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Structural Study of Metallic Growth on Yttria-Stabilized Zirconia Single Crystal by Coaxial Impact-Collision Ion Scattering Spectroscopy

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1. Introduction

The surface of oxides attracts increasing interests because of its recent extending application to various technologies^{1,2}. The importance of oxides is due to their specific electrical, optical, magnetic, mechanical and chemical properties. Yttria-stabilized zirconia (YSZ) has a variety of utility in gate dielectric of electronic circuit³, super-conductive film⁴, highly conductive oxide film⁵, bolometric sensors⁶ and nuclear reactor⁷. Another important application of YSZ is catalytic support at metal/ceramic joints like Rh/YSZ system⁸. YSZ works as solid-state electrolyte as well, which is based on the ionic conduction of oxygen. YSZ is then applied to oxygen sensor and solid oxide fuel cell (SOFC)⁹.

In all the above devices including YSZ, the surface plays an essential role because the property of the devices is dominated by the microstructure of the metal-YSZ interface or the thin film structure of YSZ itself^{3-6,10}. Concretely, the structures of YSZ/Ni interface have recently been reported with interest in the development of super-conductive film^{11,12}, whereas Pt is an electrode material generally used for ferroelectric memory devices¹. Ni/YSZ interface structure was reported also with interest in SOFC¹³ based on the catalytic properties of Ni¹⁴, because Ni/YSZ is known as a candidate system for SOFC as well as Pt/YSZ¹⁵. However, for both electronic and chemical devices, the properties of the devices are strongly affected by the interfacial structures. Hence, it is needed to elucidate the interfacial structure at the atomic level. However, the examples of micro-structural study on the metal/ceramic systems are quite limited, although much information on the metal/semiconductor is given by many surface-sensitive techniques.

In this report, we present the structural analysis and comparison of the initial growth process of Ni and Pt on the YSZ clean surface, which was obtained by coaxial-impact collision ion scattering spectroscopy (CAICISS). To better understanding of the structure, a good investigating model is evaporated metals onto well-defined single crystal surface. The CAICISS spectra revealed that Ni grows epitaxially on the YSZ(001) surface, whereas Pt grows with disorder, after the deposition in ultra-high vacuum (UHV) condition. Such

clear difference at the atomic scale on the clean oxide surface gives a clue to understand the unrevealed properties based on the metal/ceramics interface structures.

2. Experiments and Results

The YSZ(001) single crystals (10x10mm, 0.5mm thick), made by skull-melting method, were provided from the Earth pharmaceutical Inc. (one side mechano-chemically polished, containing 10.0 mol% of Y₂O₃ as dopant).

The experiments were carried out in an UHV chamber that was equipped with CAICISS (Shimadzu, TALIS-9700) and a reflection high energy electron diffraction (RHEED) system with base pressure of 7×10^{-8} Pa. After ultrasonically cleaned in acetone and ethanol in turn, the specimen was introduced in the chamber. The YSZ crystal was cleaned by annealing in vacuum at 500°C (measured by a thermocouple attached to the back of the crystal) for 1 hour by means of radiation from the rear Tungsten heater.

After this procedure, a clear 1x1 unreconstructed RHEED pattern that is from the ideal YSZ lattice periodicity was obtained. Highly pure Ni (+99.99%) was then vapor-deposited onto the clean surface from the Knudsen-cell evaporator held at 1300°C, at a rate of 0.3 ML/min measured by a quartz-balance. In the case of Pt, evaporator was held at 1600°C. During the deposition, the sample was held at room temperature with the pressure lower than 9×10^{-5} Pa for both cases.

Before and after the deposition, CAICISS measurements were available for the sample on a two-axis goniometer. The primary He⁺ ion beam (2mm in diameter) of 2 KeV was introduced to the sample and a time-of-flight (TOF) energy analyzer was set coaxially to obtain a scattering angle of 180°. The energy spectrum of scattered ions reflects the mass numbers of target atoms. A series of CAICISS spectra were taken by scanning the incident (θ) or azimuth (ϕ) angle and compared with simulation spectra.

The azimuth angular dependence of Zr signal intensity at the incident angle of 45° from the <001> axis is shown in Fig.1 (a2) with a TOF spectrum (Fig.1 (a1)) taken in 120 sec. A strong angular dependence of 4-fold symmetry was

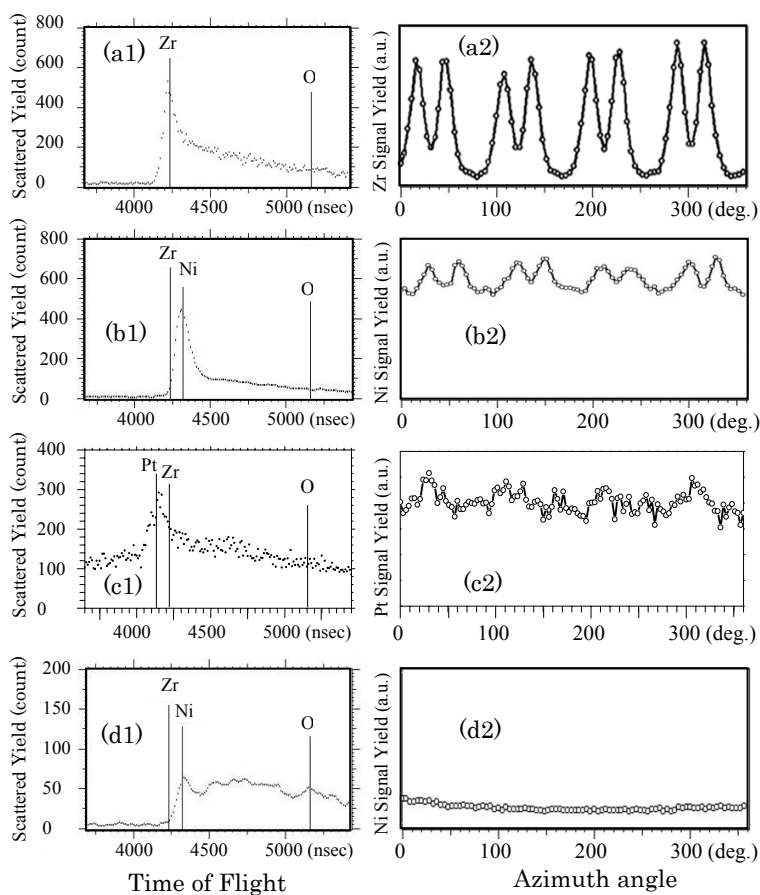
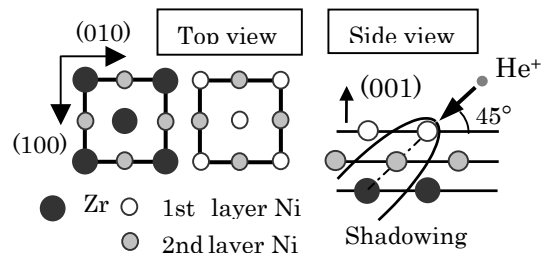


Fig.1. CAICISS spectra of TOF (left) and azimuth angle dependence (right) are shown for (a) clean YSZ, (b) Ni/YSZ (UHV), (c) Pt/YSZ (UHV), and (d) Ni/YSZ (after exposure in air). In the TOF spectra (left), vertical bars represent the calculated peak position. Azimuth spectra (right) were taken for Zr (a2), Pt (c2) and Ni signal (b2, d2).

Fig.2. Possible Ni atomic arrangement on YSZ, deduced from the CAICISS spectra (Fig.1 (b2)).



3. Conclusions

The YSZ (001) surface and its interfaces with deposited Ni and Pt were directly identified by CAICISS. The outermost plane on the clean YSZ surface was found to be Zr layer. The Ni layers at the coverage of 2MLs were well ordered, which kept 4-fold symmetry of the substrate, indicating certain Ni-YSZ interaction. However, this

interaction was less rigid than oxidation. In the case of Pt, the initial growth on YSZ (001) was little ordered. Such clear difference at the atomic scale on the clean oxide surface gives a clue to understand the unrevealed properties based on the metal/ceramics interface structures.

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References

- [1] H.Koinuma, The Oxide Electronics (Baifukan, Tokyo, 2001) [in Japanese].
- [2] V.E.Henrich & P.A.Cox, The Surface Science of Metal Oxide (Cambridge University Press, 1994).
- [3] S.J.Wang et al., Appl. Phys. Lett. 78, 1604 (2001).
- [4] R.P.Reade et al., Appl. Phys. Lett. 80, 1352 (2002).
- [5] H.Ohta et al., J. Appl. Phys. 91, 3547 (2002).
- [6] J.-H.Kim et al., Appl. Phys. Lett. 82, 4295 (2003).
- [7] S.Zhu et al., Appl. Phys. Lett. 80, 4327 (2002).
- [8] M.Shimokawabe et al., Appl. Catal. 59, 45 (1990).
- [9] H.Rickert, Electrochemistry of Solids (Springer, 1982).
- [10] J.G.Li: J.Am.Ceram Soc. 75, 3118 (1992).
- [11] C.Park et al., Appl. Phys. Lett. 76, 2427 (2000).
- [12] C.Cantoni et al., Appl. Phys. Lett. 79, 3077 (2001).
- [13] X.Chen et al., Appl. Phys. Lett. 84, 2700 (2004).
- [14] D.Sotiropoulou and L.Ladas: Surf.Sci. 408, 182 (1998).
- [15] C.G.Vayenas et al., Nature 343, 625 (1990).

clearly observed, as expected from the fluorite structure of YSZ (001) crystal with a Zr-layer at the top of the surface.

The same sample was estimated after the deposition of Ni at 2 monolayers (ML). Fig.1 (b1), in which only the Ni peak is observed, represents that the surface is fully covered by Ni atoms. Fig.1 (b2) shows a clear 4-fold symmetry in accord with the symmetry of the clean surface. This profile was reproduced by simulation (data not shown) for the structural model shown in Fig.2. The lower contrast of spectrum (Fig.1 (b2)) than that of Fig.1 (a2) was reproduced, too.

On the other hand, Fig.1 (c2) shows that the Pt layer has little symmetry after the deposition on YSZ (001), although the measurement was made just after Pt atoms covered the YSZ clean surface (Fig.1 (c1)). This result shows directly a diversity of the metal-YSZ interaction and suggests a rigid Ni-YSZ interaction.

However, after exposure in the air, the Ni/YSZ sample showed a drastic change, although the sample was still free of charge-up of He ions. Fig.1 (d1) showed both of the nickel and oxygen signals without Zr signal. Decreased yield accords with the intuitive image of the surface degradation based on oxidation. In Fig.1 (d2), the periodic feature was fairly lost. We can then conclude that the surface Ni layer was oxidized and changed into 3-dimensional islands without any orientation on it.