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Investigation of the initial stage of Cerium oxidation

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Received March 29, 2024

Revised April 10, 2024

Accepted April 12, 2024

The initial stages of oxidation of a massive Cerium sample at room temperature in an ultrahigh vacuum (oxygen partial pressure 10^{-6} Pa) after obtaining an atomically pure surface by bombardment with Ar^+ ions were studied using electron Auger spectroscopy. It was found that chemisorption is observed initially when exposed to oxygen up to 5 L, from 5 to 14 L Ce_2O_3 nuclei are formed, followed by coalescence at exposures from 14 to 40 L. The process ends with the formation of a thick oxide film Ce_2O_3 .

Keywords: oxide, vacuum, adsorption, chemisorption, exposure, coalescence.

DOI: 10.61011/PSS.2024.07.58981.72

1. Introduction

Cerium is the first lanthanide metal that has 4f-states filled. Its energy of internal level 4f is almost the same as for 5d and 6s levels, therefore, small energy is required to change the relative filling of the electronic levels. Because of low ionization potential Ce has high electrical positivity. Therefore, it is quite sensitive to the outer exposure, such as temperature, pressure and chemical environment. Because of this singularity many interesting effects are manifested, such as antiferromagnetic, superconducting effects [1] and etc.

In practice Cerium is used as a catalyst, in optics, metallurgy, as well as in the form of additives in ceramics and glass, fluorescent material. Various intermetallic compounds Ln_xM_y (where $M = \text{Mn, Fe, Co, Ni, Cu}$ and etc.) may be applied as thin films in the areas of nanotechnology, constant magnets, superconductors and composite materials, solid-state lasers, catalysts and hydrogen accumulators. Finally, Cerium is used for passivation of metals and semiconductors to get the high-quality passive-oxidized films [2].

Because of its fundamental and practical application value the study of Cerium surface properties is pivotal. Since 1980, the surface properties of Cerium have been studied using X-ray photoelectron spectroscopy and electron Auger electron spectroscopy. In the literature for Cerium, as for many lanthanides, the Auger spectrums are described, obtained from the surface films, deposited in the ultrahigh vacuum on metal substrates [3]. No doubt, these findings were useful, however, it would be interesting to study the surface of a Ce bulky sample in different states, and, first of all, to study its oxidized surface.

2. Experimental part

The studied sample Ce (99.9%) was cut from a bulky metal piece and represented a $10 \times 10 \times 1$ mm plate. The surface of sample was grinded and polished with a fine-grain emery paper in ethanol because of high chemical activity. Further, the sample surface was cleaned in the gate chamber by scribing with a diamond needle in Argon environment followed by ion (Ar^+ , 3000 eV, $2 \mu\text{A}/\text{cm}^2$) etching in the spectrometer working chamber.

The spectra were obtained using an Auger spectrometer (energy analyzer with a cylindrical „mirror“) on the basis of ultrahigh-vacuum system USU-4 [4]. The limiting residual pressure in the chamber of the Auger spectrometer was $5 \cdot 10^{-8}$ Pa. The energy of the probing electron beam with a diameter of 1 mm was 2 keV at a current of $1 \mu\text{A}$. The spectra were recorded in the range from 0 to 1000 eV at a modulation voltage of retarding potential 2 V. After the sample has been placed in the working chamber the oxygen and carbon on the sample surface were identified, while carbon was easily removed by ion bombardment for several minutes. For removal of oxygen this procedure was carried out for 1 hour. Figure 1 illustrates the characteristic Auger spectrum obtained in the ultrahigh vacuum 10^{-8} Pa for the atomic pure surface of Ce within the energy range 20–150 eV.

During experiments on studying the initial oxidation state Oxygen was placed in the working chamber using the precision inlet valve, while partial pressure O_2 remained at a level of $1 \cdot 10^{-6}$ Pa. To solve this task we have selected the low-energy part of the spectrum as the most sensitive to the surface.

The results of analysis of Auger-spectra E_{XYZ} compared with experimental data

Auger-transition	Calculation E_{XYZ} according to [8], eV	Experiment according to [1], eV	Our data eV
$N_3N_{4,5}P_1$	57.0	—	—
$N_{4,5}O_{2,3}O_{2,3}$	68.0	68.5	67.2
$N_{4,5}N_{6,7}N_{6,7}$	87.5	87.0	87.1
$N_3N_{4,5}N_{6,7}$	107.0	105.0	105.9
Interatomic transition	—	122.5	119.0

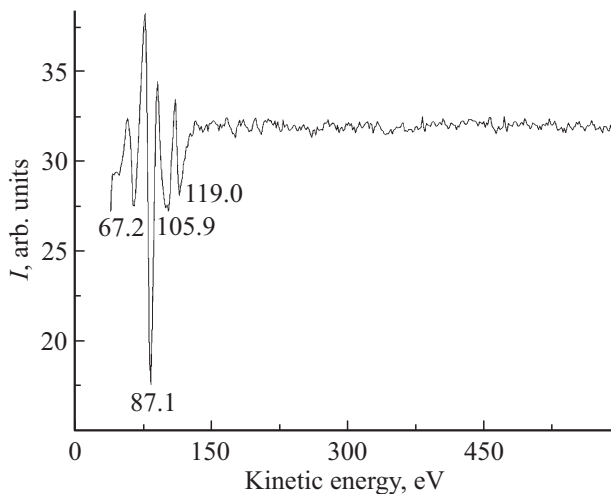


Figure 1. Auger spectrum of atomic pure surface of Ce.

3. Results and discussion

Various expressions for calculation of Auger-electron E_{XYZ} energy are used in the literature. In the most rough approximation, when electron structure deformation due to vacancies is neglected, the energy E_{XYZ} as a difference in bond energy of levels E_X , E_Y , E_Z in the transition. It is possible to take the into account the structure changes in approximation of equivalent cores [5], where it is supposed that for the outermost electron shells the appearance of the core hole is equivalent to the charge increase per unit. Chang and Jenkins [6] suggested to allow for this effect by using for Y- and Z-shells the bond energies as both, the average values of this atom and the values of the neighboring atom. In a more correct expression [5] the fourth summand is added for the energy related to relaxation and re-distribution of electronic density during the electronic transitions. However, the last summand, as shown from analysis of some metals, gives a contribution to the kinetic energy of Auger-electron $< 1\%$ [7]. Therefore, in this study we used the expression from paper [6]:

$$E(\text{Ce})_{XYZ} = E(\text{Ce})_X - E(\text{Ce})_Y - E(\text{Ce})_Z,$$

where bond energies $E(\text{Ce})$ for Y- and Z-shells were calculated as average values of $E(\text{Ce})$ and for the neighboring atom $E(\text{Pr})$, because Ce atom after appearance of a vacancy in the X-shell is in the single-time ionized state.

In this paper for calculation of kinetic energy of the low-energy Auger-transitions in Cerium the bond energies from [8] were used. The results of calculations are presented in the table.

In our experiments on Auger-spectra we observed the peaks due to the following transitions: $N_{4,5}O_{2,3}O_{2,3}$ — 67.2 eV, $N_{4,5}N_{6,7}N_{6,7}$ — 87.1 eV, $N_3N_{4,5}N_{6,7}$ — 105.9 eV (Figure 1). It should be noted that in [3] the transition 87.1 eV was interpreted as a superposition $N_{4,5}O_{2,3}N_{6,7}$ and $N_{4,5}O_{2,3}V$. We believe that the major contribution in the formation of this peak is made by super-transition electrons of Koster–Kronig (special case of Auger-transition) $N_{4,5}N_{6,7}N_{6,7}$, as prevailing above others due to higher process probability.

Apart from the above-mentioned transitions, a quite intensive peak at 119.0 eV was observed, the energy of which didn't depend on the energy of primary electrons. That is why this peak was attributed to the inter-atomic Auger-transitions.

As seen from the Table, in Cerium the Auger-electrons are formed during generation of primary vacancies at levels N_3 and $N_{4,5}$. The most intensive one was the peak from the Koster–Kronig transition: $N_{4,5}N_{6,7}N_{6,7}$ — 87.1 eV. Lower intensity $N_{4,5}O_{2,3}O_{2,3}$ — 67.2 eV is explained by the fact that Koster–Kronig super-transition probability is much higher than in Auger transitions, since the primary and secondary vacancies are filled by electrons of the same shell, thus, resulting in higher peaks intensity. Our data are consistent with the calculated values of transitions as per the data from [3,9]. Under the action of Oxygen with partial pressure $\sim 1 \cdot 10^{-6}$ Pa the energy positions of peaks $N_{4,5}O_{2,3}O_{2,3}$, $N_{4,5}O_{2,3}O_{2,3}$, $N_{4,5}N_{6,7}N_{6,7}$ were not changed, but their intensity decreased with the increase of oxygen exposure.

Figure 2 illustrates the variation of the standardized amplitude of peak Ce — $N_{4,5}N_{6,7}N_{6,7}$ — 87.1 eV, starting from the atomic-pure surface depending on the time of oxygen exposure. The exposure up to 5 L leads to a drastic reduction of the ratio of $I(\text{Ce})/I_0(\text{Ce})$ intensities, where

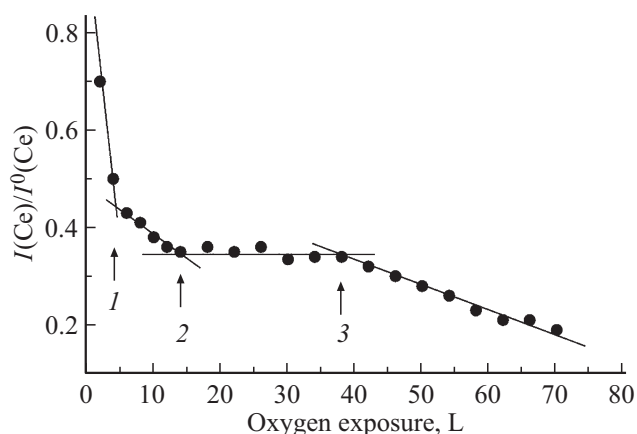


Figure 2. $I(\text{Ce})/I^0(\text{Ce})$ ratio versus exposure in oxygen environment at room temperature.

$I_0(\text{Ce})$ — amplitude of Auger peak for the atomic-pure surface of Ce, down to the value of 0.45. In the section of 5 to 14 L also a noticeable slope of the curve with reduction of $I(\text{Ce})/I^0(\text{Ce})$ to 0.35 is observed. In the interval from 14 to ~40 L a saturation area is observed, and further the curve has a slope again.

Our findings allow to make the following conclusions. Oxygen interacts with Cerium with the formation of Stranski–Krastranov thin films [10]. As with Cerium films [1,3,11], the appearance of Oxygen on the surface of Ce bulky sample doesn't lead to any chemical shifts of the low-energy peaks on the spectra, and the profiles of Auger-peaks are not noticeably changed. With the exposure to Oxygen up to 5 L the chemisorption is first observed on the atomic-pure surface. Upon completion of 2D-layer formation (within exposure interval from 5 to 14 L) the nucleuses Ce_2O_3 are starting to form followed by 3D island growth, after which the coalescence at 14 to 40 L follows. At the end of the process a thick oxide film Ce_2O_3 is formed. This conclusion is proved by calculations of surface concentrations after every exposure of surface to Oxygen. Thus, there exist at least three different oxidation stages for Cerium. Meanwhile, from the X-ray photoelectron spectroscopy data [11] it follows that further exposure to Oxygen of over 50 L leads to the formation of CeO_2 layer, which, according to authors of [11], is proved by Ce(3d) spectrum, peculiar to CeO_2 . In our experiments exposure to Oxygen of over 40 L didn't result in drastic changes of $I(\text{Ce})/I^0(\text{Ce})$, which indicates the absence of Ce_2O_3 transformation.

Funding

The work was carried out as part of NOSU State assignment of Russian Ministry of Education and Science (scientific thesis code: FEFN-2024-0002).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by T.Zorina