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Effect of Sodium Atom Adsorption on the Electronic Structure of a Gold Film

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The electronic structure of a gold film deposited on W was studied during the adsorption of sodium atoms. An analysis of the photoemission spectra from the valence band and core levels of Au $4f$ and Na $2p$ upon synchrotron excitation in the photon energy range of 80–600 eV showed that Na adsorption leads to the formation of $\mathrm{Na}_x\mathrm{Au}_y$ intermetallic compounds of various stoichiometry under the Na monolayer.

Keywords: adsorption, sodium, gold, intermetallic compound.

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Compounds of two metals form intermetallic compounds, the properties of which may differ from those of the parent metals. For example, the CsAu compound is a wide-band-gap semiconductor [1]. Besides, it was shown that 2D layers of alkali metal (AM) intermetallides with Au can also form ionic semiconductor compounds, in particular, $\mathrm{Na}_x\mathrm{Au}_y$, which are currently receiving more attention, than the rest of the AM–Au intermetallic compounds (see, for example, [2–5]). In intermetallic compounds of AM–Au, gold acts in the unusual role of an anion rather than a cation, as in most compounds [6]. The formation of AM–Au intermetallides during deposition of AM atoms on the Au surface occurs in two stages. At the first stage, during the deposition of submonolayer coatings of AM, no diffusion of AM atoms into Au occurs and, therefore, no intermetallide is formed. At the second stage, when a dose of AM atoms is deposited on more than one monolayer, the diffusion of AM atoms in Au occurs with the formation of AM–Au intermetallide, while the monolayer of AM atoms remains on the surface.

The purpose of this paper is to determine the possibility of formation of the $\mathrm{Na}_x\mathrm{Au}_y$ intermetallic compound during the deposition of sodium atoms on the gold surface and to reveal the accompanying changes in the electronic structure.

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 within the photon energy range of 80–600 eV. Photoelectrons along the surface normal were recorded, an exciting beam fell on a sample surface at the angle of 45°. Studies of the gold film deposited on tungsten before and after sodium deposition were carried out *in situ* in vacuum ($P < 5 \cdot 10^{-10}$ Torr) at room temperature. The photoemission spectra were recorded within the valence band range, and spectra of the Au $4f$, W $4f$ and Na $2p$ core levels were also recorded. The full energy resolution was 50 meV. For all the below spectra the background was subtracted as per the Shirley method.

An Au film 2.7 nm thick was deposited on the surface of polycrystalline W; the film thickness was determined from the suppression of the peak W $4f$ by the Au film, taking into account the known value of the photoelectron escape depth of 1.9 nm with a kinetic energy of 580 eV [7,8]. The photoelectron spectra of the valence band of the gold film at excitation energies $h\nu = 80$, 120 and 600 eV (Fig. 1) coincide with the well-known spectra of the valence band (see, for example, [9]). The spectrum of the valence band contains two characteristic peaks with binding energies of 3.3 and 6.6 eV below the Fermi level (E_F). There is insignificant amount of natural oxide on the W surface, which is clearly seen from the spectrum of the core level of the W $4f$ doublet for the excitation energy $h\nu = 120$ eV (Fig. 2, *a*). The same Figure shows experimental spectrum decomposition by pairs of the Gaussian function with spectrum splitting of 2.2 eV and an intensity ratio of 4:3. The W^0 peak is clearly visible at the binding energy $E_b = 31.5$ eV relative to the Fermi level (E_F). The peaks at $E_b = 32.27$ and 35.67 eV can be attributed to the states W^{4+} and W^{6+}, respectively, which coincides with the results of papers [10,11]. For $h\nu = 600$ eV, only the W^0 states are observed in the spectrum of the core level of the W $4f$ doublet. This is due to the fact that the greater the kinetic energy (E_{kin}) of the emitted electrons is, the greater the depth of their emit is, and the smaller is the contribution of the surface to the photoemission signal.

The deposition of a sodium coating leads to a change in both the spectrum of the valence band and the spectrum of the core states of the substrate. Fig. 2 shows the spectrum of core states of the doublet W $4f$ and Na $2p$. The Na $2p$ peak, in contrast to the symmetric peaks of the W $4f_{5/2}$ and $4f_{7/2}$

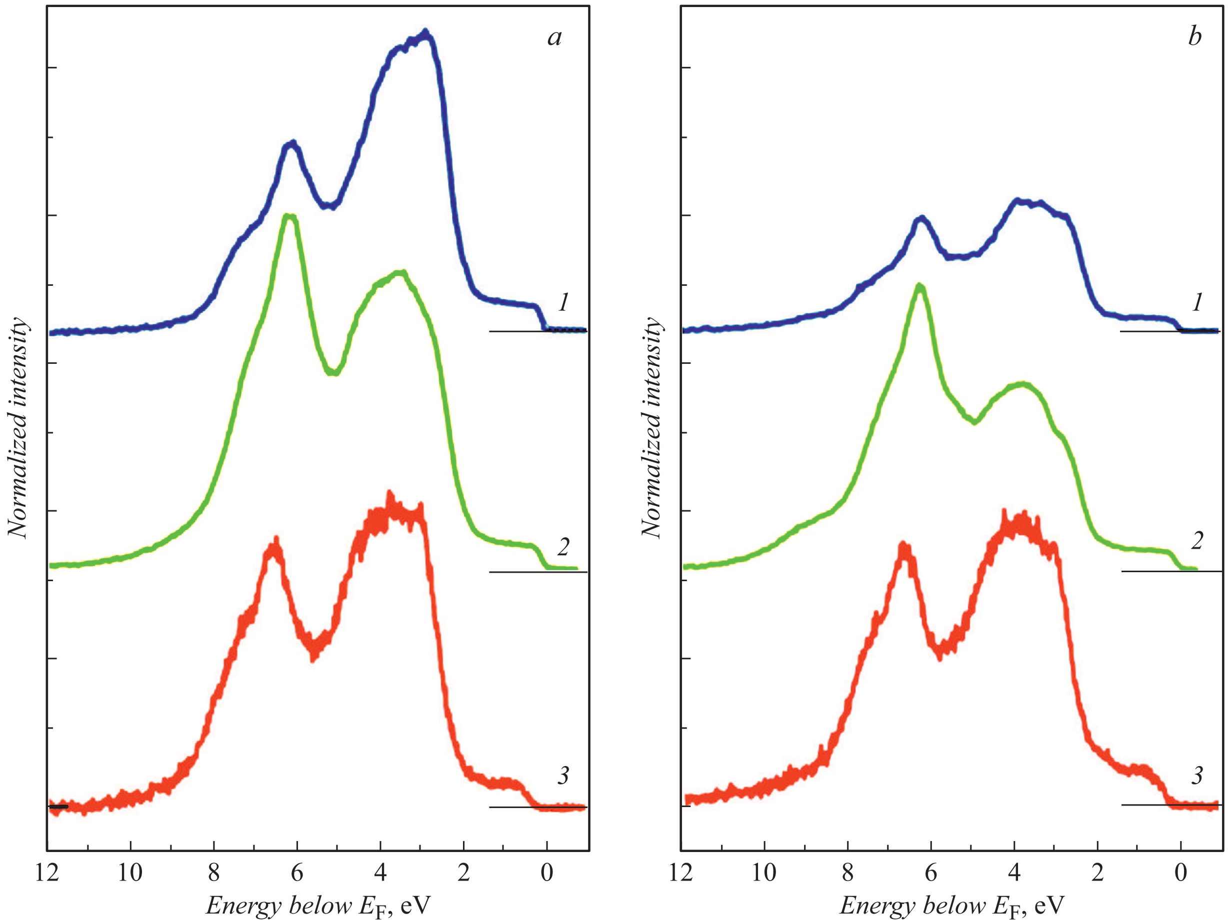

Figure 1. Photoemission spectra in the valence band region for the surface of gold deposited on W before (*a*) and after (*b*) sodium deposition at excitation energies $h\nu = 80$ (*1*), 120 (*2*) and 600 eV (*3*). The spectra are normalized to the intensity of the peak from $E_b = 3.8$ eV before Na deposition.

doublets, has asymmetric shape with a tail towards higher binding energies. The Na $2p$ peak can be decomposed into two peaks: narrow with $E_b = 30.9$ eV and wide with $E_b = 31.8$ eV relatively to E_F. The first peak is associated with the states of Na^0, and the second — with the states of Na^+, which coincides with previously published results (see, for example, [12,13]). Note that for $h\nu = 80$ eV, the W $4f$ peaks are not visible in the spectrum, which reflects the escape of photoelectrons from the surface and near-surface region. The excitation energy increasing up to $h\nu = 300$ eV leads to decrease in the Na $2p$ contribution and increase in the W $4f$ contribution to the photoemission signal. The area ratio of peaks Na^0 to Na^+ is 1.0 for $h\nu = 80$ eV, 1.1 for $h\nu = 120$ eV and 4.4 for $h\nu = 300$ eV. This behavior indicates the Na^+ proportion decreasing with distance from the surface and, accordingly, the intermetallide formation in the Na−Au interface. It follows from the obtained results that on the gold surface there is an adsorbed monolayer of neutral Na atoms and Na atoms diffused into the gold film, which, after reaction with gold atoms, form the Na_xAu_y intermetallide (as was obtained earlier in [3]), where the Na atoms are in the ionic state. This intermetallide is mainly localized under a monolayer of Na atoms. Na^0 proportion increasing compared to Na^+ far from the surface may indicate the formation of Na_xAu_y metallic intermetallides with a higher content of Na atoms compared to Au content, i. e. with $x \gg y$. The fact that the interaction of Na atoms with Au occurs in the near-surface region is also indicated by the invariance of the Au $4f_{5/2}$ and $4f_{7/2}$ peaks at an excitation energy of $h\nu = 600$ eV.

The spectra of the valence band at excitation energy of $h\nu = 80$, 120 and 600 eV after the Na atoms deposition are shown in Fig. 1, *b* and confirm the above conclusions. The spectrum of the valence band at the excitation energy $h\nu = 600$ eV remains unchanged, which indicates that there is no change in the valence band through the depth of the sample. Thus, for $E_{kin} \sim 590-600$ eV the contribution of photoelectrons from the surface is insignificant. The most significant changes in the valence band occur at the excitation energy $h\nu = 80$ eV: the peak with $E_b = 6.1$ eV decreases 1.8 times, and the peak with $E_b = 3.8$ eV decreases by a factor of 3.5. At $E_{kin} \sim 70-80$ eV the contribution of photoelectrons from the surface and near-surface region dominates in the spectrum, but the contribution to the

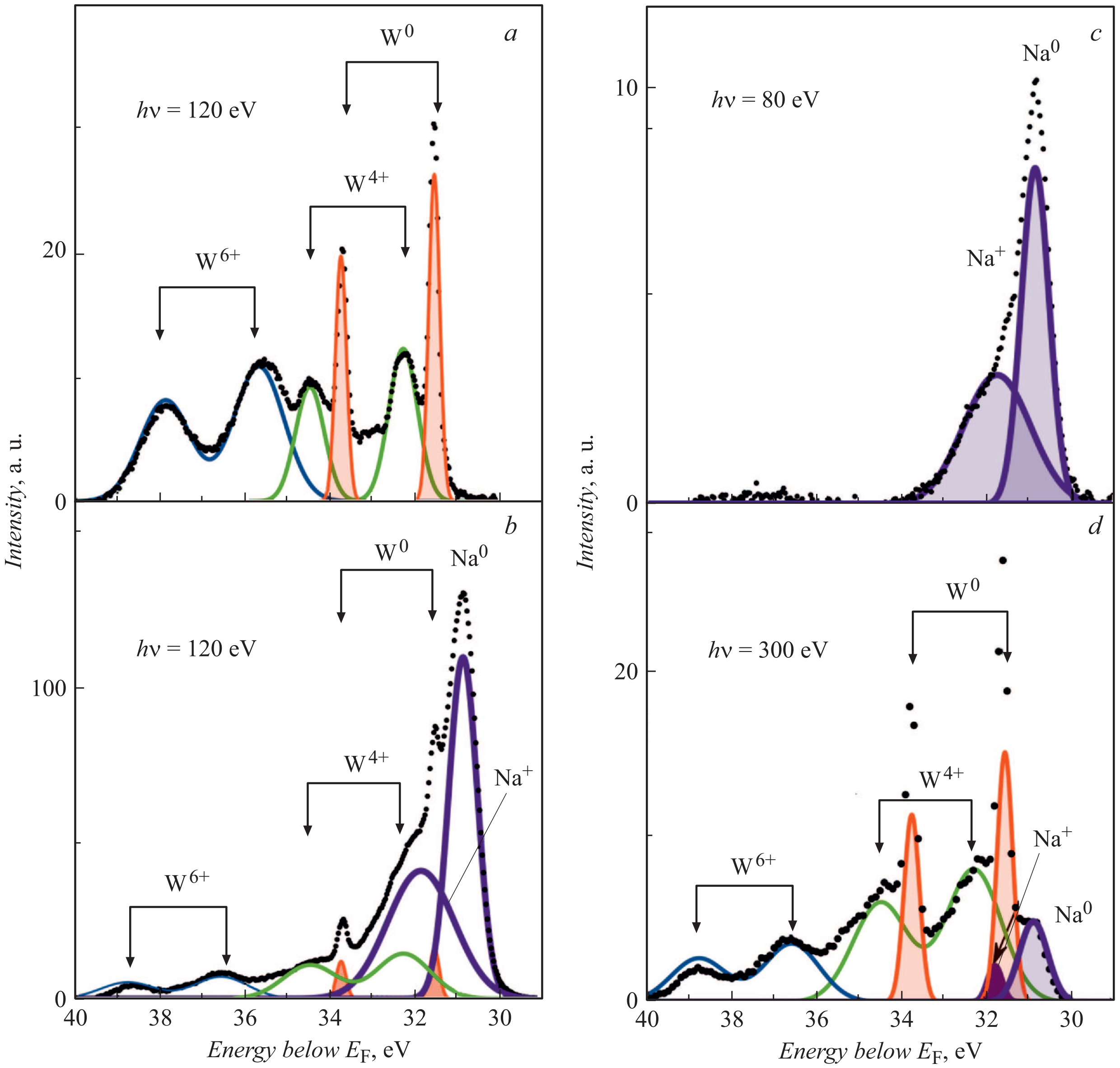

Figure 2. Analysis of the photoemission spectra of the core levels of W $4f$ and Na $2p$ for the surface of gold deposited on tungsten before (a) and after ($b-d$) sodium deposition at excitation energies $h\nu = 120$ (a, b), 80 (c) and 300 eV (d). The dots show the experimental spectra, the contributions of the W^{6+} and W^{4+} states are represented by blue and green lines, respectively, the contribution of the W^0 state - by red lines, and regions (a, b, d), states of Na $2p$ are shown by purple lines ($b-d$) and regions (c, d). Colored version of the Figure is presented in electronic version of the article.

electron density of valence states of the Na monolayer is small compared to the contribution from the near-surface Na$_x$Au$_y$ layer, whose valence band is formed mainly by Au $5d$ electrons [14]. Similar results were obtained in calculations by the density functional theory method, for example, for adsorbed Cs monolayer on Mo(001) [15]. The spectrum of the valence band at the excitation energy $h\nu = 120$ eV changes its shape, the peak with $E_b = 6.1$ eV decreases by 15%, and the peak with $E_b = 3.8$ eV decreases by 1.6 times. This behavior is due to the fact that at $E_{kin} \sim 110-120$ eV the contribution from the surface becomes smaller than that from the near-surface region, but the contribution from the depth of the sample is also small. Thus, the comparison of previously obtained data on the formation of various intermetallides from Cs$_x$Au$_y$ to Li$_x$Au$_y$ [3,16–18] during the deposition of AM atoms on the Au surface, together with the calculations of the NaAu [14] valence band with the experimental data obtained in this work, allows us to conclude that after the Na atoms deposition on the Au surface, the monolayer of Na atoms is formed, under which Na$_x$Au$_y$ intermetallides of various stoichiometry are formed.

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Conflict of interest

The authors declare that they have no conflict of interest.

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