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XPS study of Pd/Co multilayers: identification of Pd and Co interface bonding states by pattern recognition methods

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Abstract

Artificially structured magnetic superlattices consisting of ultrathin Pd/Co multilayers with varying thicknesses exhibit strong perpendicular magnetic anisotropy. This particular property in such systems is strongly correlated with the structure of the interface and its local environment. In the present work, the interface of Pd/Co in two multilayer systems was sampled applying X-ray photoelectron spectroscopy (XPS) and sophisticated pattern recognition methods for spectrum processing, i.e. the *k*-nearest neighbour rule (kNN) and a clusterization algorithm. For the first time, the fuzzy kNN approach has been applied for investigating surface effects. The above methods consider the lineshape of photoelectron spectra recorded for a set of reference samples, evaluate the criteria for the optimum separation of groups, and identify the unknown samples. Photoelectron Pd 3d and Co 2p spectra were recorded from metallic Pd, Co and CoPd solid solutions with varying concentrations of constituents, and from Pd/Co magnetic multilayers. The applied methods were able to identify the alloying of Pd and Co atoms at the Pd/Co interface of the multilayer systems with different concentrations of component involved. The results obtained indicate that both interfaces have finite thickness, which may influence the magnetic properties of the investigated systems.

Keywords: Cobalt; Palladium; X-ray photoelectron spectroscopy

1. Introduction

Pd/Co multilayers, members of the family of artificially structured metallic magnetic superlattices with ultrathin sublayers, display strong perpendicular magnetic anisotropy [1–7]. Thicknesses below 1 nm and the high density of interfaces of the sublayers indicate that the local environment

effects at the interfaces are important for understanding the magnetic properties [8,9].

Changes in the chemical environment of an atom are usually visualized in the XPS spectra by binding energy shifts [10]. However, small shifts in the peak positions and the surface charging effects may complicate such an analysis. Analysis of core shifts is sometimes unable to distinguish between different oxidation states and may not unambiguously distinguish between oxide and hydroxide, not to mention other chemical species [11].

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An additional tool for sampling the chemical environment of the atom can be applied by investigating the shape of Auger or photoelectron transitions [10]. In the Auger process involving valence levels, the valence electron density of states is convoluted into the peak structure, changing the shape of the peak [10]. It is especially visible in CVV (core level–valence–valence) Auger transitions [10], e.g. C KLL, O KLL, Si LMM or In MNN. In the photoemission process, changes in the subtle photoelectric structure due to the different environments of the atom can arise for various reasons, such as overall changes in the electronic structure due to chemical bonding or changes in structure, which is also visualized in subtle chemical shifts and changes in the screening of the hole. Several processes are responsible for the above: (i) the inelastic collision process, which leads to a change in the background, (ii) multiplet splitting of core level peaks, which occurs when the system has unpaired electrons in the valence band, and (iii) multiple electron transition process following the core electron emission, leading to discrete transitions in the valence band (“shake-up” and “shake-off” satellites, “asymmetric metal core levels”) [10].

Analyses of the chemical environment of carbon atoms on the basis of the Auger CVV spectra shape in systems of various carbon forms [12], different polymers [12–18], indium and phosphorus atoms in an InP(110) sample [19–20], silicon, oxygen and nitrogen atoms in silicon oxides [21] and silicon nitride layers [22] were performed using the pattern recognition method. Similar analyses by the pattern recognition method of the alloying effect in AuPd alloys of various concentrations by investigating the Pd 3d and Au 4f photoelectron spectra were also performed [23].

The aim of the present work was to investigate the bonding state of Pd and Co atoms at the interfaces of Pd/Co multilayer systems. X-ray photoelectron spectroscopy and the pattern recognition method [24] were used for that purpose. The procedure is based on a sophisticated comparison of the shapes of spectra taken from well defined standards (metallic Pd, metallic Co, CoPd solid solutions) and Pd/Co multilayers. Before applying the CoPd alloys as standards for

investigating Pd/Co multilayer systems, the alloying effect was verified.

2. Experimental

Pd/Co multilayers were prepared using a Leybold Z-400 system in which one holder was used to fix two small targets (Pd and Co samples) 40 mm in diameter. The substrates (Si(100) wafers) were positioned below the targets on a rotating table at a distance of 40 mm in such a way that they were alternately exposed to the Co or the Pd target through the window. The exposure time was set by the rotating speed of the substrate table and also by the size of the window (the exposure angle). Both targets were constantly sputtered with the shielding arranged in such a way that no cross-contamination of the multilayers could occur. The rate of the sputtering was determined first for the Co layer (with the Pd window closed) and then for the Pd layer (with the Co window closed). The thicknesses of the Co and Pd layers were determined by measuring the exposure time combined with Dektak or low-angle X-ray measurements. The program developed by Philips Analytical was applied. For simple Co or Pd layers the above procedure supplies the nearly perfect fit, indicating correct determination of the thickness. The first Pd/Co multilayer system (no. 940120) consisted of 10 bilayers with 11 Å of Pd and 10 Å of Co layers, whereas the second one (no. 940127) consisted of 7 bilayers with 11 Å of Pd and 4 Å of Co layers. The multilayers were deposited on a 200 Å thick seed layer of Pd, which is a layer between the Si substrate and the multilayer.

Photoelectron spectra were measured by ADES-400 (V.G. Scientific) angular resolved photoelectron spectrometer at room temperature using Al K α radiation. The spectra were recorded in regions of Co 2p, Pd 3d, O 1s and C 1s lines at fixed positions of the sample at normal photoelectron take-off angle. The energy analyzer was operated in the constant energy mode at 50 eV. The Co 2p spectra were recorded at 100 eV pass energy due to the fact that Co layer situated beneath the Pd layer gives a very weak Co signal. The acceptance angle of the analyzer was set to

$\pm 4.1^\circ$. All the XPS spectra were calibrated to the Au 4f_{7/2} line at 83.8 eV.

To avoid the expected ion-beam-induced modifications of chemical bonds of atoms within the analyzed volume in the multilayer systems, these surfaces were studied without sputter-cleaning. Since from the previous study [5] it was obvious that the Co layer below the Pd layer in the multilayer systems is partially oxidized, the Co 2p spectra of metallic Co and Co in two CoPd solid solutions were recorded without sputter-cleaning in oxidized form. The Pd 3d spectra for metallic Pd and CoPd solid solutions were recorded as slightly oxidized Pd, except for the metallic Pd sample which was investigated after sputtering the surface with an Ar⁺ ion beam (energy 3 keV, current 2×10^{-5} A, diameter 1 cm at the target and 70° relative to the surface normal).

The XPS spectra were recorded for the surfaces of Co, Co₂₀Pd₈₀, Co₄₇Pd₅₃, Pd, sputtered Pd (Pd_{sput}), Pd/Co multilayer no. 940120 (referred to as PdCom1) and Pd/Co multilayer no. 940127 (referred to as PdCom2). The CoPd alloys were prepared by melting both constituents in a vacuum at 1250°C (Co₄₇Pd₅₃) and 1370°C (Co₂₀Pd₈₀) for 30 min. Both CoPd alloy samples were verified to be homogeneous by scanning electron microscopy and electron X-ray microanalysis. The surface composition of the alloys was determined in a separate experiment by XPS quantitative analysis using the so-called “multiline approach” [25]. This method does not require standards. It takes into account the instrumental and matrix effects and derives quantitative information from the statistical analysis of all photoelectron intensities visible in the spectra. The reliability of this approach is better than that of methods involving uncorrected relative sensitivity factors. The above method confirmed that the surface concentration was close to that of the bulk concentration. A slight enrichment of Co constituent at the surface was observed. This may be due to selective sputtering in the sputtering conditions, since the sputtering yield for Pd is higher than for Co [26].

The surfaces of as-prepared multilayers are slightly contaminated by carbon and oxygen. Both constituents, Pd and Co, are partially oxidized. The weak signal intensity at binding energy

~ 778 eV is ascribed to the metallic Co bonding state, while the most pronounced peak with a maximum at ~ 781.5 eV belongs to oxidized Co (Co–O, Co–OH). The third rather wide peak is identified as a satellite structure [27]. Detailed inspection of the Co 2p spectra of about 10 different Pd/Co multilayers using normal and grazing take-off angles and the both Al and Mg K α radiation showed the following common features: the upper part of the first Co sublayer just beneath the top Pd sublayer was partially oxidized, while the other Co atoms were in the metallic state [5].

3. The pattern recognition method

The pattern recognition method was applied to Pd 3d and Co 2p photoelectron spectra in order to verify the alloying effect in the Pd/Co multilayer system. A comparison of the variations in the shapes of the Pd 3d and Co 2p photoelectron spectra in CoPd alloys and in Co and Pd elemental samples with those of the Pd/Co multilayer system samples provided information about the possible alloying effect at the interface of the multilayer samples.

A detailed description of the pattern recognition algorithms can be found in the literature [24]. Below, only a brief outline of one of the algorithms, the so-called *k*-nearest neighbor (kNN) rule is given.

In the pattern recognition procedures the spectrum is usually recorded in digital form as a multidimensional vector (object). The coordinates of such a vector are called features. Such a represented spectrum can be visualized as a point in multidimensional space. Several spectra for a particular chemical state of atom are recorded. These spectra form a set of objects (a cluster of points or a class) in multidimensional space. The dispersion of the cluster is due to statistical error occurring in the spectra measurements. Within the above approach several chemical states of atoms can be considered, with every state represented by an appropriate set of spectra (class or a cluster). The collection of observed classes can be considered as a reference set which is treated as a “computer experience” in the recognition procedure of the

spectra (objects) recorded at an uncertain chemical state. Actually, the unknown spectra can be identified on the basis of the reference set. The pattern recognition rule can only prescribe such spectra to one of the classes within the “computer experience”.

Both the identification “a priori” of the spectra in the reference set, where the ascription to a class is known, and the identification “a posteriori”, where the unknown spectrum is recognized, are performed by the kNN rule. This rule considers the closest neighbourhood of every vector, ascribing it to the class which has prevailing number of vectors in the considered neighborhood. An example of the performance of the kNN rule for the selected optimum number of nearest neighbors equal to 12 is shown in Fig. 1.

The quality of the classifier is described by the probability of misclassification, ΔE , which is a function of the chosen number of nearest neighbors, k . The value of the optimum number of nearest neighbors is selected in the classification procedure “a priori”, performed on the reference set in such a way that the minimum value of misclassification probability is chosen and thus the adequate value of k . In the identification “a posteriori” the recognition is based on the developed classifier and thus the selected value of k in the

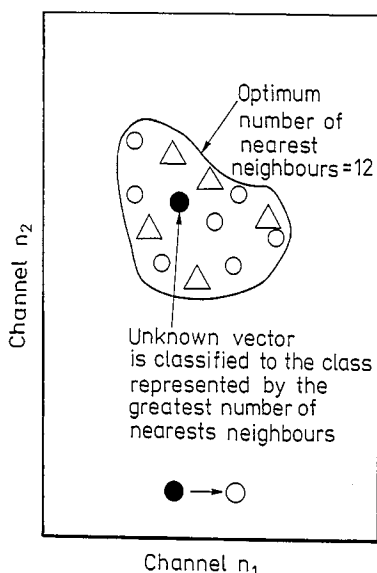


Fig. 1. Illustration of the performance of the k -nearest neighbor rule.

kNN rule is applied. The misclassification error estimated in the “a priori” procedure establishes the error of “a posteriori” identification.

Numerous recognition procedures (classifiers) can be constructed. In this work, a parallel network of kNN classifiers is used [24]. This classifier is constructed by considering each combination of pairs of classes from the reference set instead of all classes together. Application of the network of binary classifiers facilitates the identification. In such a case the partial misclassification probability values for every combination of pairs of classes are calculated. From the above values the total misclassification probability is obtained by “voting” of all binary classifiers. The performance of the classifier can be further improved by selecting the most informative coordinates (channels) within the spectra. This procedure is called feature selection.

Additionally, in the present work the fuzzy kNN rule was applied for the first time for the identification of the chemical state of the surface atoms. A description of the above mathematical procedure can be found elsewhere [28]. All procedures of establishing the classifier, its criteria and identification of the unknown spectra are similar to those in the non-fuzzy rule, except that they are based on a different mathematical formalism. In the theory of the non-fuzzy kNN rule the main reason for the spectral indeterminacy reflected by the standard deviation of a class is due to randomness (statistical error). The theory of fuzzy rule provides suitable mathematical tools and techniques in analyzing systems and decision processes where the pattern indeterminacy is due to the fact that the identified spectra consist of combinations of different chemical states reflected by the spectra from the reference set. This fact is referred to as the variability and/or vagueness (fuzziness) of the recognized pattern. When the pattern indeterminacy is due to inherent vagueness rather than randomness, then the fuzzy rule can be a better tool for describing the problem. In the fuzzy rule each member of the set of vectors to be identified is represented by value which is the combination of members occurring with a certain probability (lying between 0 and 1) in the reference set. The classification by the fuzzy rule determines the

degree of belonging (membership) of the identified pattern to the members of the reference set.

Before applying the pattern recognition method all photoelectron spectra were first processed. This procedure comprised the following steps: (i) smoothing (moving-average method), (ii) normalizing by shifting all maxima to a common point, (iii) normalizing the amplitudes of spectra, and (iv) reducing the dimensions of the spectra in order to reduce the time of the computing process. The original spectra were recorded with an energy channel separation of 0.1 eV. The smoothing procedure was performed by averaging a few points without deforming the subtle shape structure. The final spectra resulted in energy channel separations a few times higher than the original spectra. Examples of the Pd 3d and Co 2p photoelectron spectra after processing are shown in Figs. 2 and 3, respectively.

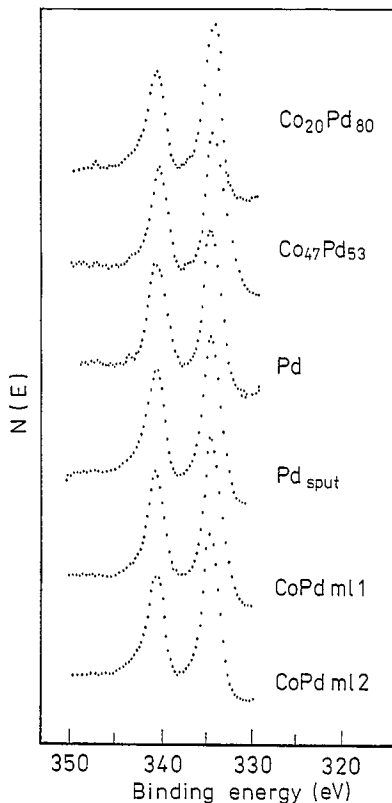


Fig. 2. Examples of Pd 3d photoelectron spectra of spectra of CoPd alloys, Pd, Pd_{sput} and Pd/Co multilayer systems after all stages of preprocessing.

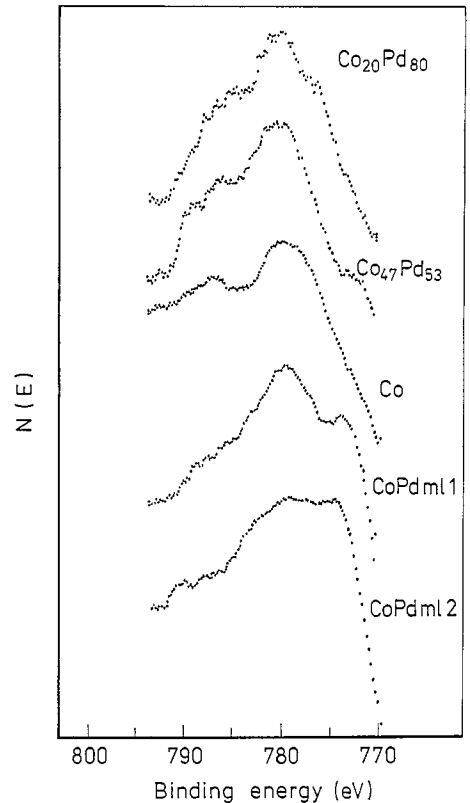


Fig. 3. Examples of Co 2p photoelectron spectra of spectra of CoPd alloys, Co and Pd/Co multilayer systems after all stages of spectra preprocessing.

4. The clusterization method

The clusterization method [24] is applied to the set of spectra. In such a procedure the spectra are not ascribed “a priori” to a given class. From all the spectra in the reference set any number of clusters can be formed in such a way that the probability of misclassification between the clusters is minimized. This is obtained by applying the k -nearest neighbor rule. In the clusterization procedure the main parameters are: (i) the mean dispersion of each cluster, (ii) the distance between the clusters, and (iii) the number of vectors belonging to each cluster.

For the problem with ascribing the known spectra to the classes “a priori”, the clusterization procedure provides the result how the spectra from various classes create the clusters. The method can also distinguish spectra from the same class by

ascribing them to various clusters. In such a way some additional information can be obtained on the arrangement of spectra in each class (the size of the class and its dispersion).

5. Application of the pattern recognition method

The application of the pattern recognition method was performed in several steps. First, the non-fuzzy kNN rule was applied, and then the fuzzy approach. For both approaches two reference sets containing Pd 3d and Co 2p photoelectron spectra were constructed. Both the Pd 3d and Co 2p spectra were recorded for the CoPd alloys, metallic samples and the multilayer samples. The pattern recognition method was used

(1) to verify if the changes due to different surroundings of Co and Pd atoms in CoPd alloys with different concentrations of constituents, metallic Co and Pd can be visualized in the shapes of the Co 2p and Pd 3d photoelectron lines;

(2) to verify the alloying effect in CoPd alloys; and

(3) to verify and identify the effect of alloying at the interface of the Pd/Co multilayer systems on the basis of the Pd 3d and Co 2p photoelectron lines recorded for the set of standards.

The performance of the classifier in distinguishing various alloys, metal and Pd/Co multilayer systems on the basis of Pd 3d and Co 2p photoelectron lines is listed in Tables 1 and 2, respectively. Both classifiers are based on the whole set of features. For the Pd 3d line the total misclassification probability for distinguishing various analyzed systems is 0.347 (Table 1), whereas for Co 2p it is 0.218 (Table 2). The best discrimination (the minimum misclassification probability) for the studied systems by both Pd 3d and Co 2p lines is obtained within the groups: (i) alloys – metallic samples, and (ii) metallic samples – multilayer systems. In the case of the Pd 3d line the effect of distinguishing is much weaker than in the case of the Co 2p line. The overlapping of the classes is obtained in the case of both CoPd alloy samples containing various concentrations of constituents. Fig. 4 shows a graphical representation of the identification in the form of histograms of distances

Table 1

Comparison of misclassification probabilities for Pd 3d spectra of CoPd alloys, Pd, Pd_{sput} and Pd/Co multilayer systems

Classes	Number of channels	Misclassification probability, ΔE	
		Pair	Total
1 Co ₂₀ Pd ₈₀ /Co ₄₇ Pd ₅₃	85	0.245	
2 Co ₂₀ Pd ₈₀ /Pd	85	0.060	
3 Co ₂₀ Pd ₈₀ /Pd _{sput}	85	0	0.347
4 Co ₂₀ Pd ₈₀ /PdCom1	85	0.400	
5 Co ₂₀ Pd ₈₀ /PdCom2	85	0	
6 Co ₄₇ Pd ₅₃ /Pd	85	0.020	
7 Co ₄₇ Pd ₅₃ /Pd _{sput}	85	0	
8 Co ₄₇ Pd ₅₃ /PdCom1	85	0.175	
9 Co ₄₇ Pd ₅₃ /PdCom2	85	0	
10 Pd/Pd _{sput}	85	0	
11 Pd/PdCom1	85	0.045	
12 Pd/PdCom2	85	0	
13 Pd _{sput} /PdCom1	85	0	
14 Pd _{sput} /PdCom2	85	0	
15 PdCom1/PdCom2	85	0	

Table 2

Comparison of misclassification probabilities for Co 2p spectra of CoPd alloys, Co and Pd/Co multilayer systems

Classes	Number of channels	Misclassification probability, ΔE	
		Pair	Total
1 Co ₂₀ Pd ₈₀ /Co ₄₇ Pd ₅₃	128	0.382	
2 Co ₂₀ Pd ₈₀ /Co	128	0	
3 Co ₂₀ Pd ₈₀ /PdCom1	128	0	
4 Co ₂₀ Pd ₈₀ /PdCom2	128	0	
5 Co ₄₇ Pd ₅₃ /Co	128	0.019	
6 Co ₄₇ Pd ₅₃ /PdCom1	128	0	0.218
7 Co ₄₇ Pd ₅₃ /PdCom2	128	0.062	
8 Co/PdCom1	128	0	
9 Co/PdCom2	128	0	
10 PdCom1/PdCom2	128	0	

of Pd 3d spectra from the line joining the centres of gravity of two selected pairs of classes.

The results of the identification of Pd/Co multilayer systems on the basis of the Pd 3d and Co 2p photoelectron lines are shown in Tables 3 and 4, respectively. Both classifiers are based on the reference set including CoPd alloys, Co and Pd, whereas the samples of Pd/Co multilayer systems are identified by the developed classifier. The values of

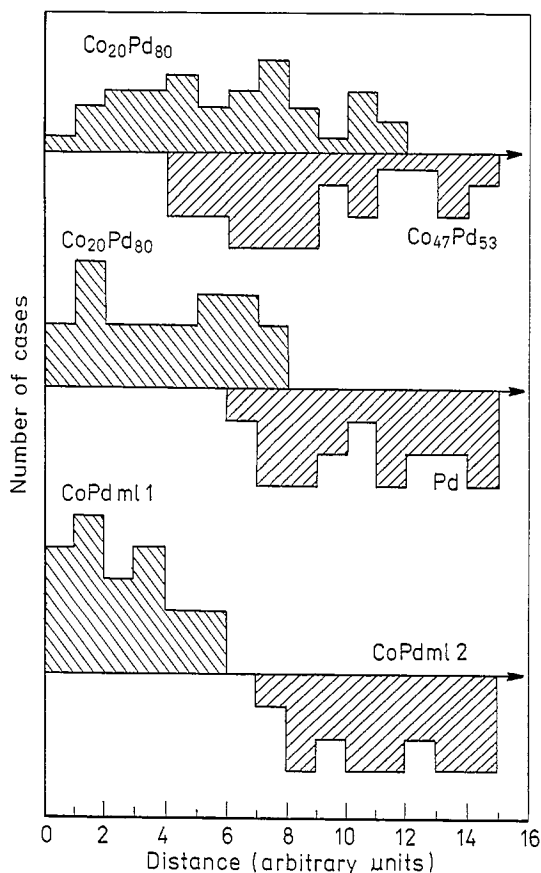


Fig. 4. Examples of histograms of distribution of Pd 3d photoelectron spectra in CoPd alloys, Pd, Pd_{sput} and Pd/Co multilayer systems.

misclassification probability obtained from the spectra represented in the full dimension are better than for the previous classifier, where the Pd/Co multilayer systems were included in the reference set. After the feature selection procedure the values of misclassification probability for the reference set based on the Pd 3d line decreases from 0.147 to 0.077 (Table 3), and for the Co 2p line from 0.247 to 0.100 (Table 4), which results in facilitating the identification process. In spite of the better misclassification probability after feature selection, the results of the identification before and after the feature selection procedure are similar. The Pd/Co multilayer no. 1 is identified as Co₂₀Pd₈₀ alloy on the basis of the Pd 3d line (Table 3). In the same sample, identified on the basis of the Co 2p line, the alloying effect is not visualized. Instead, the sample is identified as metallic cobalt (Table 4). In the case of the sample of Pd/Co multilayer system no. 2 the alloying effect is identified in the form of Co₄₇Pd₅₃ alloy by both Pd 3d and Co 2p photoelectron lines.

The results of the kNN fuzzy classifier identification of Pd/Co multilayer systems performed on the basis of the classifier developed for Pd 3d and Co 2p photoelectron spectra are shown in Tables 5 and 6, respectively. Both fuzzy classifiers constructed for the set of Pd 3d and Co 2p spectra provide similar values of misclassification probability for the recognition of the spectra from the

Table 3
Comparison of misclassification probabilities for Pd 3d spectra of CoPd alloys, Pd, Pd_{sput} and identification of the Pd/Co multilayer systems based on the developed classifier; values of misclassification probability and results of identification indicated in parentheses denote the results after the feature selection procedure

Classes	Misclassification probability, ΔE		Results of identification
	Pair	Total	
1 Co ₂₀ Pd ₈₀ /Co ₄₇ Pd ₅₃	0.245 (0.150)		
2 Co ₂₀ Pd ₈₀ /Pd	0.070 (0.010)	0.147	
3 Co ₂₀ Pd ₈₀ /Pd _{sput}	0 (0)	(0.077)	
4 Co ₄₇ Pd ₅₃ /Pd	0.020 (0.005)		
5 Co ₄₇ Pd ₅₃ /Pd _{sput}	0 (0)		
6 Pd/Pd _{sput}	0 (0)		
PdComl1			Co ₂₀ Pd ₈₀ (Co ₂₀ Pd ₈₀ , Co ₄₇ Pd ₅₃)
PdComl2			Co ₄₇ Pd ₅₃ (Co ₄₇ Pd ₅₃ , Pd)

Table 4

Comparison of misclassification probabilities for Co 2p spectra of CoPd alloys, Co and identification of the Pd/Co multilayer systems based on the developed classifier; values of misclassification probability and results of identification indicated in parentheses denote the results after the feature selection procedure

Classes	Misclassification probability, ΔE		Results of identification
	Pair	Total	
1 Co ₂₀ Pd ₈₀ /Co ₄₇ Pd ₅₃	0.353 (0.137)		
2 Co ₂₀ Pd ₈₀ /Co	0 (0)	0.247	
3 Co ₄₇ Pd ₅₃ /Co	0.009 (0)	(0.100)	
PdCom1			Co (Co)
PdCom2			Co ₄₇ Pd ₅₃ (Co ₄₇ Pd ₅₃)

Table 5

Identification of Pd/Co multilayer systems based on the kNN fuzzy classifier after feature selection developed on the basis of Pd 3d spectra

Samples	Final result of identification [no. of cases]	Distribution of identification cases and fuzzy probabilities	
		Case (fuzzy probability)	[no. of cases]
PdCom1	Co ₂₀ Pd ₈₀ [64]	Co ₂₀ Pd ₈₀ (0.67) + Co ₄₇ Pd ₅₃ (0.33)	[35]
	Co ₄₇ Pd ₅₃ [31]	Co ₂₀ Pd ₈₀ (1.0)	[29]
	Pd [5]	Co ₄₇ Pd ₅₃ (0.67) + Co ₂₀ Pd ₈₀ (0.33)	[31]
PdCom2	Co ₄₇ Pd ₅₃ [72]	Pd (0.67) + Co ₂₀ Pd ₈₀ (0.33)	[5]
	Pd _{sput} [28]	Co ₄₇ Pd ₅₃ (1.0)	[65]
		Co ₄₇ Pd ₅₃ (0.67) + Co ₂₀ Pd ₈₀ (0.33)	[7]
		Pd _{sput} (1.0)	[28]

Table 6

Identification of Pd/Co multilayer systems based on the kNN fuzzy classifier after feature selection developed on the basis of Co 3d spectra

Samples	Final result of identification [no. of cases]	Distribution of identification cases and fuzzy probabilities	
		Case (fuzzy probability)	[no. of cases]
PdCom1	Co [19]	Co (1.0)	[19]
	Co ₄₇ Pd ₅₃ [14]	Co ₄₇ Pd ₅₃ (1.0)	[14]
PdCom2	Co ₄₇ Pd ₅₃ [20]	Co ₄₇ Pd ₅₃ (1.0)	[20]
	Co [1]	Co (1.0)	[1]

reference set to those of the non-fuzzy classifiers (Tables 3 and 4). Therefore it is expected that the results of Pd/Co multilayers identification by non-fuzzy and fuzzy classifiers will be similar. The advantage of the fuzzy classifier is the possibility of indicating in the identification results the combination of different chemical states, which appear

in the reference set, with its fuzzy probabilities. The final results of the fuzzy rule identification are similar to those of the non-fuzzy rule. By applying the reference set containing the Pd 3d line, Pd/Co multilayer no. 1 is recognized in the majority of cases as a combination of Co₂₀Pd₈₀ alloy and Co₄₇Pd₅₃ alloy occurring with fuzzy probabilities

0.67 and 0.33, respectively, and some cases as $\text{Co}_{20}\text{Pd}_{80}$ alloy with a fuzzy probability equal to 1. The identification based on the reference set containing Co 2p spectra indicates in the majority of cases as pure metallic Co state with a fuzzy probability equal to 1, and some cases as $\text{Co}_{47}\text{Pd}_{53}$ alloy occurring with a fuzzy probability equal to 1. The Pd/Co multilayer no. 2 is recognized with a much higher certainty (fuzzy probability equal to 1) as an alloy with the concentration of constituents $\text{Co}_{47}\text{Pd}_{53}$ by both Pd 3d and Co 2p photoelectron lines. Some cases of mixtures of both CoPd alloys are identified by the classifier based on Pd 3d spectra.

6. Application of the clusterization method

The clusterization results performed on Pd 3d and Co 2p photoelectron lines are shown in Tables 7 and 8, respectively. Two selected numbers of cases are chosen: (i) clusterization into a number of clusters equal to the number of classes “a priori” (six in case of the Pd 3d line, and five in case of the Co 2p line), and (ii) clusterization into a number of clusters larger than the set of classes “a priori”.

From the clusterization of the first stage performed on the Pd 3d and Co 2p spectra (Tables 7 and 8) it is visible that not all the spectra form groups which are equivalent to the classes “a priori”. This information is consistent with the results shown in Tables 1–6, where the misclassification probabilities between all combinations of classes are not zero.

The clusterization of Pd 3d spectra (Table 7) divides the reference set into classes which contain: (i) two sets of spectra of CoPd alloy, oxidized metallic Pd and Pd/Co multilayer system no. 1; (ii) a set of spectra of CoPd alloys, Pd_{sput} and Pd/Co multilayer system no. 2; (iii) two sets of spectra of Pd/Co multilayer system no. 2 and Pd_{sput} ; and (iv) a set of spectra of Pd/Co multilayer system no. 2. Similarly, in the case of the Co 2p spectra, the clusterization procedure (Table 8) divides the classes into groups of spectra containing: (i) CoPd alloys and Pd/Co multilayer system no. 1; (ii) CoPd alloys; (iii) CoPd alloys and Pd/Co multilayer system no. 2; (iv) $\text{Co}_{47}\text{Pd}_{53}$ alloy, metallic Co and both Pd/Co multilayer systems; and (v) $\text{Co}_{47}\text{Pd}_{53}$ alloy and metallic Co. Further clusterization for both Pd 3d and Co 2p spectra into eight classes (Tables 7 and 8) does not change the distribution of spectra in the clusters but splits the

Table 7
Comparison of results of the clusterization analysis performed on the Pd 3d photoelectron line in CoPd alloys, Pd, Pd_{sput} and Pd/Co multilayer systems; the results show the analysis performed for six and eight clusters

Number of clusters	Cluster number	Sample (number of vectors)	Total number of vectors
6	1	$\text{Co}_{20}\text{Pd}_{80}$ (23), $\text{Co}_{47}\text{Pd}_{53}$ (25), Pd(7), PdComl1(18)	73
	2	$\text{Co}_{20}\text{Pd}_{80}$ (58), $\text{Co}_{47}\text{Pd}_{53}$ (70), Pd(72), PdComl1(74)	274
	3	Pd(21), $\text{Co}_{20}\text{Pd}_{80}$ (19), $\text{Co}_{47}\text{Pd}_{53}$ (5), Pd_{sput} (1), PdComl2(1)	55
	4	Pd_{sput} (74), PdComl2(19)	93
	5	Pd_{sput} (27), PdComl2(9)	36
	6	PdComl2(71)	71
8	1	$\text{Co}_{20}\text{Pd}_{80}$ (23), $\text{Co}_{47}\text{Pd}_{53}$ (25), Pd(7), PdComl1(18)	73
	2	$\text{Co}_{20}\text{Pd}_{80}$ (58), $\text{Co}_{47}\text{Pd}_{53}$ (70), Pd(72), PdComl1(74)	274
	3	$\text{Co}_{20}\text{Pd}_{80}$ (10), $\text{Co}_{47}\text{Pd}_{53}$ (2), Pd(5), PdComl1(3), PdComl2(1)	21
	4	$\text{Co}_{20}\text{Pd}_{80}$ (3), $\text{Co}_{47}\text{Pd}_{53}$ (2), Pd(5), Pd_{sput} (1), PdComl1(5)	16
	5	$\text{Co}_{20}\text{Pd}_{80}$ (6), $\text{Co}_{47}\text{Pd}_{53}$ (1), Pd(11)	18
	6	Pd_{sput} (74), PdComl2(19)	93
	7	Pd_{sput} (27), PdComl2(9)	36
	8	PdComl2(71)	71

Table 8

Comparison of results of the clusterization analysis performed on the Co 2p photoelectron line in CoPd alloys, Co and Pd/Co multilayer systems; the results show the analysis performed for five and eight clusters

Number of clusters	Cluster number	Sample (number of vectors)	Total number of vectors
5	1	Co ₂₀ Pd ₈₀ (24), Co ₄₇ Pd ₅₃ (20), PdCom1(2)	46
	2	Co ₂₀ Pd ₈₀ (15), Co ₄₇ Pd ₅₃ (18)	33
	3	Co ₂₀ Pd ₈₀ (3), Co ₄₇ Pd ₅₃ (15), PdCom2(11)	29
	4	Co ₄₇ Pd ₅₃ (4), Co(19), PdCom1(31), PdCom2(10)	64
	5	Co ₄₇ Pd ₅₃ (3), Co(29)	32
8	1	Co ₂₀ Pd ₈₀ (15), Co ₄₇ Pd ₅₃ (13)	28
	2	Co ₂₀ Pd ₈₀ (5), Co ₄₇ Pd ₅₃ (11)	16
	3	Co ₂₀ Pd ₈₀ (3), Co ₄₇ Pd ₅₃ (15), PdCom2(11)	29
	4	Co ₂₀ Pd ₈₀ (10), Co ₄₇ Pd ₅₃ (7)	17
	5	Co ₂₀ Pd ₈₀ (9), Co ₄₇ Pd ₅₃ (7), PdCom1(2)	18
	6	Co ₄₇ Pd ₅₃ (3), PdCom1(23), PdCom2(4)	30
	7	Co ₄₇ Pd ₅₃ (3), Co(29)	32
	8	Co ₄₇ Pd ₅₃ (1), Co(19), PdCom1(8), PdCom2(6)	34

existing clusters into smaller groups. The results indicate that two Pd/Co multilayer systems are distinguished from each other by analysis based on the Pd 3d and Co 2p lines. This also applies to metallic state of Co and Pd, especially in the case of Pd_{sput}. It is not such a straightforward result for the two CoPd alloys.

7. Discussion

The results of the two pattern recognition methods and the clusterization procedure are consistent. It has been proved that it is possible to resolve the chemical states of metallic Co and Pd from the chemical state of Co and Pd atoms in solid solutions with various concentrations. It was also possible to sample the differences in the chemical state of Co and Pd atoms at the interface of Pd/Co multilayer systems and to ascribe the chemical state of interface atoms to the appropriate CoPd solid solutions available in the reference set. Both Pd/Co multilayers are identified as various systems. In both systems the alloying effects at the interface of Pd/Co layers are indicated by the differences in the concentrations of alloy constituents. The results of identification of the multilayer no. 2 are in agreement for classifiers based on Co 2p and Pd

3d photoelectron spectra. The discrepancy in identification by the classifier based on Pd 3d and Co 2p spectra arises for the first Pd/Co multilayer system, where the classifier based on the Pd 3d line recognizes the Co₂₀Pd₈₀ alloy, whereas the classifier based on the Co 2p line indicates the Co metallic state. This discrepancy is also indicated in the results of the identification by the fuzzy rule. Since the parameters of the applied classifiers are similar and the misclassification probability for the reference set after feature selection is minimized, being nearly equal to zero, such discrepancies cannot be explained on the basis of the performance of the classifier or the quality of the chemical effect due to the particular photoelectron spectra used. Some other reason to account for such results might be found in terms of the specific multilayer systems investigated and the difference in the transport parameters of photoelectrons having different kinetic energies. These transport parameters include the depth distribution function (DDF), $\phi(\alpha, z)$ [29], which describes the contribution from different layers of the investigated systems to the total measured photoelectron signal [30]. Such a function is intrinsically related to the type of the system, and it has never been measured nor calculated for multilayers. The majority of information is carried from the so-called mean escape depth,

$\langle z \rangle$, which is defined as [29,31]

$$\langle z \rangle = \int_0^{\infty} z \phi(\alpha, z) dz,$$

where $\phi(\alpha, z)$ is the depth distribution function [29,31], α is the polar emission angle counted from the surface normal, and z is the distance normal to the surface. The DDF, in general, deviates from an exponential dependence. If the DDF is assumed to be exponential, then the mean escape depth can be estimated from the measurable parameter such as the inelastic mean free path (IMFP), as follows [29]:

$$\langle z \rangle = \lambda \cos \alpha.$$

Due to the differences in kinetic energies of the Co 2p and Pd 3d electrons, the IMFP values will vary for the above two solids. These values have been estimated by the elastic peak spectroscopy for the CMA geometry, where $\alpha = 42.3^\circ$, to be 14 Å for Co 2p photoelectrons [32] and about 20 Å for Pd 3d photoelectrons [32,33]. Since the layers of Pd/Co multilayer system no. 1 consist of 11 Å Pd and 10 Å Co layers, the contribution from the mean escape depth of the Co 2p photoelectron signal is due to sampling one Pd/Co interface, whereas the Pd 3d photoelectrons can sample two Pd/Co interfaces. This is not the case for Pd/Co multilayer system no. 2, with a 4 Å Co layer beneath Pd. Additionally, it seems that the majority of Co atoms from the thin 4 Å Co layer at the interface exist in the state which is reflected by the spectra represented by the CoPd alloy. In the case of a system with a 10 Å Co layer at the interface, constituents of the Co 2p photoelectron signal are due to the thin alloy interface and Co–Co metallic state which finally might prevail.

The quantitative information about two Pd/Co multilayer systems is resolved by the pattern recognition method. This information cannot be due to differences at the interface in the two systems, since the probabilities of alloying at the interfaces prepared under the same deposition conditions are the same for 4 Å Co and for 10 Å Co. This result can be rather interpreted on the basis of the information that one of the investigated

systems has a thicker layer of Co within the sandwich system.

8. Summary

The present results demonstrate that XPS together with sophisticated computing methods of pattern recognition and clusterization enable us to resolve and identify the changes in the Pd 3d and Co 2p spectra due to various concentrations of Co and Pd atoms in the solid solution, accounting also for the metallic Co and Pd states. These changes are due to rather weak interactions among surrounding atoms and are reflected in the subtle structure of the photoelectron spectra. The effects of alloying of palladium and cobalt atoms at the interface of Pd/Co multilayer systems are also visualized. This alloying effect at the interface of two Pd/Co multilayer systems with various Co layer thicknesses can be distinguished. These results are obtained although the information carried out in the shape of Pd 3d and Co 2p photoelectron lines accounts for the contributions from the surface region containing few Pd/Co interfaces. The results obtained on the alloying effect imply that the interfaces are not consequently abrupt. This information is of great importance for deep understanding of the anisotropic magnetic properties of the investigated systems.

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