

Oxidation of Co Overlayers on Pd(111) Surfaces

Tschang-Uh NAHM*

Department of Physics, Hanyang University, Seoul 133-791

Wookje KIM and S-J. OH

Department of Physics and Center for Strongly Correlated Materials Research, Seoul National University, Seoul 151-742

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We studied the adsorption of oxygen on ultrathin Co layers on Pd(111) substrates by using X-ray photoemission spectroscopy and the surface magneto-optic Kerr effect. Upon an oxygen exposure of 300 Langmuir, the Co layers are oxidized as a mixture of CoO and Co₃O₄, and the latter can be further reduced to CoO by heating at 700 K. Additional heating at higher temperature leads to a partial decomposition of CoO into Co and O, and the Kerr signals of both longitudinal and polar directions were observed. However, pre-annealing completely inhibits oxidation.

I. INTRODUCTION

In recent years, the search for magneto-optical recording materials has been focused on Co-based multilayer and alloy films [1–3]. In particular, Co/Pt multilayered systems have been studied extensively, and it has been shown that perpendicular magnetic anisotropy and large Kerr rotation can be obtained with Co/Pd systems. However, the influence of gas adsorbates on the magnetic properties, as well as the morphology, of such systems has not been studied in detail in part because their behaviors are much more complicated than the metal overlayers.

Among the adsorbates on the magnetic films exposed to air, oxygen is the most serious one because magnetic metals are easily oxidized at room temperature. There have been various kinds of studies in regard to the influence of oxygen on magnetic ultrathin films; the presence of oxygen on magnetic overlayers can result in exchange-coupling reversal [4] and sometimes leads to an enhanced spin-dependent effect due to an oxygen surfactant action [5]. In addition, oxidation of metal overlayers can be followed during heating by decomposition of the oxide [6,7] or simply the diffusion of oxygen atoms into substrates as in O/Co systems [8,9]. Upon further heating, this can be followed by segregation into oxide islands and a bare substrate surface or even into overlayer metal-only islands and oxygen-chemisorbed substrate surfaces.

As a part of the undertaking to understand the modifications of the magnetic properties and the morphology of ultrathin magnetic films upon oxidation and those of the oxidized films upon heating, we have studied the chem-

ical environment, morphology, and magnetic properties of ultrathin Co films on Pd(111) surfaces by using X-ray photoemission spectroscopy (XPS) and the surface magneto-optic Kerr effect (SMOKE). The original motivation for the present work was to study the change of the magnetic properties due to the presence of interfacial oxygen atoms, but it turned out that most of the oxygen atoms diffuse into the Pd(111) substrate and that it was extremely difficult to prepare the O/Pd(111) surface, as previous studies had reported [10–12].

In this work, we found that the ultrathin Co overlayers were converted to a mixture of CoO and Co₃O₄ after O₂ exposure at room temperature. Upon heating at 700 K, the Co₃O₄ phase disappeared, and on further heating at higher temperatures, decomposition of the oxide occurred. This decomposition was accompanied by the interdiffusion of Co atoms into the substrate and by the reappearance of a ferromagnetic hysteresis loop. However, it turned out that pre-annealing of the Co/Pd(111), which leads to surface alloy formation, inhibited oxidation of the surface and that the oxygen atoms were only chemisorbed on the alloy layers.

II. EXPERIMENTAL

The Pd(111) substrate was of the disk type with a 10-mm diameter and 1-mm thickness. The surface was cleaned by several cycles of Ar⁺ sputtering at 1 keV and annealing at 870 K in a home-made ultra-high vacuum chamber until the crystal surface showed a well-defined low-energy electron diffraction (LEED) pattern with no contamination detected in the XPS spectrum. The base

*E-mail: tschnahm@hanyang.ac.kr, FAX: +82-2-2295-6868

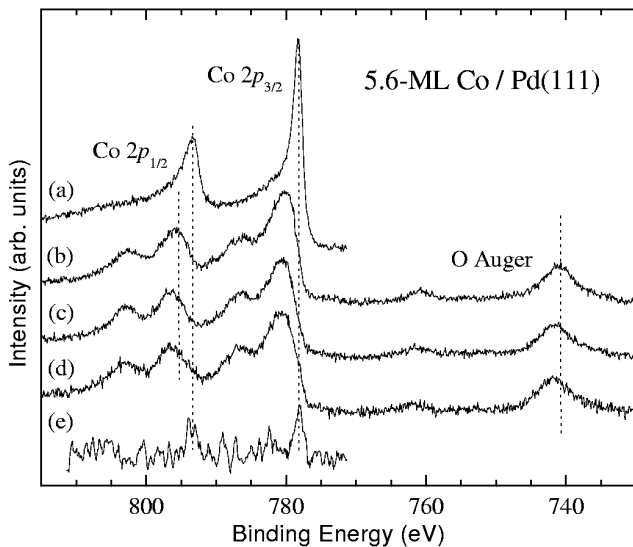


Fig. 1. Co 2*p* and O Auger spectra of 5.6 ML Co layers on Pd(111): (a) as-deposited, (b) after a 300-Langmuir oxygen exposure, (c) after heating at 700 K for 5 min, and (d) after additional heating at 700 K for 20 min. (e) A difference spectrum between curves (d) and (b) with an arbitrary normalization. The vertical lines indicate the peak positions of Co 2*p*_{1/2} and 2*p*_{3/2} of curve (a), and those of Co 2*p*_{1/2} and O Auger of curve (b).

pressure of the chamber was 8×10^{-11} torr, and the light source for the SMOKE measurement was a 10-mW He-Ne laser with $\lambda = 623.8$ nm.

The Co film was deposited on the Pd substrate at room temperature by using an e-beam heating method. A cobalt wire of 99.99 % purity was heated by electron bombardment from a tungsten filament. The film thickness was first calibrated using a quartz thickness monitor, and was then cross-checked by XPS using Co 2*p* and Pd 3*d* core-level photoemission (PE) line intensities at a sub-monolayer coverage, assuming no island growth. The values obtained from these two methods agreed with each other within an error of 10 %. In this work, the Co film thickness was represented in units of one monolayer (ML), and 1 ML was set as 1.32×10^{15} Co atoms cm^{-2} , assuming a pseudomorphic growth of the Co film on the Pd(111) surface. The oxygen exposure was done at room temperature by backfilling the whole chamber at 1.0×10^{-6} torr for 5 min.

The XPS spectra shown here were obtained with unmonochromatized Mg K α radiation with $h\nu = 1253.6$ eV. The overall resolution was 0.9 eV. Since the O 1*s* PE line overlaps with the Pd 3*p* core level, we instead obtained a photo-excited O Auger spectra for a quantitative analysis.

III. RESULTS AND DISCUSSION

Table 1. Spectral intensity ratio between O Auger and Co 2*p* and that between Co 2*p* and Pd 3*d*.

	I(O Auger)/I(Co 2 <i>p</i>)	I(Co 2 <i>p</i>)/I(Pd 3 <i>d</i>)
5.6-ML Co	—	0.51
O ₂ 300-L	0.25	0.72
700 K for 5 min	0.22	0.55
additional 20 min	0.22	0.43

1. Oxygen Adsorption on Co/Pd(111)

Figure 1 shows the Co 2*p* core-level PE spectra and the O Auger spectra of the 5.6-ML Co films on Pd(111) at various stages. After deposition of Co atoms, the binding energy of the Co 2*p*_{3/2} PE line was 778.3 eV, which is exactly the same value as for the bulk Co [13]. Upon a 300-Langmuir(L) O₂ exposure, the Co 2*p* spectrum became similar to that of CoO [14,15], which has a discernible satellite structure at 786.3 eV. However, the main line binding energy was 780.0 ± 0.1 eV, different from the value listed in Ref. 10. Since there was no additional structure at the binding energy of metallic Co, we concluded that all of the Co atoms had been oxidized.

When the oxide layer was heated at 700 K for 5 min, the spectral lineshape changed slightly; the main lines and the satellites were shifted toward higher binding energy by 0.3 eV, and the linewidths of the main lines were reduced by 0.2 eV. The value of the binding energy, 780.3 eV, indicates that the oxide is almost all CoO, and the reduction of the linewidth implies that the Co atoms have uniform chemical states upon heating.

Actually, further information about the chemical change of Co and its oxide overlayers can be obtained from the O Auger lines. On heating at 700 K, the kinetic energy of the main line shifted by 0.7 eV. Since the Auger line reflects the detailed change of the electronic structure of the O 2*p* states, it is necessary to compare the valence electronic structures of various Co oxides [15–17]. It was shown that the binding energies of the O 2*p* states of the CoO phase formed by oxidation of Co/W(110) at room temperature are at 5.3, 7.3, and 9.9 eV, while those of Co₃O₄ phase formed by oxidation at 80 K are at 4.9, 6.9, and 9.2 eV [17]. From these values, one can deduce that the O Auger peaks of CoO must have lower kinetic energies than those of Co₃O₄ by 0.4 – 0.7 eV, because the O 1*s* PE lines have the same value of binding energy for both oxides [14]. This comparison implies that the oxide phase after O₂ exposure can be a mixture of CoO and Co₃O₄. Furthermore, the measured binding energy of the Co 2*p*_{3/2} main line was within the range of the values listed for Co₃O₄ [13].

To support this argument, we compared the intensities of the Co 2*p* PE and the O Auger lines (Table 1). For the quantitative analysis, inelastic backgrounds were subtracted from the raw spectra shown in Fig. 1. The ratio between the Co 2*p* PE intensity I(Co 2*p*) and the

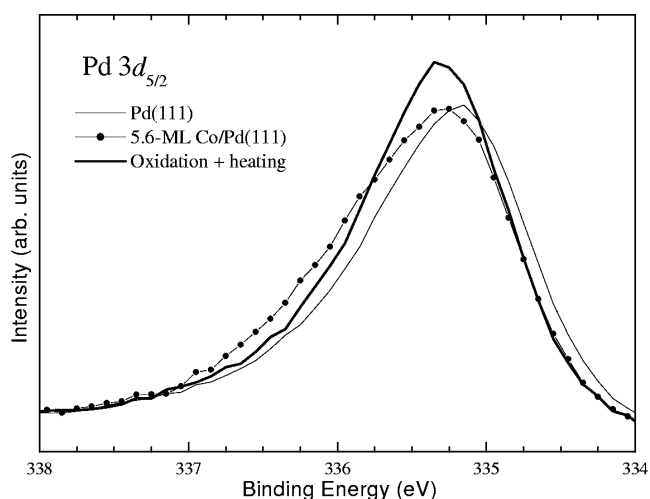
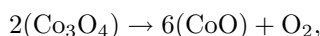


Fig. 2. Pd $3d_{5/2}$ PE spectra of 5.6-ML Co layers on Pd(111): (a) pure Pd(111), (b) as-deposited 5.6-ML Co layer, and (c) Co/Pd(111) after heating the oxidized layer at 700 K for 25 min. The lineshape after a 300-Langmuir oxygen exposure is almost the same as that of the curve in (b).

O Auger intensity $I(\text{O Auger})$ decreased by 12 % upon heating the film at 700 K for 5 min. If the whole oxide after oxygen exposure is in the Co_3O_4 phase, then from the simple chemical reaction



we can expect 25 % of the oxygen atoms to disappear. Since the measured difference of O the Auger intensity is only 12 %, we can conclude that the initial Co oxide is a mixture of CoO and Co_3O_4 with nearly equal amounts.

Further heating at 700 K for an additional 20 min showed another feature at 778.2 ± 0.1 eV, which can be best interpreted as the decomposition of oxides into Co and O atoms. In Fig. 1(e), we show the difference in spectra between the curves (d) and (b) with arbitrary normalization. Comparing the Co $2p$ peak intensities of curves (b) and (d), we found that this arbitrary normalization in fact gives 4 % additional weight to curve (b). This implies that around 4 % of the Co $2p$ PE line intensity comes from metallic Co atoms. However, we cannot determine whether the oxygen atoms from the decomposed Co oxides reside on the bare Pd(111) surface or are desorbed into the vacuum or even diffuse into the substrate because a 4 % change could not be detected in the O Auger spectra. There have been some reports about the presence of O-chemisorbed bare W(110) substrates after heating oxidized Ni/W(110) [6] or Fe/W(110) [7] bimetallic layers, but it is most likely that O atoms diffuse into the substrate as in the aforementioned O/Pd(111) case [10–12] since there was no abrupt pressure increase during heating.

Figure 2 shows the lineshape changes of the Pd $3d$ PE spectra. The inelastic backgrounds are removed, and the spectra are normalized to the same value of total inten-

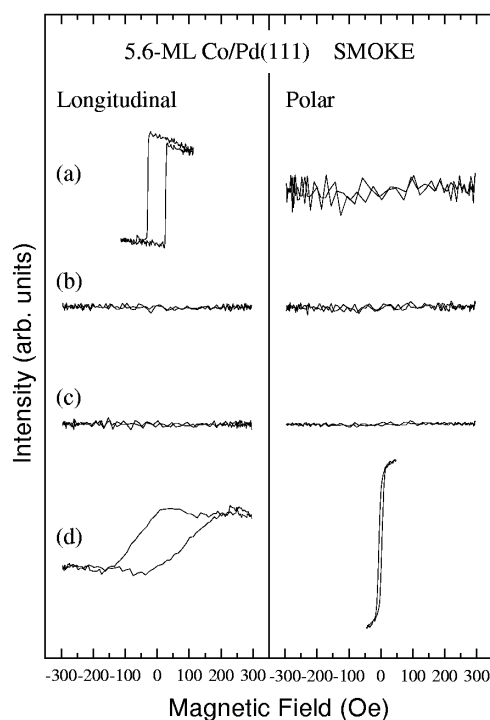


Fig. 3. SMOKE signal of 5.6-ML Co layers on Pd(111): (a) as-deposited, (b) after a 300-Langmuir oxygen exposure, (c) after heating at 700 K for 5 min, and (d) after additional heating at 700 K for 20 min.

sity. After Co deposition, the Pd $3d_{5/2}$ PE peak was shifted by 0.15 eV due to the bonding between the interfacial Pd and Co atoms. The lineshape and the binding energy did not change much upon oxidation of the Co layers. It seems that the atoms of the innermost Co layer retain their bonding with substrate atoms. Upon heating at 700 K, the peak became sharper, indicating a uniformity in the chemical environment of the Pd atoms. The relative intensities $I(\text{Co } 2p)/I(\text{Pd } 3d)$ at the various stages are listed in Table 1. Since the oxidation will definitely increase the thickness of the overlayer, an increase of $I(\text{Co } 2p)/I(\text{Pd } 3d)$ is expected upon oxygen exposure. After heating at 700 K, this value is decreased, probably due to island formation of Co oxides upon heating.

The magnetic property of the oxidized 5.6 ML Co/Pd(111) was studied with SMOKE, and the results are shown in Fig. 3. Since the Co overlayer is thick enough to suppress the surface anisotropy which favors a perpendicular magnetic moment, there is no polar Kerr signal for the as-deposited film. The oxidation completely removes the Kerr signal, as can be expected from the fact that both CoO and Co_3O_4 are paramagnetic at room temperature. However, upon heating at 700 K for 25 min, hysteresis loops were observed both for the longitudinal and for the polar directions. Since a small number of Co atoms are found to be in the metallic phase, this ferromagnetic behavior must be due to the intermixing between the Co atoms and the Pd substrate.

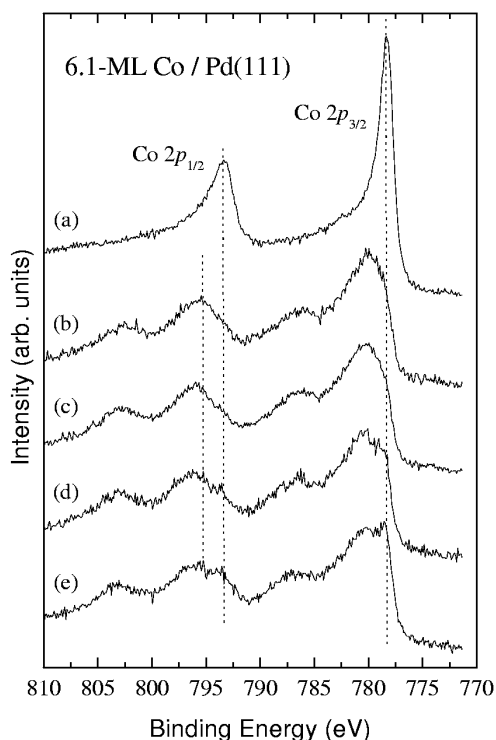


Fig. 4. Co 2p spectra of 6.1-ML Co layers on Pd(111): (a) as-deposited, (b) after a 300-Langmuir oxygen exposure, (c) after heating at 700 K for 5 min, (d) after additional heating at 750 K for 10 min, and (e) after further heating at 800 K for 10 min.

In order to see more clearly the decomposition of CoO upon heating, we prepared an oxidized 6.1-ML Co film and heated it at higher temperatures (Fig. 4). The line-shapes of the spectra are similar to those for the 5.6-ML Co film, but upon heating at 750 K for 10 min and upon additional heating at 800 K for 10 min, the metallic Co 2p PE peak was significantly enhanced. From the spectral intensity comparison, we estimate that at least 12 % of the Co atoms of the heated film at 800 K were metallic. This assures that the heating of the Co oxide films results in decomposition of oxides into metallic Co and oxygen.

The oxidation of the Co surface has been dealt with for various planes, and the overall trends can be summarized as follows: at room temperature, oxygen atoms usually diffuse into the bulk and CoO is formed. Only very high doses of oxygen lead to the formation of Co₃O₄. At low temperature, the formation of oxide starts immediately with Co₃O₄ [16,17]. In this work, we studied the oxidation of ultrathin Co films on Pd(111), which grew in an fcc structure [18], and found that the oxide was not purely CoO, but a mixture of CoO and Co₃O₄. However, heating at 700 K for 5 min removed the Co₃O₄ phase, and we believe that the observed partial formation of Co₃O₄ was due to the relatively high exposure value (300 L) we used.

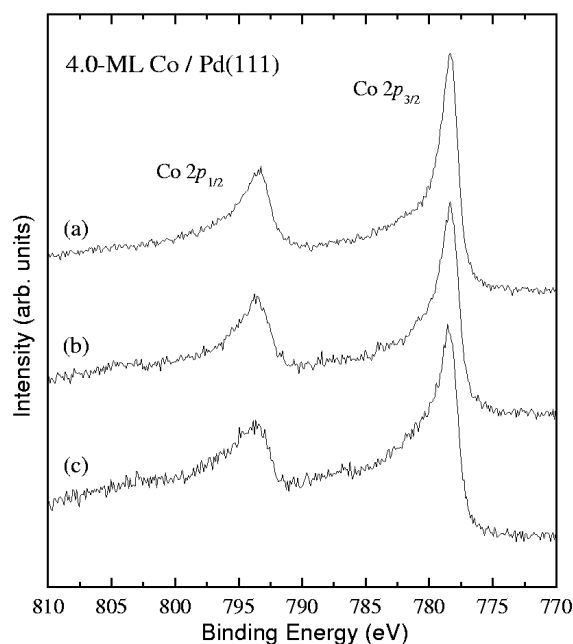
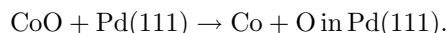


Fig. 5. Co 2p spectra of 4.0-ML Co layers on Pd(111): (a) as-deposited, (b) pre-annealed at 600 K for 1 h, and (c) after a 300-Langmuir oxygen exposure. Note the absence of oxide peaks.

Upon heating at 700 – 800 K, we observed an incomplete decomposition of CoO. This decomposition is not possible for the bulk, but the presence of the Pd(111) surface can lead to the following chemical reaction:



Since the heat of formation of CoO is $-2.5 \text{ eV atom}^{-1}$ [19] and the activation energy of thermal desorption of oxygen atoms in Pd(111) substrate is 2.4 eV atom^{-1} [20], such a chemical reaction is not highly favorable. However, the reaction increases the entropy of the system since CoO decomposes into Co and O and since the oxygen atoms diffusing into the Pd substrate may induce a disordered structure. Therefore, the difference in the Gibbs free energy before and after the reaction can be negative at high temperature. Similar, but more complex behavior of the decomposition of oxides has been reported on a W(110) substrate [6,7].

2. Oxygen Adsorption on Intermixed Layers

We also studied the oxygen adsorption on a Co-Pd alloy thin film prepared by pre-annealing the 4.0-ML Co films at 600 K for 1 h, as shown in Fig. 5. The Co 2p PE peaks were broadened after annealing, but the binding energy remained the same. This change in linewidth can be interpreted as an interdiffusion of Co atoms into the substrate Pd atoms since a similar broadening was

observed for the Co 2*p* PE spectra of Co-Pd alloys [21]. In addition to the increase of the linewidth, the spectral intensity ratio $I(\text{Co } 2p)/I(\text{Pd } 3d)$ decreased by 36 % as a result of interdiffusion.

In order to estimate the Co concentration of the surface alloy $\text{Co}_x\text{Pd}_{1-x}$, we used Johansson and Mårtensson's method for treating core-level binding-energy shifts in alloys [22–24]. This method is based on a Born-Haber cycle involving the heat of formation usually calculated after Miedema *et al.* [25]. The Co 2*p* binding-energy shift calculated in a simplified scheme [22] was $\Delta E = 0.09(1-x)$ eV, which was too small to be detected for a quantitative estimate. When we applied the same method to the Pd 3*d* binding-energy shift, we found that

$$\Delta E = 1.16x \text{ eV.}$$

Since the Pd 3*d* peak of pre-annealed film shifted by 0.38 eV from the pure Pd(111) case, we can estimate that the Co concentration of the surface alloy is 33 %.

Upon oxygen exposure of the pre-annealed layer, however, there was no indication of oxidation of Co atoms [Fig. 5 (c)]. This implies that all of the O atoms were chemisorbed on the surface, which is different from the non-annealed layers. Further heating at 600 K led to a loss of oxygen by 50 %. Since there was no abrupt increase in the pressure reading on heating the layer, the oxygen adsorbates seem to have diffused into the bulk, without affecting either the Co 2*p* or the Pd 3*d* line-shapes.

One possible explanation for this inhibition may be that although the surface alloy can be oxidized, the top-most layer is Pd only. If this were the case, the Pd 3*d* PE line should be composed of at least two peaks which correspond to the emission from the top Pd layer and to the emission from the intermixed layers. However, the observed Pd 3*d* PE line was a single peak without any additional broadening. Furthermore, no oxidation was observed even when the oxygen atoms diffused into the bulk upon heating. The most plausible explanation for the inhibition of oxidation is that the Co-Pd(111) surface alloy whose Co concentration is 33 % is not oxidized.

Actually, to the best of our knowledge, there have been no reports on the oxidation of Co-Pd surfaces, but the inhibition of oxidation can be understood as follows: First, since the heat of formation of the Co-Pd alloy is negative [25], the bonding between the atoms must be stronger than in pure Co metal. This may lead to much weaker bonds between Co and O atoms than for the non-annealed case. Secondly, the (111) surface of the fcc structure is the least reactive because of its close-packed nature. We are not sure whether Co-Pd alloys with such open surfaces as (100) can be oxidized, but it is highly probable that the inert nature of the (111) surface may inhibit oxidation at room temperature.

IV. CONCLUSION

To summarize, we studied the influence of oxygen adsorption on the magnetic property and the morphology of ultrathin Co layers on Pd(111) substrates by using XPS and SMOKE. Upon an oxygen exposure of 300 L, the Co layers were converted to a mixture of CoO and Co_3O_4 , and the latter could be further reduced to CoO by a short annealing at 700 K. Additional heating at 700 – 800 K led to a partial decomposition of CoO into Co and O, and Kerr signals for both the longitudinal and the polar directions were observed. The oxygen adsorption on the pre-annealed layer was also investigated. The Co concentration of the pre-annealed 4.0-ML Co layers was estimated to be 33 %. This pre-annealing completely inhibited oxidation, and only chemisorption was found to occur.

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