Aqueous Solution-Based Ceramic Thin Film Deposition Using Organic Polymers with Amide Groups

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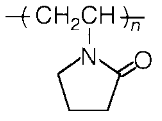
An aqueous solution-based dip-coating technique was presented for ceramic thin film deposition. Organic polymers with amide groups such as polyvinylpyrrolidone, polyvinylacetamide and polyacrylamide, incorporated in aqueous solutions of metal salts, were demonstrated to offer much better wetting of the substrates and gel film formability. Transparent, crack-free TiO_2 and ZrO_2 thin films of 0.07–0.1 μm in thickness could be obtained from aqueous solutions of $Ti(SO_4)_2$ and $ZrCl_2O$, respectively, containing these organic polymers.

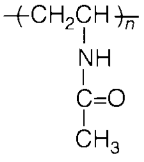
Dip- or spin-coating solutions for ceramic thin film deposition are prepared mostly through hydrolysis and polycondensation of metal alkoxides. Since metal alkoxides are hydrophobic and immiscible with water, alcohols are used as mutual solvents for homogenizing alkoxides and water.[1] Alcohols, however, are volatile, inflammable, and hence not favorable solvents to be handled in manufacturers. Therefore, replacement of alcohols by water, which is not inflammable, is strongly demanded in industries. However, water has significantly much higher surface tension (72 mN m^{-1}) than alcohols (20–23 mN m^{-1}), causing poor wettability of the substrates and film formability. In fact, even when water-soluble metal salts like nitrates and acetates are used as the starting materials, water is never used as the major solvent but alcohols.[2,3] In the present paper, it is demonstrated that aqueous solutions of water-soluble metal salts can be used as the coating solutions when organic polymers with amide groups are contained.

The starting materials employed in preparing solutions were $ZrCl_2O$ (Wako Pure Chemical Industries), aqueous solution of $Ti(SO_4)_2$ (30 wt%, Wako Pure Chemical Industries) containing 13 wt% H_2SO_4, polyvinylpyrrolidone (PVP, **1**, 1×10^4 in average molecular weight, Tokyo Kasei Kogyo), aqueous solution of polyvinylacetamide (PVAcAm, **2**, 40 wt% , 3×10^4 in average molecular weight, Showa Denko, GE-191LL), aqueous solution of polyacrylamide (PAAm, **3**, 50 wt%, 1×10^4 in average molecular weight, Aldrich) and ion-exchanged water. The starting solutions of the batch compositions shown in Table 1 were prepared at room temperature. All the solutions were clear, transparent and slightly colored.



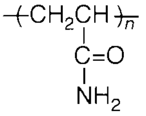
PVP

1



PVAcAm

2



PAAm

3

Gel films were deposited on silica glass substrates (20 × 40 × 1.2 mm^3) by dip-coating at a substrate withdrawal speed of 3 cm min^{-1}, immediately heated at 100 °C for 10 min and then fired at 700 °C for 10 min. In the absence of the organic polymers, continuous films failed to be formed due to the poor wetting. The inclusion of the organic polymers in solutions, on the other hand, greatly enhanced the wettability and film formability, resulting in crack-free, transparent films with traces of tiny dots. The films stuck strongly to the substrate as in the case of alkoxide-derived coating films, and were not delaminated with Scotch tape or by ultrasonic wave irradiation in water.

As summarized in Table 1, the thickness of the fired films ranged from 0.07–0.1 μm, which was measured using a contact probe surface profilometer as in the same way as that described elsewhere.[4] Figure 1 shows the spectra of the fired films, where a bare silica glass substrate was used as the reference. The spectra indicate that the films obtained are highly transparent in the visible range. The ripples in the spectra result from the interference of the light. It might be the smooth surface and dense microstructure that brought about the large amplitude of the ripples, because both of them provide high reflectivity at the air/film and film/substrate interfaces, which causes effective interference of the light.

Figure 2 shows the X-ray diffraction patterns of the fired films measured using an X-ray diffractometer with a thin film attachment and with Cu Kα radiation. Rutile and anatase phases were detected in the TiO_2 film prepared from the PVP-containing solution, and only rutile in that from the PVAcAm-containing solution. Cubic and monoclinic ZrO_2 phases were found in the ZrO_2 film prepared from the PVP-containing solution, and only cubic ZrO_2 in that from the PAAm-containing

Table 1 Batch compositions of the solutions and the thickness of the fired films

Sample	Batch / g						Film
	$Ti(SO_4)_2$ aq	$ZrCl_2O$	PVP	PVAcAm aq	PAAm aq	H_2O	thickness / μm
TiO_2(PVP)	40.0	–	2.78	–	–	20.8	0.10
TiO_2(PVAcAm)	41.5	–	–	11.0	–	68.0	0.07
ZrO_2(PVP)	–	16.1	5.56	–	–	50.0	0.08
ZrO_2(PAAm)	–	16.1	–	–	7.1	43.8	0.09

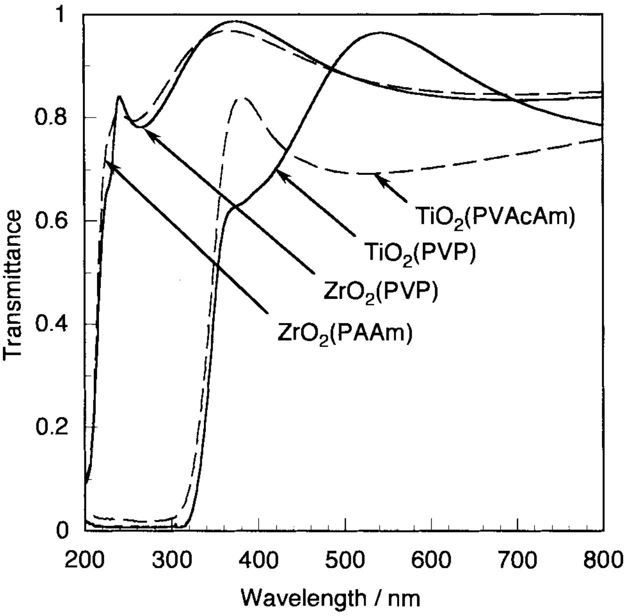


Figure 1. Optical absorption spectra of the fired films.

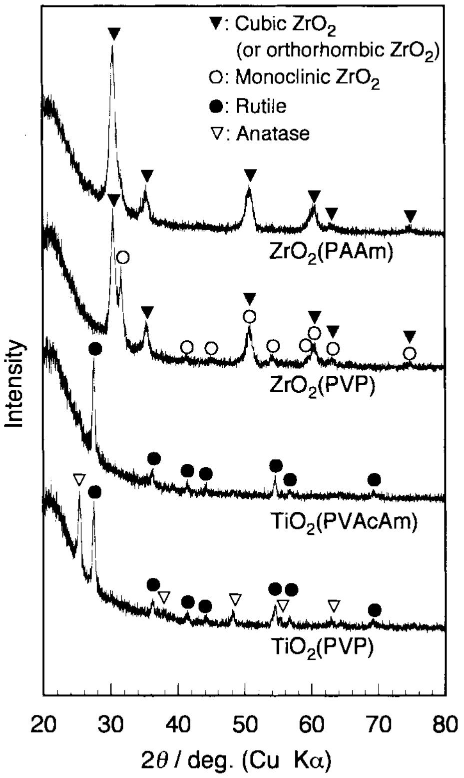


Figure 2. X-ray diffraction patterns of the fired films.

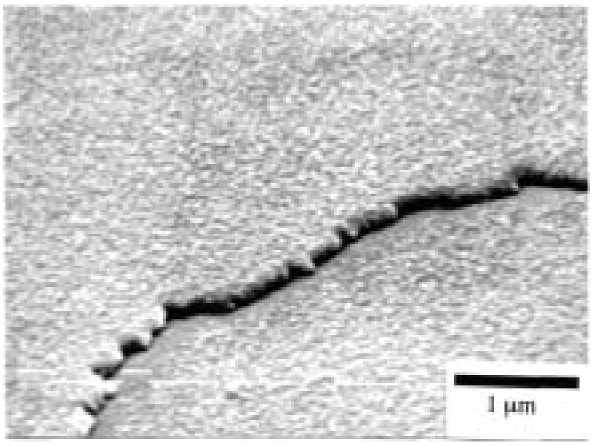


Figure 3. SEM picture of the fired TiO_2 film (TiO_2(PVP)).

solution, though in both cases the precipitation of orthorhombic ZrO_2 cannot be ruled out. Figure 3 shows the SEM picture of the TiO_2 film prepared from the PVP-containing solution, where smooth surface and relatively dense microstructure are seen.

Aqueous solutions of metal salts containing organic polymers with amide groups have been demonstrated to work as the precursor coating solutions for transparent, crack-free ceramic thin films. Another benefit of the technique is the stability of viscosity and the long lifetime of the solutions. Alkoxide-derived sols generally increase in viscosity with time due to the progress of polycondensation reaction towards metalloxane polymers. In contrast, the present metal salts are stable as complexes in aqueous media, and do not undergo polymerization towards metalloxane polymers except at high pH. Although analytical study has not been carried out, probably the major part of the polymeric species are built up with the metal atoms or complexes linked with the organic polymers. The O and/or N atoms of the amide groups could coordinate with the metal atoms, and the C=O groups could make hydrogen bonds with the OH groups of the inorganic species,[5] possibly constructing organic–inorganic polymeric networks.

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