Electron-stimulated desorption of potassium atoms from a potassium layer adsorbed on a tungsten covered with a gold film

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Abstract. For the first time, electron-stimulated desorption (ESD) of K atoms from the K layer adsorbed on W covered with an Au film was detected and recorded, and the ESD yield was measured by a direct method depending on the electron energy, concentration K, and the thickness of the Au film. A model is proposed that explains the processes of ESD of potassium atoms from the surface.

1. Introduction

Studies of gold-alkali metal intermetallic compounds were started in the middle of the last century [1]. In compounds of alkali metal atoms with gold, gold plays an unexpected role for it as an anion [2], while in the vast majority of compounds gold is a cation. The interest in alkali-gold compounds is associated with the rapid growth of gold chemistry [2], the use of gold nanoparticles in various fields from catalysis [3-4] and medicine [5,6] to the creation of various sensors and detectors [7, 8]. Potassium, as is known, is a promoter of many chemical reactions and, therefore, interest in studying the interaction of K atoms with both gold and gold nanoparticles is understandable.

Adsorption of potassium atoms on Au has been well studied by various surface research methods: low electron diffraction, photoelectron spectroscopy, electron energy loss spectroscopy, scanning tunneling microscopy, etc. [9-14]. Compounds K₉Au₉ are semiconductors [15].

The process of forming a gold-alkali metal compound consists of two stages: at the first stage, alkali metal atoms are adsorbed on the surface of the substrate, and at the second stage, which begins after the formation of one monolayer of alkali metal atoms, alkali atom diffusion occurs on the substrate when an excess of alkali metal atoms is deposited metal deep into the gold substrate with the formation under the monolayer of alkali metal adatoms compounds. Note that the Au layer closest to W does not take part in the formation of the alkali-Au compound, and as a result, a three-layer coating of monolayer of alkali metal/alkali-Au compound/Au/W is obtained on the surface W [16].

The aim of this work was to consider in detail the processes that occur during electron irradiation of the K/K₉Au/Au/W system, and on this basis to propose a model of the electron-stimulated desorption (ESD) of K atoms in this system.
2. Experimental setup

The studies proposed in this work were carried out in an ultrahigh-vacuum setup "ESD Spectrometer", the experimental design and sample structure are shown in figure 1. The residual gas pressure in the setup did not exceed $5 \times 10^{-10}$ Torr. Textured ribbons were used as a substrate for the samples under study, which were purified by heating at 1800 K in an oxygen atmosphere at a pressure of $1 \times 10^{-6}$ Torr for 3 hours. Gold was deposited onto the ribbon at 300 K from a directly filament tungsten tube into which 99.99% pure gold foil pieces were placed, and potassium was deposited onto the ribbon also from K from a directly heated evaporator by thermal decomposition of potassium chromates. The K concentration on the surface of the ribbon was determined by the time of deposition by a constant flow, the intensity of which was measured by the surface ionization current on the ribbon, and amounted to $0.5 \times 10^{15}$ atom/cm$^2$ in the monolayer of atoms. The concentration of deposited gold was determined by the time of deposition and amounted to $3 \times 10^{15}$ atom/cm$^2$ in the monolayer of atoms. The temperature of the sample could vary in the range from 160 K to 600 K.

![Figure 1. a. Scheme of the experiment: 1 — sample, 2 — source of electrons, 3 and 4 — evaporators Au and K, 5 — ion collector, 6 — ion-retaining electrode, 7 — ion collector, 8 — surface ionization ribbon. b. Scheme of K/KxAu\textsubscript{y}/Au/W system.](image)

3. Results and discussion

As mentioned above, when coverage of less than one alkali metal monolayer, the formation of an alkali metal-gold intermetallic compounds does not occur. Prior to the deposition of potassium atoms, a gold film two monolayer thick was deposited on the surface of tungsten. Figure 2a shows that ESD of potassium atoms is not observed when a potassium coverage of less than one monolayer. A similar behavior was observed when deposition cesium atoms on gold [17]. As soon as the dose of deposition of potassium atoms became more than one monolayer, it became possible to register ESD of potassium atoms, which indicates the formation of the K$_x$Au$_y$ intermetallic compounds under a monolayer potassium film, and the registration of ESD of potassium atoms indicates that the formed K$_x$Au$_y$ compound is a semiconductor. It is known that ESD is observed only on non-metallic surfaces, i.e. on semiconductor or dielectric [18]. On the metal surface, the lifetime of the excited state of the adatom-surface bond is small, since the excitation is very quickly quenched due to the escape of the excited electron into the conduction band, and therefore there is no ESD on metals. A semiconductor (dielectric) layer on the metal surface significantly increases the excitation lifetime, and ESD yield is then observed. With an increase in the dose of deposited potassium, a linear increase in the yield of ESD ($q$) of potassium atoms occurs. An increase in the yield occurs up to a dose of deposited potassium equal to 2 monolayers. Further deposition of potassium atoms does not increase the yield $q$. That is, the formation of an intermetallic compounds, but already by a deficit of gold atoms. It could be assumed that when a potassium atom is deposited at a dose of 2 monolayers, a KAu compound is
formed, and when three monolayers of potassium atoms are deposited, a K$_2$Au compound is formed. It should be noted that the gold monolayer closest to tungsten does not take part in the formation of the intermetallic compounds.

**Figure 2.** (a) The yield $q$ of K atoms upon ESD from tungsten coated with two gold monolayers at $T = 300$ K depending on the concentration of adsorbed potassium $n_K$ for the energy of the bombarding electrons 64 eV. (b) The yield of $q$ potassium atoms upon ESD from tungsten coated with gold at $T = 300$ K depending on the time of gold deposition for three potassium concentrations $n_K$: $0.75 \cdot 10^{15}$ atom/cm$^2$ and $1.0 \cdot 10^{15}$ atom/cm$^2$. The energy of the bombarding electrons is 64 eV.

In the next experiment, different amounts of gold atoms were deposited: no more than 5 monolayers. For each gold coverage 3 doses of potassium atoms were deposited, corresponding to deposition of 1.0, 1.5, and 2.0 monolayers. It is expected that during the deposition of one monolayer film of potassium atoms, ESD of potassium atoms was not observed at any thickness of the gold film. Figure 2b shows how the yield of ESD of potassium atoms changes from the thickness of a previously deposited gold film. As soon as the thickness of the gold film is more than one monolayer, it becomes immediately possible to register ESD of potassium atoms. As the thickness of the gold film increases, the ESD yield of potassium atoms increases linearly to a dose of deposited potassium, which is equal to the thickness of the gold film for deposited potassium 1.5 monolayer and 0.9 to the thickness of the gold film for deposited potassium 2.0 monolayer.

**Figure 3.** The output of K atoms upon ESD from tungsten coated with two gold monolayers and two potassium monolayers at $T = 300$ K depending on the energy of the bombarding electrons.

The maximum ESD yield of potassium atoms is observed at a gold layer thickness of 2 monolayers for both studied doses of deposition of potassium atoms. It can be assumed that KAu$_2$ compounds are
formed for deposition 1.5 potassium monolayer and KAu for deposition 2.0 monolayer K. Further deposition of potassium atoms leads to a decrease in ESD yield of potassium atoms of 10 and 20% for potassium deposition doses of 1.5 and 2.0 monolayer, respectively.

The decrease in the ESD yield of potassium atoms can be explained by the beginning of the formation of gold nanoparticles on the surface of tungsten, i.e. the film grows according to the Stranski-Krastanov growth after depositions of 2 monolayers of gold. The non-smoothness of the surface of the studied sample can lead to a decrease in the surface irradiated by electrons, since the angle of incidence of electrons on the surface is 45 degrees. Also, different cross sections for the excitation of the ESD process for different stoichiometries of the formed intermetallic compounds can play a decrease in the yield of ESD of potassium atoms.

Figure 3 shows the “resonance” dependence of the ESD potassium yield on the energy of bombarding electrons measured at $T = 300$ K from the surface W coated with two Au monolayers for potassium deposited at $T = 300$ K. There are 2 peaks with maxima at 64 eV and 82 eV. These peaks are associated with the excitation of the core levels of Au $5p_{3/2}$ and Au $5p_{1/2}$ by bombarding electrons.

To explain the ESD process of potassium atoms in the K/K$_x$Au$_y$/Au/W system, we use the ideas proposed earlier in [17].

**Figure 4.** Scheme of ESD processes in the K monolayer/ K$_x$Au$_y}$/Au monolayer/ Wsubstrate. $E_{\text{VBM}}$ is the energy corresponding to the maximum of the valence band.

Figure 4 shows a scheme of the processes occurring in the electronic structure of the K/K$_x$Au$_y$/Au/W system. Electron irradiation of the sample leads to the excitation of an electron from the core level of Au $5p$ (1) to the local state $E_L$ near the bottom of the $E_{\text{CBM}}$ conduction band, which has dropped from the conduction band in the field of the formed core Au $5p^+$ hole into the band gap of the K$_x$Au$_y$ semiconductor. It is the excitation of an electron from Au $5p$ states by electron irradiation of the system into the conduction band that leads to the formation of a “quasiresonant” peak in Fig. 3. After this, the Au $5p^+$ hole is neutralized by electrons from the valence band of the intermetallic
compound (2) or from the K 3s level (3), which is accompanied by Auger processes, which include filling K 3s holes (4) that appeared in the electronic structure of the sample and excitation of the valence band electrons in vacuum (5) or into the conduction band (6) due to the released energy. Since the local state is located near the $E_{CBM}$ (for the Cs/CsAu system, it is located 50 meV lower [19]), the electron can be easily trapped in the conduction band (7). An electron from the conduction band is captured (8) by an adsorbed K atom with the formation of a neutral K$^0$ atom in the K monolayer. The K$^0$ atom formed in this case increases in volume and desorbed from the K monolayer on the surface. It should be noted that during the ESD of potassium atoms, the adsorbed layer of K atoms and the nearest K$_x$Au$_y$ layer are associated with electronic transitions in the interface region.

4. Conclusion
ESD of K atoms was found in the K/K$_x$Au$_y$/Au/W system, which indicates that K$_x$Au$_y$ is a semiconductor. An analysis of the concentration dependences on the amount of deposited K and Au suggests the formation of KAu in the case of deposition of 2 gold monolayers with further transformations in K$_2$Au by an increase in the amount of deposited K. A quasi-resonant dependence of the ESD of K atoms on the energy of exciting electrons is observed, associated with the excitation of core levels of Au 5p$_{3/2}$ and Au 5p$_{1/2}$. A model of the processes occurring in the K/K$_x$Au$_y$/Au/W system is proposed. The ESD process captures atoms located in the adsorbed layer of K atoms and the nearest K$_x$Au$_y$ layer.

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