Ceramics International 32 (2006) 105–109

CERAMICS
INTERNATIONAL

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Charge distribution at interface and in bulk of YSZ thin films deposited on Si substrate

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Received 22 November 2004; received in revised form 21 December 2004; accepted 20 January 2005

Abstract

Charge distribution at the YSZ/Si interface and in the bulk of $ZrO_2 + x.Y_2O_3$ ($x = 1.22$, 2.39, 3.73 and 6.49 mol% Y_2O_3) thin films were studied by the charge transient methods and the impedance spectroscopy. The smallest amount of mobile ionic charge for the film with 6.49 mol% Y_2O_3 was found, while the positive charge fixed at the YSZ/Si interface is almost the same for each of the investigated films. The currents flowing across the films were influenced by their phase compositions, mainly in the film with 6.49 mol Y_2O_3. The observed diode behaviour with the characteristic leakage current was present probably due to the absence of interface traps, capable to capture the mobile positive charge. The electrical conductivity as the function of yttria amount and phase composition indicates the presence of isolated oxygen vacancies as well as the associated point defects. The behaviour of electrical conductivity is in a relatively good agreement with that observed for the crystalline YSZ samples used as the targets at the deposition of investigated films by e-beam evaporation on the Si substrate.

Keywords: B. Interface; Yttria-stabilized zirconia; Thin film; Polycrystalline structure; Bulk; Charge transient methods; Impedance spectroscopy

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1. Introduction

The phase composition and the crystallographic structure are decisive for many physical properties and thus also for many applications of materials. Both these topics together with the charge transport and selected mechanical and optical properties, in the crystalline as well as in the thin film forms of yttria-stabilized zirconia (YSZ) were described and discussed in our recent papers [1,2]. Thin films of zirconia have various applications in many fields of interest ranging from the solid oxide fuel cells, e.g. [3], through sensors, e.g. [4], electrochemical devices, e.g. [5], membrane reactors, e.g. [6] up to the protective coatings, e.g. [7], microelectronic elements, e.g. [8], etc., where the quality of interface between investigated film material and the substrate used is also important.

The purpose of the present study was to bring some information about the charge distribution at the interface between the YSZ film and silicon substrate in comparison with that in the bulk of the YSZ film using the charge transient methods and the impedance spectroscopy.

2. Experimental

2.1. Preparation of samples

$ZrO_2 + x.Y_2O_3$ ($x = .22$, 2.39, 3.73 and 6.49 mol%) films were deposited on n-doped Si (1 1 1) substrates by electron beam evaporation of the crystalline targets. The temperature of deposition was 750 °C. The details of the deposition can be found elsewhere [9]. The thicknesses of films determined by the surface profilometry using Talystep were found to be 103–304 nm.

2.2. Charge transient methods

Monitoring of the transient charge in response to a potential step (pulse) is a convenient way of characterizing

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0272-8842/$30.00
doi:10.1016/j.ceramint.2005.01.004

charge relaxation phenomena in a solid-state device. The experimental equipment based on such an approach was used in the course of all the measurements described in this section. The instrument, developed in the Institute of Physics, Slovak Academy of Sciences, comprises two PC cards (main application card, A/D and D/A converter card), the charge-sensitive preamplifier (with the charge detection threshold of 10^{-15} C) and the cryostat or the electrochemical cell, both equipped with the suitable electrode systems. The type of the charge relaxation depends presumably on the conductivity mechanism of the sample under consideration. Generally it can be postulated that an overall charge transient response can be described as a complex of the following relaxation processes:

- dielectric polarization,
- electrochemical double layer charging,
- oxidation or reduction of some electrically active ionic species.

In the presented work, the following charge transient methods were used to study the thermally untreated samples: capacitance–voltage measurements (*C–V*), cyclic voltammetry (CVAM) and isothermal charge transient spectroscopy (IQTS) in the rate window-scanning mode.

2.2.1. Capacitance–voltage measurements

The (*C–V*) characteristics were measured in the feedback-charge mode [10]. The repetition period of bias pulses was set to 10 ms, the filling pulse duration to 5 ms, the potential scan rate to 0.02 V/s. The transient charge was sampled according to the rules published in [10], i.e. just before the end of the bias pulse and then after 1.5 and 4.5 ms, respectively, after the trailing edge of the filling pulse.

2.2.2. Cyclic voltammetry

(CVAM) is a commonly used transient technique in which the working electrode potential is ramped linearly starting at either positive or negative voltage, and then after reaching some reversal potential, ramped back to the starting voltage [11]. This procedure has the advantage that the reversibility of the charge transfer (redox reaction) taking place on the working electrode during the forward scan can be probed during the backward scan.

2.2.3. Rate window scanning in charge transient spectroscopy

(IQTS) is a complementary submode to Q-DLTS in such a sense that the rate window of the "lambda" filter is scanned while maintaining a constant temperature. A series of rate window scans at different temperatures is necessary for getting parameters of trap levels, unless a fitting procedure (multiexponential analysis) is available. Nevertheless, the single IQTS measurement at a constant temperature can serve as a qualitative tool for the description of the processes taking place at the studied structure.

2.3. ac conductivity measurements

ac conductivity measurements were performed using a Solartron Si 1260 impedance/gain phase analyzer interfaced to a computer and run through a Lab-view program. The impedance measurements were made in the frequency range of 10 Hz–1 MHz at temperatures RT–480 °C in air.

All electrical measurements were done in the metal-insulator-semiconductor (MIS) configuration with aluminium and gold as the top and the bottom electrodes, respectively.

3. Results and discussion

3.1. Transfer and charge distribution at the interfaces of YSZ/Si thin films

The transfer of charge and its distribution in the YSZ films including the interfaces YSZ/Si were studied by the charge transient methods [10].

The capacitance–voltage (*C–V*) *characteristics*, measured in the feedback-charge mode [10] are shown in Fig. 1. The counterclockwise hysteresis loop points to a slow charge relaxation. We are likely dealing with the movements of ionic species in the gate dielectric. Starting the gate potential scan at the positive gate biases, the excess positive charge of oxygen ion vacancies at the Si/YSZ interface leads to a shift of the threshold of the accumulation-to-depletion transition. Only free electrons in Si substrates are able to leave the interface toward the bulk, when the potential of the gate is swept to more negative values, while the positive (ionic) charge is captured at the YSZ/Si interface. This is a reason, why the *C–V* plot corresponding to the potential scan from the accumulation ($U > 0$) to the depletion is shifted to more negative potentials in comparison with the *C–V* plot

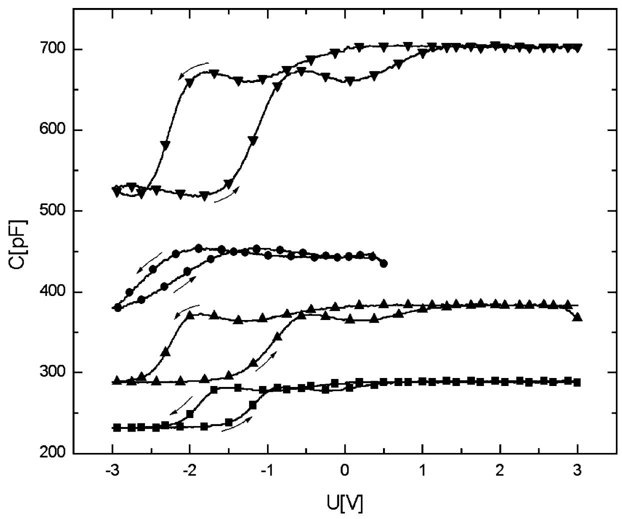

Fig. 1. The set of *C–V* curves obtained for the Y_2O_3 amounts in YSZ film: 1.22 mol% (■), 2.39 mol% (▲), 3.73 mol% (▼) and 6.49 mol% (●).

registered on the return. Similar behaviour of the *C–V* plots was described in [12,13], as well as in our previous work [14]. The behaviour of the *C–V* plots for the molar concentration of Y_2O_3 equal to 6.49 mol% (dashed-dot line) differs from the other three plots. The relatively small hysteresis of that curve implies that there is the smallest contribution of the mobile ionic charge in the YSZ thin film. Nevertheless, the transition from the accumulation to the depletion and back is always shifted by about -2 V from the zero bias, indicating a considerable amount of fixed positive charge at the YSZ/Si interface.

The cyclic voltammograms (*CVAM*) of the thin YSZ layers, obtained for the potential scan rate 0.1 V/s, are shown in Fig. 2. The equivalent conductance of all samples, except that one with the molar concentration of yttria equal to 6.49 mol%, is very low ($\sim 10^{-11}$ S) and no evidence for a redox reaction is found in the voltammograms. The situation is different for the sample with the best developed cubic structure, 6.49 mol% yttria. With reference to Fig. 2, the electrical conductivity of the latter sample is higher (see the scale in the left-up corner) at the applied voltage in the range of units of volts and the current–voltage dependence is similar to that of the diode. The current strongly increases at the ultimate positive potentials while a relatively weaker change of the current together with the voltammetric signal coming from a redox reaction at the potential ~ -1.1 V is observed under the negative biasing. This finding, as well as the smallest amount of the free charge captured at the interface traps, is in a good agreement with the lowest hysteresis of the *C–V* curve observed for this sample (Fig. 1). Here, the connection with the corresponding *C–V* curve, described above, is worth mentioning. Contrary to the other samples, the positive charged oxygen ion vacancies are not bounded to the YSZ/Si interface. They presumably contribute to the steady-state current through the sample with a faradaic component and consequently give rise to the asymmetric *I–V* characteristics, resembling a diode behaviour. (When the interface deep traps are absent at the interface YSZ/Si, the positive charge cannot be captured and therefore it can contribute to the leakage current.)

The charge transient spectroscopy (*rate window scanning mode*) was also used to characterize the transient properties of YSZ thin films (i.e. at the same temperature the sampling events are gradually changed during the entire experiment). The measured spectra are depicted in Fig. 3. As it is shown, the deep interface traps in the form of sharp peaks can be found in these spectra for all investigated samples with the exception of sample with the highest used yttria content (Fig. 3). In the case of this sample, it is possible to observe only a relatively wide-spread signal coming from the continuum of bulk defects. Consequently, such a composition of the sample leads to the *I–V* curves, which are characteristic for a diode with a sharp increase of the leakage current, when the applied voltage exceeds approximately 500 mV.

3.2. Transfer and charge distribution in the bulk of YSZ thin films

Transfer and charge distribution in the bulk of films can be revealed, for instance, by the study of the structure–conductivity relationship, which is strongly dependent on the structure and phase composition for the fluorite-related structures. In the present study, the structure of all investigated oxide film configurations was found to be polycrystalline and films contain at least two structurally different phases, one fcc phase with increasing degree of perfection as Y_2O_3 content increases and the other one

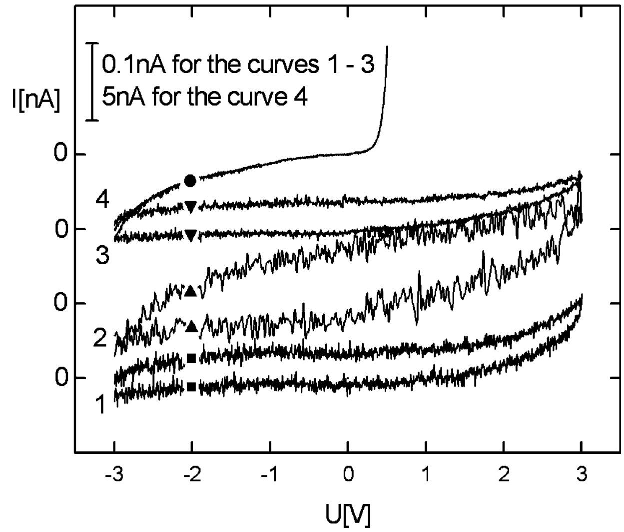

Fig. 2. The set of cyclic voltammograms obtained for the Y_2O_3 amounts in YSZ film: 1.22 mol% (■), 2.39 mol% (▲), 3.73 mol% (▼) and 6.49 mol% (●); the "zero levels" for the corresponding plots are shifted, the absolute value of signal is indicated in the left-upper corner.

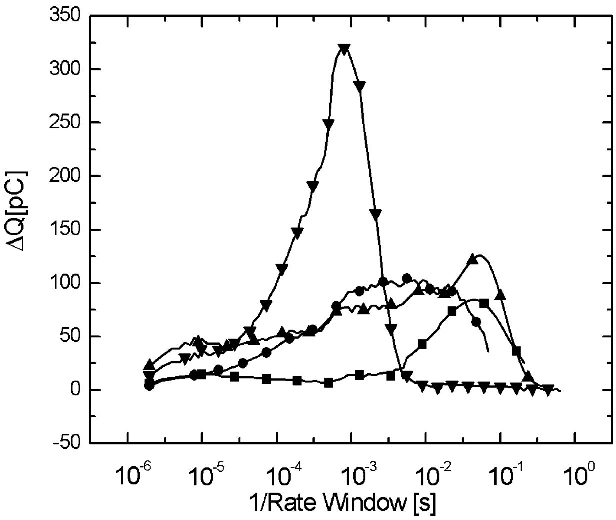

Fig. 3. Correlated transient charge ΔQ vs. time window plots belonging to the different molar concentrations of Y_2O_3 in YSZ thin films: 1.22 mol% (■), 2.39 mol% (▲), 3.73 mol% (▼) and 6.49 mol% (●).

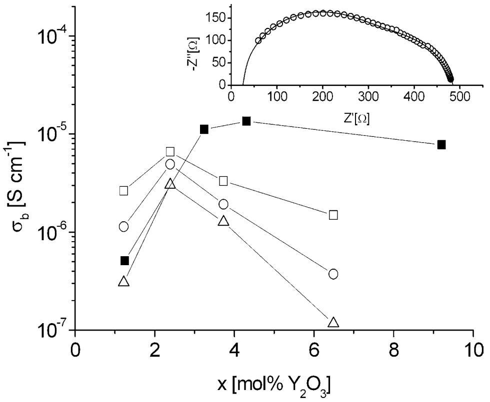

Fig. 4. Isothermal dependences of the bulk electrical conductivity σ_b of YSZ thin films on the amount of Y_2O_3 in the low temperature region: (△) 201 °C, (○) 261 °C, (□) 323 °C (with the inset of impedance diagram for $ZrO_2 + 2.39$ mol% Y_2O_3 at 261 °C) and of crystalline YSZ samples at 320 °C (■).

which maybe presumably a highly distorted form of some regular phase [2].

The effect of yttria content, structure and phase composition on the electrical conductivity σ is documented in Fig. 4. An example of the impedance diagram is shown in the inset of Fig. 4. The serial combination of two parallel circuits (R1C1, R2C2) and their temperature and frequency behaviours indicate two contributions of the total electrical conductivity (inset in Fig. 4). These two semicircles can be resolved in the impedance diagrams for all thin films investigated. The high-frequency one ($\geq$200 kHz) can be attributed to the bulk. The relative permittivities ε_r calculated from this semicircle are in a good agreement with those obtained by the other independent methods [2]. The low-frequency semicircle (10 Hz–30 kHz) was observable only at higher temperatures with the equivalent resistance surpassing that of the bulk. The physical mechanism responsible for this semicircle cannot be determined unambiguously from the measured data. The origin could be crystallite boundaries, the presence of a thin ($\sim$1 nm) SiO_2 interlayer or small isolated SiO_2 islands on the surface of Si substrate leading to an imperfect electrical contact [15–17]. A combined effect of all these factors together also cannot be neglected. The impedance diagram at the highest frequencies (the inset in Fig. 4) is slightly influenced by the presence of a parasitic inductance.

The isothermal dependences of the bulk electrical conductivity σ_b (measurements of the small-signal frequency response, 500 mV) as the functions of yttria content (Fig. 4) indicate the present influence of isolated oxygen ion vacancies $V_O^{\cdot\cdot}$ as well as the associated point defects $(Y'_{Zr}V_O^{\cdot\cdot})^{\cdot}$. The isolated oxygen vacancies $V_O^{\cdot\cdot}$ control the bulk electrical conductivity σ_b of the lightly doped samples and are generated by the presence of Y^{3+} ions (Fig. 4). The associated point defects $(Y'_{Zr}V_O^{\cdot\cdot})^{\cdot}$ control the low-temperature transfer properties of the samples with the higher concentrations of yttria. The formation of associated point defects (defect complexes) can be realized, in general, when the concentration of point defects increases (Fig. 4). The dependence of electrical conductivity on the yttria content is in a relatively good agreement with that observed for the corresponding crystalline YSZ targets [1] and our recent results [18] as well as the results of the other authors for the thin films prepared under the similar conditions (e.g. [19,20]). Lower values of the electrical conductivity observed for the investigated films are probably due to not sufficiently developed structures during the deposition process of films.

4. Conclusions

The investigation has provided the following interesting data:

- The *C*–*V* plot can serve as a tool to obtain the information about the mobile charge in the measured structure. The smallest amount of the mobile ionic charge was found to be for the film with the yttria content of 6.49 mol% while the positive charge fixed at the YSZ/Si interface is approximately same for each of the investigated films.
- It was shown, that the current flowing across the film is influenced by the phase composition of thin polycrystalline films. The strong voltage dependence of the current was observed mainly for the film with the yttria content of 6.49 mol%. Such a diode behaviour with the characteristic leakage current could be caused by the absence of interface traps, capable to capture the mobile positive charge.
- The absence of interface traps was confirmed by the charge transient spectroscopy in the rate window-scanning mode. Only for the film with the yttria content of 6.49 mol%, the wide-spread signal, coming from the continuum of bulk defects, was measured. No sharp peak, attributable to the interface traps, was observed.
- The bulk electrical conductivity as the function of yttria content indicates the present influence of isolated oxygen vacancies as well as the associated point defects.
- The behaviour of electrical conductivity is in a relatively good agreement with that for the crystalline samples. However, from the quantitative point of view, the lower values observed for the films could be due to not sufficiently developed structures during the deposition process of films.
- All data obtained by the isothermal transient methods used are in a good mutual agreement as well as in the comparison with the data obtained by impedance spectroscopy.

Acknowledgements

This work was partially supported by research grants nos. 2/4105/04 and 2/4100/04 of the Slovak Grant Agency.

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