
ADSORPTION OF STRONTIUM ONTO AN ALUMINUM OXIDE SURFACE

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Auger-spectroscopy has been applied to study the adsorption of strontium onto an aluminum oxide surface. It has been established that, at a temperature as low as 300 K, the Sr deposition with the coverage up to one monolayer (ML) results in a redox reaction on the substrate surface. As a result, the interface layer includes both Al and Sr atoms in the metal state, as well as the molecules of relevant oxides. The Sr adlayers on Al₂O₃ were observed to grow layer-by-layer up to 3 ML in thickness. The dissolution of strontium in the volume of aluminum oxide has been found at 800 K.

1. Introduction

A lot of works is devoted to studying the adsorption systems which are formed when metal atoms are adsorbed onto the surface of metal substrates, with these systems being studied there in detail making use of a variety of methods. Recently, the systems made up of components with other physical and chemical nature have been attracting an enhanced interest, namely, thin metal adfilms on the surfaces of oxides [1, 2]. It is a consequence of the wide practical use of such systems in heterogeneous catalysis, nanoelectronics, materials science, optoelectronics, etc. For a long time, carrying on experiments with such objects has been complicated because of the difficulties connected with applying the analytical methods developed in order to study metal surfaces. Only the recent results, which have demonstrated that thin (a few monolayers in thickness) oxide films preserve the basic properties of bulk oxides and possess a sufficiently high tunnel transparency, so that practically all the known techniques of surface science can be used, have activated works in this domain.

This work is aimed at studying the adsorption of strontium atoms onto the surface of aluminum oxide. This system is interesting for studying the regularities of the interaction between electropositive metal adsorbates and oxides, and also can find application in elaborating the environment preservation technologies, in particular,

for preventing from the expansion of the radioactive nuclides of alkaline-earth elements.

2. Experimental Part

The measurements were carried on using an USU-4 high-vacuum installation equipped with an Auger-spectrometer (of the cylindrical mirror type) and an argon-ion gun, by applying the Anderson variant of the method of contact potential difference (CPD).

The pressure of residual gases during the measurements did not exceed 2×10^{-10} Torr. An aluminum foil (Al 99.99%) 100 μm in thickness was used as a substrate. The adsorption of strontium was studied on both the surface of a preliminary oxidized aluminum foil and the surface of aluminum oxide obtained by oxidizing an aluminum film about 3 ML in thickness which was sputtered onto the same foil directly in installation. The surface of the foil specimen was cleaned before the measurements by subjecting it to a bombardment with Ar ions and heating up to 800 K. A specimen can be heated up resistively, and its temperature was measured by a chromel-alumel thermocouple.

In the chamber of installation, the sources of Al, Sr, and O₂ were placed. The flux calibration and the determination of the Sr adatom concentration were carried out making use of the CPD method. In order to calibrate the flux, we used an auxiliary (reference) W(110) crystal located in the vacuum chamber, next to the researched Al specimen. The concentration dependence of the work function in the Sr–W(110) system was known from previous researches [3]. The sputtering of strontium was carried on in equal doses, and the deposition of each dose was followed by annealing the specimen for 1 min at 800 K.

The formation of one Al monolayer was taken to be completed when the work function in the Al–W(110) system achieved a constant value [4].

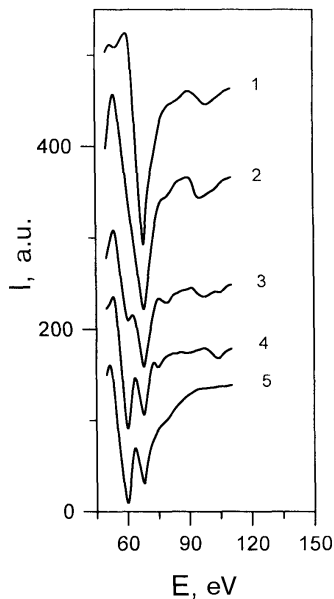


Fig. 1. Auger-spectra measured from an 3-ML aluminum film oxidized at various expositions in an oxygen atmosphere: 0 (1), 1200 (2), 2400 (3), and 3600 L (4); and from a preliminary oxidized aluminum foil (5). 1 L = 10^{-6} Torr/s

3. Experimental Results and their Discussion

In Fig. 1, we present the Auger-spectra of the specimen being a preliminary oxidized aluminum foil, as well as those obtained after the oxidation of a 3-ML Al film in an oxygen atmosphere at 300 K followed by its heating up to 800 K. One can see that the ultimate spectrum, which was registered from the oxidized Al film thus obtained, coincides with the spectrum from the oxidized aluminum foil specimen. The energy positions of both peaks of the spectrum agree with the results of work [5], where an Al_2O_3 single crystal was studied. The peak at 68 eV is caused by the *LMM* Auger-transition in Al atoms, and the peak at 60 eV, which appears at the exposition in oxygen of about 2400 L and grows with the increase in the exposition, may be related to interatomic Auger-transitions in aluminum oxide that was being formed [5]. Interatomic Auger-transitions are characteristic of compounds with ionic bonds. The essence of these transitions is that the primary excitation of a core level in one of the compound atoms can relax due to the transitions of electrons from another atom belonging to this compound. Therefore, our results confirm the conclusions of works [6, 7] that the properties of an aluminum oxide film of several monolayers in thickness are rather close to those of a massive oxide.

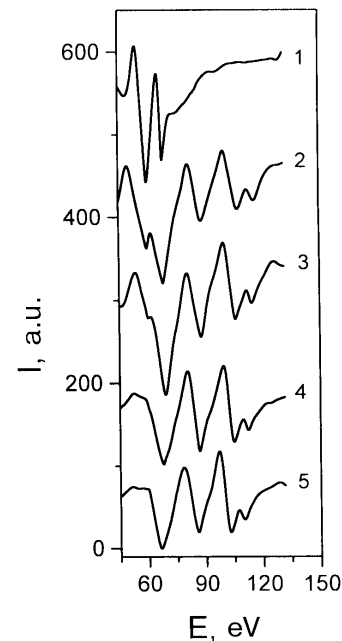


Fig. 2. Auger-spectra of the systems Al_2O_3 +Sr at various degrees of the Sr coverage $\theta_{\text{Sr}} = 0$ (1), 0.25 (2), 1.0 (3), 2.0 (4), and 3.0 ML (5)

In Fig. 2, we present the Auger-spectra obtained upon the Sr adsorption onto the surface of the preliminary oxidized aluminum foil specimen. The sputtering of strontium onto the surface of the aluminum film, which was oxidized immediately in the experimental installation, resulted in the identical Auger-spectra.

From the spectra exposed in the figure, one can see that the deposition of 0.25 ML of strontium results in the appreciable reduction of the 60-eV peak and, simultaneously, in the growth of the peak at 68 eV. It can be stimulated by a redox reaction on the specimen's surface. In this case, the number of Al_2O_3 molecules on the surface decreases (this results in an essential reduction of the peak at 60 eV), a part of Al atoms become metallized (which is responsible for the growth of the peak at 68 eV), and the Sr adatoms become oxidized (it is evidenced for by the shift of strontium Auger-peaks towards higher energies [8]). Similar processes were observed in work [9], where the adsorption of magnesium onto the chromium oxide surface was studied. As was shown in work [10], the electronic state of metal adatoms, when they are adsorbed on the oxide surfaces within the coverage range 0.1–0.3 ML, can be compared with the state that is characteristic of the atoms of these metals in the content of an oxide. It should be noted that

the growth of the 68-eV peak intensity can be caused in part by its overlapping with the strontium peak at 66 eV.

As the strontium coverage increases, the peak at 60 eV gradually fades not changing its position and practically disappears at a single-monolayer adsorbate coverage.

The strontium Auger-peaks emerge in the spectra at the coverages greater than or equal to 0.1 ML. Their positions (69, 89, 108, and 116 eV), as was pointed out above, are shifted towards higher energies relative to the Auger-peaks of metallic strontium (66, 85, 103, and 110 eV, respectively). The increase of the strontium coverage on the surface up to one monolayer gives rise to a growth of the intensity of peaks and is accompanied by their insignificant shifts towards lower energies. This may testify to a strong interaction between Sr adatoms and the surface of aluminum oxide within this interval of coverages, which does result in the essential modification of the electronic structure of adatoms. The deposition of the second and third monolayers of the adsorbate results both in the intensity increase of the strontium Auger-peaks and in their appreciable shift towards lower energies. At a strontium coverage of 3 ML, the positions of Auger-peaks practically coincide with their positions for metallic strontium. It testifies to that, provided such a thicknesses of the adfilm, Sr atoms which are located in the top layer practically do not feel the influence of the substrate [9]. The variations in the positions of Auger-peaks as the degree of strontium coverage changes are shown in Fig. 3.

The issue concerning the mechanism of growth of metallic adsorbate adfilms on the oxide surface is of importance. This mechanism depends on the relation between the energy of adatoms' binding with the substrate and the energy of their lateral interaction. If the former is greater than the latter, one should expect a layer-by-layer growth of the adfilm. Otherwise, the growth of three-dimensional island films becomes possible. Na and Mg films were shown in works [9,11] to grow layer-by-layer on the chromium oxide surface (in the case of Mg adsorbate, at least to the 2-ML coverage). The researches of adsorption of 3*d*-metals onto the aluminum oxide surface [12] testify to that the films of such adsorbates grow layer-by-layer at low temperatures of the substrate (80 K). As the adsorption temperature becomes elevated up to 600 K, the formation of three-dimensional crystallites in the Cu, Ni, and Co films becomes possible, although the Mn and Ti films retain the layer-by-layer mechanism of growth. In our case of the adsorption of the alkaline-earth element Sr onto the Al₂O₃ surface, a stronger interaction

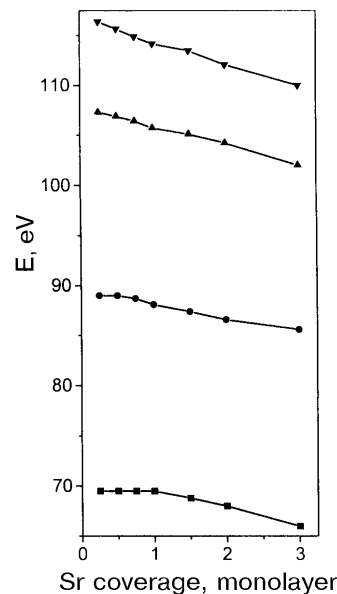


Fig. 3. Variations of the positions of the strontium Auger-peaks at 69, 89, 108, and 116 eV for various degrees of the θ_{Sr} , monolayer coverage on the aluminum oxide surface

between the adsorbate and the substrate should be expected in comparison with the interaction of 3*d*-metal atoms. The presence of such strong interaction is confirmed by the fact that, even at a 1-ML coverage with strontium, its Auger-peaks are considerably shifted with respect to those of metallic strontium. All that, together with the fact that the deposition of a single monolayer of strontium is accompanied by the practically total disappearance of the Auger-peak from the substrate, gives reasons to talk about the formation of a continuous strontium film on the Al₂O₃ surface. In this case, such a layer-by-layer mechanism of growth of the strontium adfilm is valid at least until a third monolayer has been completed. This is corroborated by the fact that the positions of strontium Auger-peaks from the 3-ML film coincide with those of the Auger-peaks of metallic Sr. If the Stranski-Krastanow growth mode had been realized, these positions of Auger-peaks would have been different; it was the case in work [9].

In work [10] devoted to studying the thermal stability of the 3*d*-oxide systems, it was shown that, at annealing temperatures of more than 600 K, the metal adsorbate dissolves in the volume of oxide. We carried out annealing at 800 K, so that we might expect for a similar result in our case as well. Really, the bombardment of a specimen with Ar ions did not give us an opportunity to clean it from Sr, even at such doses when the specimen became partially destroyed. Thus, it is possible to talk

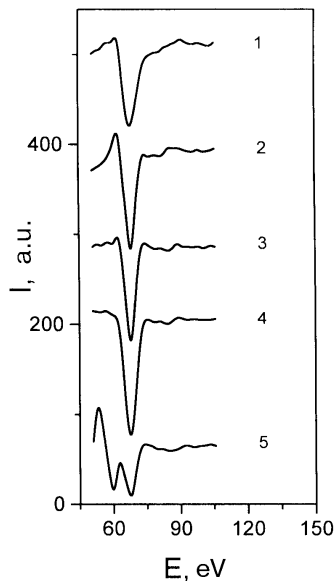


Fig. 4. Auger-spectrum from a 3-ML Al film sputtered onto the strontium adlayer as a function of the annealing duration and temperature: without annealing (1), 60 min at 600 K (2), 30 min at 700 K (3), 10 min at 800 K (4), and 30 min at 800 K (5)

about the effective dissolution of the adsorbed strontium in the bulk of aluminum oxide at a heating temperature of 800 K. On the other hand, we did not observe the appreciable diffusion of strontium into aluminum. The Auger-spectra obtained at the heating of the specimen with a 3-ML film of Al sputtered over the strontium adlayer (see Fig. 4) evidence for that. As one can see, a prolong annealing (for 30 min) at 800 K gives rise only to the oxidation of Al due to oxygen contained in the substrate, with Sr adatoms not approaching the surface.

4. Conclusions

Thus, the obtained results testify to that, if Sr is adsorbed onto the aluminum oxide surface at temperatures as low as 300 K, there occurs a redox reaction which involves the Al_2O_3 molecules of the oxide surface layer and the atoms of the first strontium monolayer. As a result, the interface layer includes the atoms of metallic (reduced) aluminum and metallic strontium and the molecules of aluminum and strontium oxides. An increase of the adsorbate coverage brings about a gradual metallization of the Sr adlayer, with this process practically coming to the end at the adfilm thickness of about 3 ML. The revealed dissolution of strontium in the volume of aluminum oxide at 800 K can

be used for both the efficient fixation of the radioactive nuclides of alkaline and alkaline-earth elements and the prevention from their expansion in the environment.

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1. Freund H.-J., Kuhlbeck H., Staemmler V. // Rep. Progr. Phys. — 1996. — **59**, N 3. — P. 283–348.
2. Freund H.-J. // Surf. Sci. — 2002. — **500**. — P. 271–299.
3. Klimenko E.V., Naumovets A.G. // Fiz. Tverd. Tela. — 1973. — **15**. — P. 3273–3278.
4. Gorodetskii D.A., Fung-Ho // Ukr. Fiz. Zh. — 1969. — **14**, N 1. — P. 94–104.
5. Citrin P.H., Rowe J.E., Christman S.B. // Phys. Rev. B. — 1976. — **14**, N 6. — P. 2642–2658.
6. Jaeger R.M., Kuhlbeck H., Freund H.-J. et al. // Surf. Sci. — 1991. — **259**, N 3. — P. 235–252.
7. Madden H.H., Goodman D.W. // Ibid. — 1985. — **59**, N 1. — P. 39–46.
8. Wagner C.D., Riggs W.M., Davis L.E., Moulder J.F. Handbook of X-ray Photoelectron Spectroscopy. — London: Perkin-Elmer, 1979.
9. Bender M., Yakovkin I.N., Freund H.-J. // Surf. Sci. — 1996. — **365**. — P. 394–402.
10. Vladimirov G.G., Magkoev T.T., Rump G.A. // Poverkhnost. — 1991. — **12**. — P. 56–63.
11. Dillmann B., Rohr F., Seifert O. et al. // Faraday Discuss. — 1996. — **105**. — P. 295–316.
12. Magkoev T.T., Vladimirov G.G., Remar D., Moutinho A.M.C. // Solid State Commun. — 2002. — **122**, N 2. — P. 341–346.

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АДСОРБЦІЯ СТРОНЦІЮ НА ПОВЕРХНІ ОКСИДУ АЛЮМІНІЮ

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Резюме

Методом оже-електронної спектроскопії вивчена адсорбція стронцію на поверхні оксиду алюмінію. Встановлено, що вже при 300 К напilenня шару Sr завтовшки до одного моносару приводить до окислювально-відновлювальної реакції на поверхні підкладки. В результаті цього в інтерфейсному шарі присутні Al та Sr в металічному стані, а також молекули оксидів цих металів. Спостерігався пошировий ріст адплівки стронцію до тримоншарового покриття. Виявлено розчинення Sr в об'ємі Al_2O_3 при 800 К.