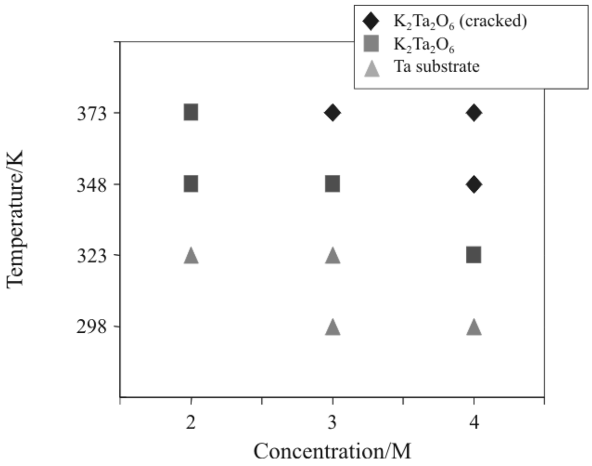

Fig. 3 Phase diagram for the formation of the potassium tantalate films

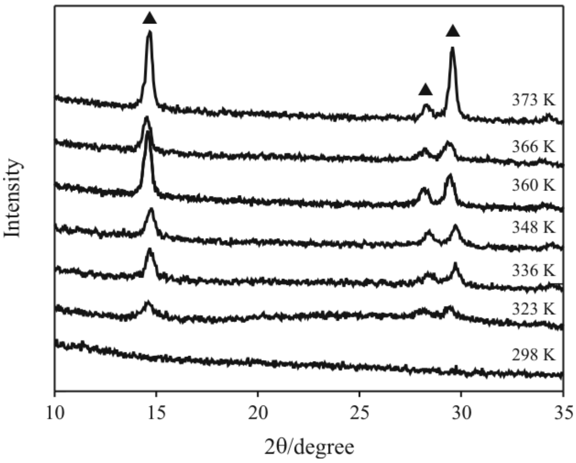

Fig. 4 XRD patterns of samples synthesized for 28.8 ks at 2 mol L^{-1} KOH aqueous at several temperatures

using hydrothermal synthesis method. XRD patterns shows the peaks of $K_2Ta_2O_6$ became sharp shape using higher temperature, the crystallinity of $K_2Ta_2O_6$ was better using the higher temperature such as 373 K.

The reaction of Ta and KOH aqueous solution occurred rapidly using an electrochemical method, Figure 5 shows that EPMA mapping of the film synthesized at 2 mol L^{-1} KOH aqueous solution at 360 K for 28.8 ks. BSE is backscattered electron image of the film, O, K and Ta shows mapping of elements of oxygen, potassium and tantalum, respectively. Dark or light color area indicates low or high count. The formation of $K_2Ta_2O_6$ was observed by XRD, however, the surface of this sample was patterned with spots by EPMA.

The reacted area or not reacted area were observed. In a previous study, (110) Ta was easy to be reacted with precedence [14]. In this study, (110) Ta peak was decreased, however, (200) Ta peak was hardly decreased with XRD. (200) Ta was hard to be reacted, $K_2Ta_2O_6$ film was hardly developed on (200) Ta. $K_2Ta_2O_6$ or no reaction area were developed with like island. A particle size was about 20–30 μm. Dark color points at potassium and oxygen mapping graphs were seemed to be hollow at BSE.

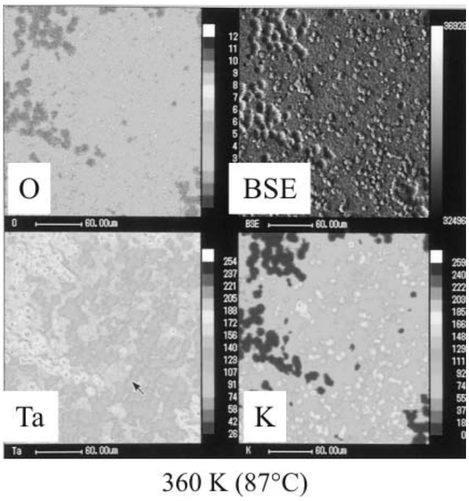

Fig. 5 EPMA Mapping of the film synthesized at 360 K, 2 mol L^{-1} KOH aqueous, 28.8 ks

The mechanism of $K_2Ta_2O_6$ formation on the tantalum substrate is shown in Fig. 6. The tantalum was reacted to with precedence and dissolves in solution. Tantalum ion contact to oxygen on the electrode, tantalum oxide ion was formed, and potassium tantalate was formed on a the substrate. The formation of $K_2Ta_2O_6$ on the substrate depends on temperature and concentration.

Surface of films

The surface of the sample was observed with FE-SEM to observe the detailed surface. The surface of films synthesized in 4 mol L^{-1} KOH aqueous solution at 323 and 348 K for 28.8 ks with DC 10 A cm^{-2} is shown in Fig. 7. Both films was dried in air at room temperature (298 K) and humidity in the room was 60%. The films had cracks due to dehydration. The thickness of films

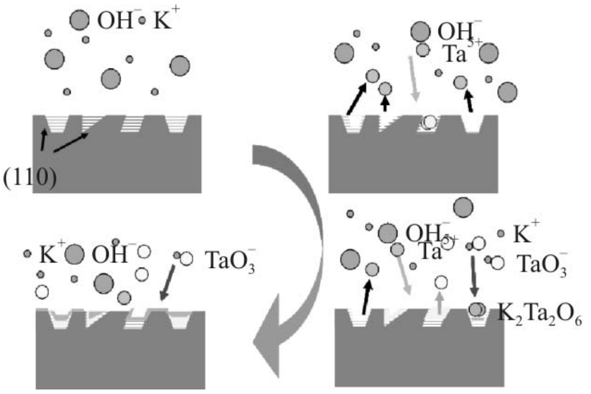

Fig. 6 Schematic diagram of the KT film formation mechanism with hydrothermal electrochemical method

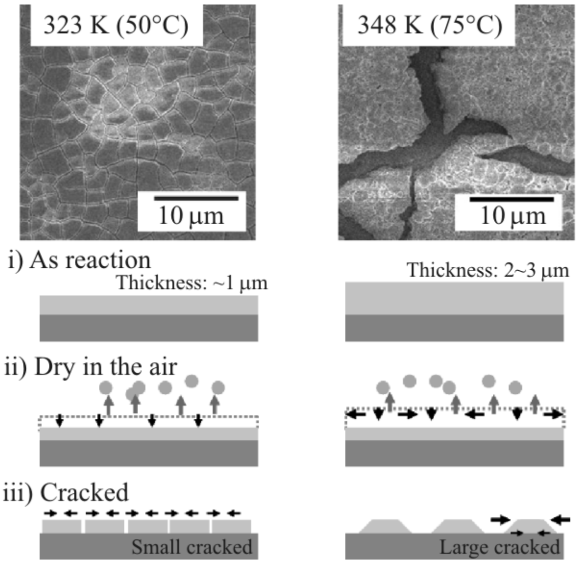

Fig. 7 FE-SEM image of the surface of dried samples

synthesized at 323 and 348 K were about 2–3 and 4–5 μm, respectively. For the thicker film (348 K), the shrinkage of the volume is bigger than thin film. The stress to be shortened was different with an upper part and bottom of the film. The bottom of the film was in contact with the substrate, the stress was smaller than upper of the film. As a result, the thicker film had a large cracks, tantalum substrate was observed though the rift of film. The thinner film had small cracks. The cracks width of thinner and thicker films were 0.2 and 2–5 μm using SEM, respectively.

Conclusions

By hydrothermal electrochemical method $K_2Ta_2O_6$ film were fabricated on Ta substrate in KOH aqueous solution directly. $K_2Ta_2O_6$ film were fabricated from 323 to 473 K at 2 to 4 mol L^{-1} KOH aqueous solution for 1 h with DC 10 A m^{-2}. The more concentration of solution and reaction time, the film became thicker. The films had cracks and developed due to dehydration. The films fabricated only pyrochlore type. This experiment needed an only simple equipment, low concentration solution, low temperature and energy and no long time.

Acknowledgements

The present work was partly supported by University of Toyama.

References

1 H.-J. Bae, J. Sigman, S.-J. Park, Y.-H. Hao, L. A. Boatner and D. P. Norton, Solid-state Electronics, 48 (2004) 51.
2 H. Kato and A. Kudo, Chim. Phys. Letter., 295 (1998) 487.
3 J. M. Ngaruiya, S. Venkataraj, R. Drese, O. Kappertz, T. P. Leervad Pedersen and M. Wuttig, Phys. Status Solidi A, 198 (2003) 99.
4 P.-H. Chang and H.-Y. Liu, Thin Solid Films, 258 (1995) 56.
5 M. Textor, L. Ruiz, R. Hofer, A. Rossi, K. Feldman, G. Hähner and N. D. Spencer, Langmuir, 16 (2004) 3257.
6 W.-P. Tai, J.-G. Kim, J.-H. Oh and Y.-S. Kim, Sens. Actuators B, 105 (2005) 199.
7 W.-P. Tai, J.-G., J.-H. Oh, C. Lee, D.-W. Park and W.-S. Ahn, J. Mater. Sci.: Mater. Electron., 15 (2004) 25.
8 Z. Wu and M. Yoshimura, Thin Solid Films, 375 (2000) 46.
9 V. Zelezny, J. Bursik and P. Vanek, J. Eur. Ceram. Soc., 25 (2005) 2155.
10 W. Wang and A. V. Virkar, Sens. Act. B., 98 (2004) 282.
11 K. Kajiyoshi, K. Yanagisawa, Q. Feng and M. Yoshimura, J. Mater. Sci., 41 (2006) 1535.
12 M. Hariharaputhiran, Y. Li, S. Ramarajan and S. V. Babu, Electrochem. Solid State Lett., 2 (2000) 95.
13 Z.-B. Wu, T. Takeda and M. Yoshimura, J. Mater. Sci., 35 (2000) 2833.
14 T. Hashizume, A. Saiki and K. Terayama, Ceramic Trans., 196 (2006) 407.

DOI: 10.1007/s10973-007-8965-z