

Conference materials

UDC 538.971

DOI: <https://doi.org/10.18721/JPM.161.168>

Electron-stimulated desorption of lithium and potassium atoms in the adsorption of lithium and potassium atoms on gold

I.A. Gromov, T.E. Kuleshova, Yu.A. Kuznetsov, M.N. Lapushkin , N.S. Samsonova

Ioffe institute, St.Petersburg, Russia

 lapushkin@ms.ioffe.ru

Abstract. The electron-stimulated desorption of lithium and potassium atoms from Li_xAu_y and K_xAu_y layers on the surface of gold adsorbed on W(100) has been studied. The yield of electron-stimulated desorption of Li and K atoms was measured by a direct method as a function of the electron energy, the concentration of Li and K atoms, and the thickness of the Au film. The formation of semiconductor intermetallic compounds Li_xAu_y and K_xAu_y is considered.

Keywords: electron-stimulated desorption, intermetallic, 2D-layers

Funding: This study was funded by RFBR grant number 20-02-00370.

Citation: Gromov I.A., Kuleshova T.E., Kuznetsov Yu.A., Lapushkin M.N., Samsonova N.S., Electron-stimulated desorption of lithium and potassium atoms in the adsorption of lithium and potassium atoms on gold, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (1.1) (2023) 398–403. DOI: <https://doi.org/10.18721/JPM.161.168>

This is an open access article under the CC BY-NC 4.0 license (<https://creativecommons.org/licenses/by-nc/4.0/>)

Материалы конференции

УДК 538.971

DOI: <https://doi.org/10.18721/JPM.161.168>

Электронно-стимулированная десорбция атомов лития и калия при адсорбции атомов лития и калия на золото

И.А. Громов, Т.Э. Кулешова, Ю.А. Кузнецов, М.Н. Лапушкин , Н.С. Самсонова

Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия

 lapushkin@ms.ioffe.ru

Аннотация. Исследована электронно-стимулированная десорбция атомов лития и калия из слоев Li_xAu_y и K_xAu_y на поверхности золота, адсорбированного на W(100). Выход электронно-стимулированной десорбции атомов Li и K измерялся прямым методом в зависимости от энергии электронов, концентрации атомов Li и K и толщины пленки Au. Рассмотрено образование полупроводниковых интерметаллидов Li_xAu_y и K_xAu_y .

Ключевые слова: электронно-стимулированная десорбция, интерметаллид, 2D-слои

Финансирование: Работа поддержана РФФИ, грант № 20-02-00370.

Ссылка при цитировании: Громов И.А., Кулешова Т.Э., Кузнецов Ю.А., Лапушкин М.Н., Самсонова Н.С. Электронно-стимулированная десорбция атомов лития и калия при адсорбции атомов лития и калия на золото // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 1.1. С. 398–403. DOI: <https://doi.org/10.18721/JPM.161.168>

Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (<https://creativecommons.org/licenses/by-nc/4.0/>)

Introduction

Compounds of two metals are called intermetallic compounds. Intermetallic compounds can and do have properties different from the metals of which they are composed. Bronze is the first intermetallic compound known to mankind. Gold-alkali metal intermetallic compounds are of particular interest, since in them gold is an anion [1], while in the vast majority of compounds gold is a cation. Studies of intermetallic compounds gold-alkali metal started in the middle of the last century [2]. Interest in gold-alkali metal compounds is associated with the rapid growth of Au chemistry [3], the use of Au nanoparticles in various fields from catalysis [4] and medicine [5] to the creation of various sensors and detectors. [6].

2D layers of gold intermetallic compounds with alkali metals (AM) Li_xAu_y , Na_xAu_y , K_xAu_y , and Cs_xAu_y are semiconductors, in contrast to bulk samples (Li_xAu_y , Na_xAu_y and K_xAu_y), which exhibit metallic properties. Only CsAu is a semiconductor regardless of its size.

The formation of the intermetallic compound gold-alkali metal at temperatures close to room temperature can be divided into two stages. At the first stage, an adsorbed alkali metal monolayer is formed on the gold surface and no intermetallic compound is formed. At the second stage, an increase in the dose of deposited alkali metal on the gold surface leads to the diffusion of alkali metal atoms into the depth of the gold substrate with the formation of a gold-alkali metal intermetallic compound. In this case, a monolayer of alkali metal will remain on the surface. The stoichiometry of the gold-alkali metal intermetallic compound depends on the number of gold and alkali metal atoms that have reacted. Note that the Au layer closest to W does not participate in the formation of an alkali metal-Au compound, and as a result, a four-layer system is obtained: an alkali metal monolayer/an AMAu intermetallic compound/a monolayer of Au atoms/W(100) [7].

Electronic-stimulated desorption (ESD) is observed only from the surface of semiconductors and dielectrics, and it is not observed from the surface of metals, since excited states rapidly relax in metals (see review, for example [8]). In semiconductors, the lifetime of excited states is sufficient for the process of ESD of atoms [8].

The purpose of this work was a detailed consideration of the processes occurring during the electron irradiation of the $\text{Li}/\text{Li}_x\text{Au}_y/\text{Au}/\text{W}$ and $\text{K}/\text{K}_x\text{Au}_y/\text{Au}/\text{W}$ system and to compare the processes of formation of intermetallic compounds Li_xAu_y and K_xAu_y , which will allow us to highlight the commonality and differences in the formation of intermetallic compounds of 2D layers of Li_xAu_y and K_xAu_y .

Materials and Methods

The studies proposed in this work were carried out in an “ESD Spectrometer” ultrahigh vacuum setup; the design of the experiment and the structure of the sample are shown in Figure 1. The pressure of the residual gas in the installation did not exceed $5 \cdot 10^{-10}$ Torr. Textured W(100) ribbon were used as a substrate for the samples, which were cleaned by heating at 1800 K in an oxygen atmosphere at a pressure of $1 \cdot 10^{-6}$ Torr for 3 hours. Gold was deposited on a tungsten ribbon at 300 K from a straight-heated tungsten tube, into which pieces of gold foil with a purity of 99.99% were placed. Lithium was deposited on a gold-coated tungsten ribbon from a Knudsen cell by thermal reduction of lithium oxide with aluminum. Potassium was also deposited onto the tape at 300 K from a Knudsen cell by thermal decomposition of potassium chromates. The potassium concentration on the surface was determined from the deposition time with a constant flux, the intensity of which was measured from the surface ionization current on the tungsten W ribbon. The Li concentration on the surface was determined from the time of deposition by a constant flux, the intensity of which was measured by the current during surface ionization on an iridium ribbon. 1 monolayer (ML) corresponds to a close-packed monolayer of Li atoms with a hexagonal structure and is equal to $1.0 \cdot 10^{15}$ atom/cm². The surface concentration in the potassium monolayer was $5.0 \cdot 10^{14}$ at/cm². The concentration of deposited gold was determined by the time of deposition and was $1.0 \cdot 10^{15}$ atm/cm² in the monolayer [11]. The measurements were carried out at $T = 300$ K at the energy of bombarding electrons in the range of 0–300 eV.

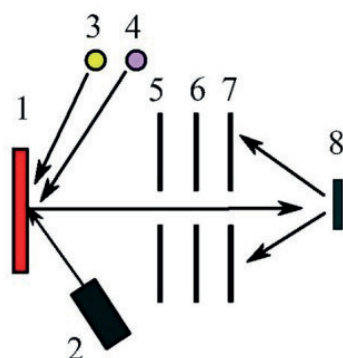


Fig. 1. Experiment scheme: 1 — sample, 2 — electron source, 3 and 4 — evaporators of Au and Li(K), 5 — ion collector, 6 — ion-retention electrode, 7 — ionic collector, 8 — surface ionization ribbon

Results and Discussion

First, two monolayers of gold were deposited on the tungsten surface. After that, Li (K) coverage was deposited to the surface of the gold film. The yield (q) of desorbing Li (K) atoms was recorded. Figure 2, a shows that ESD of Li (K) atoms are not observed when Li (K) is less than one monolayer. At a dose of deposited Li (K) atoms greater than 1 MLs, ESD of Li (K) atoms begins to be detected, which indicates the formation of intermetallic compounds of 2D Li_xAu_y (K_xAu_y) layers under the monolayer Li (K) film. Since ESD of Li (K) atoms is observed, it can be argued that Li_xAu_y (K_xAu_y) semiconductor compounds are formed. Further deposition of Li (K) atoms leads to a linear increase in the ESD yield of Li (K) atoms. The maximum value of the ESD yield of Li (K) atoms is achieved by deposition of a dose of Li (K) atoms equal to 2 MLs. A subsequent increase in the dose of deposited Li atoms leads to a sharp decrease in the ESD yield of Li atoms. However, further increase in the dose of deposited K atoms does not change the ESD yield of K atoms.

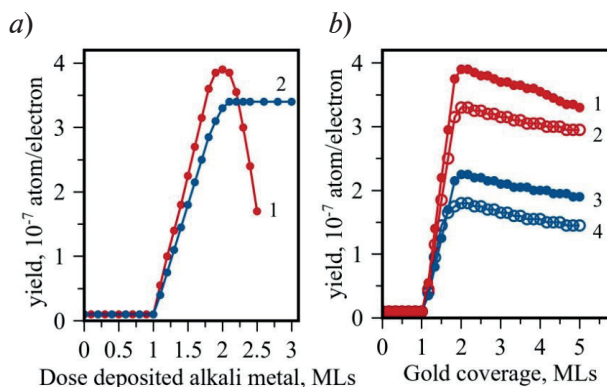


Fig. 2. Yield q of Li (K) atoms during ESD from tungsten covered with two gold monolayers at $T = 300$ K as a function of the dose of deposited Li (1) and K (2) atoms for an energy of bombarding electrons of 64 eV (a). Yield q of Li (K) atoms in ESD from gold-covered tungsten at $T = 300$ K as a function of gold deposition time for two doses of deposited Li (1,2) and K (3,4) atoms: 1,3—1.5 MLs and 2,4—2.0 MLs (b). The energy of the bombarding electrons is 64 eV

Let us consider the possible Li_xAu_y (K_xAu_y) compounds obtained and the differences in the formation of 2D layers of Li_xAu_y (K_xAu_y) upon deposition of Li (K) atoms. It can be assumed that LiAu is formed upon deposition of 2 MLs of Li atoms (corresponds to the maximum ESD yield of Li atoms) and KAu upon deposition of 3 MLs of K atoms (corresponds to the plateau of the ESD yield of K atoms). Note that the indicated stoichiometry of intermetallic compounds is an estimate and is directly related to the number of Li (K) atoms in the monolayer. The difference in the formation of 2D layers of Li_xAu_y (K_xAu_y) during deposition of Li (K) atoms is as follows: when the dose deposited of Li atoms more than 2 MLs atoms, Li atoms do not diffuse deep into the film, but Li atoms accumulate on the surface with the formation of a second monolayer on

the surface, which screens the exit of lithium atoms through the adsorbed layer of Li atoms. When the dose deposited of K atoms more than 2 MLs atoms, K atoms diffuse deep into the film and the K_xAu_y intermetallic compound continues to form.

In the next experiment, a different number of Au atoms were deposited, which was no more than 5 MLs. For each Au coverage, a fixed dose of Li (K) atoms was deposited, equal to the deposition dose of 1.5 and 2.0 MLs of Li (K) atoms. After each measurement of the ESD yield of Li (K) atoms, the deposited material on W was removed from the surface, and Au and then Li (K) were deposited again.

Figure 2, *b* shows the ESD yield of Li (K) atoms as a function of the amount of deposited Au on W for two deposition doses of Li (K) atoms: 1.5 and 2.0 MLs. As can be seen, upon deposition of less than 1 MLs of gold followed by deposition of Li (K) atoms, no ESD of Li (K) atoms is observed and no formation of Li_xAu_y (K_xAu_y) occurs. Let us consider how the ESD of Li (K) atoms changes with an increase in the thickness of the deposited gold film. Thus, in the gold coverage range from 1 to 1.8 MLs, the ESD of Li (K) atoms increases linearly, reaching its maximum value at a gold film 2 MLs thick. A further increase in the thickness of the gold film leads to a decrease in the ESD of Li (K) atoms. This indicates the formation of a 2D semiconductor layer of Li_xAu_y (K_xAu_y) between the upper monolayer of Li (K) atoms and the Au monolayer closest to the W surface.

Let us consider the possible stoichiometry of the formed Li_xAu_y (K_xAu_y) intermetallic compounds. Thus, at the maximum ESD yield of Li atoms, we can assume the formation of $LiAu_2$ at a Li deposition dose of 1.5 MLs and the formation of $LiAu$ at a Li deposition dose of 2.0 MLs. With an increase in the thickness of the deposited gold film over 2 MLs, an insignificant decrease in the ESD yield of Li atoms occurs by only 15%, which can mean either slow diffusion of lithium atoms deep into the gold layer, or a weak dependence of the probability of the ESD yield of Li atoms for Li_xAu_y , which depends on the ratio x/y with increasing y . It is possible to propose the formation of KAu by deposition of 1.5 MLs of potassium onto a gold film 1.25 MLs thick and by deposition of 2 MLs of potassium onto a gold film 1.5 MLs thick. Thus, at the maximum ESD yield of K atoms, we can assume the formation of KAu_4 at a deposition dose K of 1.5 MLs and the formation of KAu_2 at a deposition dose of K equal to 2.0 MLs. With an increase in the thickness of the deposited gold film over 2 MLs, an insignificant decrease in the ESD yield of K atoms occurs by only 15%, which can mean either slow diffusion of K atoms deep into the gold layer, or a weak dependence of the ESD yield of K atoms for K_xAu_y , which depends on the ratio x/y with increasing y .

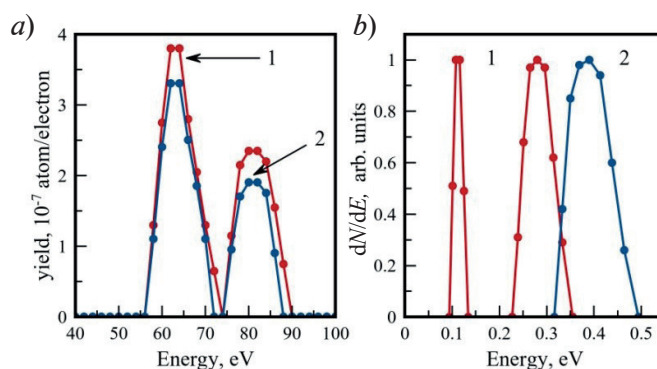


Fig. 3. Yield of Li and K atoms upon ESD from tungsten coated with two monolayers of gold and two monolayers of Li (1) and K (2) at $T = 300$ K as a function of the bombarding electron energy (*a*). Kinetic energy distribution of desorbed Li (1) and K (2) atoms during ESD from tungsten covered with two Au and two Li (K) monolayers (*b*). The energy of exciting electrons is 64 eV

Figure 3 shows the dependence of the yield of lithium (potassium) atoms q of the ESD on the energy of exciting electrons (E_e), in which two resonance peaks are observed with maxima at 63.5 and 81.4 eV, corresponding to the ionization energies of the Au levels $Au 5p_{3/2}$ and $5p_{1/2}$. The full width at half maximum of the peak is 8.8 and 9.6 eV, respectively, for the $Au 5p_{3/2}$ and $5p_{1/2}$ levels upon ESD of Li atoms. In the case of the ESD of K atoms, these values are slightly smaller:

8.6 and 8.2 eV, respectively, for the Au $5p_{3/2}$ and $5p_{1/2}$ levels. The ratio of the areas under the peaks coincides with the theoretical spin-orbit value of 0.5 for the ESD of K atoms and is much larger than the theoretical spin-orbit value of 0.70 for the ESD of Li atoms. Such a deviation may be due to the fact that the Li $1s$ level with the binding energy $E_b = 54.7$ eV is not excited by the electrons bombarding the surface and forms a channel that partially suppresses the ESD of lithium atoms. This effect is similar to the ESD of Cs atoms, when only one peak is observed in the dependence of the yield of cesium atoms $q(E_e)$ of ESD on the energy of exciting electrons at $E_b = 63.5$ eV [11]. The presence of one peak was explained by the fact that the excitation of the Au $5p_{1/2}$ level ($E_b = 74.2$ eV) is completely quenched by its resonance with the Cs $4d_{5/2}$ level ($E_b = 77.5$ eV). In the case of the ESD of lithium atoms, the Au $5p_{3/2}$ state with $E_b = 57.2$ eV partially delocalizes, and the probability of its excitation decreases, which leads to a decrease in the ESD of lithium atoms.

Figure 3, *b* shows the kinetic energy distribution (KED) of desorbing Li (K) atoms in ESD from tungsten covered with two Au monolayers and two Li (K) monolayers. It can be seen that E_{kin} has two peaks for desorbing Li atoms: a low energy peak (LE) at energy of 0.11 eV and a high energy peak (HE) at energy of 0.28 eV. The HE peak is associated with the excitation of the ESD of Li atoms from the upper monolayer of Li atoms, and the LE peak is associated with the excitation of the ESD of Li atoms from the 2D layers of Li_xAu_y intermetallide. For the ESD of K atoms, KED has only one peak for desorbing K atoms: a HE peak at energy of 0.39 eV, which is associated with the excitation of the ESD of K atoms from the upper monolayer of K atoms. Most likely, the presence of one peak is associated with the formation of an intermetallic compound with deficiency of potassium atoms – KAu_y . We assume that the LE peak in KED is observed only in intermetallic compounds Li_xAu_y when the content of alkali metal atoms is greater than or close to the content of gold atoms.

The results obtained show that the ESD process captures atoms located at the interface between the adsorbed layer of Li (K) atoms and the 2D layer of Li_xAu_y (K_xAu_y). Lithium atoms are 1.6 times smaller than potassium atoms and are the same size as Au atoms. Consequently, there are more lithium atoms on the surface in the monolayer than potassium atoms. However, this leads to the fact that to form, for example, intermetallic compounds Li_xAu_y and K_xAu_y of the same stoichiometry, it is required to deposit two times fewer monolayers of Li atoms than K atoms. It would seem that lithium and potassium atoms differ only in the size of the atoms and the size of the formed crystal cell. $LiAu$ and KAu form a more compact CsCl-type crystal cell (with cell parameter $a = 0.31$ nm for $LiAu$ and $a = 0.39$ nm for KAu). However, the ESD process of Li and K atoms is also affected by the difference in the electronic structure of Li and K atoms: the proximity of the Li $1s$ levels with $E_b = 54.7$ eV and Au $5p_{3/2}$ with $E_b = 57.2$ eV leads to partial suppression of the ESD process of Li atoms associated with excitation level Au $5p_{3/2}$.

Conclusion

It has been found that the adsorption of lithium and potassium atoms on thin gold films leads to the formation of 2D intermetallic films Li_xAu_y and K_xAu_y , which can be considered 2D semiconductor films. Intermetallic compounds are formed between the upper alkali metal monolayer and the gold monolayer closest to the W surface. As a result of the interaction of alkali metal and gold atoms, intermetallic compounds of various stoichiometries are formed, depending on the number of atoms of deposited gold and alkali metal. It is assumed the formation of $LiAu_2$ at a Li deposition dose of 1.5 MLs and the formation of $LiAu$ at a Li deposition dose of 2.0 MLs onto a gold film with a thickness of 2 MLs. It is assumed the formation of KAu_4 at a deposition dose K of 1.5 MLs and the formation of KAu_2 at a deposition dose of K equal to 2.0 MLs. onto a gold film with a thickness of 2 MLs. A resonant dependence of the yield of Li and K atoms on the energy of exciting electrons is observed, which is related to the excitation of the Au $5p_{3/2}$ and $5p_{1/2}$ core levels. A difference was found in the kinetic energy distribution of desorbed Li and K atoms: a high-energy one, which is associated with the excitation of the ESD process of Li and K atoms in the upper monolayer of Li and K, and a low-energy one, which is associated with the excitation of the ESD process of Li atoms in the Li_xAu_y intermetallic compound. The ESD process captures atoms located at the interface adsorbed layer of Li (K) atoms: 2D layer of Li_xAu_y (K_xAu_y).

Acknowledgments

This study has been funded by RFBR according to the research project No. 20-02-00370.

REFERENCES

1. **Jansen M.**, The chemistry of gold as an anion, *Chemical Society Review*. 9 (37) (2008) 1826–1835.
2. **Spicer W.E., Sommer A.H., White J.G.**, Studies of the Semiconducting Properties of the Compound CsAu, *Physical Review*. 1 (115) (1959) 57–62.
3. **Priecel P., Salami H.A., Padilla R.H., Zhong Z., Lopez-Sanchez J.A.**, Anisotropic gold nanoparticles: Preparation and applications in catalysis, *Chinese Journal of Catalysis* 10 (37) (2016) 1619–1650.
4. **Ciriminna R., Falletta E., Pina C.D., Teles J.H., Pagliaro M.**, Industrial Applications of Gold Catalysis, *Angewandte Chemie*, 46 (55) (2016) 14210–14217.
5. **Dykman L.A., Khlebtsov N.G.**, Gold Nanoparticles in Biology and Medicine: Recent Advances and Prospects, *Acta Naturae*, 2 (3) (2011) 34–55.
6. **Priyadarshini E., Pradhana N.**, Gold nanoparticles as efficient sensors in colorimetric detection of toxic metal ions: A review, *Sensors and Actuators B: Chemical*, (238) (2017) 888–902.
7. **Ageev V.N., Afanas'eva E.Yu.**, Initial stages of the interaction of sodium and cesium with gold, *Physics of the Solid State*, 12 (48) (2006) 2347–2353.
8. **Ageev V.N.**, Desorption induced by electronic transitions, *Progress in Surface Science*, 1-2 (47) (1994) 55–203.

THE AUTHORS

GROMOV Ivan A.

gromov-24-2@yandex.ru

ORCID: 0000-0001-9269-2259

LAPUSHKIN Mikhail N.

lapushkin@ms.ioffe.ru

ORCID: 0000-0002-9042-7889

KULESHOVA Tatiana E.

www.piter.ru@bk.ru

ORCID: 0000-0003-3802-2494

SAMSONOVA Natalia S.

kolomna.88@mail.ru

ORCID: 0000-0002-5965-0767

KUZNETSOV Yurii A.

kuznets@ms.ioffe.ru

ORCID: 0000-0003-2560-2182

Received 31.10.2022. Approved after reviewing 08.11.2022. Accepted 08.11.2022.