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Core Level Spectroscopy during Sodium Atom Adsorption on Gold Nanoparticle Surfaces

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The electronic structure of Au nanoparticles deposited on a W surface with natural oxide was studied by *in situ* photoelectron spectroscopy in ultrahigh vacuum before and after adsorption of Na atoms. The photoemission spectra from the core levels of Au 4*f*, Na 2*s*, and Na 2*p* were analyzed under synchrotron excitation in the photon energy range of 80–600 eV. It was shown that heating of the Au nanoparticle film leads to an increase in photoemission from the Au 4*f* level, which is associated with an increase in the size of gold nanoparticles. Deposition of Na atoms leads to the formation of an adsorbed Na layer and diffusion of Na atoms deep into the gold film with the formation of the intermetallic compound Na_xAu_y. Two states were found: Na⁰ and Na⁺, which are associated with the adsorbed Na layer and the intermetallic compound Na_xAu_y, respectively.

Keywords: adsorption, sodium, gold, surface reconstruction, photoemission.

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1. Introduction

Gold nanoparticles have centuries-old history of study and application, dating back to the era of Ancient Rome. During recent years the gold nanoparticles again became the subject of multiple studies due to unique physical and chemical properties and universal application [1–3]. Properties of gold nanoparticles can be controlled due to their adjustable size, form and composition. Nanoparticles find wide application in creation of biosensors [4], in medicine [5–8], gas detectors [9], microelectronics [4], catalysis [9–12] etc.

The gold nanoparticles synthesis and surface functionalization are subject of multiple studies. Different chemical and physical approaches were developed for gold nanoparticles synthesis with required size, form and characteristics of surface, for example, sol-gel-processes or electrical deposition. So, it is possible to obtain gold nanoparticles ranging in size from units to hundreds of nanometers, which facilitates their application in various fields.

Note that gold nanoparticles significantly differ from their bulk analogs. The thermodynamic characteristics change if material size decreases. Due to large ratio of surface atoms to bulk atoms the melt point decreases in nanoparticle as compared to bulk material. So, even comparatively low-temperature heating of gold nanoparticles leads to their size change. Besides, the thermal stability of Au nanoparticles is affected by substrate and gaseous atmosphere. In paper [13] it was determined that during treatment to 700°C on SiO₂ nanoparticles Au grew from 4 to 6 nm, and on TiO₂ — from 3 to 13 nm.

In paper [14] the sodium adsorption was studied on surface of gold film with maximum thickness of 5 monolayers (ML), the adsorption was performed by method of electron-stimulated desorption (ESD) of sodium atoms. It is shown that in case of submonolayer coverage of sodium no intermetallic compound Na_xAu_y is formed, and at large doses of sodium deposition intermetallic compound Na_xAu_y is formed, and obtained 2D-layer is semiconductor layer. At energy of bombarding electrons below 100 eV ESD of atoms is observed only from surface of semiconductors and dielectrics. From metal surface ESD is not observed due to fast energy dissipation [15–16].

In paper [17] using thermal desorption spectroscopy the adsorption of Na atoms on surface of deposited gold film with deposition dose over 3.3 ML on surface W(100) was studied. It is shown that Na atoms are desorbed from three phases: monolayer Na film, multilayer Na film and intermetallic compound Na_xAu_y.

The intermetallic compound Na_xAu_y is formed during interaction of sodium and gold at room temperatures. Stoichiometry of compound depends on conditions of its formation [18–20].

In paper [18] reconstruction of surface Au(111) during adsorption of Na atoms was studied using scanning tunneling microscopy. It was identified that during adsorption of sodium 0.23 ML on gold surface a poorly ordered domain structure with hexagonal symmetry and higher density of atoms Au is formed. This is due to the weakening of the bond between the two upper layers of Au caused by the interaction of sodium adatoms and gold surface

atoms. In [19] adsorption of sodium atoms of surface Au(111) was studied in submonolayer mode of coverages at different temperatures. It is shown that at $T = 300$ K at Na coverage over 0.25 ML the mixed surface layers Na and Au are formed. At large sodium deposition doses the mixed structure NaAu is formed in top layer. During adsorption of several monolayers Na atoms ingress in more deeper layers of substrate, and thin film of intermetallic compound Na-Au is formed. The paper [20] shows that sodium and gold react at room temperature and form 4 intermetallic phases of compound Na-Au under high pressure. The volume ratio of Au to Na was 1–2%, and, hence, system was under conditions, enriched with Na. At pressure below 0.83 GPa formation of the compound Na_2Au was observed. At pressure above 0.83 and 3.6 GPa additionally two other phases of compound Na_3Au are formed. Finally, at high pressure of 54 GPa, a fourth phase with highly disordered structure was discovered.

The intermetallic compound formation on the gold film on tungsten (Au/W), used during ESD study, can differ from the intermetallic compound formation on massive sample of Au, and also depend on gold facet yield to surface [21].

In present paper the objective is set to study effect of heating the deposited film of gold nanoparticles on spectrum of core states of gold and study of sodium atoms adsorption at large doses of sodium atoms deposition on nanoparticles.

2. Experiment details

The photoemission studies were carried out in the Russian-German laboratory on the synchrotron HZB BESSY II (Berlin, Germany) using the photoelectron spectroscopy method during excitation in the photon energy range of 80–600 eV. Photoelectrons normal to the surface were recorded, the exciting beam fell on the sample surface at angle 45° . The tungsten sample with size 8×8 mm and thickness 0.15 mm, coated by natural oxide, was preliminary annealed at temperature $T = 850$ K for 10 min in vacuum. Then on surface gold film with thickness over 2 nm was deposited. Next, sodium coverage several monolayers thick was deposited on the gold film, after which additional gold film with thickness over 2 nm was deposited. Such 2D-layer was studied *in situ* in vacuum $P < 5 \cdot 10^{-10}$ Torr at room temperature. Additionally, of 2D-layer surface sodium was deposited by equal portions. Spectra of core levels Au 4*f*, W 4*f*, Na 2*s* and Na 2*p* were registered. Full energy resolution was 50 meV. The spectra were reduced to the energy relative to the Fermi level E_F , whose position was determined by the low-energy decrease in the photoelectronic spectrum of the stainless steel substrate, with which the sample was in ohmic contact. For all spectra described below, the background was subtracted by the Shirley method. The atomically clean Na was deposited onto a clean surface of the sample from a standard source. Note that one Na monolayer is closely-packed layer of Na atoms. A probing

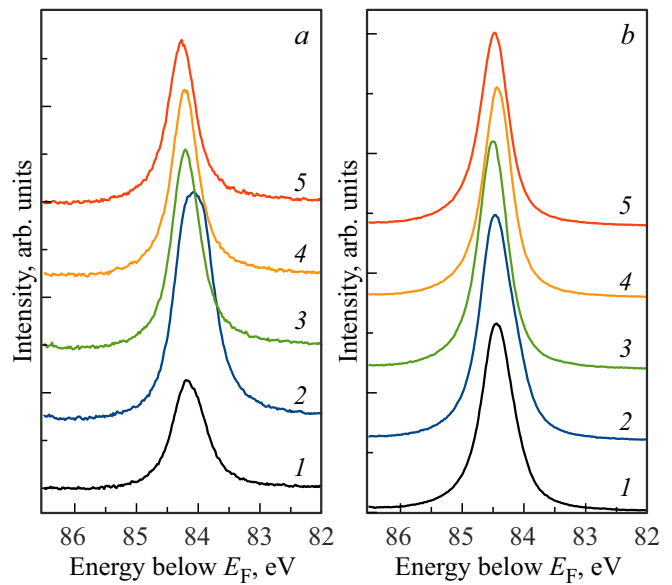


Figure 1. Spectra of normal photoemission of core level of Au $4f_{7/2}$ of studied sample at excitation energy $h\nu$, equal to a) 140 eV and b) 600 eV: curves 1 — prepared sample, 2 — after heating for 10 min at $T = 850$ K, 3 — after Na deposition for 2.5 min, 4 — after Na deposition for 5.0 min and 5 — after Na deposition for 7.5 min.

depth depends on the kinetic energy of photoelectrons: the more the kinetic energy of photoelectrons, the more the photoelectron escape depth. It should be noted that the main contribution to the photoemission at $h\nu = 80$ eV is made by photoelectrons from the sub-surface region, contribution to the photoelectron photoemission from the sample depth increases with the excitation energy growth compared with the photoelectrons escaping from the sample surface.

3. Results and discussion

Figure 1 provides spectra of core level of Au $4f_{7/2}$ of studied sample at excitation energy 140 and 600 eV. Peak at $h\nu = 140$ eV has larger contribution from surface and near-surface region than at $h\nu = 600$ eV. Peak shape is asymmetrical with bias towards lower bond energies. This peak shape is typical for metals and is associated with the excitation of electrons into a continuum of unoccupied states [22], however, currently there is no consensus on the nature of this effect [23–26]. The spectrum shape is properly described by the Doniach–Sunjic –function. Full width of peak at half-maximum is $\Gamma = 0.70$ eV for $h\nu = 140$ eV and $\Gamma = 0.72$ eV for $h\nu = 600$ eV. As shown in [27], gold deposition onto tungsten substrate with natural oxide results in the formation of gold nanoparticles having the shape of spheroid with a truncated lower part. Let's evaluate averaged thickness of gold film of gold. For dependence of all photoelectrons yield from film with thickness of x the

following formula can be written:

$$N(x) = N_0(\lambda - \exp(-x/\lambda))/\lambda, \quad (1)$$

where $N(x)$ — number of registered photoelectrons, N_0 — number of photoelectrons yielding infinitely thick sample, λ — mean free path of electron in solid body. At gathering depth 4.5λ the yield of electrons is 99%. At kinetic energy of photoelectrons 570 eV for gold $\lambda = 0.93$ nm [28]. As in spectra of prepared surface at excitation energy $h\nu = 600$ eV no peak was observed corresponding to W $4f_{7/2}$, having bond energy 31.4 eV, we can assume that thickness of studied sample is obviously larger than 4.2 nm. For sample loaded in chamber signal from peak of Na $2s$ is not registered at excitation energy 150 and 300 eV, this indicates thickness of gold film above it 2.5 nm minimum.

Besides, after heating at $T = 850$ K for 10 min the gold film thickness decreases, this is indicated by registration of peak W $4f_{7/2}$ at excitation energy $h\nu = 600$ eV. It is impossible to evaluate accurately the averaged thickness of film, but registration of peak W $4f_{7/2}$ indicates that thickness of film Au/Na/Au became lower than 4.2 nm. After heating intensity of peak Au $4f_{7/2}$ increases at excitation energy 140 and 600 eV, area under peak (A) increases by 2.4 times for $h\nu = 140$ eV, and for $h\nu = 600$ eV A increases by 1.3 times (see Figure 1, curves 2). Such behavior can be explained by change in shape of gold nanoparticles. Heating leads to increase in the size of the nanoparticles and to a greater smoothness of the surface [21], as well as to decrease in their number and decrease in dips between gold nanoparticles. Recall that nanoparticles are better described by spheroids [27]. Therefore, total area of surface, from which photoemission can be observed, increases. Note that photoelectrons at normal to surface of sample holder are registered, i.e. at normal to surface of tungsten substrate. Photoelectrons in center of ellipsoid fly out at normal to the ellipsoid surface, and upon approaching the edge of ellipsoid the photoelectrons fly out at angle to the ellipsoid surface. Therefore, they need to run over larger distance, and their yield will lower, because λ is replaced by $\lambda \cos(\alpha)$, where α — angle of fly out relative to normal to ellipsoid surface. So, number of flying out photoelectrons for small nanoparticle will be lower than in case of large nanoparticles. Note that contribution of surface to general signal for $h\nu = 140$ eV is larger than for $h\nu = 600$ eV. Peak width Γ is 0.76 eV for $h\nu = 140$ eV and 0.74 eV for $h\nu = 600$ eV.

Sodium deposition for 2.5 min leads to changes in spectrum Au $4f_{7/2}$ (Figure 1, curves 3). Area under peak Au $4f_{7/2}$ decreases by 0.67 and 0.88 times for $h\nu = 140$ and 600 eV, respectively. You can evaluate the nominal thickness of deposited sodium layer by decrease in area of peak Au $4f_{7/2}$ for $h\nu = 140$ eV, which is 0.22 nm. Peak width Γ decreases to 0.62 eV for $h\nu = 140$ eV and 0.64 eV for $h\nu = 600$ eV.

Next sodium deposition for 2.5 min leads to further changes in spectrum Au $4f_{7/2}$ (Figure 1, curves 4).

Area under peak Au $4f_{7/2}$ decreases by 10% both for $h\nu = 140$ eV, and for $h\nu = 600$ eV. Peak width increases to 0.70 eV for $h\nu = 140$ eV and remains unchanged ($\Gamma = 0.64$ eV) for $h\nu = 600$ eV.

Next sodium deposition for 2.5 min leads to insignificant changes in spectrum Au $4f_{7/2}$ (Figure 1, curves 5). Area under peak Au $4f_{7/2}$ decreases by 6 and 8% for $h\nu = 140$ and 600 eV, respectively. Peak width Γ decreases to 0.62 eV for $h\nu = 140$ eV and 0.76 eV for $h\nu = 600$ eV.

Gold film heating leads not only to abrupt disappearance of gold atoms, but also to occurrence in spectrum of peaks of core states of sodium atoms. Behavior of peak Na $2p$ at excitation energies 120, 300 and 600 eV is not considered, because the peak is located near the peak W $4f$, this makes difficult data interpretation. Pay attention to spectra of core states Na $2p$ (Figure 2) and Na $2s$ (Figure 3) at excitation energies 80 and 150 eV respectively. Note that peak Na $2s$ is not observed at excitation energy 300 eV, and background spectrum is not shown in Figure 4. Note that excitation section of peak Na $2s$ at $h\nu = 300$ eV is by order of magnitude lower than at $h\nu = 80$ and 150 eV. As in previous paper [29], the observed peak Na $2s$ can be divided to two: Na⁰ and Na⁺. Peak Na⁰ is associated with film of adsorbed sodium on surface, peak of ion Na⁺ is associated with formation of compound Na_xAu_y as result of diffusion of sodium atom deep into the gold film with further reaction of sodium atoms and gold. With a decrease in the kinetic energy of photoelectrons, the depth of the probed region decreases and the contribution from the surface layer increases. Areas under peaks Na⁰ (A^0) and Na⁺ (A^+) for core level Na $2p$ at excitation energy $h\nu = 80$ eV are approximately equal, and for core level Na $2s$ at excitation energy $h\nu = 150$ eV area under peak Na⁰ is almost by two times higher than under peak Na⁺. This means that sodium mainly concentrates on surface. We can approximately evaluate the sodium coverage by ratio of areas under peaks Na⁰ and W⁰ $4f$ for excitation energy $h\nu = 120$ eV as per available data obtained in paper [29], it is approximately equal to 0.3–0.4 ML.

Sodium deposition for 2.5 min leads to changes in photoemission spectra (see Figure 2, *b*, 3, *b* and 4, *a*). Intensity of peak Na $2p$ at excitation energy 80 eV increased by 5 times, and of peak Na $2s$ at excitation energy 150 eV it increased by 3.5 times. Also we began registration of peak Na $2s$ at excitation energy 300 eV.

Ratio of areas $A^0 : A^+$ for $h\nu = 80$ eV decreased to ratio 2 : 3, ratio of areas $A^0 : A^+$ for $h\nu = 150$ eV increased to ratio 3 : 4, and ratio of areas $A^0 : A^+$ for $h\nu = 300$ eV is 2 : 3. Rise of peak Na⁰ for $h\nu = 80$ eV by 3.5 times and rise of peak Na⁺ by 6 times indicate that sodium film is adsorbed on the formed 2D-layer Na_xAu_y, which is created as result of diffusion of sodium atoms in depth of gold film with further reaction of sodium atoms and gold. We can evaluate thickness of the adsorbed Na film, which is equal to about 1.0–1.4 ML. Recall that thickness of sodium film calculated by decrease in peak Au $4f_{7/2}$, is 0.22 nm. If we suppose that sodium is in covalent state in film (covalent

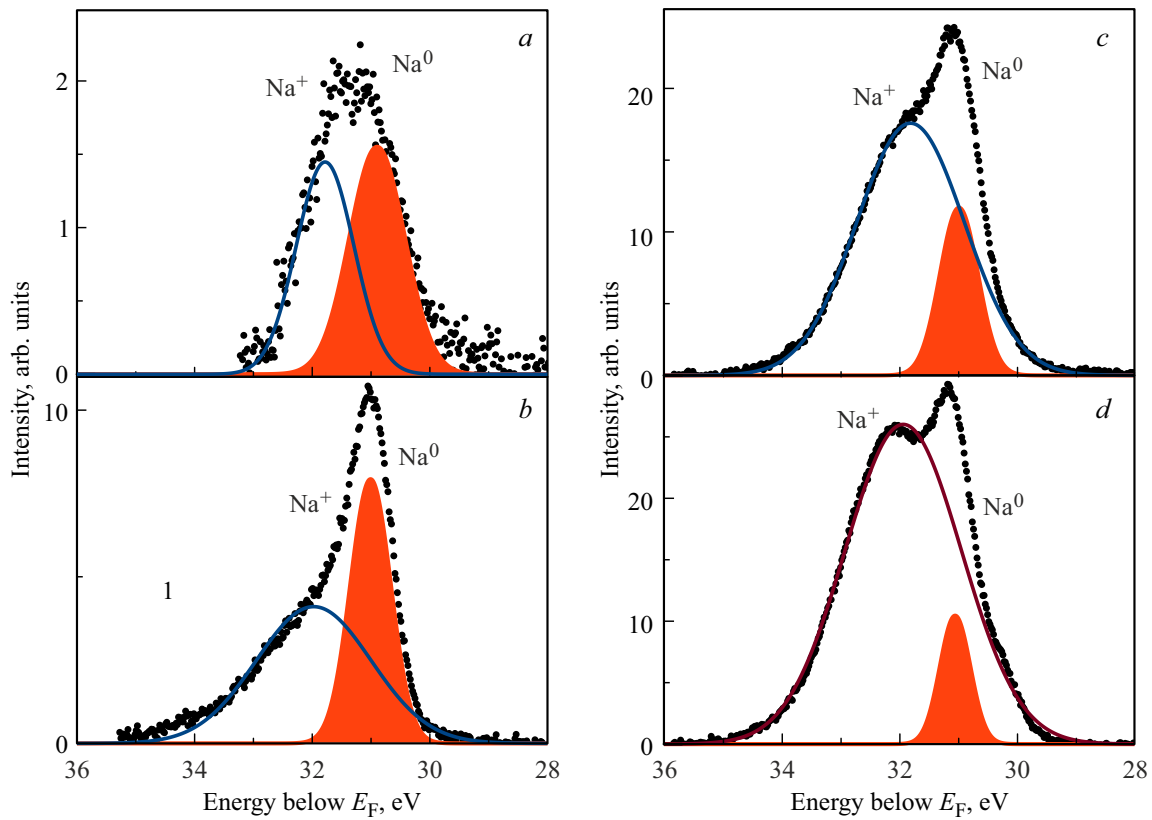


Figure 2. Analysis of photoemission spectra of core levels Na $2p$ a) after heating at $T = 850$ K for 10 min, b) after Na deposition for 2.5 min, c) after Na deposition for 5.0 min and d) after Na deposition for 7.5 min, at excitation energy $h\nu = 80$ eV. Dots indicate the experimental spectrum, bold solid lines — contribution of states Na^0 and Na^+ .

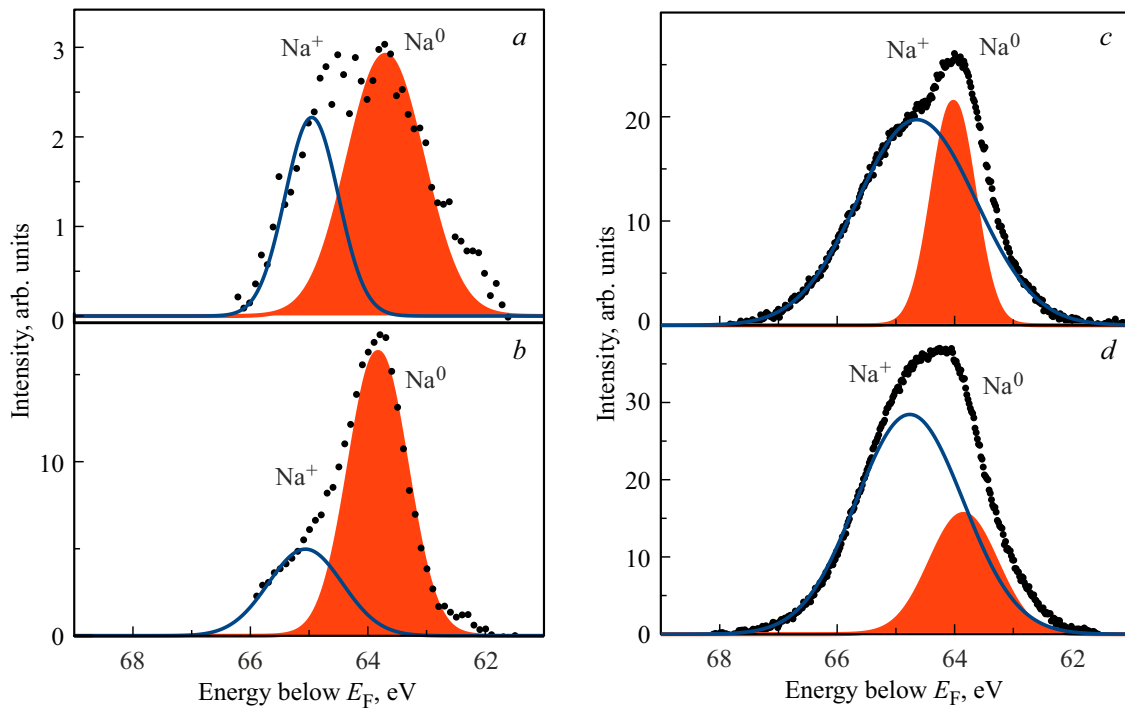


Figure 3. Analysis of photoemission spectra of core levels Na $2s$ a) after heating at $T = 850$ K for 10 min, b) after Na deposition for 2.5 min, c) after Na deposition for 5.0 min and d) after Na deposition for 7.5 min, at excitation energy $h\nu = 150$ eV. Dots indicate the experimental spectrum, bold solid lines — contribution of states Na^0 and Na^+ .

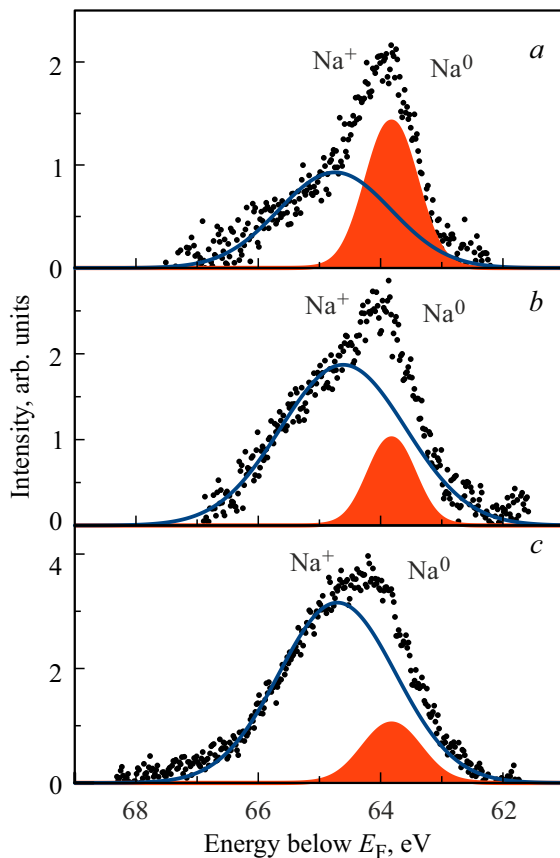


Figure 4. Analysis of photoemission spectra of core levels Na 2s *a*) after Na deposition for 2.5 min, *b*) after Na deposition for 5.0 min and *c*) after Na deposition for 7.5 min, at excitation energy $h\nu = 300$ eV. Dots indicate the experimental spectrum, bold solid lines — contribution of states Na^0 and Na^+ .

radius is 0.15 nm), then for 2.5 min 0.7 ML was deposited, and this rather well coincides with the above evaluation. Since the probing depth increases with excitation energy increasing, the contribution from the surface decreases, therefore the observed dependence of growth A^+ indicates effective diffusion of sodium atoms in the gold film with formation of intermetallic compound Na_xAu_y .

Next sodium deposition for 2.5 min (total time — 5 min) increases deposition dose of sodium by two times (see Figure 2, *c*, 3, *c* and 4, *b*). Intensity of peak Na 2*p* at excitation energy 80 eV increased by 3 times, and of peak Na 2*s* at excitation energy 150 eV increased by 2.6 times. Peak Na 2*s* at excitation energy 300 eV increased by 1.5 times. Ratio of areas $A^0:A^+$ for $h\nu = 80$ eV decreased to ratio 1:4, for $h\nu = 150$ eV decreased to ratio 1:3, and for $h\nu = 300$ eV — to 1:5. All this indicates that the contribution from the surface, where the adsorbed sodium layer is localized, decreases, and the thickness of the formed 2D layer Na_xAu_y continues to increase. Rise of peak Na^0 for $h\nu = 80$ eV by 1.5 times ensures evaluation of thickness of adsorbed Na film, which is approximately equal to 1.5–2.1 ML. Thickness increasing

of formed 2D-layer Na_xAu_y is confirmed by rise of peak Na^+ for $h\nu = 150$ eV by 6 times and rise of peak Na^+ for $h\nu = 300$ eV by 2.2 times.

Next sodium deposition for 2.5 min (total time — 7.5 min) increases total deposition dose of sodium by three times (see Figure 2, *d*, 3, *d* and 4, *c*). Intensity of peak Na 2*p* at excitation energy 80 eV increased by 1.4 times, and of peak Na 2*s* at excitation energy 150 eV increased by 1.45 times. Peak Na 2*s* at excitation energy 300 eV increased by 1.5 times. Ratio of areas $A^0:A^+$ for $h\nu = 80$ eV decreased to ratio 1:10, ratio of areas $A^0:A^+$ for $h\nu = 150$ eV was kept equal to 1:3, and ratio of areas $A^0:A^+$ for $h\nu = 300$ eV is 1:6. Therefore, the contribution from the surface, where the adsorbed sodium layer is localized, decreases, and the thickness of the formed 2D layer Na_xAu_y continues to increase. Decreasing of peak Na^0 for $h\nu = 80$ eV by 1.4 times ensures evaluation of thickness of adsorbed Na film, which is approximately equal to 1.0–1.4 ML. This behavior indicates that the thickness of the adsorbed sodium film tends to monolayer, and all deposited sodium goes for the formation of 2D layer Na_xAu_y . Thickness increasing of formed layer Na_xAu_y is confirmed by rise of peak Na^+ for $h\nu = 150$ eV and for $h\nu = 300$ eV by 1.6 times. Deceleration of rise of peak Na^+ for $h\nu = 150$ eV indicates that thickness of 2D-layer Na_xAu_y is close to probing depth in our experiment.

4. Conclusions

Adsorption of sodium atoms on the preliminary deposited gold film, comprising nanoparticles, on tungsten surface with natural oxide layer is studied. It is shown that gold film heating at temperature $T = 850$ K leads to desorption of gold atoms and increase in surface area. The sodium atoms deposition leads to the formation of adsorbed layer of sodium atoms, and due to the ongoing diffusion of sodium atoms into the gold substrate, 2D-layer Na_xAu_y is formed. Two states of the sodium atoms were found: Na^0 , associated with sodium states in adsorbed Na layer, and Na^+ , associated with sodium states in intermetallic compound Na_xAu_y .

Conflict of interest

The authors declare that they have no conflict of interest.

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