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Electron-stimulated desorption of europium atoms from the surface of a germanium monolayer deposited on tungsten

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The adsorption of europium on the surface of a germanium monolayer deposited on a tungsten substrate using electron-stimulated desorption was studied. It was found that the electron-stimulated desorption of Eu atoms at europium coverages of less than 0.3 monolayers is caused by the excitation of the Eu $5p$ and Eu $5s$ states, and at coverages of more than 0.4 monolayers it is caused by the excitation of the states: W $4f$, W $5p$ and W $5s$. A model of electronic transitions has been proposed to explain the processes that occur during the electron-stimulated desorption of europium atoms.

Keywords: electron-stimulated desorption, adsorption, germanium, tungsten, europium.

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1. Introduction

In the recent decade, there is significant attention to europium among the rare-earth metals (REM), which is related to applicability of this element as an additive (impurity) for directional modification and improvement of properties of various materials. Thus, for example, ions of trivalent europium (Eu^{3+}) have been used as a red-luminophore component in color electron-beam tubes and liquid crystal displays [1], so have ions Eu^{2+} — for creating magnetic-intercalated compounds of silicene and germanene [2,3]. Moreover, great importance is attached to atomic layers of europium, as they ensure high mobility of the carriers in germanene derivatives [4]. Finally, with the help of europium it is possible to synthesize a two-dimensional (2D) compound EuC_6 — graphite functionalized by intrinsically-magnetic metal — which is a ferromagnetic and has transport properties similar to graphene [5]. It is obvious that a father progress in obtaining new promising europium-based materials requires detailed understanding of electronic properties of monolayers and submonolayers of this REM adsorbed on the various surfaces, their stability when irradiated by beams of electrons and photons, as well as mechanisms of interaction of the Eu atoms with foreign films, such as, for example, germanium monolayers.

The present study gives the results of investigation of the electron-stimulated desorption (ESD) processes of the europium atoms from the tungsten surface covered by a layer of the germanium atoms. The ESD of neutral atoms from various substrates is an informative „*state-of-the-art*“ method of investigating the peculiarities of the electronic structure of the surface structures [6,7]. Application of this method for diagnostics of the europium-based film structures is contributed by a relatively low potential of ionization of its atoms (5.67 eV) [8] low activation energy for desorption from the W(100) surface in a series of rare earth atoms [9], which is 3.0 eV for Eu adsorption. The earlier studies of these systems have found an interesting peculiarity of ESD yield of Eu atoms from the surface of oxidized tungsten, namely, a very sharp dependence of this value on the electron energy [10,11]. It has been also shown that with europium coverages below 0.3 monolayers ESD of its atoms is related to excitation of the Eu $5p$ and $5s$ core levels, so is it — to excitation of the W $5p$ and $5s$ core levels. At the same time, the role of the layer of oxygen atoms on the surface of tungsten in this system is currently unclear. Layers of germanium atoms deposited on a tungsten substrate were studied in the work [12]. It has discovered that ESD of the adsorbed cesium atoms is related to excitation of the W $5p$ and $5s$ core levels and secondary electrons formed after excitation of the Ge $3d$ core level.

It is known that at room temperature there is no dissolution of europium in germanium, germanium in tungsten and europium in tungsten [13]. So, we believe that there is no diffusion of these substances in the adsorption system under study.

2. Experiment

2.1. Materials

The target was textured tungsten ribbon with a predominant exposure to the surface of the face (100). At $T = 2000$ K and under pressure of $1 \cdot 10^{-9}$ Torr, the ribbon were preheated for 5 h by passing alternating current to bring predominantly the (100) face to the surface [14], and after that they were cleaned of carbon by annealing at $T = 1800$ K in oxygen under pressure $1 \cdot 10^{-6}$ Torr for 3 h.

The ribbon cleaning was finished after oxygen pumping by oxygen desorption at $T = 2200$ K for 3 min.

Germanium was deposited onto the ribbon from a straight-channel tungsten tube, which had pieces of germanium placed. The tube was in parallel to the ribbon and it had holes for uniform depositing of germanium along the ribbon.

Europium was deposited onto the oxidized surface of the target at $T = 300$ K from a directly heated evaporator made of a tantalum tube into which metallic europium was placed. The tube, 3 mm in diameter, had several holes along its length for uniform deposition of europium along the target. Purity of the flow of europium atoms was controlled by means of a quadrupole mass-spectrometer. The concentration of deposited europium was determined using thermal desorption spectroscopy [15] as well as controlled by a current of surface ionization of europium on the target heated to the temperature $T = 1800$ K. The concentration of europium, which corresponded to the monolayer, was established by means of thermal desorption spectroscopy and Auger-electron spectroscopy [15]. The formation of a monolayer during europium deposition was monitored by the observation of a maximum yield of Eu atoms during ESD.

The target was irradiated with electrons in a stationary mode. An electron emitter was a polycrystalline tungsten filament of the diameter of 0.15 mm, which was located in parallel to the target. The current density of the irradiating electrons did not exceed 10^{-5} A/cm^2 at the electron energy of 100 eV, so the electron irradiation of the target did not cause its noticeable heating.

The europium atoms were ionized by means of a heated tungsten ribbon at $T = 2000$ K.

2.2. Preparation of samples

The samples under study were created by using the following method: the germanium monolayer was deposited onto the clean tungsten ribbon and then a number of europium atoms required for ESD measurements was deposited to the sample (it varied in the different experiment). After the measurements, the tungsten surface was cleaned and prepared again.

2.3. Experimental setup

All studies were carried out in an ultra-high vacuum setup „Spectrometer ESD“, the experimental diagram of which is shown in Figure 1. During the experiment, the setup pressure was below $5 \cdot 10^{-10}$ Torr. The experiments were carried out at the temperature of $T = 300$ K. The tungsten ribbon with the germanium and europium layers deposited thereon was irradiated with the electron beam of the energy within the range of 0–200 eV. The power supplied by the electron beam did not change the temperature of the ribbon. The germanium coverage was determined by the dependence of ESD yield of the Cs atoms from the monolayer cesium film deposited to the germanium film at $T = 300$ K, on the germanium depositing time [16]. The maximum ESD yield of the Cs atoms was achieved in formation of the monolayer germanium film. The concentration of deposited europium was determined using thermal desorption spectroscopy [14] as well as controlled by a current of surface ionization of europium on the target heated to the temperature $T = 1800$ K. The concentration of europium, which corresponded to the monolayer, was established by means of thermal desorption spectroscopy and Auger-electron spectroscopy [15]. The formation of a monolayer during europium deposition was monitored by recording the maximum ESD yield of Eu atoms. The desorbing europium atoms were ionized on the W ribbon of thermal ionization (8) at $T = 2000$ K and recorded in the collector (7). The probability of ionization of the europium atoms was $9 \cdot 10^{-4}$ ion/atom [16]. The ESD yield magnitude (q) is considered to be a density of a desorbing atom flux to a flux density of the ESD-exciting electrons. The „Spectrometer ESD“ set-up made it possible to record the ESD yield of Eu atoms and measure the dependence of this yield q on the energy of exciting electrons and the number of Eu and Ge atoms deposited on the substrate.

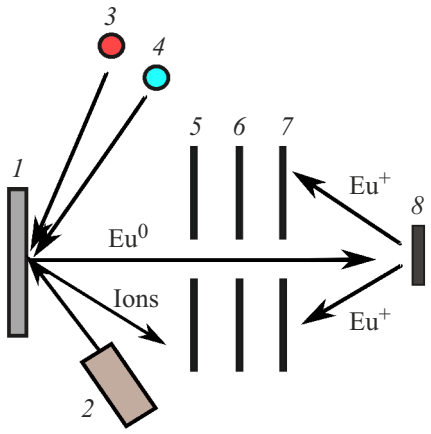

Figure 1. Experiment diagram. *1* — the W ribbon, *2* — the electron source, *3* and *4* — the Ge and Eu evaporators, *5, 6* — the electrodes that retain ions desorbed when the sample is irradiated by electrons, *7* — the ion collector, *8* — the surface ionization W ribbon.

3. Results and discussion

3.1. Results

Figure 2 shows the dependences of the yield (q) of electron-stimulated desorption of the europium atoms in dependence on the energy of electrons (E_e) that excite ESD, for the two europium coverages (θ): 0.2 monolayers (MLs) and 1.0 monolayers. For the europium coverage of 0.2 monolayers, the ESD of Eu atoms begins to be recorded at $E_e > 26.0$ eV and the ESD yield dramatically increases

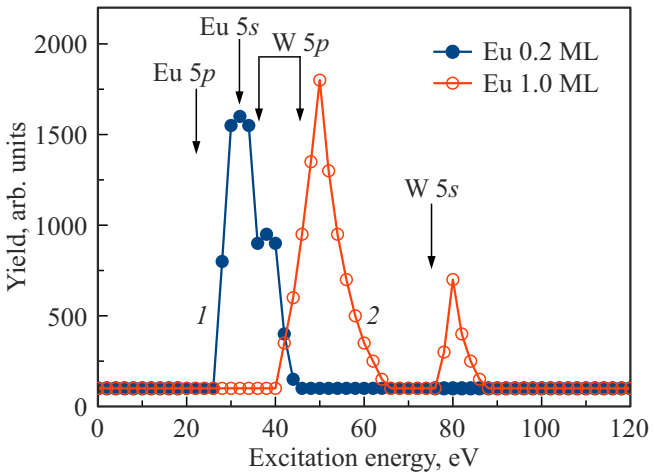

Figure 2. Yield q of the Eu atoms in ESD from the tungsten surface covered with the germanium monolayer and a dose of europium depositing of 0.2 monolayers (*1*) and 1.0 monolayers (*2*), at $T = 300$ K, depending on the energy of the bombarding electrons E_e. The arrows show a position of the levels of Eu $5p$, Eu $5s$, W $5p$ and W $5s$.

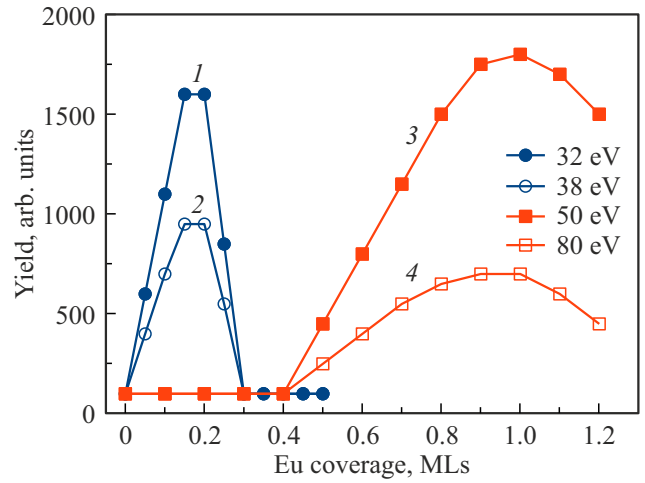

Figure 3. Yield q of the Eu atoms in ESD from tungsten covered with the germanium monolayer, at $T = 300$ K, depending on the dose of the deposited europium atoms for the energy of the bombarding electrons 32 (*1*), 38 (*2*), 50 (*3*) and 80 eV (*4*).

with increase in E_e. There is evidently a compound peak having two maxima at the excitation energy of 31.9 eV and 38.0 eV. At $E_e > 46.0$ eV, there is no observed ESD of the europium atoms. The observed peaks can be related to excitation of the states Eu $5p$ (the binding energy $E_b = 22.0$ eV) and Eu $5s$ ($E_b = 32.0$ eV). For the europium coverage of 1.0 monolayers, the ESD of Eu atoms begins to be recorded at $E_e = 40.0$ eV and the ESD yield dramatically increases with increase in E_e. There is evidently a wide peak with a maximum at the excitation energy of 50.0 eV. With further increase in the energy, there is a drop of the ESD yield of the Eu atoms and the region $66.0 \le E_e \le 76.0$ eV exhibits no ESD of the europium atoms. With a further increase in excitation energy, an additional, less intense, ESD peak of europium atoms is recorded at $E_e = 80.0$ eV. The peak at $E_e = 50.0$ eV can be related to excitation of the states of closely-located tungsten doublets: W $4f_{7/2}$ ($E_b = 31.4$ eV), W $4f_{52}$ ($E_b = 33.6$ eV), W $5p_{3/2}$ ($E_b = 36.8$ eV) and W $5p_{1/2}$ ($E_b = 45.3$ eV). The presence of four levels, which are insignificantly different in the energy and simultaneously contribute to this peak, agrees well with the observed width of the latter. As can be seen on Figure 2, it is approximately two times bigger than the peak width at $E_e = 80.0$ eV. The narrower peak can be related to excitation of W $5s$ ($E_b = 75.6$ eV). The similar results were obtained when studying ESD of the Eu atoms from oxidized tungsten [11].

Figure 3 shows the dependences of the yield of electron-stimulated desorption of the europium atoms from tungsten covered by the germanium monolayer, at $T = 300$ K depending on the dose of the deposited Eu atoms at the various energies of the bombarding electrons. The indicated energies correspond to the maxima of the ESD yield of europium atoms in Figure 2. It is clear that on Figure 3 the entire region of the europium coverages can be distinctly divided into two sections: from 0 to 0.3 and from 0.4 to 1.2 monolayers. These sections are separated by a gap, which does not exhibit ESD of the europium atoms. The region of the coverages below 0.3 MLs exhibits ESD of the europium atoms, which is related to excitation of the Eu $5p$ and Eu $5s$ states.

The ratio of the ESD yields of the europium atoms at the excitation energy of 32 and 38 eV does change with the coverage and is 0.58, which can indicate that there is no ESD of the europium atoms in excitation of the doublet Ge $3d$ ($E_b = 29.2$ and 29.8 eV). The range of the coverages 0.3–0.4 MLs exhibits no ESD of the Eu atoms. This means that with a europium coverage of 0.3–0.4 ML, a phase transition occurs on the surface and the formation of a new Eu/Ge/W phase. With the coverages above 0.4 monolayers, the dependence $q(\theta)$ of the europium atoms exhibits new peaks that correspond to ESD of the europium atoms in excitation of the W $4f$, W $5p$ and W $5s$ states. The decrease in the ESD yield of europium atoms at $\theta > 1$ MLs is associated with the screening effect of the second forming layer of europium atoms. The ratio of the ESD yields of the europium atoms at the excitation energy of 50 and 80 eV does not change with the coverage up to 1 MLs and it is 2.5. It means emergence of the third surface phase that is formed within the region from 0.4 to 1.0 monolayers. Further increase in the coverage results in increase in the ratio to 4 at the coverage of 1.2 MLs. It can be related to the fact that a depth of penetration of the exciting ESD electrons increases with increase in the kinetic energy of electrons, and, therefore, a portion of the ESD exciting electrons decreases in the tungsten layer covered with two europium layers in comparison with one layer of the europium atoms. The similar results were obtained when studying ESD of the Eu atoms from oxidized tungsten [11].

3.2. Model

We note that the processes related to excitation of the tungsten and europium atoms occur at a fixed amount (one monolayer) of deposited germanium. With the low europium coverages, ESD of the europium atoms is related to excitation of the europium atoms, while with the high europium coverages, ESD of the europium atoms is related to excitation of the tungsten atoms. We propose a probable scheme of electronic transitions with ESD of the europium atoms (see Figure 4).

Let us consider the processes occurring in ESD of the europium atoms, as exemplified by excitation of the Eu $5p$ electrons. Irradiation of the surface by electrons results in excitation of the Eu $5p$ level (1) with formation of a hole at this level. Subsequently, the Auger process occurs in the europium atom with neutralization of the hole (2) and excitation of the electron to vacuum (3), with the formation of a positive Eu ion. The Eu ion is neutralized by transition of the electron from the valence band of the adsorbed germanium atoms (4) with increase in the size of the europium atoms, thereby resulting in its repulsion from the surface and desorption. The germanium atom is neutralized by transition of the electron from the tungsten valence band. The similar process can occur in excitation of the Eu $5s$ states.

Let us consider the processes occurring in ESD of the europium atoms in excitation of the tungsten states, as exemplified by excitation of the electrons of W $5p$. Irradiation of the surface by electrons results in excitation of the W $5p$ level (5) with formation of a hole at this level. Then, the electron is tunneled from the Ge $3d$ level with neutralization of the hole at a level of the W $5p$ level (6), as suggested in the study [18]. The formed hole at the Ge $3d$ level is neutralized by tunneling the electron from the Eu $5p$ level (7) with formation of the hole Eu $5p$. Neutralization of the hole at the Eu $5p$ level with subsequent desorption of the europium atom occurs according to the same scheme as described above for the excitation of the Eu $5p$ level (transitions (2–4)). Let us not that the hole at the W $5p$ level can not be neutralized by the transition of the electron from the Eu $5s$ level due to prohibition of the $s-s$ transitions and a large distance between the atoms of europium and tungsten. The similar process can also occur in excitation of the W $4f$ states and the W $5s$ states, whose level is not shown on the diagram.

Note that all the electronic transitions occur in an interface germanium–tungsten and europium–tungsten.

The drop of ESD yield with the europium coverages exceeding one monolayer is apparently related to the fact that formation of the second europium layer hampers the transition (7).

It is assumed that the germanium atoms most likely adsorb in hollow positions on the W(100) surface. However, there is no solid single-atom germanium film formed on the tungsten surface. This possibility is indicated by results of the study [15]. Excitation of the europium states at the small coverages may be related to formation of surface complexes that consist of atoms of europium, germanium and tungsten. This complex can be formed, for example, by substituting a vacancy in the germanium monolayer with the europium atom. As the europium coverage increases, these complexes can be covered by the second europium layer, thereby resulting in the drop of the ESD yield of the Eu atoms. If the defect in the surface layer of the germanium atoms is connected by more than one atom, then it is possible to have a situation when the defect is occupied by a large number of the europium atoms. Then, as the coverages increases, a role of the europium-europium bond increases as the Eu–Ge bond in the Eu–Ge–W complex weakens. It also results in reduction of the ESD yield of the Eu atoms.

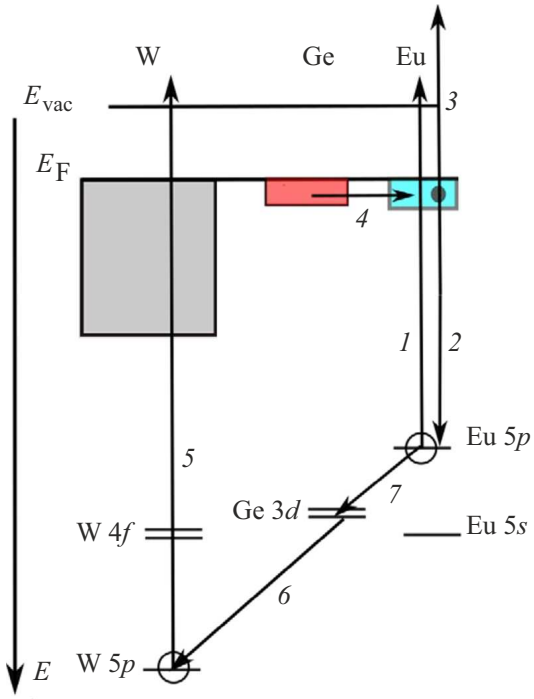

Figure 4. Diagram of the processes of ESD of the europium atoms from the surface of the Ge monolayer on tungsten with the deposited europium 2D-layer.

With the coverages above 0.4 monolayers of europium, it is assumed that the europium atoms also prefer to be adsorbed in the well position above the germanium layer with the large coverages. Therefore, the europium atoms will be adsorbed in the position above the surface atom of tungsten. In this case, when being irradiate by electrons, the formed hole at the W $5p$ level is neutralized by tunneling the electron from the Eu $5p$ level (7) with formation of the Eu $5p$ hole and this process is not interfered by the monolayer film of the germanium atoms. In this case, as the coverage increases, the ESD yield of the europium atoms increases.

4. Conclusion

Electron-stimulated desorption of europium atoms on a monolayer germanium film on a W(100) surface has been studied. It is shown that with europium coverages of less than 0.3 monolayers it is caused by the excitation of the Eu $5p$ and Eu $5s$ states, and with coverages of more than 0.4 monolayers it is caused by the excitation of the states: W $4f$, W $5p$ and W $5s$. No ESD of the europium atoms is observed with the europium coverages within the range from 0.3 to 0.4 europium monolayers. A model of ESD of europium atoms is proposed, which is associated with the excitation of Eu $5p$ and Eu $5s$ or W $4f$, W $5p$ and W $5s$ states with subsequent hole relaxation due to transitions in the Eu/Ge and Eu/Ge/W interface.

Conflict of interest

The authors declare that they have no conflict of interest.

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