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Electron-Stimulated Desorption of Cesium Atoms from Adlayers on a Gold Surface

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Abstract—We have studied the process of electron-stimulated desorption (ESD) of Cs atoms from a Cs/CsAu/Au/W system. It is established that ESD takes place from a Cs adlayer and the adjacent CsAu layer of this system. A model of Cs atom desorption from the Cs/CsAu/Au/W system is proposed. The results confirm the semiconductor nature of CsAu compounds.

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Intermetallic compounds of gold with alkali metals (AMs) have been studied since the mid-20th century [1, 2]. In particular, it has been found that CsAu is a wide-band semiconductor. In AM–Au intermetallics, gold plays the rather unusual role of an anion [3], in contrast to being a cation in overwhelming majority of compounds. Thus, AM–Au compounds are unique systems in this respect.

In a series of Li, Na, K, Rb, and Cs atoms, the electron properties of their compounds with gold vary from metal to semiconductor. At present, it is known that these AM–Au intermetallics can form not only at low temperatures ($T \leqslant 300$ K) as thin films on glass, quartz [1, 2], and metal (Ru [4, 5], W [6]) substrates, but also appear at high temperatures ($T \geqslant 1000$ K) during AM deposition onto gold ribbons [7–10] and can even form massive layers [11]. AM–Au compounds were studied by photoelectron spectroscopy and thermodesorption at low temperatures and by surface ionization at high temperatures. It has been established [4–6] that AM–Au compounds are formed during the co-adsorption of AM and Au atoms on Ru and W, provided that the amount of each adsorbed metal is greater than a monolayer, and a CsAu layer is formed under the surface monolayer of Cs.

During the initial stage of adsorption at 300 K, a layer of AM and Au adatoms is formed on the transition metal substrate at low surface coverages of both AM ($\Theta_{AM} < 1$) and gold ($\Theta_{Au} < 1$). When the gold coverage exceeds one monolayer ($\Theta_{Au} > 1$), AM adatoms diffuse into the gold layer only upon the formation of a complete AM monolayer ($\Theta_{AM} > 1$) and form an AM–Au intermetallic compound (or alloy) on the Au/W (or Au/Ru) interface. The thickness of this alloy depends on the thickness of gold above its monolayer on W (or Ru) and on the amount of adsorbed AM atoms. Note that the gold layer adjacent to the W (Ru) substrate does not participate in the formation of AM–Au compounds, so that the resulting system comprises a three-layer coating on the W(100) or Ru(001) substrate: AM/AMAu/Au/W(Ru).

Previously [12–16], we have used the method of electron-stimulated desorption (ESD) to study the behavior of the surface of such systems under the action of irradiation by electrons at variable energy E_e. It was found that electron irradiation of the surface of Na/NaAu/Au/W [12] and Cs/CsAu/Au/W [13–16] systems led to the ESD of neutral Na and Cs atoms, respectively. The ESD of AM atoms began only after the onset of formation of an AM–Au alloy layer under the upper monolayer of Na or Cs atoms. The films of Cs and Au on the W(100) surface were deposited in situ from atomically clean sources in a UHV chamber of the ESD spectrometer setup at pressures not exceeding 5×10^{-10} Torr at $T = 300$ K. The substrate temperature could be varied from 160 to 600 K. The experimental procedure was described in detail previously [16, 17].

The present work was aimed at thoroughly considering physical processes in the Cs/CsAu/Au/W system under electron irradiation and formulating on this basis a new mechanism of the ESD of cesium atoms from this system.

Figure 1 shows plots of the ESD yield $q(n_{Cs})$ of Cs atoms at $T = 300$ and 160 K from the tungsten surface covered with two monolayers of gold (Au/W) versus surface concentration of cesium adsorbed on the Au/W surface. As is known, a monolayer of cesium on a W(100) surface covered with a monolayer of gold has a concentration of $n_{Cs}^{ML} = 0.5 \times 10^{15}$ cm^{-2} [18]. As can be seen from this figure, the yield of desorbed Cs

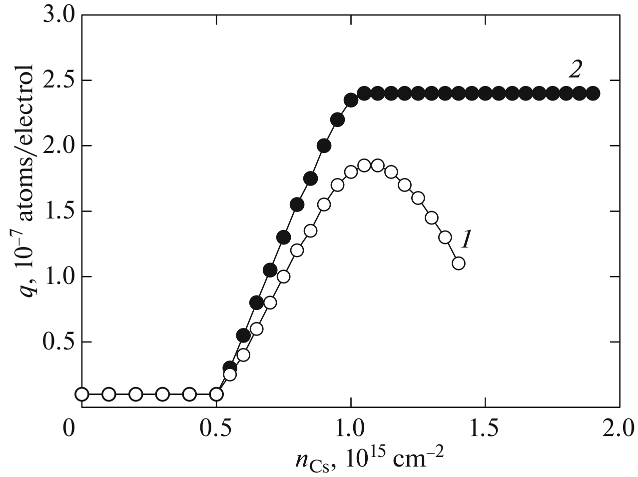

Fig. 1. Dependence of the ESD yield q of Cs atoms at $T =$ (*1*) 160 and (*2*) 300 K from the tungsten surface covered with two monolayers of gold on concentration n_{Cs} of cesium adsorbed on the Au/W surface (electron energy, 64 eV).

atoms appears at a point corresponding to their concentration in a monolayer coverage on Au/W. It should be noted that only our previous ESD measurements [13–16] allowed the onset of CsAu compound formation during the deposition of Cs and Au onto tungsten to be exactly determined.

The need for a nonmetallic (dielectric or semiconductor) interlayer to be present between an adatom and metal substrate for the ESD yield onset is explained as follows. Desorption of electron-impact-excited particles requires that the lifetime of an excited state of the adatom–surface bond would be sufficiently large for both the bond rupture and the removal of particle from the surface [19, 20]. These conditions are not satisfied on the metal surface, where the excitation is very rapidly quenched because of the excited electron transfer to a conduction band, so that the ESD from metals is absent. The presence of a dielectric (or semiconductor) on the metal surface significantly increases the excitation lifetime, so that the ESD yield becomes possible. A linear increase in the ESD yield in Fig. 1 begins at a Cs concentration of between one and two monolayers, i.e., when a monolayer of CsAu compound is formed under a Cs monolayer. The constancy of Cs yield q at cesium concentration n_{Cs} above two monolayers implies that (i) neither properties of the surface layer nor its composition vary with increasing Cs deposition at $T = 300$ K in the n_{Cs} range indicated in Fig. 1 and (ii) Cs atoms neither adsorb on nor diffuse under a Cs monolayer in the Cs/CsAu/Au/W system. In the case of Cs deposition at $T = 160$ K, the $q(n_{Cs})$ curve exhibits a maximum. A drop in the ESD yield of Cs at $n_{Cs} > 1.0 \times 10^{15}$ cm^{-2} is related to the possible formation of a multilayer film at this temperature. therefore, a decay in the ESD yield of Cs atoms may be indicative of both a screening of this yield by Cs film at one-and-a-half monolayer coverage and a decrease in the amount of desorption-exciting electrons with an increase in the Cs coverage.

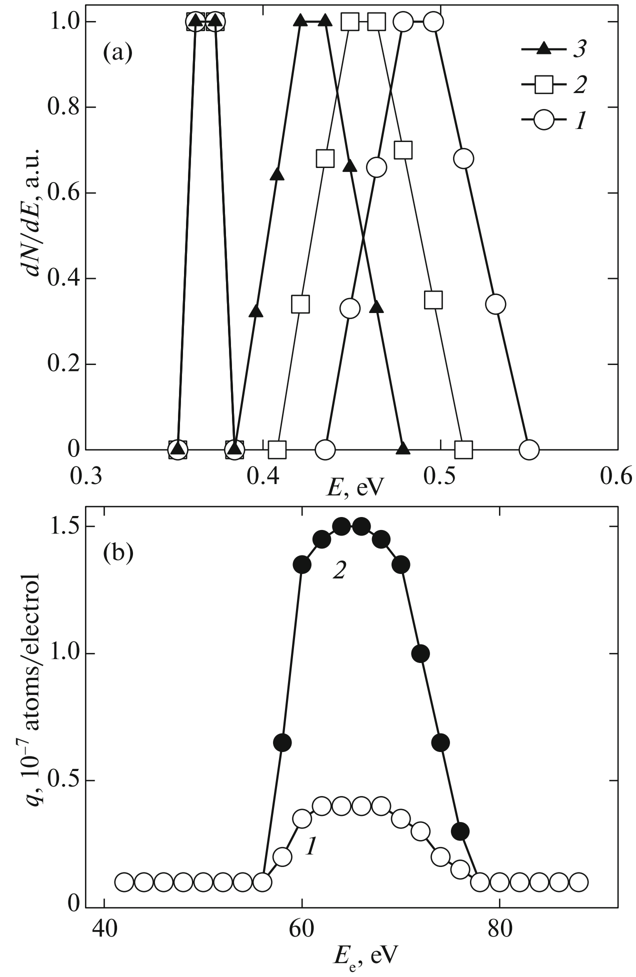

Fig. 2. (a) Normalized energy distributions of Cs atoms desorbed at 160 K from tungsten covered with two Au monolayers at 300 K for three Cs concentrations: (*1*) 0.75 × 10^{15}, (*2*) 1.0 × 10^{15}, and (*3*) 1.25 × 10^{15} cm^{-2} (electron energy, 64 eV); (b) yield q of Cs atoms desorbed at 160 K from tungsten covered with two Au monolayers and two Cs monolayers at 160 K as a function of energy E_e of bombarding electrons for (*1*) LE peak and (*2*) HE peak of the energy distribution.

The ESD of Na and Cs atoms from the surface of systems described above has two channels of yield: (i) from the surface adlayer of Cs and (ii) from the upper layer of CsAu compound formed between the AM monolayer and Au/W layer. Figure 2a shows normalized energy distributions of Cs atoms desorbed at 160 K from tungsten covered with two Au monolayers at 300 K for three concentrations of deposited cesium. If the amount of deposited Cs is slightly above one monolayer (0.75 × 10^{-15} cm^{-2}), measurements at 160 K reveal the presence of two ESD peaks—the low-energy (LE) peak with a maximum at 0.37 eV and the

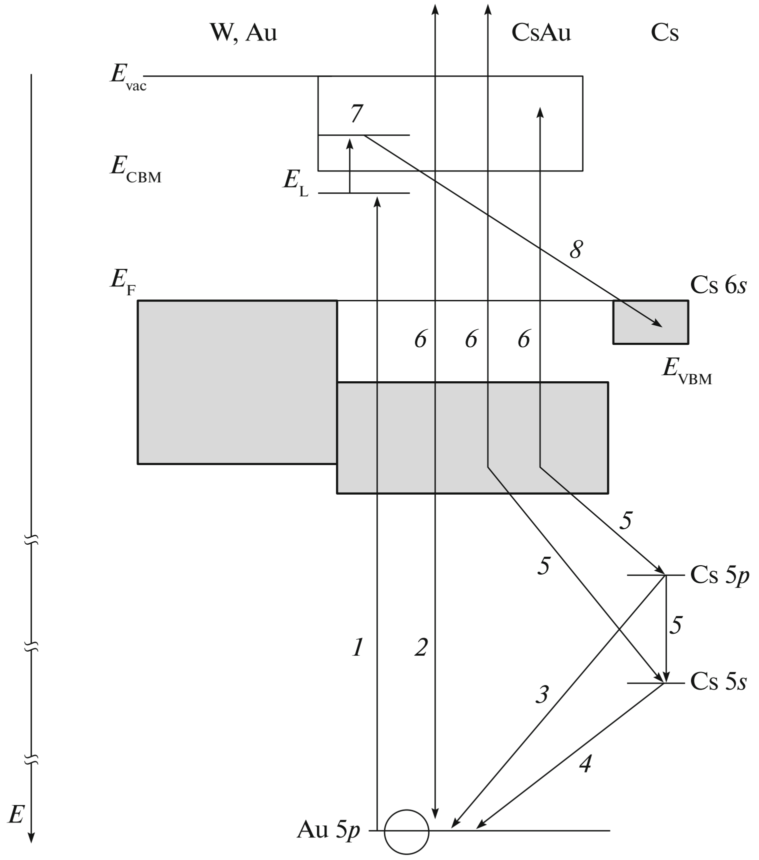

Fig. 3. Schematic diagram of ESD processes in the Cs layer–CsAu layer–Au monolayer–W substrate system.

high-energy (HE) peak with a maximum at 0.49 eV. It was previously shown [13] that the HE peak is related to ESD from the surface layer of CS adatoms, while the LE peak corresponds to ESD from the CsAu alloy layer. Both channels exhibit the same resonance-type dependence $q(E_e)$ of the ESD yield of AM atoms on electron energy E_e, representing a relatively narrow peak (57 eV $\leqslant E_e \leqslant$ 78 eV) with a maximum at 64 eV for Cs atoms (Fig. 2b). The "resonance" character of the yield of AM atoms was previously related [12–16] to the formation of a core exciton upon electron-impact excitation of the Au $5p_{3/2}$ and Au $5p_{1/2}$ levels for ESD of Na atoms and the Au $5p_{3/2}$ levels for ESD of Cs atoms with binding energies of 57 and 75 eV in an Au 5*p* doublet of the free Au atom.

In the present work, we propose a detailed description of the ESD of Cs atoms from the surface of a three-layer coating Cs/CsAu/Au/W on the W(100) substrate upon sequential adsorption of Au and Cs atoms at 300 K.

Figure 3 shows a schematic diagram of ESD processes in the Cs/CsAu/Au/W system. Electron irradiation of a sample leads to the excitation of electron from the Au 5*p* core level *1* to a local state E_L near the conduction band minimum (E_{CBM}), which sank from the conduction band to bandgap of CsAu semiconductor in the field of the Au $5p^+$ core hole. Calculations of the electron band structure [21, 22] showed that the conduction band of CsAu have large peaks in the density of states. The valence band is formed due to hybridization, predominantly of the Au 5*d* and 6*s* states, while the conduction band is formed mostly by the Au 6*p* states [21]. The much earlier work [22] indicated that the states of both bands are formed due to the hybridization of 5*d*, 6*s*, and 6*p* states of Au and Cs, which is bonding for the valence band and antibonding for the conduction band. It is the excitation of electrons from Au 5*p* states to the conduction band by electron irradiation that leads to the formation of a "resonance" peak observed in Fig. 2b.

This is followed by neutralization of the Au $5p^+$ hole by electrons from the valence band of CsAu alloy (*2*), Cs 5*s* level (*3*), and Cs 5*p* level (*4*), which is accompanied by Auger processes including the filling of all holes in the electron structure (*5*) and the excitation of electrons from the valence band maximum (E_{VBM}) to vacuum or the conduction band (*6*) via evolved energy.

Filling of the Au $5p^+$ hole returns the local state E_L (already filled by an electron) to the conduction band

(*7*). Then, the process can proceed via one of the two possible scenarios: (i) electrons generated in the conduction band can be trapped by the potential of the Cs+ core with the formation of a neutral atom Cs° in the Cs monolayer or CsAu compound or (ii) an antibonding Cs(5*s*, 6*p*)–Au(6*s*, 6*p*) state that has returned to the conduction band exhibits decay and converts into Cs 6*s* state (*8*). The resulting neutral Cs° atom of increased volume (compared to that of a Cs^+ ion) is pushed out by its surrounding either from Cs monolayer on the surface to form an HE peak in the energy distribution of Cs atoms or from underlying CsAu alloy layer to form an LE peak in the energy distribution (Fig. 2a) with an intensity that is lower than that of the HE peak (Fig. 2b).

A smaller peak width, lower kinetic energy of Cs atoms, and lower intensity of the LE peak are probably related to a smaller amplitude of Cs atom oscillations in CsAu compound compared to that in a Cs monolayer, as well to an escape to the surface from a deeper layer. Thus, we have demonstrated the possibilities of ESD-based analysis of the mechanism of electron processes in near-surface layers of the CsAu/Cs interface.

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