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Formation and properties of surface phosphide on rhenium

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The adsorption of PCl_3 molecules on $(10\bar{1}0)\text{Re}$ was studied in a wide temperature range of 300–2000 K. It was shown that at room temperature PCl_3 molecules are chemisorbed on the surface, apparently in a partially dissociated form. At $T \sim 800$ K, thermal desorption of chlorine begins, and at $T > 1100$ K, only phosphorus remains on the surface. When PCl_3 is adsorbed in the range $T = 1100$ – 1200 K, a surface compound with ReP stoichiometry is formed. The surface compound begins to decompose at 1200 K as a result of thermal desorption; P atoms finally leave the rhenium surface at $T \approx 1850$ K, which corresponds to a change in the desorption activation energy from 3.3 eV to 5.1 eV.

Keywords: phosphorus, rhenium, adsorption, surface compound, thermal desorption.

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1. Introduction

Traditionally, in physical materials science, group V elements, primarily nitrogen and phosphorus, are classified as harmful impurities [1,2] that impair the properties of most ferrous and non-ferrous alloys. Phosphorus atoms occupy an intermediate position between substitution and interstitial elements, but by the nature of their interaction with the lattice of refractory metals, it is closer to silicon and sulfur than to nitrogen [3]. However, by the nature of its chemical interaction, phosphorus is in many ways an analogue of carbon [4]. Bulk metal phosphides, as well as carbides and nitrides, are refractory to a very high extent and are characterized by the formation of very strong metal-nonmetal chemical bonds.

The interaction of phosphorus with the surface of transition metals has been much less studied than the adsorption of silicon, carbon or chalcogens on them. There is a large number of publications devoted to the adsorption of nitrogen, ammonia, and nitrogen oxides on platinum metals [5,6] and transition metals [7], generated mainly by the needs of heterogeneous catalysis, where, in particular, the mechanisms of binding gases with surface are investigated. However, they are of little use in relation to the phosphorus adsorption.

Previously, we studied the interaction of phosphorus atoms with the $(100)\text{W}$ surface, and showed that a very thermally stable surface compound is formed on it: the surface phosphide with WP composition. It turns out that P atoms from the surface phosphide are capable of competing with silicon atoms for adsorption sites in the process of joint adsorption [8]. Rhenium is close to tungsten in a number of physical properties (refractoriness, crystal lattice rigidity, density), but has a different crystal geometry [6] and differs significantly in chemical and catalytic properties,

being one of the most important catalysts [9]. In this context, it seemed important to study the mechanisms of phosphorus adsorption and its thermal stability on the surface of a given metal.

2. Instruments and experimental methods

The studies were carried out in an ultra-high vacuum ($p \approx 10^{-10}$ Torr) high-resolution Auger spectrometer [10]. The sample used was a $1 \times 0.02 \times 40$ mm polycrystalline rhenium ribbon heated by alternating current. For the calibration purposes, a tungsten ribbon of the same size was placed parallel to the rhenium one. Both ribbons were cleaned by heating in ultra-high vacuum (UHV) at 2500 K and in an oxygen atmosphere ($p_{\text{O}_2} \approx 10^{-6}$ Torr, 1500 K). After cleaning, only Auger peaks of the corresponding metal were observed on the surface of the ribbons. Simultaneously with cleaning, the ribbons were textured and the $(100)\text{W}$ face with a work function of $e\phi = 4.65$ eV and the $(10\bar{1}0)\text{Re}$ face with a work function of $e\phi = 5.15$ eV came out to the surface. The work function was measured by the Richardson method. Both values are typical for the above-mentioned tungsten and rhenium faces [11]. According to X-ray diffraction data, the degree of orientation of the $(10\bar{1}0)\text{Re}$ face with respect to the surface was 99.9%, and for tungsten the degree of orientation of the (100) face was 99.6%. The temperature of the ribbons was measured with a micropyrometer. The temperature measurement error was ± 5 K. In the non-pyrometric region, linear extrapolation of the temperature dependence on the heating current was carried out.

A surface coverage of P atoms was created by the adsorption of PCl_3 molecules, which were injected into

the working chamber of the Auger spectrometer to a pressure of $\sim 1 \cdot 10^{-7}$ Torr. For the measurements, the Auger peaks of phosphorus with $E = 120$ eV, chlorine with $E = 181$ eV, a triplet of Auger peaks of tungsten with $E = 162$ – 177 eV, and a triplet of Auger peaks of rhenium with $E = 161$ – 176 eV were used [12]. It was possible to record Auger spectra directly from heated samples up to $T = 2200$ K. The intensity of the Auger signal was measured peak-to-peak using differentiated Auger spectra.

3. Experimental results

3.1. Interaction of phosphorus trichloride with the surface (10 $\bar{1}$ 0)Re

Adsorption of PCl_3 molecules on rhenium at room temperature resulted in the appearance of peaks in the Auger spectrum with energies of $E = 120$ eV and $E = 181$ eV, corresponding to LVV Auger transitions in adsorbed phosphorus and chlorine atoms [12]. Then the sample was heated and the transformation of the Auger spectrum was monitored.

The change in the Auger signals of chlorine (1) and phosphorus (2) during the adsorption of PCl_3 molecules on rhenium to saturation at 300 K followed by heating is shown in Figure 1. The intensities of the Auger signals of both adsorbates do not correspond to the stoichiometry of the adsorbed molecule, presumably as a result of mutual screening.

Heating the sample to $T = 700$ – 1100 K leads to a gradual removal of chlorine from the metal surface, presumably as a result of the destruction of adsorbed molecules and thermal desorption of chlorine, most likely in the form of Cl_2 molecules. At the same time, the Auger signals of phosphorus and rhenium increase slightly, presumably due to a decrease in screening by chlorine atoms. At

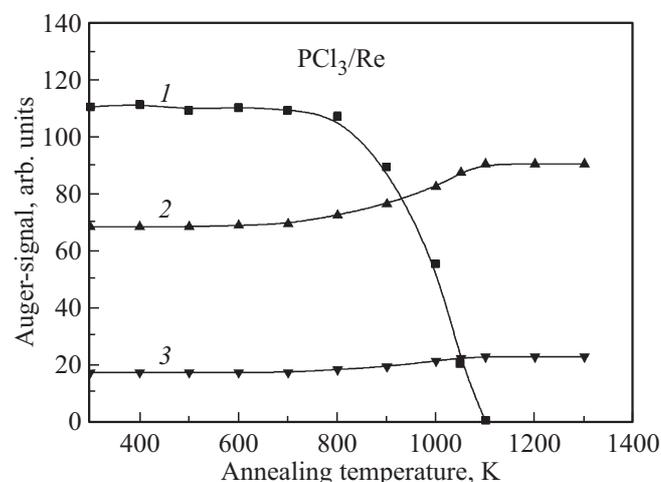


Figure 1. Dependence of the intensity of the Auger signal of Cl (1), P (2), and Re (3) on the sample annealing temperature for 20 s at each point. Initial state — adsorption of PCl_3 at 300 K up to saturation.

$T > 1100$ K, the Auger signal of chlorine on the surface cannot be observed — this corresponds to the complete destruction of adsorbed molecules and thermal desorption of chlorine. At the same time, only phosphorus atoms remain on the surface. Similar effects are widely used in the technology of gas-phase epitaxy of A_3B_5 semiconductor compounds [13], where PCl_3 molecules are used as one of the technological and effective carriers of phosphorus atoms to the surface of the growing crystal, while unwanted impurities (chlorine) are easily removed from the surface.

3.2. Formation and properties of the surface rhenium phosphide

In order to ensure the deposition of phosphorus atoms on the metal surface, adsorption of PCl_3 molecules was used at $T = 1100$ K: exposure of rhenium in phosphorus trichloride vapor at $p_{\text{PCl}_3} = 10^{-7}$ Torr for 2–3 min resulted in the formation of a stable surface coating of phosphorus atoms; chlorine was not observed on the surface. The Auger signal of phosphorus in this mode reaches saturation; the value of the Auger signal turns out to be approximately 30% greater than the maximum value that it had when heating the adsorption layer of PCl_3 molecules obtained at room temperature. In this case, the ratio of the Auger signal of phosphorus to the Auger signal of pure rhenium is $I_{\text{P}}/I_{\text{Re}}^0 = (4.4 \pm 0.3)$, and the intensity of the Auger signal of rhenium decreases by ~ 1.2 times. Auger spectra of phosphorus and rhenium for this state are shown in Figure 2. Insignificant screening, typical for the formation of surface rather than bulk chemical compounds, led us to the assumption that we are dealing with the adsorption of P atoms on the surface, as was previously observed for the W–P system [8], and not with the formation of bulk rhenium phosphide. It should be noted that the shape of the Auger spectra of phosphorus in surface compounds on rhenium and tungsten turned out to be the same; no change in the shape of the Auger spectrum of rhenium upon adsorption of phosphorus was noticed.

As it turned out, the surface concentration of phosphorus in the coating under study does not depend on the temperature of its deposition in a temperature range of 1100–1200 K, which also indicates the surface rather than the bulk nature of the resulting adsorption state. By analogy with tungsten, it is logical to call this state rhenium surface phosphide (SP).

3.3. Thermal stability of the rhenium surface phosphide

Figure 3 shows the change in the Auger signals of the adsorbate (phosphorus) and the substrate (rhenium) during stepwise heating of the surface phosphide. As can be seen, even at 1200 K the Auger signal of the adsorbate begins to decrease, indicating the removal of phosphorus atoms from the surface. At $T > 1850$ K, phosphorus is not observed on

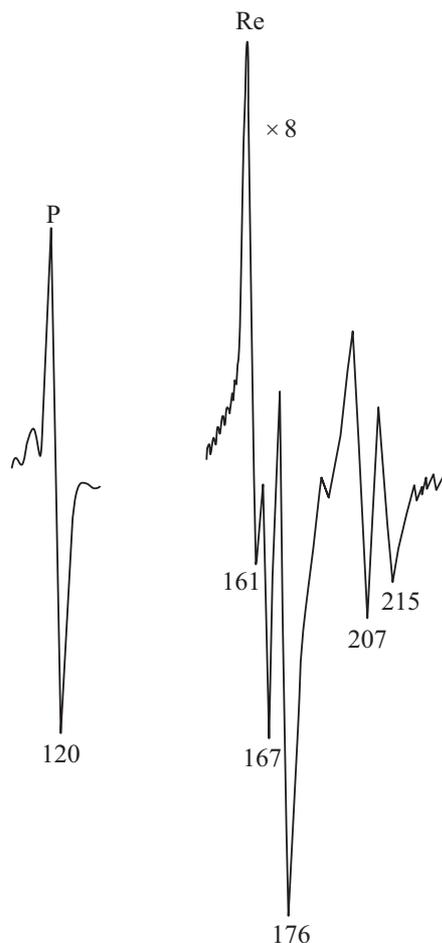


Figure 2. Auger spectra of phosphorus and rhenium for the surface chemical compound of ReP.

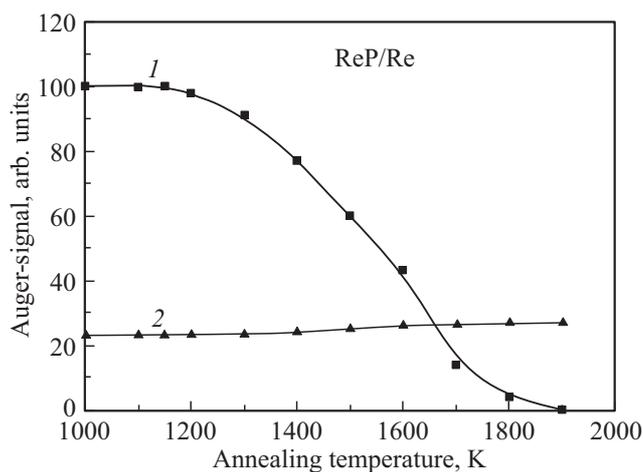


Figure 3. Change in the intensity of the Auger signals of phosphorus (1) and rhenium (2) upon annealing of the ReP surface phosphide for 20 s at each point.

the surface, and the Auger signal of the substrate restores its initial value, indicating the atomic purity of the surface.

Thus, the removal of phosphorus from rhenium SP takes place in a very wide temperature range of 1200–1850 K.

The mechanism of its removal, the dissolution of phosphorus atoms in the bulk of the metal or thermal desorption, has not currently been established, but based on the very high temperatures it can be assumed that, at least for small coatings, it is removed by thermal desorption. In favor of thermal desorption rather than dissolution of atoms in the bulk of the substrate also indicates the fact that when the sample was cooled, phosphorus was not released on its surface. Assuming the first order of desorption, the Arrhenius relation for the adatom lifetime relative to desorption and setting the pre-exponential $C = 10^{13} \text{ s}^{-1}$ [6], the desorption energy at low degrees of coverage $\theta \rightarrow 0$ can be estimated. As it turned out, $E_{\text{des}} \sim 5.1 \text{ eV}$.

Applying a similar model to a coating that is close to saturation, it is possible to calculate the activation energy for the destruction of the SP at $\theta \approx 1$. It is $E_{\text{des}} \sim 3.3 \text{ eV}$, i.e. almost 2 eV lower. Previously, we observed a similar very strong change in the activation energies of destruction of other surface compounds on tungsten, rhenium, and molybdenum: silicides, sulfides, and carbides, where the activation energy of the corresponding processes changed by 2 eV and even more [14].

3.4. Absolute concentration of phosphorus in the rhenium surface phosphide

To understand the physics of the phenomenon, it is important to measure the absolute concentration of phosphorus atoms in the resulting surface phosphide. Determining the absolute concentration of the adsorbate is a very difficult task. We used surface phosphide at (100)W with WP stoichiometry and a phosphorus atom concentration of $1 \cdot 10^{15} \text{ cm}^{-2}$ as a reference for comparison. The technology for its production and the absolute concentration of phosphorus in it were determined by us earlier in [8] by comparing the intensities of Auger signals of phosphorus and other elements (C, Si, S) on the tungsten surface with known absolute concentrations.

For this purpose, we produced tungsten surface phosphide on a W sample placed next to the rhenium sample in the working chamber of the Auger spectrometer. It was produced by adsorption of PCl_3 molecules on (100)W at $T = 1100 \text{ K}$, a gas pressure of $p = 1 \cdot 10^{-6} \text{ Torr}$, and an exposure time of 120 s. The relationship between the magnitude of the Auger signals of tungsten and phosphorus in the coating produced in our experiment was well consistent with this ratio presented in [8].

Weak and almost identical screening of the Auger signals of rhenium and tungsten substrates by adsorbed phosphorus atoms, as well as the close time of formation of maximum coverage at the same flux density of PCl_3 at $T = 1100 \text{ K}$ indicates the proximity of phosphorus concentrations on both substrates. The table shows intensities of the Auger signals of phosphorus and both substrates (W and Re) recorded in one experiment, and the Auger signals of the substrates were recorded both before exposure in the atmosphere of PCl_3 and after the formation of surface

Auger signal intensities, a. u.

Pure W sample	37
Pure Re sample	27
Signal of W from the W surface phosphide	34
Signal of P from the W surface phosphide	90
Signal of Re from the Re surface phosphide	23
Signal of P from the Re surface phosphide	102

compounds. The ratio of the intensities of the Auger signals of tungsten and rhenium from pure substrates is in good agreement with their elemental sensitivity coefficients presented in the reference book [12]

As can be seen from the table, the intensity of the Auger signal of phosphorus on rhenium is greater than that on tungsten. When phosphorus adatoms are located strictly on the surface, their concentration is directly proportional to the values of the Auger signals, and the surface concentration of phosphorus on rhenium can be estimated as $N_P > 1 \cdot 10^{15} \text{ cm}^{-2}$, which is apparently close to the stoichiometry of ReP.

Let us use another method for estimating the concentration of phosphorus on rhenium in the surface phosphide. To do this, we directly compared the intensities of the Auger signals of phosphorus from the surface phosphide and silicon from the surface silicide grown on rhenium. The surface silicide was produced according to the method previously described by us in [15]: silicon was sputtered onto heated $(10\bar{1}0)\text{Re}$ at a temperature of 1200 K with a constant flux of $2 \cdot 10^{12} \text{ cm}^{-2}\text{s}^{-1}$. In this case, a surface silicide with a concentration of Si atoms of $N_{\text{Si}} = 1.3 \cdot 10^{15} \text{ cm}^{-2}$ is formed on the surface, and all excess silicon goes into the bulk of the substrate, into the solid solution state.

Experiments have shown that in the case of $\text{W}(100)$ the ratio of the intensities of the Auger signals of silicon and phosphorus from the corresponding surface compounds is close to unity. Comparing the intensity of these adsorbates on the surface $(10\bar{1}0)$ of rhenium, we obtained the same ratio, i.e. unity with an accuracy of about 15%. Thus, the surface concentrations of silicon and phosphorus on rhenium are almost the same, which means that phosphorus actually forms a surface compound with the ReP stoichiometry.

3.5. Thermal stability of adsorbed phosphorus at its various concentrations

Figure 4 shows the data presenting the thermal stability of adsorbed phosphorus on $(10\bar{1}0)\text{Re}$ at its various surface concentrations. The above-mentioned adsorption states were produced according to the method described above for the formation of surface phosphide, i.e. the exposure of rhenium heated to 1100 K in PCl_3 vapor at $p = 10^{-6}$ Torr. But the exposure time was different: it was 180 s for

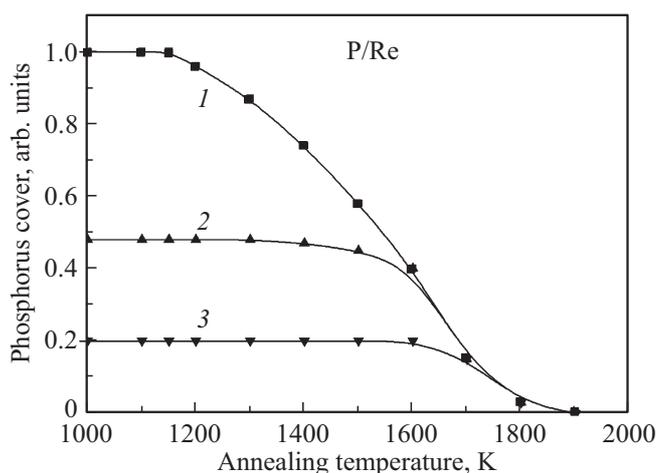


Figure 4. Change in the degree of surface coverage of phosphorus ϑ on rhenium as a function of the sample annealing temperature by 20 s at each point. Initial state ϑ : 1 — 1; 2 — 0.5; 3 — 0.2. Monolayer coating $\vartheta = 1$ corresponds to $N_P = 1.3 \cdot 10^{15} \text{ cm}^{-2}$.

the curve 1 (this corresponds to the formation of surface phosphide), 80 s for the curve 2, and 30 s for the curve 3. Between experiments, the rhenium tape was annealed in ultra-high vacuum at $T = 2300 \text{ K}$ for 30 s to remove all possible adsorbates.

As can be seen, the destruction of surface phosphide begins at $T > 1200 \text{ K}$, as described above. It is interesting that when the surface concentration of phosphorus is equal to half that in the surface phosphide, the thermal stability is significantly higher; its removal from the surface is recorded only at $T > 1500 \text{ K}$. The thermal stability of a very small coating is even higher, approximately 20% of the surface phosphide: it is stable up to 1650 K; complete removal of phosphorus requires $T > 1850 \text{ K}$. All this is indicative of a strong concentration dependence of the bond energy of P atoms with the substrate

It is interesting that the thermal destruction curves of all three coatings practically coincide in those regions where P atoms leave the surface. This indicates that the destruction mechanism does not depend on how much phosphorus was on the surface initially, but is determined only by the kinetics of the atom detachment from the surface. The activation energy of this process is highly dependent on the coating, as previously observed for silicon and for sulfur.

4. Discussion of results

In contrast to $(100)\text{W}$, which has a rectangular surface crystal geometry with a pronounced adsorption relief, rhenium, which has a HCP lattice, is textured during annealing with the appearance of a dense grooved face $(10\bar{1}0)$ with long rows of closely packed metal atoms, stretching in the direction of $[\bar{1}2\bar{1}0]$. There is no data in the literature on the nature of the reconstruction of this face during adsorption; it can be assumed that the

adsorbed atoms occupy places along the rows, reproducing the symmetry of the face, taking into account its relaxation. In this situation, the concentration of impurity atoms in the surface compound should weakly depend on the nature of this impurity, which is observed experimentally with respect to silicon and phosphorus.

5. Conclusion

Adsorption of phosphorus trichloride molecules on the surface of $(10\bar{1}0)\text{Re}$ at 1100–1200 K results in the formation of surface phosphide with the adsorbate concentration of $(1.3 \pm 0.2) \cdot 10^{15} \text{ cm}^{-2}$ and the composition of ReP relative to surface metal atoms. It can be expected that P atoms from SP will participate in competitive processes on the surface with other atoms during their joint adsorption, as was previously observed for many pairs of atoms (Si, C, S, O, Be, Al. . .) from the surface chemical compounds at temperatures that ensure their possible thermal desorption or dissolution in the bulk substrate [16].

Conflict of interest

The authors declare that they have no conflict of interest.

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