On the off stoichiometry of cerium oxide thin films deposited by RF sputtering

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Abstract

We have studied the stoichiometry of cerium oxide films deposited by RF sputtering as a function of deposition conditions using the resonant Rutherford backscattering method. We found that some films have an off-stoichiometry of CeO_y with y greater than 2.0. Such an off-stoichiometry cannot be due to a mixture of the known phases of bulk cerium oxide samples. Those thin samples may have either cerium vacancies or interstitial oxygen atomic impurities. We have tried to determine the valence of the cerium ions by measuring the X-ray photoemission.

1. Introduction

Cerium oxide CeO_2 thin films has been proved to be a good buffer layer for the growth of $YBa_2Cu_3O_x$ thin films on sapphire and Si substrates [1–3]. The cerium oxide thin films have been grown by vacuum evaporation [1], laser ablation [2] and sputtering [3]. Bulk cerium oxide samples were known to have several phases of CeO_2, Ce_2O_3 and even oxygen-deficient CeO_y with $1.5 < y < 2.0$ [4,5]. It is very likely that cerium oxide thin films may not be of the stoichiometry of CeO_2. However, to the best of our

knowledge, the dependence of the stoichiometry of cerium oxide thin films on the deposition conditions have not been studied in detail yet.

The familiar $^{16}O(\alpha, \alpha)^{16}O$ elastic nuclear resonance near 3.03 MeV offers an attractive sensitive mean of extending the Rutherford backscattering (RBS) technique to probe the oxygen in oxides. The resonant RBS cross-sections are as much as 25 times greater than the RBS cross-sections. This method is very suitable to probe the light oxygen atoms among the heavy cerium atoms. In this paper, we have used the resonant RBS method to determine the oxygen contents of the cerium oxide thin films grown by RF sputtering as a function of sputtering conditions. We found that some samples have an off-stoichiometry of CeO_y with $y > 2.0$. The stoichiometry depends on the sputtering conditions. The ratios of the oxygen atoms to cerium atoms, y are equal to or less than

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2.0 for all the known phases of bulk cerium oxides. Therefore such an off-stoichiometry cannot be due to the mixture of the known phases of bulk samples. Those thin films with $y > 2.0$ may be either cerium deficient or oxygen overdosed. Furthermore, to understand why y is greater than 2.0, we have tried to determine the valences of the cerium ions by measuring the X-ray photoemission spectroscopy (XPS) of some selected samples. The lattice spacings as a function of the values of y are also studied by X-ray diffraction (XRD).

2. Experimental

The CeO_y films studied here were grown by the on-axis radio frequency (RF) magnetron sputtering method. The substrates used are either (1102) sapphire or (100) MgO. To prove the universality of our results, the samples were grown by two different deposition chambers A and B and by two different research groups. The sample names, deposition chambers, substrates, deposition temperature T_d, oxygen-to-argon pressure ratio O_2/Ar, deposition pressure, orientation and the full width at the half maximum of the rocking curve of the (200) peak $\Delta \omega$ of the films deposited are summarized in Table 1. ($\Delta \omega$ of some samples were measured at the (111) peak and were marked by an asterisk.) The RF

power of the chambers A and B is, respectively, 60 and 40 W. After deposition, the films were cooled to room temperature in an atmospheric pressure and 50 Torr oxygen atmospheric pressure and 50 Torr oxygen atmosphere for chambers A and B, respectively. Some samples have pure (111) or (200) orientations while most of them have mixed orientations of (111) and (200). The $\Delta \omega$ of the samples from chamber A were much larger than those of the samples from chamber B except sample A1018 which has pure (200) orientation.

To take the random RBS spectra, the He^+ ion beam was incident at the angles of 3 to 5 degrees to the normal of the film. Some measurements were repeated at different incident angles such that we could be sure to get the true random spectra by comparing the different spectra obtained. The detector was set at a laboratory scattering angle of 170 degrees. The respective Si and Au edges of the random spectra of a quartz crystal and a gold thin film grown on glass were used to calibrate the channel numbers to the corresponding energy of the scattered He^+ ions. The CeO_y thin film was covered by a 5–10 nm thick Au layer which was used to avoid charge up. Cameron [6] has first reported the resonant energies, resonant cross-sections and resonant widths between the He ions and oxygen atoms. Recently, Leavitt et al. [7] have measured accurately the resonant energies, the resonant widths, and the

Table 1
Summary of the sample names, deposition chambers, substrates, deposition temperature T_d, oxygen-to-argon pressure ratio O_2/Ar, deposition pressure, orientation, the full width at the half maximum of the rocking curve of the (200) peak $\Delta \omega$ of the films and the stoichiometry deduced. ($\Delta \omega$ measured at the (111) peak was marked by an asterisk.)

Sample	Deposition chamber	Substrate	T_d (°C)	O_2/Ar	Deposition pressure (mTorr)	Orientation (111)/(200)	$\Delta \omega$ (degree)	Stoichiometry
A1020a	A	sapphire	720	5/100	30	15/85	4.67	$Ce_{1.0}O_{2.0 \sim 2.2}$
A1020b	A	sapphire	720	25/100	30	9/91	2.68	$Ce_{1.0}O_{2.5}$
A1020c	A	sapphire	720	10/100	30	9/91	3.89	$Ce_{1.0}O_{2.0 \sim 2.2}$
A1015	A	sapphire	720	25/100	20	98.4/1.6	7.32 [a]	$Ce_{1.0}O_{1.8}$
A1018	A	sapphire	720	5/100	15	0/100	0.59	$Ce_{1.0}O_{3.3}$
B0427	A	MgO	700	25/100	15	11/89	2.74	$Ce_{1.0}O_{2.1}$
B0414	A	MgO	750	25/100	15	47/53	3.76	$Ce_{1.0}O_{2.4}$
B0125	A	MgO	720	25/100	15	2/98	1.57	$Ce_{1.0}O_{2.5}$
VAO	B	sapphire	600	100/100	60	100/0	0.31 [a]	$Ce_{1.0}O_{2.0 \sim 2.2}$
VA3S1	B	sapphire	760	100/100	60	0/100	0.3	$Ce_{1.0}O_{3.3}$
VB314	B	sapphire	650	100/100	100	91/9	0.71	$Ce_{1.0}O_{2.4}$
VB3	B	sapphire	710	100/100	100	15/85	0.29	$Ce_{1.0}O_{1.9}$

[a] Measured on the (111) peak.

resonant cross-sections. In this study, the enhanced resonant scattering cross-sections were calculated by the partial-wave method using the parameters determined by Leavitt et al. [7]. The conventional RBS cross-sections between the He ions and oxygen atoms were replaced by the enhanced resonant cross-sections in the computer program Gisa 3.91 [8] to fit the random RBS spectra. Rutherford cross-section with the correction of electron screening was used for the cerium atoms. The stoichiometry of the CeO_y films was deduced from the fitting. The thickness of the thin-film samples is approximately 100 nm. The exact energy of the He^+ ions determined by the energy of the resonant oxygen peak was found to be 3.04 MeV. Therefore the resonance occurs near the surface of the films.

The XPS spectra were acquired by the VG Microlab MKIII system using the Mg $K\alpha$ X-ray radiation. The exposure time of the sample to the X-ray radiation for spectrum measurement was limited to a short period of 5 min to avoid radiation damage on the sample surface [9]. The orientations and the rocking curves of the films are measured by the standard XRD method.

3. Results

3.1. RBS

The fitting of the computer simulation to the random RBS spectrum of magnesium oxide substrate standard yields a stoichiometry of MgO as shown in Fig. 1. It serves as the calibration of our measurement procedures, enhanced oxygen cross-sections and the computer simulation. Figs. 2 and 3 show the examples of the measured random spectrum and the computer simulation of the samples A1020a and A1018, respectively. The computer simulation fits well to both the cerium and resonant oxygen peaks. The stoichiometry of sample A1020a was determined to be $Ce_{1.0}O_{2.0 \sim 2.2}$ which was very closed to CeO_2. However, sample A1018 was found to be $Ce_{1.0}O_{3.3}$ which has either too much oxygen or not enough cerium. Figs. 3(b) and (c) show the details of the fitting to the oxygen and cerium peaks, respectively. For comparison, the computer simulation of the stoichiometry of $Ce_{1.0}O_{2.0}$ was also plotted as the
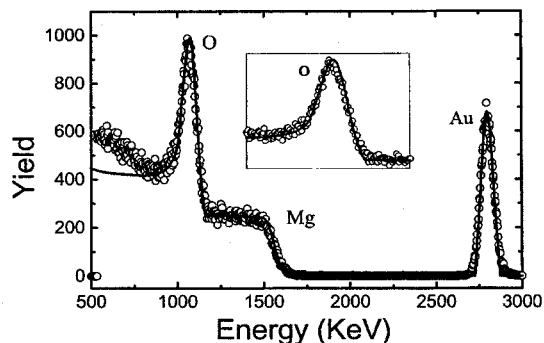

Fig. 1. The random RBS spectrum of a MgO substrate. The solid line is the computer simulation fitting to the spectrum assuming a stoichiometry of MgO. The insert shows the details of the fitting to the resonant oxygen peak.

dash line in Figs. 3(a), (b) and (c). The stoichiometry of all the samples obtained by the best fitting to the random spectrum were summarized in Table 1. Some samples have the stoichiometry of CeO_y with $y > 2.0$ while some do not.

We have studied the stoichiometry as a function of deposition conditions. The results show that the stoichiometry of cerium oxide thin film frustrated sensitively with T_d, O_2/Ar ratio and deposition pressure.

Samples A1020a, A1020b, and A1020c were deposited at a fixed temperature and pressure but with different oxygen partial pressures. Samples A1020a and A1020c have stoichiometry very near $Ce_{1.0}O_{2.0}$. However, sample A1020b which was deposited with the highest oxygen partial pressure has a stoichiometry of $Ce_{1.0}O_{2.5}$. Increasing the oxygen partial pressure above a certain limit will increase the oxygen contents of the films.

Sample A1015 was deposited at the same substrate, T_d and O_2/Ar ratio but at slightly lower total deposition pressure of sample A1020b. Sample A1015 has a stoichiometry with y less than 2.0. Slightly decreasing the deposition pressure will change not only the stoichiometry but also change the orientation from mainly (200) to mainly (111). However, the only difference in deposition conditions of samples A1020a and A1018 was also deposition pressure but at a different fixed O_2/Ar ratios. On decreasing the deposition pressure, y of samples A1020a and A1018 increases from 2.0 to 3.3 which
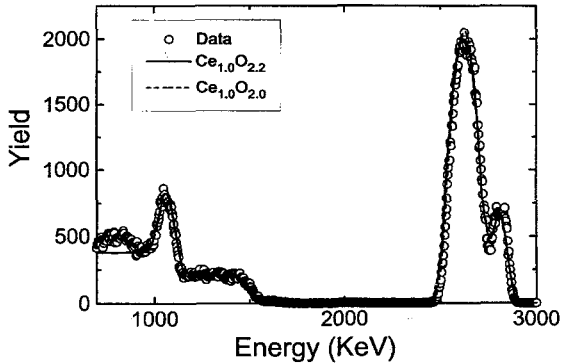
Fig. 2. The random RBS spectrum of sample A1020a. The solid and dashed lines are the computer-simulation fitting to the spectrum assuming a stoichiometry of $Ce_{1.0}O_{2.2}$ and $Ce_{1.0}O_{2.0}$, respectively. Both lines fit quite well to the spectrum.

is the highest value observed so far. The orientation of the films does not change and is mainly (200) (samples A1020a and A1018) on decreasing the deposition pressure this time. The above studies show that the stoichiometry fustrates very sensitively with deposition pressure and O_2/Ar ratio.

Samples B0427, B0414 and B0125 were deposited on the same substrate and under the same O_2/Ar ratio and deposition pressure but at different T_d. At low T_d of 700°C for sample B0427, y is equal to 2.1. On slightly increasing T_d from 700 to 720 and 750°C, y increases to 2.5 and 2.4, respectively. The experiment was repeated using another substrate of sapphire, deposition chamber, and at higher deposition pressure of 60 m Torr for samples VAO and VA3S1. Again on increasing the T_d from 600 to 760°C, y increases from 2.0–2.2 to 3.3. However, samples VB314 and VB3 were deposited at a much higher deposition pressure of 100 m Torr. At such a high pressure, y is equal to 2.4 (greater than 2.0) at the low T_d of 650°C. On increasing the T_d to 710°C, y decreases to 1.9 which is very closed to 2. The high deposition pressure gives a value of y greater than 2 at the low T_d of 650°C in contrast with the results at low deposition pressure discussed above. The value of y depends sensitively on T_d and deposition pressure. Changing T_d and deposition pressure change the kinetic energy of the oxygen and cerium ions during the sputtering pressure. It is believed that the kinetic energy of those ions should affect the stoichiometry of the films.

The above study shows that the stoichiometry and the orientation of the cerium oxide films are a complicated function of the substrate used, T_d, O_2/Ar ratio and deposition pressure.

3.2. XPS

Fig. 4 shows an example of the cerium 3d XPS spectrum of sample A1015. The XPS spectra of all samples were analyzed by deconvolution fitting. The energy values and the relative areas of the peaks deduced as shown in Fig. 4 are summarized in Table 2 for all the thin-film samples as well as the standard CeO_2 powder. Refs. [9] and [10] give the energies of the peaks for CeO_2: 882.2 and 888.6 eV, while those of Ce_2O_3 are 884.4 and 880.6 eV. None of the energies of the peaks match those of CeO_2 or even Ce_2O_3 for the thin-film samples. No XPS spectrum
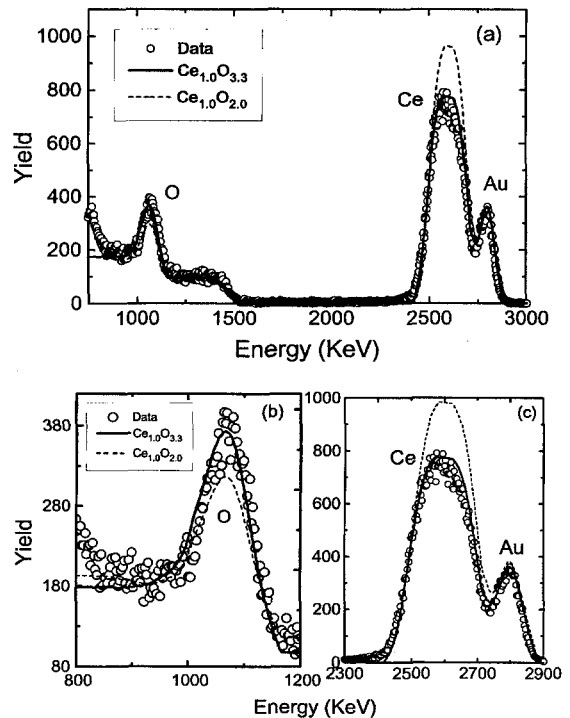

Fig. 3. (a) The random RBS spectrum of sample A1018. The solid and dashed lines are the computer-simulation fitting to the spectrum assuming a stoichiometry of $Ce_{1.0}O_{3.3}$ and $Ce_{1.0}O_{2.0}$, respectively. The solid line fits well to the spectrum but the dashed line does not. (b) The details of the fitting to the resonant oxygen peak. (c) The details of the fitting to the cerium peak.
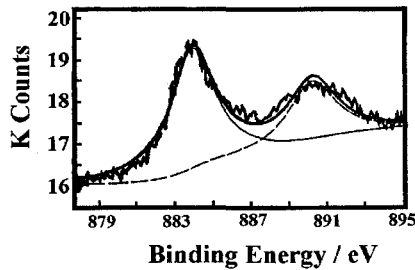
Fig. 4. The cerium 3d XPS spectrum of sample A1015.

other than the stoichiometry of CeO_2, Ce_2O_3 and reduced CeO_2 have been so far reported for comparison. (Reduced CeO_2 is a mixture of CeO_2 and Ce_2O_3.) We still cannot conclude to the valence of the cerium ion by XPS studies. However, it is the

first XPS studies in those films with stoichiometry of CeO_y with y greater than 2. No clear correlation between the energy of the peaks and the stoichiometry was observed either.

3.3. XRD

XRD shows that all the films studied have the CeO_2 phase with (200), (111) or mixed orientations. No impurity phase was observed. Table 3 summarizes the length of the lattice in the (200) and (111) directions. If the off-stoichiometry is due to the oxygen interstitial atoms or cerium vacancies, then the lattice spacing will be longer or shorter, respectively. We cannot find a direct relation of the lattice spacing with the value of y. Therefore, it may be

Table 2
Summary of the energy and the relative area of the peaks of the cerium 3d XPS spectra deduced by deconvolution

Sample	Ce1		Ce2		Ce3	
	Energy (eV)	Area	Energy (eV)	Area	Energy (eV)	Area
A1020a	883.4	52%	887.6	38%	890.3	10%
A1020b	883.8	34%	887.2	61%	891.5	5%
A1020c	883.2	50%	887.4	50%	–	
A1018	882.4	59%	887.3	41%	–	
A1015	883.5	65%	889.8	35%	–	
B0427	884.3	62%	890.4	38%	–	
B0125	883.4	60%	889.5	40%	–	
CeO_2 powder	882.2	64%	888.6	36%	–	

Table 3
Summary of the values of y, and the length of the lattice spacing in the (200) and (111) directions for different samples. The data for CeO_2 powders are also given for reference

Sample	Value of y	(200) lattice spacing in nm	(111) lattice spacing in nm
A1020a	2.0–2.2	0.2714	0.3105
A1020b	2.5	0.2709	0.3115
A1020c	2.0	0.2717	0.3118
A1015	1.8	0.2719	0.3106
A1018	3.3	0.2713	–
B0427	2.1	0.2709	0.3092
B0414	2.4	0.2711	0.3097
B0125	2.5	0.2708	–
VAO	2.0	–	0.3150
VA3S1	3.3	0.2718	–
VB314	2.4	0.2711	0.3141
VB3	1.9	0.2713	0.3147
CeO_2	2.0	0.2706	0.3123

likely that both the cerium vacancies and oxygen interstitial atoms play a certain role in the off-stoichiometry depending on the deposition conditions.

4. Discussion

Is the off-stoichiometry with y greater than 2.0 due to surface roughness, any embedded impurity atoms, wrong input cross-sections, computer errors or even a channeling effect?

The height of the cerium and oxygen peaks of the random spectra can be affected by the roughness of the samples. The thin-film samples have very smooth surfaces with the peak to a valley roughness of 3 to 6 nm as observed by atomic force microscope. Therefore, the off-stoichiometry should not be due to surface roughness.

The sample and target holders were made of either Fe or Al. Fe or Al atoms may be sputtered into the films and then are oxidized to form oxide impurity phases which cause y to be greater than 2.0. No Fe or Al impurity atom imbedded in the cerium oxide film was observed in any RBS spectra of the samples. Thus such an off-stoichiometry should not be due to any impurity Fe or Al atoms imbedded in the films. No other impurity atom was observed in the RBS spectra. Furthermore, no impurity spectrum line was found in the XPS observation.

Although we have utilized the latest most accurate enhanced resonant oxygen cross-sections reported so far [7], any underestimation of the resonant oxygen cross-section can give a wrong result of y greater than 2. However, it should be noted that we can still deduce the cerium compositions and hence the oxygen contents of the samples by fitting only the height of the RBS spectrum of the peaks of the cerium sublattice and the Al_2O_3 or MgO substrates. Our computer simulation fits well to the cerium peaks. We have checked the formulation of calculating the cerium cross-section in the computer program Gisa 3.91 by fitting the non-resonant RBS spectrum of cerium oxide films reported in Ref. [1]. We get the same stoichiometry close to $CeO_{2.0}$ as reported in Ref. [1].

Furthermore, cerium was known to have several isotopes with nuclear mass of 136, 138, 140 and 142

of relative abundance of 0.0019, 0.0025, 0.8848 and 0.1107, respectively. Most of the isotopes have a nuclear mass of 140 and 142. The ratios of the Rutherford cross-sections and the kinematic factors of these two isotopes are, respectively, less than 0.005% and 0.16%. The difference in the cross-sections is very small. The energy of the He ions scattered from these two isotopes should be within 5 keV which is much smaller than the resolution of the detector. Therefore, although we take as input the average Rutherford cross-section and average kinematic factor for the cerium atoms in the computer simulation, the difference in the cross-sections and kinematic factors of the isotopes should not affect the results of the deduced stoichiometry of the samples obtained by the computer simulation.

We have also double checked our computer simulation by analyzing again the spectra of some of our samples using the commercially available software, RUMP. The same compositions were obtained. Therefore, the off stoichiometry of CeO_y with $y > 2.0$ should not be due to impurities, computer errors, wrong input cross sections or artifacts, if any.

Such an off-stoichiometry cannot be due to the channeling or partial channeling effect, if any occurred in the random spectra measurement for the following reasons. Firstly, although samples A1018, VA3S1, VB314 which have the stoichiometry with $y > 2$ have rather good crystallinity (small values of $\Delta \omega$), samples A1020b, B0414 and B0125 have a very poor crystallinity. The rocking curves of those samples with poor crystallinity are very broad without any sharp peak embedded in the rocking curve observed. Therefore, the grains should not be well aligned. Channeling effect is impossible on those samples with poor crystallinity. Secondly, if any partial channeling effect occurs, both the cerium and oxygen peaks will decrease and then the spectra cannot be fitted to the computer simulation which assumes complete random scattering of the He^+ ions. Even though if some how the partial channeling is mainly steered by the potential of the Ce sublattices, and therefore the height of the oxygen peaks do not decrease, the oxygen peak of our computer simulation should be higher than the experimental data because we had a higher oxygen concentration than it should be in our computer simulation. Thirdly, we have repeated the measurements at different inci-

dent angles. We got the same spectra. This was not possible if a partial channeling effect occurred in any measurement. Lastly, if any channeling effect occurs, we may observe the surface peak or part of the surface peak in the spectrum on samples with high crystallinity.

5. Conclusion

We found that the stoichiometry of cerium oxide thin film frustrated sensitively with T_d, O_2/Ar ratio and deposition pressure. Some cerium oxide films even have the off stoichiometry of CeO_y with $y >$ 2.0. Those thin films with such an off-stoichiometry cannot be a mixture of the known phases of the bulk samples. Chin and Morishita [11] have also observed that the oxygen contents of the a-axis $YBa_2Cu_3O_x$ oxide films deposited by RF sputtering depends on the deposition temperature. It may be a general phenomenon that the oxygen contents of oxide films deposited by RF sputtering depend on the deposition conditions.

Mansour et al. [12] and Neterfield [13] also reported the RBS observation of an excess oxygen-to-cerium ratio on the films deposited by oxygen ion-assisted electron-beam evaporation when the current density of oxygen ion was larger than a critical level. Cerium dioxide was evaporated by the electron beam onto an unheated substrate which was irradiated by an oxygen ion beam. They gave the interpretation that the off-stoichiometry was due to the oxygen-ion implantation into the films. The growth mechanism of the films deposited by sputtering is quite different from that of the ion-assisted e beam. The films were grown at a high temperature about 600°C. It is possible that excess oxygen ions are implanted into the films during the sputtering process. However, it is not clear whether the off-stoichiometry with $y > 2$ is due to cerium vacancies or interstitial oxygen atoms. Future transmission electron microscopy study may help us to answer this question. Unfortunately,

XPS studies cannot determine the valence of the cerium ion in those samples but we have given the first data of the XPS on those off-stoichiometric thin films with y greater than 2. XRD shows that there is no direct relationship between the lattice spacings and the values of y. It may show that both the cerium vacancies and interstitial oxygen atoms may play a role in the off stoichiometry depending on the deposition conditions.

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