PTFE-Doped CeO₂ Films: Synthesis, Characterization and Properties

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Abstract: Multi-functional hybrid films were developed by doping PTFE into CeO₂ by co-sputtering of CeO₂ and PTFE targets. The hybrid films formed on borosilicate glass substrate containing from 5 to 15 vol. % PTFE in CeO₂ showed UV shielding, high indentation hardness, hydrophobicity, optical transmittance in visible light, and high bending crack resistance. Optical properties of 100 nm thick CeO₂-5 vol. % PTFE film revealed UV light shielding of more than 80 % at 380 nm and visible light transmittance higher than 80 %. Indentation hardness measured under the load of 0.001mN was more than 16,000N/mm² of 2.7 times higher than the glass substrate. No crack in the film was observed by bending 1.5 cm in diameter. Furthermore, the hydrophobic surface property was evaluated by the water contact angle to be higher than 90 degrees. Preliminary characterization of the CeO₂-PTFE film using XPS and XMA revealed that chemical states of F in sputter doped PTFE in CeO₂ can be considered to exist as C-F and Ce-F compounds. On the other hand, chemical states of Ce changed partially from Ce⁴⁺ (CeO₂) to Ce³⁺ (Ce₂O₃ or CeF₃) with increasing doped PTFE in the film.

In this rapid communication, we preliminary described the optical, mechanical and chemical properties of newly developed hybrid CeO₂-PTFE films prepared by sputtering.

Cubic bulk material of CeO₂ has been attracting great attention as one of the most promising materials from the viewpoints of optical and heat-resisting properties, toughness against mechanical abrasion, and even chemical attack. CeO₂ was inevitably micronized into nanoparticles to develop for a wide range of catalytic applications [1]. Furthermore, film formation of CeO₂ was soon carried out by various methods and tried to apply optical coatings [2], heterogeneous catalysts [3-7]. As is well known, thin film properties are strongly influenced by their structure, composition and chemical bonding states of the constituent elements arising from preparation methods such as chemical vapour, physical vapour, and sol-gel depositions. Further improvement of the film properties was carried out by hybridization of the film with other elements by adjusting the structure and composition of starting material in chemical methods [8] or by doping in the physical process of thin-film formation [9].

To widen the application range of CeO₂ films, doping technology of other elements is one of the most useful methods not only for materials search of CeO₂-based hybrid thin film but also for basic research of materials science. Until today, various metal cations have been doped into CeO₂ with a special interest in catalysis [10-12] but there exist only a few reports of anion doping [13-15] in spite of their interesting applications such as oxygen barrier coatings for food package and water repellent coating [16, 17]. Ce is also well known to exist +4 in the oxidation state of CeO₂, but the valence changes to +3 in fluoride state of CeF₃, where highly electronegative fluoride ions were formed. Therefore, CeO₂ can incorporate fluoride ion, resulting in a change of Ce³⁺/Ce⁴⁺ redox couple. In spite of many basic research reports of CeO₂-based hybrid thin films, there exists no report on thin-film performances such as optical, mechanical and chemical properties for practical applications. We described first of all the optical, mechanical and chemical properties of PTFE doped CeO₂ films prepared by co-sputtering of CeO₂ and PTFE targets.

Doping of PTFE into CeO₂ was carried out by radio-frequency magnetron sputtering method under the conditions shown in Table 1. Composition of doped PTFE was determined by the concentration of F in the film determined by EPMA (Electron Probe Micro Analyzer JXA-8530F), where concentration ratio F/ (Ce + F) in vol. % in hybrid film was used in this paper.

Figure 1 showed the optical transmittance of CeO₂-PTFE films with 80 -100 nm thick with the light wavelength from...
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Table 1: Sputter Doping Conditions of PTFE into CeO₂ Films

| Parameters               | Conditions                                      |
|--------------------------|-------------------------------------------------|
| Targets                  | Sintered CeO₂, PTFE                             |
| Dimension of targets     | 76.2 mm in diameter and 5 mm in thickness        |
| Substrate                | 0.7 mm thick borosilicate glass                  |
| Working gas and pressure | Argon at 1Pa                                     |
| RF magnetron power       | 200W for CeO₂ and 20-50W for PTFE               |
| Deposition rate          | 4~5 nm/min                                      |
| Deposition time          | 20 min                                          |
| Film thickness           | 80 - 100 nm                                     |
| Distance between target to substrate | 5 cm                                           |

250nm to 2500nm was evaluated by using Hitachi 4100 spectrometer and deposition rate and film thickness by a laser microscope (Keyence VK-X210/200) using a 408 nm visible light. Composition and structure of the hybrid films were analyzed by EPMA and thin-film XRD (Rigaku ATX-E), respectively. UV light-shielding properties were usually evaluated by the transmittance at the wavelength of 380 nm. CeO₂ film showed a typical UV shielding properties, where threshold wavelength 330 nm of UV shielding corresponds to band gap E₉ of 3.4 eV, which was large compared to bulk CeO₂ of 3.1-3.2 eV. This difference can be explained by the bandgap widening by the non-equilibrium state of as-sputtered film CeO₂-x film. Threshold wavelength of sputtered CeO₂-PTFE films remains unchanged up to 15 vol.% but drastic change can be seen over 20 vol.%, where UV shielding properties disappeared by the change of band structure of CeO₂. Characterization of CeO₂-PTFE films was carried out by X-ray photoelectron spectroscopy (XPS) to elucidate the chemical states of the films. At first, a typical XPS core-level spectrum of C₁s in PTFE film sputter-deposited by argon gas recorded using Mg radiation (photon energy = 1253.6 eV) as shown in Figure 2, where XPS spectrum of C₁s of thermally evaporated PTFE film is also shown in the figure by a dotted line for reference. The core-level spectra of the sputter-deposited film were fitted after adjusting the baseline relative to signal background. The chemically distinct species of functional groups were also resolved using Gaussian distribution fitting procedure with the peak positions and area were determined. The C₁s core-level spectra at binding energy E₉ at 284.6 eV were taken as reference for charge correction in the core-level spectra, and the peak position was calibrated with respect to it. Functional groups of C₁s spectra of PTFE film were assigned as follows [18]: C-C at 284.6 eV, C-CFₓ at 288.0 eV, CF at 290.0 eV, CF₂ at 292.7 eV and CF₃ at 294.5 eV.

Figure 1: Optical transmittance of CeO₂-PTFE hybrid films.

Figure 2: C₁s XPS spectra of sputtered PTFE films.

The core-level spectra of C₁s, Ce₃d, F₁s of CeO₂-PTFE hybrid films and sputtered CeF₃ film were shown in Figure 3. Functional groups [19] of C-O, C-O-H (Ether and alcohol), C=O (Carbonyl), C=O-H (Ester, Acid), C=O-O-O (Carbonate), C=O-O-H (Carboxyl) and small amount of functional groups of C-Fₓ increased by doping PTFE up to 15 vol.% but further addition of PTFE results in large emerging peaks of C-Fₓ functional groups appeared at E₉ from 290eV to 295eV [6, 8, 19]. These results indicated that sputter doped PTFE was found to exist in the forms of C-Fₓ, which may give hydrophobic surface properties [19, 20]. Typical Ce₃d spectra were observed from CeO₂ films with satellite
peak at 918 eV indicating Ce$^{+4}$ chemical state and of course, no fluorine was detected. With the increase in PTFE content in CeO$_2$ films, C$_{3d}$ spectra indicated a gradual change in chemical states of Ce from Ce$^{+4}$ to Ce$^{+3}$ as assigned in the figure and the satellite peak at 918 eV decreased accordingly. Besides, large functional groups at E$_s$ from 290eV to 295eV also indicated the formation of CeF$_2$ in hybrid films. However, F$_{1s}$ peaks remain unchanged even by doping PTFE up to 20 vol.% of PTFE, indicating that fluorine in CeO$_2$-PTFE hybrid films exists in the same chemical states of CeF$_3$ but not different from PTFE as shown in Figure 4 (F$_{1s}$ in PTFE at 689 eV and in CeF$_3$ at 685 eV).

Figure 3: Change in C1s spectra in CeO$_2$-PTFE hybrid films and bulk PTFE and CeF$_3$.

C-F$_x$ BONDS IN CHEMICAL COMPOUNDS

Based on the XPS analyses shown in Figures 3 and 4, we can conclude that chemical states of fluorine of sputter doped PTFE in CeO$_2$ can be considered to exist as CeF$_3$ and C-F$_x$ and the host element of Ce changed partially from Ce$^{+4}$ (CeO$_2$) to Ce$^{+3}$ indicating the formation of Ce$_2$O$_2$ or CeF$_3$.

According to the basic process of sputtering [21], the constituent elements of the targets made of metals and ceramics will leave target surface to the substrate in the form of the atomic particle by momentum transfer from sputtering working gas atoms to the target. Therefore, CeO$_2$ target was considered to be sputtered in atomic Ce and atomic O, but there exists no report on the form of sputtered particles of polymer target such as PTFE. Experimental results shown in Figure 2 revealed that PTFE was sputtered mainly in the form of C-F$_2$ from the target to deposit on the substrate as a physical mixture of C, F, CF, CF$_2$ and CF$_3$. As a result, film growth by sputtering of CeO$_2$-PTFE target can be considered by chemical reaction on the substrate among co-landing atomic Ce, O, C from CeO$_2$ target and C, F, CF, CF$_2$ and CF$_3$ from PTFE target.

Degree of indentation hardness (IH) of bulk substrates and CeO$_2$-PTFE hybrid films was evaluated using Nano Indenter (Nanomechanics I Micro) under the load of 0.001mN. As shown in Figure 5, IH of borosilicate glass substrate about 6,364 N/mm$^2$ increased steeply to over 20,876 N/mm$^2$ by sputter deposition of 100 nm thick CeO$_2$ film and then decreased gradually by doping of PTFE in CeO$_2$ up to 20 vol.%. IH of CeO$_2$-PTFE hybrid films on borosilicate glass substrate was found to be over 10,000 N/mm$^2$ even up to 20 vol.%PTFE in CeO$_2$. It can be understood that IH of CeO$_2$ film is a reflection of the hardness of bulk CeO$_2$ which is widely known as a grinding abrasive. Furthermore, IH of over 820 N/mm$^2$ of sputtered PTFE films compared to IH of 33 N/mm$^2$ of bulk PTFE substrate can be explained in terms of sputter induced polymerization of PTFE films [18]. It is very interesting to note that CeO$_2$-PTFE hybrid films containing PTFE from 0 to 15vol.% showing excellent UV shielding properties showed super IH from 15,000 to 20,000 N/mm$^2$ at the same time.

Hydrophilic/hydrophilic property was evaluated by contact angle measurement of water droplet of 1 µL using Drop master 500 System of Kyowa Interface Science. All samples were found to be more than 90 degrees after annealing at 100°C shown in Figure 6. Film surfaces showed water repellent properties and the contact angle of more than 90 degrees in composition range from 5 to 30 vol. %PTFE in CeO$_2$. Hydrophobic properties of CeO$_2$-PTFE films thus obtained may be due to the effect of the hydrophobic additive of PTFE and spontaneous water repellency of sputtered CeO$_2$ films [22].

In conclusion, multi-functional hybrid films were developed by doping PTFE into CeO$_2$ by sputter deposition using CeO$_2$ and PTFE targets. Hybrid films containing from 5 to 15 vol.% PTFE in CeO$_2$ showed 4 functions of UV shielding, super indentation hardness, hydrophobicity and optical transmittance in visible light. Detailed investigation of surface properties using XPS and EPMA revealed that chemical states of F of sputter doped PTFE in CeO$_2$ can be considered to exist as C-F$_x$ and the host element of Ce changed correspondingly from Ce$^{+4}$ (CeO$_2$) to Ce$^{+3}$ indicating the formation of Ce$_2$O$_2$ or CeF$_3$. Furthermore, hydrophobic surface properties can be also explained in terms of surface
**Figure 4:** Change in Ce3d and F1s spectra in CeO2-PTFE hybrid films and bulk PTFE and CeF3.

**Figure 5:** Changes in indentation hardness of CeO2-PTFE hybrid films on borosilicate glass and PTFE.

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concentration of F of CeO$_2$-PTFE films evaluated by XPS analyses.

Figure 6: Changes in contact angle with film composition.

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