

Thermal properties of CO-Yb-substrate nanostructures

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Influence of adsorbed carbon monoxide molecules on the thermal properties of rare-earth metal ytterbium films of nanoscale thickness has been studied. The films are produced at room temperature by metal deposition on single-crystal silicon substrates with the Si(111) surface orientation or textured tungsten ribbons with the predominant (100) face. It is shown that the adsorbed molecules hinder evaporation of ytterbium. The strength of such hindering is dependent on the chemical nature of substrate material. It is established that the substrates affect the state of adsorbed molecules through the nanofilms. This in turn influences on the evaporation rate of nanolayer material.

Keywords: thermal stability of nanofilms, surface, adsorbed molecules, carbon monoxide, ytterbium, silicon, tungsten, Auger electron spectroscopy, mass spectrometry.

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Introduction

Considerable attention is currently being paid to the study of nanometer-sized objects (e.g., [1–10]). One area of such research is the study of adsorbed molecules effect on the properties of nanometer-thick metal films. These studies have shown that molecules of carbon and oxygen monoxide adsorbed in molecular form on the surface of rare earth metal ytterbium nanofilms induce the transition from the divalent state to the trivalent state therein [11]. This transition means that adsorbed molecules can also induce qualitative changes in other properties of nanoobjects. In particular, valence transition can be accompanied by a change in the type of bonds between atoms in the ytterbium crystal lattice. The proof of such conclusion was obtained in the paper [12]. It was shown that when oxygen in molecular form is adsorbed on the surface of 16 monolayer (ML) thick ytterbium films, a metal–semiconductor transition occurs therein. Thus, adsorption of CO and O₂ molecules on the surface of ytterbium nanofilms may be accompanied by significant changes in a number of their characteristics and, in particular, thermal properties. Research of relationship between thermal properties of materials and their electronic and atomic structure is a relevant scientific and practical task. In particular, such studies are important for development of completely new methods to improve stability of various nanoobjects [13]. The objective of this paper was to study the nature and scope of changes to thermal stability of ytterbium nanofilms happening during CO molecules adsorption.

1. Research methods

This paper studied ytterbium nanofilms deposited on substrates of two types: silicon monocrystals with surface

orientation Si(111) and thickness $3 \cdot 10^{-2}$ cm and textured tungsten ribbons with thickness of 10^{-3} cm. As is commonly known [14,15], the surface of such ribbons after their heating at high temperatures is formed by rather large crystallites, face (100) of which is oriented parallel to the surface. Ribbons were decarbonized by heating in an oxygen atmosphere at a pressure of 10^{-4} Torr. Ytterbium nanofilms were deposited on the surface of the substrates by thermal evaporation of metal from tantalum evaporators in vacuum $3 \cdot 10^{-7}$ Torr. During metal deposition, substrates had room temperature. Ytterbium deposition rate was generally 1 ML/min. During nanostructure studies, residual gas pressure in the vacuum chamber did not exceed $3 \cdot 10^{-8}$ Torr.

The properties of ytterbium nanofilms were modified by adsorbing carbon monoxide CO molecules on their surface at room temperature. Under these conditions, the adsorbed molecules were in molecular form because their closed electron shells are extremely stable [16].

CO–Yb-substrate structures obtained at different doses of adsorbed gases have been studied. But most often this dose was 480 Langmuir (L, $1 \text{ L} = 10^{-4} \text{ Torr} \cdot \text{s}$). Carbon monoxide inlet into the vacuum chamber of the unit was carried out with the inlet system after its thorough cleaning *in situ*. Inlet gas purity was monitored by a mass spectrometer located in the immediate vicinity of the studied specimens.

Two experimental methods were used to investigate thermal properties: Auger electron spectroscopy (AES) and mass spectrometry. The first method was implemented using an Auger-spectrometer with an analyzer of the „cylindrical mirror“ type. The second method was implemented using a magnetic 90-degree sector mass spectrometer. The Auger spectra of the structure components before and

after heating them at different temperatures for 45 s were studied using the EOS method.

Mass spectrometry was used to study the ytterbium evaporation rate dependences in studied structures at different temperatures.

It was assumed that a number of processes may occur when the structures created at room temperature are heated:

(a) ordering of structures. They can transform from more loose to more densely packed structures.

b) the state of the molecules adsorbed on the surface may change as a result of the ordering of the structures. If they were partially immersed in the surface before heating, after heating and ordering they should float up above the surface.

c) floating of molecules may be accompanied by an increase in Auger signals of the atoms that make up the adsorbed molecules.

d) molecules can dissociate when heated. The released atoms will either remain on the surface, diffuse into ytterbium nanofilms, or evaporate into vacuum.

e) Yb atoms will evaporate from nanofilms.

It was suggested that the experimental methods used in this paper would make it possible to analyze the mentioned processes and, consequently, to obtain data on the thermal properties of the studied structures.

2. Study results and their discussion

Fig. 1 provides results obtained for structures CO (480 L)–Yb (16 ML)–Si(111) using AES method. Given temperature dependences have some characteristic features. It can be seen that the intensity of ytterbium (kinetic

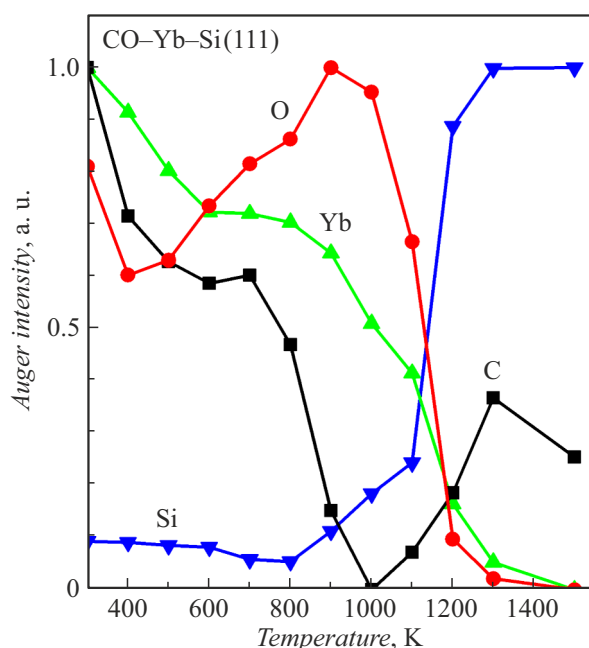


Figure 1. Temperature dependences of intensity of Auger-signals of carbon, oxygen, ytterbium and silicon for structure CO (480 L)–Yb (16 ML)–Si(111).

energy 170–180 eV), carbon (273 eV) and oxygen (503 eV) Auger-lines begin to decrease markedly already when heated to relatively low temperatures. This decrease for oxygen Auger peak ends at $T = 400$ K, and for carbon and ytterbium Auger-signals — at 600 K. When heated to higher temperatures, carbon and ytterbium Auger-signals remain approximately constant in the 600–800 K temperature region and then begin to decrease (in the case of carbon, this decrease is observed already at temperatures above 700 K). Temperature dependence of oxygen Auger-peak intensity is qualitatively different from those just discussed. This peak in the temperature range of 400–1000 K significantly increases, and then at higher temperatures it decreases. The aforementioned difference between the temperature dependences of carbon and oxygen at $T > 400$ K makes it possible to assume that in this temperature region the of CO molecules dissociate, and dissociation degree increases with increasing temperature. Growth of oxygen Auger-peak in this case indicates, most likely, that O atoms released by dissociation of molecules remain on the surface rather than diffusing into the volume of the film, forming an oxide. This conclusion is also supported by the fact that evaporation of ytterbium and oxygen atoms from the silicon surface ends at $T = 1300$ –1500 K. However, if oxidation were to occur on the surface and form stable ytterbium oxide Yb_2O_3 , its evaporation would have to take place at much higher temperatures [17].

Complex course of carbon Auger-peak intensity dependence in the region of the highest temperatures draws attention. Thus, at $T > 700$ K this peak begins to decrease, at $T = 1000$ K it becomes equal to zero, and at even higher temperatures it appears again. Such course of the temperature dependence testifies to the fact that carbon atoms released during dissociation of CO molecules at $T > 700$ K diffuse through the ytterbium film to the substrate surface. Due to the limited free path length of the carbon Auger-electrons, their Auger-signal becomes zero. It reappears when the ytterbium film partially or completely evaporates.

Fig. 2 shows the temperature dependences of Auger-signals of components in structures CO (480 L)–Yb (16 ML)–W. A number of peculiarities of these dependences, which distinguish them from the dependences of fig. 1, draw attention. Firstly, this is much weaker pronounced decrease of Auger-signals with temperature growth in the region of low temperature values. Secondly, parallelism in the course of the dependences. In particular, fig. 2 shows that the curves obtained for carbon and oxygen have a very similar appearance in contrast to the analogous dependences for the system CO–Yb–Si(111). Finally, thirdly, there is no evidence that carbon atoms diffuse through the ytterbium films to the substrate, as is the case for the CO–Yb–Si(111) structures. As already noted, a reflection of the latter is that the carbon Auger-signal reaches a minimum at some temperatures (~ 1000 K) and then grows at even higher values. All the mentioned features of the temperature dependences for the CO–Yb–W structures suggest that the dissociation of CO molecules does not

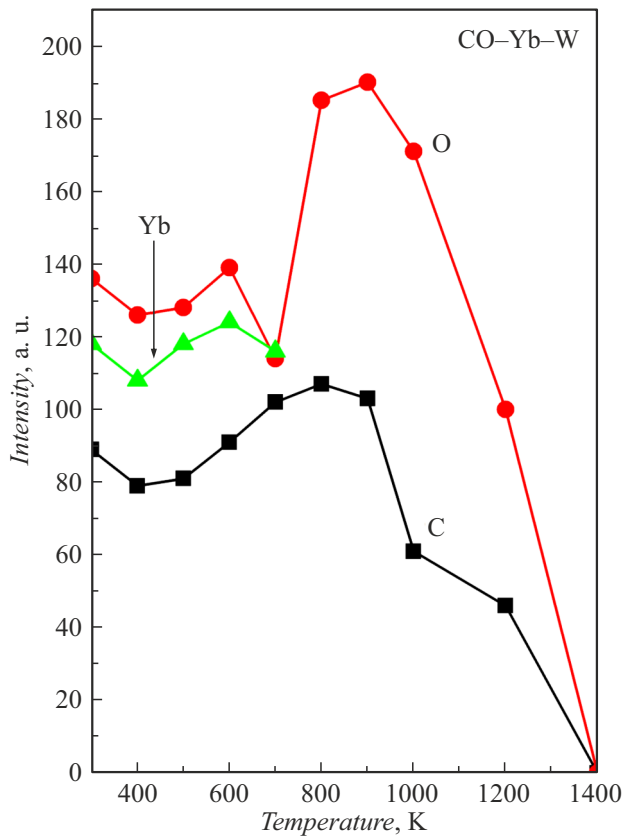


Figure 2. Temperature dependences of intensity of Auger-signals of carbon, oxygen and ytterbium for structure CO (480 L)-Yb (16 ML)-W.

occur in them when heated. The aforementioned difference in the properties of the two structures indicates that the substrates have a significant influence on their properties. This conclusion finds clear endorsement in the results obtained by the mass spectrometric method. Some of them is given in fig. 3. In this figure in coordinates „speed of atom evaporation Yb–reverse temperature“ there are results for three structures: Yb (16 ML)-W (curve 1), CO (480 L)-Yb (16 ML)-W (curve 2) and CO (480 L)-Yb (8, 16 and 24 ML)-Si(111) (curves 3–5). Besides, in this figure there is dependence of metal ytterbium evaporation speed on temperature, calculated by pressure of its equilibrium vapors [18] (curve 6), and a similar dependence for ytterbium evaporation from disilicide film YbSi_{2-x} , formed by heating structure Yb (16 ML)-Si(111) at 800 K for 300 s (curve 7). Comparison of dependences 1 and 6 shows that they are very close. This means that evaporation of ytterbium from 16 ML thick films is not different from the same process from three-dimensional specimens. Deposition of CO molecules on the surface of ytterbium nanofilms leads to a significant shift of the evaporation rate dependence on temperature in the region of its high values (dependence 2). However, its nature and, in particular, slope tangent determined by evaporation process

activation energy remain practically unchanged. The noted features indicate that the thermal stability of ytterbium films increases considerably in the adsorption of CO molecules. This is due to the reduced probability that the Yb atom, having received the energy sufficient to transfer it from the film to the gas phase, will evaporate. It is also noteworthy that dependence 2, as well as dependence 1, has almost linear character throughout the temperature range in which ytterbium evaporation occurs. This means that during evaporation of metal atoms, properties of the nanofilm formed by them practically do not change, and the system CO-Yb-W is not subject to thermally activated restructuring.

Dependences 3–5 (fig. 3) obtained for CO-Yb-Si(111) structures with ytterbium films thicknesses of 8, 16 and 24 ML are qualitatively different from the first two: they are significantly nonlinear. First, there is a slow increase in ytterbium evaporation rate in the very wide temperature region of 300–900 K. And only at $T > 900$ K there is a significant acceleration of this process. This course of the evaporation curves is a reflection of the temperature-dependent struc-

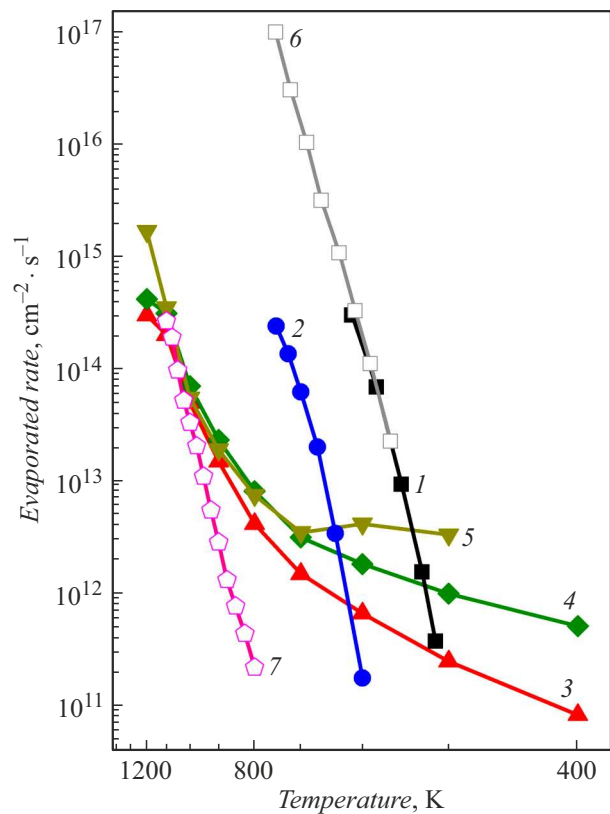


Figure 3. Temperature dependences of ytterbium atom evaporation speed from Yb structures (16 ML)-W (curve 1), CO (480 L)-Yb (16 ML)-W (curve 2) and CO (480 L)-Yb-Si(111) (curves 3–5). Thickness of ytterbium nanofilms in CO structures CO (480 L)-Yb-Si(111): 3–8, 4–16, 5–24 ML. For comparison, similar dependences obtained for massive three-dimensional specimens of metallic ytterbium (curve 6) and ytterbium disilicide nanofilms in structure Yb (16 ML)-Si(111) (curve 7) are also shown.

turing processes occurring in the structures, which end at $T \approx 900$ K. In the process of these rearrangements, their thermal stability increases. This ensures slow growth of the ytterbium evaporation rate with increasing temperature. It is characteristic that silicon Auger-signal (92 eV) does not increase up to temperatures $T = 800$ K (fig.1) during these rearrangements. This indicates that active mixing of Si and Yb atoms does not occur at the same time.

Intense evaporation of ytterbium from structures CO–Yb–Si(111) occurs in the region of temperatures $T > 900$ K, significantly exceeding similar values for dependences 1 and 2. It is significant that in the region of high temperatures (~ 1000 K and above) the rates of ytterbium evaporation from CO–Yb–Si(111) structures coincides with similar values for ytterbium disilicide film (dependence 5). Consequently, ytterbium disilicide may form in CO–Yb–Si(111) structures at $T \geq 1000$ K, which is confirmed by the results of thermodesorption spectroscopy [19], and also agrees with the AES results in fig. 1.

Thus, the experimental results obtained in this paper indicate that adsorption of CO molecules on ytterbium nanofilms leads to a significant shift of Yb atoms intense evaporation curves to the region of higher temperatures. Thus, in the case of CO–Yb–W structures this shift is 100 K, and for CO–Yb–Si(111) — 400 K (fig. 3). These results mean that the thermal properties of the studied structures essentially depend on the substrate. This dependence is determined by the fact that, according to the experimental data obtained in this paper, dissociation of CO molecules on the nanofilm surface does not occur, and therefore the thermal stability of the latter is determined by the adsorbed carbon monoxide layers thereon. The results also indicate that the adsorbed molecule layers act as a certain envelope that inhibits the evaporation of the nanofilm material. A kind of an evaporation cell is created, inside which vapor pressure is determined by the properties of the material to be evaporated (ytterbium in this case). As a result, flow of evaporated atoms is determined by the vapor pressure and the properties of the layer of adsorbed molecules.

In case of CO–Yb–Si(111) structures the situation is more complex. CO molecules dissociate at higher temperatures. C atoms released diffuse to the substrate, and O atoms remain on the surface. As a result, several processes become possible. The main ones among them, in opinion of the authors, are the following. First, O atoms can form O₂ molecules, which, being on the surface in the adsorbed state, may cause a more significant increase in the thermal stability of ytterbium nanofilms compared to CO molecules. Second, oxygen atoms can react chemically together with Si atoms to form complex silicate compounds with Yb atoms. Possible participation of Si atoms in reactions is indicated by growth of silicon Auger-signal observed in the temperature range, where ytterbium evaporates intensely (900–1200 K). The considered processes can lead to increase of thermal stability of ytterbium nanofilms.

The question arises why CO molecules dissociate into atoms on the same ytterbium nanofilms at elevated temperatures, as it takes place in CO–Yb–Si(111) structures, while this does not occur on films that are part of CO–Yb–W structures. One possible reason for this difference is that films with different structures or microstructures are created on different substrates at room temperature. In that case they may have different distances between the adsorption centers on the surface. One of them may contribute to the process of molecule dissociation, while the other will be less favorable for this process.

Obviously, the proposed model raises a complicated question related to the mechanism of Yb atoms passage through adsorbed layers in process of their transition from nanofilms to vacuum. It is possible that this occurs through any defects in these layers or, if the adsorbed layer is not completely filled, through unoccupied adsorption centers.

Conclusion

Effect of adsorbed carbon monoxide molecules on the thermal properties of nanometer-thick films of the rare earth metal ytterbium was studied using AES and mass spectrometry. Films were created at room temperature by deposition of the metal on monocrystalline silicon substrates with Si(111) surface orientation or textured tungsten ribbons with preferential yield to the face surface (100). Ytterbium films with thicknesses of 8, 16, and 24 monolayers were studied. It was shown that adsorbed molecules slow down ytterbium evaporation. The value of this slowdown depends on the chemical nature of the substrate material. It is shown that the substrates through nanofilms affect the state of the adsorbed molecules. In some cases (CO–Yb–Si(111) structures) the CO molecules on the nanofilm surface dissociate at elevated temperatures, in other cases (CO–Yb–W structures) at temperatures at which the nanofilm material evaporates, carbon monoxide remains on the surface in its molecular form. Dissociation is the starting point of several processes, which may result in formation of other molecules or structures that slow down the evaporation of Yb atoms.

Conflict of interest

The authors declare that they have no conflict of interest.

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