Achievement of Crack-Free $BaTiO_3$ Films over 1 μm in Thickness *via* Non-Repetitive Dip-Coating

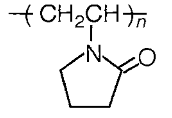
Hiromitsu Kozuka* and Masahiro Kajimura
Department of Materials Science and Engineering, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680

(Received June 23, 1999; CL-990547)

$BaTiO_3$ coating films were prepared from $Ba(CH_3COO)_2$-$Ti(OC_3H_7^i)_4$-H_2O-CH_3COOH-$C_3H_7^iOH$ solutions containing poly(vinylpyrrolidone) with average molecular weight of 630000. Formation of crack-free $BaTiO_3$ films 1.2 μm in thickness was successfully achieved via single-step, non-repetitive dip-coating. The film had relatively dense mocrostructure in SEM scale and transmitted visible light.

Sol-gel coating technique has long been recognized in laboratories as a simple and inexpensive method for preparing ceramic coating films. Employing this technique in industries, however, sounds somehow difficult because thick gel films are likely to be cracked on heating, and the critical thickness, the maximum thickness achievable without crack formation via single-step deposition, is often as low as 0.1 μm for non-silicate oxides. Film thickness over submicrometer is favored in general for achieving better crystallinity, and is crucial, for instance, in piezoelectric actuators, where electric field is converted to displacement, which is proportional to the film thickness. In laboratories, crack-free ceramic films over submicrometer in thickness are obtained by repeating the gel film deposition and heat-treatment using coating solutions of low viscosities. Such repetitive procedure, however, is time consuming and not realistic in industries. So far, chelating agents and diols are reported to be effective in enhancing the critical thickness.[1,2]

When deposited gel films are heated, film densification occurs via condensation reaction between the OH groups of the metalloxane polymers, resulting in evolution of tensile stress as high as 100 MPa.[3] Saegusa and Chujo have demonstrated that poly(vinylpyrrolidone) (PVP, **1**) can be hybridized with metalloxane polymers in molecular scale through hydrogen bonds between the C=O groups of the former and the OH groups of the latter.[4] Expecting such hydrogen bonds to retard the condensation reaction and promote the structural relaxation in films, the present authors recently have prepared TiO_2 films from alkoxide solutions containing PVP, finding that PVP is significantly effective in increasing the critical thickness.[5] In the present work, this technique is applied to preparation of coating films of a complex oxide, $BaTiO_3$, an important material for piezoelectric applications.



1

$Ti(OC_3H_7^i)_4$, $Ba(CH_3COO)_2$, PVP with average molecular weight of 630000, CH_3COOH, $C_3H_7^iOH$ and distilled water were used as the starting materials. Starting solutions of molar compositions, $Ti(OC_3H_7^i)_4 : Ba(CH_3COO)_2 : PVP : H_2O : CH_3COOH : C_3H_7^iOH = 1 : 1 : (0 \text{ or } 1) : 20 : 9.08 : 20$ were prepared with the following procedure, where the ratio PVP/$Ti(OC_3H_7^i)_4$ represents the mole ratio of the monomer of PVP to $Ti(OC_3H_7^i)_4$. First, PVP was dissolved completely in $C_3H_7^iOH$, and then CH_3COOH and $Ti(OC_3H_7^i)_4$ were added to the solution successively under stirring to obtain a slightly yellow, transparent solution. Then $Ba(CH_3COO)_2$-H_2O solution was added dropwise under stirring. After the solution was kept standing at 25 °C in a sealed glass container for various periods of time, gel films were deposited on a silica glass substrate (20 mm×40 mm×1.2 mm, Sumikin Quartz Product, Inc.) by dip-coating at a substrate withdrawal speed of 3 cm min^{-1}, and the gel films were transferred into an electric furnace of 700 °C and heated there for 10 min.

The thickness of the heat-treated films was measured by a Kosaka Laboratory surface profilometer SE3400: a part of the gel film was scraped off with a surgical knife, and after heat-treatment the level difference between the coated part and the scraped part was measured. Crack formation was examined by SEM observation and with the surface roughness profiles obtained by the surface profilometer.

Figure 1 shows the relationship between the sol reaction time and the thickness of the heat-treated films prepared from the solutions with and without PVP. The crosses in the figure denote the films with cracks, while the other marks represent the crack-free films. The critical thickness of the films, which may

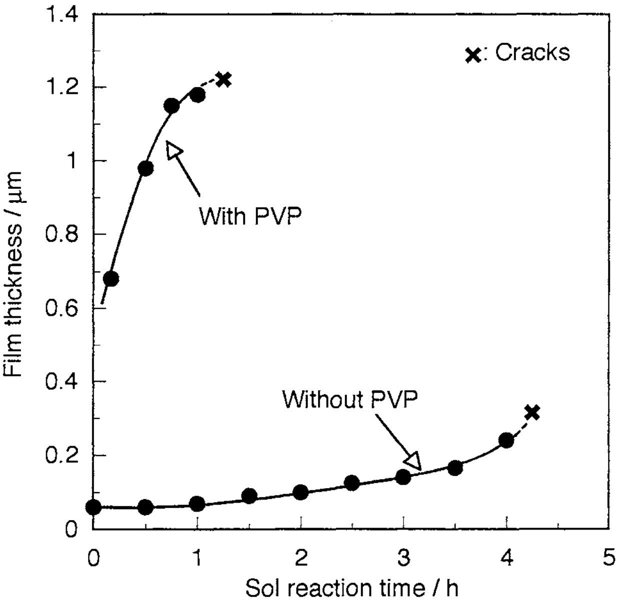


Figure 1. Relationship between the sol reaction time and the thickness of the heat-treated films prepared from the sols with and without PVP. ✖ denotes the films with cracks and the other marks represent the crack-free films.

lie between the crosses and the other marks in the figure was significantly increased by PVP incorporation. The 1.2 μm thick, crack-free film obtained via single-step deposition was perovskite $BaTiO_3$ as seen in the X-ray diffraction (XRD) pattern (Figure 2), where the broad peak around 20 ° is the diffraction from the glass substrate. The SEM picture of the 1.2 μm thick film showed relatively dense microstructure as seen in Figure 3 although incorporation of substantial amount of organics is in general expected to result in highly porous ceramic films through thermal decomposition. The film was slightly opalescent in appearance, but transmitted visible light as shown in the optical transmission spectra (Figure 4).

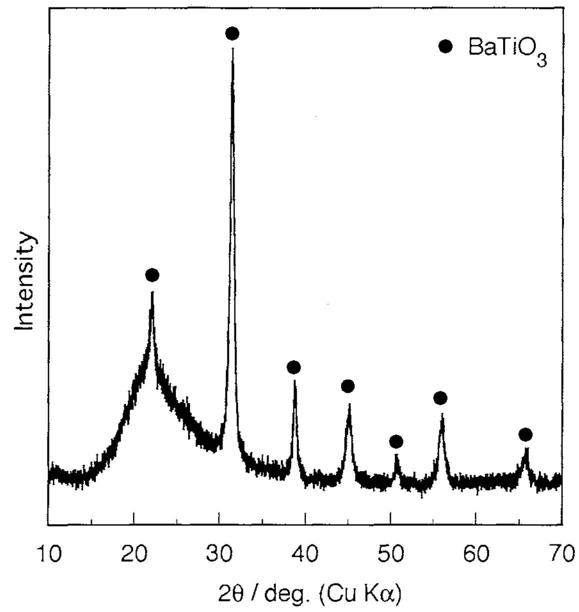


Figure 2. XRD pattern of the heat-treated film 1.2 μm in thickness prepared from the PVP-containing sol.

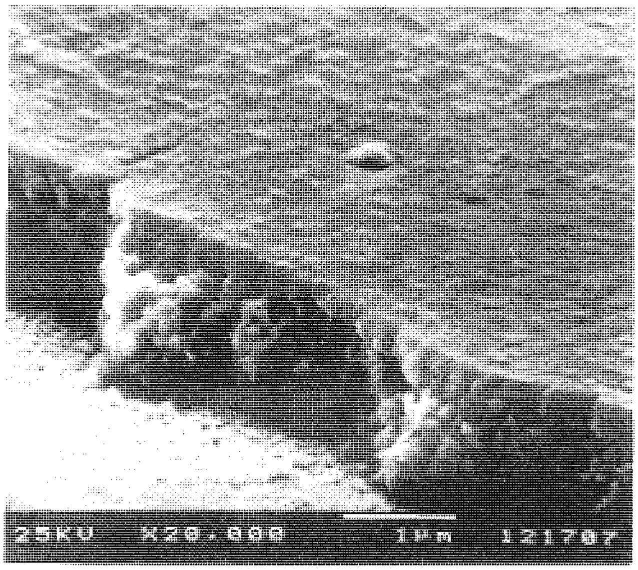


Figure 3. SEM picture of the heat-treated film obtained from the PVP-containing sol via non-repetitive, single-step dip-coating.

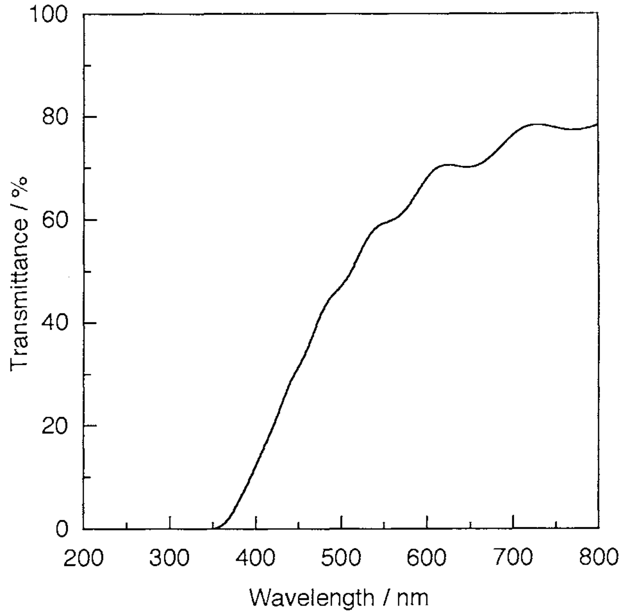


Figure 4. Optical transmission spectra of the heat-treated film 1.2 μm in thickness prepared from the PVP-containing sol.

The relatively dense microstructure and light transmitting property are thought to be allowed by molecular level hybridization between PVP and metalloxane polymers in gel films, which minimizes macropore formation on thermal decomposition. Hybridization between PVP and metalloxane polymers is evidenced in the transparency of the sols and gel films. The hybridization is also evidenced in the faster increase in sol viscosity found in the PVP-containing sol as revealed in Figure 1.

H. Kozuka thanks Nippon Sheet Glass Foundation for Materials Science and Engineering and Kinki-chiho Invention Center for their financial support. This work is also financially supported by the Institute of Industrial Technology, Kansai University, and the Kansai University Research Grants (Grant-in-Aid for Encouragement of Scientists, 1999.

References

1 H. Schmidt, G. Rinn, R. Naβ and D. Sporn, *Mat. Res. Soc. Symp.*, **121**, 743 (1988).
2 Y.-L. Tu, M.L. Calzada, N.J. Phillips, and S.J. Milne, *J. Am. Ceram. Soc.*, **79**, 441 (1996).
3 R.R.A. Syms, *J. Non-Cryst. Solids*, **167**, 16 (1994).
4 T. Saegusa and Y. Chujo, *Makromol. Chem., Macromol. Symp.*, **64**, 1 (1992).
5 H. Kozuka, K.-S. Jang, C.-S. Mun, and T. Yoko, Proceedings of the 3rd International Meeting of Pacific Rim Ceramic Societies, Kyongju, Spetember 1998, in press.