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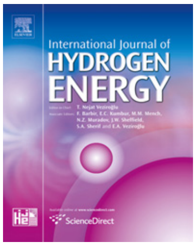

Pd as a promoter to reduce Co cluster films at room temperature

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ABSTRACT

The optical and resistivity properties of Pd/Co films are investigated and related to the interaction of palladium and the underlying cobalt (Co) clusters layer when exposed to hydrogen. Co is used because it is known to absorb hydrogen only on its surface. Co clusters with mean size of 1.8 nm in the gas phase were deposited on sapphire substrates at room temperature (RT), 300 °C, and 500 °C, respectively, and capped by a continuous Pd film. Light transmission and reflection in the visible range were measured during hydrogen exposure at different pressures in consecutive cycles. An unusual change in the transmittance and the resistance during the first hydrogenation cycle of a sample suggests that a reduction of the surface oxide on the Co clusters layer occurs at room temperature. The reduction of the native oxide on Co thin films or bulk does not happen without the Pd capping when exposed to hydrogen under similar conditions.

1. Introduction

Heterogeneously catalyzed reactions play a very important role in industrial production and for that reason the understanding of the basic process at atomic level have long been pursued. How and where these reactions take place at the atomic scale is still a matter of intense research. Studies of these reactions in research laboratories, under mild conditions of cleanliness, pressure and temperature did not reproduce the conditions in industrial facilities and therefore the studies were not significant to improve the production. There are still several "gaps" in-between research and industry in many catalyzed processes. Namely the "pressure gap", the "material gap" and the "phase gap". Somorjai [1] has spent a research life trying to bridge the ultra high vacuum (UHV) and high pressure gap in reactions such as the hydrogenation of carbon monoxide (CO) and Ammonia (NH_3) synthesis. In this case, the reaction takes place on a solid surface at an atomic scale. A summarized understanding of these "gaps" can be found in the article by Imbihl et al. [2]. The understanding of how exactly a reaction occurs on a molecule or on a nano-structures in the catalytic process is still being

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investigated. For example the study of M. B. J. Roeffaers et al. [3] was investigated with single-molecule fluorescence spectroscopy. Earlier studies also used this technique with biomolecules [4,5].

The most important intermediate state in a catalyzed reaction is the adsorption and dissociation of the molecules which are the reactants. In our case, the oxide reduction or the absorption of atomic hydrogen is preceded by the dissociation of the hydrogen molecule.

Cobalt (Co) is a metal used in the past to catalyze the CO hydrogenation. This reaction on Co produce hydrocarbons heavier than methane (CH_4) and thus Co is a good catalyst for the synthesis of gasoline. Nevertheless it is widely accepted that Co does not absorb hydrogen in the bulk. Co is known for adsorbing a monolayer of hydrogen on the surface of a bulk sample and also on Co thin films. It is also a known fact that Co oxide does not reduce at room temperature in a hydrogen environment [6,7].

As Co does not absorb hydrogen and palladium does this system presents the opportunity to study the properties of a mixed system. If other metals are used instead of Co, it would add complexity to understanding the results.

The idea of depositing a known element capable of absorbing hydrogen, namely palladium (Pd), on a layer of preformed Co clusters with nanometric length scales, could unravel some interesting and/or new phenomena, when this system is exposed to hydrogen. Pd has been extensively studied during the past years and there is a basic understanding of its interaction with hydrogen gas. In this work Pd is used as a mean to deliver atomic hydrogen to an underlying layer of Co clusters, and observe their interaction. Some theoretical work on composite system has been done on Mg doped with various transition metals [8].

Pd based compounds have received a lot of interest due to Pd's capability of absorbing 900 times its volume of hydrogen under specific conditions of pressure and temperature, inducing changes in its physical and structural properties [9]. Hydrogen-metal systems have motivated numerous studies due to their direct applications which include fuel cell technology and hydrogen gas purification and their need for highly sensitive and compact hydrogen gas sensors [10]. When exposed to a hydrogen gas atmosphere, molecular hydrogen (H_2) is chemisorbed on the Pd surface where it dissociates into two H atoms (dissociative chemisorption) [11]. After donating its electron, the atomic H diffuses into the Pd lattice as a proton [12,13]. At low hydrogen pressures the α phase of PdHx is formed where the H atoms occupy interstitial sites in the fcc Pd lattice. The hydrogen atoms are believed to reside in octahedral sites, but calculations [14] have shown that tetrahedral sites may also be a favourable location. Further hydrogen absorption in Pd causes an expansion of the lattice, characteristic of the hydride phase (β) with the resulting change in the lattice constant being around 3.3% [15,16].

In the case of thin Pd films, the α phase diagram appears to be thickness dependent. With PdHx in the α phase, the absorbed H concentration follows Sievert's law [11] but deviates from such behavior when exposed to higher H pressures, typically >1 Torr at room temperature. The physical properties of Pd influenced by hydrogen absorption include electrical resistivity and optical permittivity, both of which have been contemplated for hydrogen sensing. Other examples exploit surface plasmons (SP) based techniques using an optical fiber configuration [17] or an SP resonance system in an attenuated total reflection geometry [18]. Magnetic properties are influenced by the insertion of hydrogen: in bulk FePd alloys the magnetic moment weakens upon hydrogen absorption [19] whereas an increase has been reported in the case of Fe/V multilayers [20].

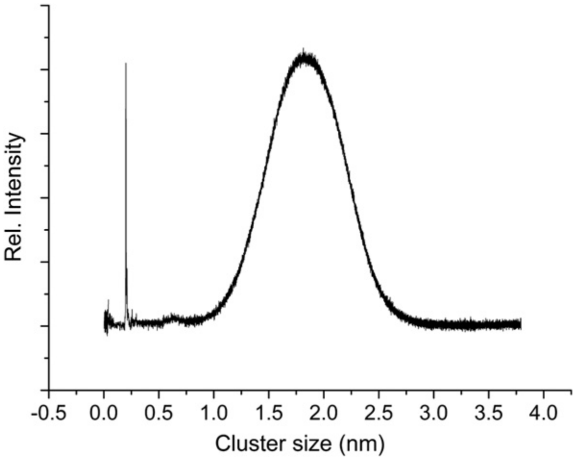

Fig. 1 – Size distribution of gas phase Co clusters.

In this paper we report on measurements of the optical response of thin Pd films deposited on preformed Co clusters that are deposited on transparent sapphire substrates at various temperatures. The optical response showed a reduction taking place at room temperature on the interface of the Pd–Co oxide layer. Similar studies but on regular glass also show change in the optical properties [21].

2. Experimental

2.1. *Sample preparation*

The Co clusters were made in a laser vaporization source [22] and deposited at low energies (<0.2 eV/atom) on polished sapphire with (0001) orientation in an ultra high vacuum deposition chamber that has a base pressure of 10^{-10} Torr. A detailed description can be found elsewhere [23]. The cluster size distribution was monitored with time-of-flight (TOF) mass spectrometry. The size distribution of the Co clusters obtained from the mass spectrum assuming spherical shapes and a Co Wigner–Seitz radius of 0.13 nm, is shown in Fig. 1. The main hump at 1.8 nm in the spectrum appears due to the overlap of the neighbouring peaks and has a width of 0.7 nm which corresponds to clusters from 1 nm to 2.5 nm. The sharp single peak at size 0.2 nm corresponds to single Co atoms.

For a number of earlier studies of cluster assembled films prepared in the same setup under similar experimental conditions, a detailed structural investigation was carried out. In particular transmission electron microscopy and small angle x-ray scattering showed that Co cluster films largely consist of spherical clusters with an average size very similar to the values obtained from gas phase mass spectrometry [24].

Table 1 – Name of samples. Layer thicknesses and Pd/Co ratio as measured by RBS. Transmission values for Pd and for Pd/Co samples as a function of Pd/Co thickness ratio.

Name	Sample description	X_{Co} = Co layer (nm)	X_{Pd} = Pd layer (nm)	Pd/Co thickness ratio	From Eqs .(1) and (2) T_{PdH} (%)	$T_{PdH_x} \times \sqrt{\frac{x_{Co}}{20}}$(%)	Measured change in transmission (%)
A1	RT	49.0	14.0	0.289	16.8	10.7	9.5
A2	300 °C	37.0	12.5	0.338	14.3	10.5	11.5
A3	500 °C	39.5	14.5	0.367	17.6	12.5	12.8
B1	Pd/Co continuous film	20.0	11.5	0.575	12.7	12.7	14.6

The Co clusters were deposited to form a film that was capped with Pd. These depositions were done at three different substrate temperatures: RT, 300 °C, and 500 °C (named A1, A2, A3) and also the physically evaporated film B1. The Pd capping layer, of all samples was deposited at room temperature with a commercial e-beam evaporator using an ultra pure Pd rod (99.99%). Table 1 gives the Rutherford backscattering spectroscopy (RBS) thickness measurements of the samples, these thicknesses were estimated using bulk densities for Co. Our RBS resolution is ±2 nm in estimating the layer thickness.

In order to confirm the elemental composition, the samples were characterized with RBS and X-ray diffraction (XRD) measurements. The RBS spectra indicate that approximately 20 atomic percent of the Co cluster layer is composed of oxygen. From variation in thicknesses, no other relevant differences are present in the chemical composition of the samples. The structural information as obtained from XRD shows that no relevant phase changes have occurred before and after the hydrogen cycles. All these measurements were done at room temperature. More oxygen is present on the sample A1 than on the others as determined by RBS.

The morphology of the different samples is very similar, as the basic building blocks are the same (Co clusters of 1.8 nm in mean size, see Fig. 1). Coalescence due to the higher temperatures of the substrates enables the formation of larger grains. Thus at low temperature (RT) the layers have smaller grains (less coalescence) whereas at higher temperature they form larger grains.

The differentiation between small and large grain sizes permits to consider that it is possible to detect the effect of a tailored substrate of Co clusters on an overlaying Pd layer. This could cause a visible change in the variation of the optical and electrical properties. Furthermore, it has been claimed that Pd covers pre-deposited Co clusters in a shell-like form. [25].

2.2. *Optical and resistance measurements*

Near normal reflectance and transmittance measurements were performed in a small cylindrical aluminium vacuum chamber equipped with two transparent quartz windows, a gas/vacuum line, and electrical feed-throughs used for connections. The incidence angle of the light is 7°. A tungsten halogen lamp was used as a source and this white light was focused on a TRIAX 180 (Jobin Yvon-Horiba) monochromator fitted with a 1200 grooves/mm diffraction grating. The light detection was done with silicon photodiodes in combination with lock-in amplifiers. The resistance was measured with a. Keithley resistivity bridge model 580 which allows measurements with 4 points connections. A similar system is described elsewhere [10,26].

All samples were provided with electrical contacts to measure the resistance at the same time as the light transmission and reflectance. The chamber was evacuated down to 10^{-2} Torr using a 50 l/s Balzers turbomolecular pump. Next the chamber was filled with hydrogen reaching a given pressure from 3 to 120 Torr. As soon as hydrogen was allowed to enter the chamber, optical and electrical data were recorded during 1000 s.

3. Results and discussion

The optical data are presented at an incident wavelength of 600 nm. The transmittance of the three samples of Co cluster films as a function of hydrogen pressure as well as a Co film capped with Pd is shown in Fig. 2. The inset in Fig. 2 shows the transmittance of a pure Pd layer of 15 nm deposited on a similar substrate. In this inset there are two relevant issues: first the variation saturates at about 27% and secondly this occurs at 200 Torr. In Fig. 2 we have also plotted the data of a Co film (grown by e-beam evaporation) capped with Pd together with the data of all the Co cluster samples. The Co continuous film capped with Pd, sample B1, has the highest transmittance increase upon hydrogen absorption, 14.6% at saturation. Next follow the cluster sample A3 made with the highest substrate temperature (500 °C) where the variation is

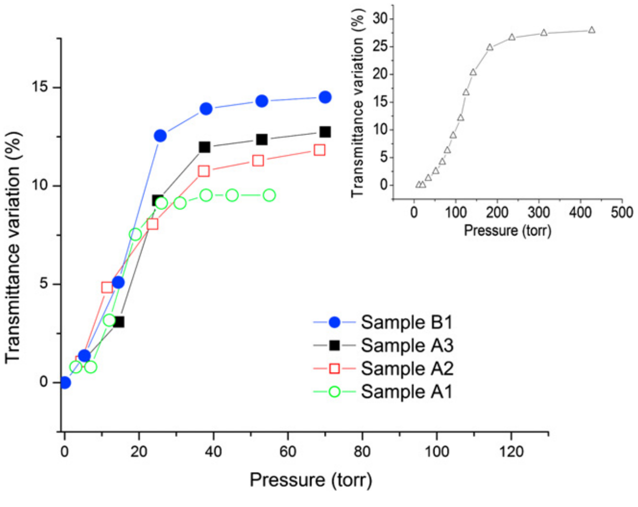

Fig. 2 – Transmittance variation versus hydrogen pressure of all the samples. The inset is a sample of pure Pd.

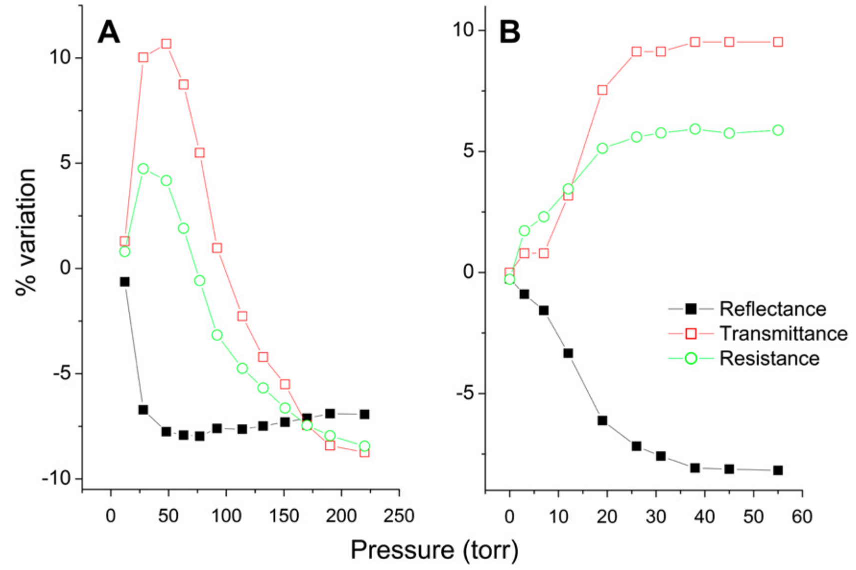

Fig. 3 – Sample A1. (A) First hydrogen exposure.(B) After first hydrogen cycle and subsequent cycles.

12.8%, sample A2 deposited at 300 °C with 11.5%, and sample A1 made at the lowest substrate temperature, room temperature, for which the variation is also the lowest with 9.5%. These values of saturation can be explained by the transmission attenuation due to the Co layer since they are not all of the same thickness.

We had studied in detail the changes in transmission of pure Pd layers when they absorb hydrogen up to 60 Torr pressure. The transmission values of the pure films follow an exponential decay as a function of the thickness. In the case of pure Pd we found the following equation that relates transmission with Pd thickness:

$$T_{Pd} = 0.671e^{-0.081x} \quad (1)$$

where x is the Pd thickness in nm. This equation is valid down to 5 nm; below this value the error in the transmission is large.

When the Pd film absorbs hydrogen the value of the transmission increases but still we find an exponential decay as a function of the thickness. In the case of Pd loaded with hydrogen up to 60 Torr, the transmission as a function of the Pd thickness can be represented by the following equation:

$$T_{PdH_x} = 0.644e^{-0.067x} \quad (2)$$

With Eqs. (1) and (2) we can calculate the change in the transmission due to the pure Pd overlayer in all measured samples. This is displayed in the 6th column of Table 1. If we multiply this value by the $\sqrt{X_{Co}/20}$ where X_{Co} is the thickness value of the A1 through A3 sample and 20 is the thickness of our reference sample B1, we obtained very similar values to the ones measured for the A samples. The comparison is not too good for the B1 sample; however, since the Pd overlayer is the thinnest therefore and and Eqs. (1) and (2) might give the largest error for this case. Pd film thickness of this order and in addition the Co film is of different nature than the Co films made from clusters. This explains why the transmission change measured for sample B1 is larger than the calculated transmission for the pure Pd overlayer.

The order of the transmission increase due to hydrogen absorption correlates very well with the thickness ratio between the Pd overlayer and the Co layer (see Table 1). The largest ratio results in the largest value of transmission increase. In the case of the pure Pd shown in the insert in Fig. 2 the transmission change at about 100 Torr is about 15% and at 400 Torr is about 27%.

The measured transmittance and the resistance provide an indication of the overall behavior of the films. The reflectance is very sensitive to surface roughness and/or changes in roughness on the first layers of atoms and is therefore harder to interpret.

In Fig. 3 we show the three variables (reflectance, transmittance, and resistance) measured on sample A1 during hydrogen exposure. In Fig. 3A the data during the first hydrogen cycle are shown, while Fig. 3B shows the data after the sample was stabilized, i.e., after several cycles of vacuum and hydrogen exposure. For the first three data points in Fig. 3A the transmittance and resistance have a positive trend and then an abrupt fall occurs. As the hydrogen starts penetrating the surface layers of the Pd film an increase in transmittance and electrical resistance occurs. At 50–60 Torr a sudden drop in these two variables is observed, which can be attributed to the fact that the hydrogen has reached the Co cluster–Pd interface and is now reacting with the surface oxide of the Co clusters. Due to the reduction of the oxide by the atomic hydrogen, the Co cluster layer becomes more metallic and thus the transmittance and resistance are reduced. That way the hydrogen reduction reaction of the cluster oxide layer is directly responsible for the observed decrease in transmittance and resistance.

The initial resistance of sample A1 was 242.2 Ω before being exposed to hydrogen. After the first hydrogen cycle the resistance of the sample decreased to 208.6 Ω. This resistance value yields a resistivity value of $\rho^{*}_{Co} = 1 \times 10^{-3}\Omega$-cm for the 39 nm thick cluster film. This is about three orders of

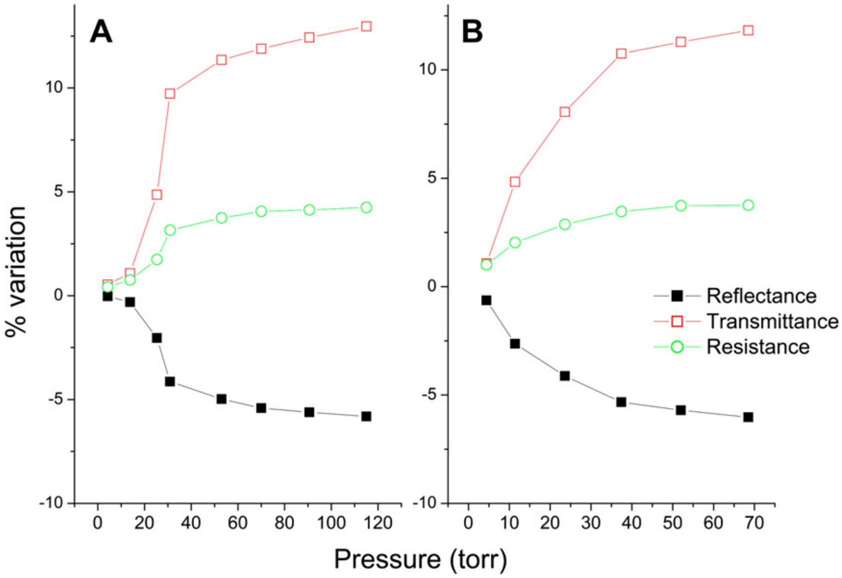

Fig. 4 – Sample A2. (A) First hydrogen exposure. (B) After first hydrogen cycle and subsequent cycles.

magnitude larger than the resistivity of a continuous Co film ($\rho_{Co} = 7 \times 10^{-6} \Omega$-cm). Clearly the high value in resistance of these Co cluster films is due to the lack of continuity in the film since the conductivity occurred only in the touching points between one cluster and the next. This observed decrease in resistivity after hydrogen exposure during the first cycle can be explained by a change in the Co cluster thickness of only 7 nm, assuming perfectly square samples. This is easily justified if one assumes conduction on 32 nm of Co cluster covered by a non-conducting 7 nm of Co oxide film.

This is the best explanation possible for the resistance behavior observed for sample A1 during the first cycle of hydrogen exposure since it is well known that the absorption of hydrogen in the bulk of metals would increase the resistance rather than decrease the resistance [26].

Also, a sustained increase in the reflectance from 50 Torr onwards can be observed in Fig. 3A. This could also be due to the Co clusters becoming more metallic. Fig. 3B shows a decay in reflectance similar to what is observed for a pure Pd film exposed to hydrogen, where the reflectance reaches saturation but never increases. After the second cycle of hydrogen exposure the system had a reproducible behavior similar to Fig. 3B.

Transmittance, resistance and reflectance were also measured on sample A2, as displayed in Fig. 4 as a function of hydrogen pressure. In contrast to sample A1, only small differences between the first and consecutive hydrogen exposures are detected.

A similar behavior was observed for sample A3, deposited at a substrate temperature of 500 °C.

As an additional reference we measured the behavior of sample B1, a Co thin film grown by e-beam evaporation and covered with Pd with similar thicknesses of both elements. Its optical and electrical properties were measured and the results are similar to Fig. 4A. Comparing the data for the reaction of this sample (B1) upon exposure to hydrogen with the data for the cluster deposited samples A2 and A3, very similar behavior is observed. i.e., the elevated temperature cluster films tend to behave like the physical vapor deposition (PVD) thin film configuration.

For samples A2, A3 and B1 the ‘‘Pd/Co Ratio’’ column from Table 1 is used to estimate the change in optical and electrical properties due to the Pd upon hydrogenation, thus no significant amount of hydrogen has been absorbed by the Co or Co oxide layer. As earlier studies on Co thin films, foils and microdots suggest that atomic hydrogen absorbed at the surface does not permeate the Co or Co oxide layers that may exist on such samples [6].

On the other hand, for sample A1, we observe a dramatic decrease (Fig. 3) in the resistance. Thus intercalation of atomic hydrogen in the Co or Co oxide is probably not what is happening but rather a reduction of the oxygen on the surface of the Co clusters. Furthermore when hydrogen penetrates into Pd the electrical resistance increases due to the fact that the hydrogen atoms act as scattering centers. As the Co clusters surface loses oxygen, the sample becomes more metallic and the overall transmittance decreases, and so would the electrical resistance. This is happening in parallel with the usual PdO reduction also occurring at room temperature during hydrogen exposure.

4. Conclusion

We have studied the reflectance, transmittance and electrical properties of a series of samples consisting of films of Co clusters deposited at different substrate temperatures and covered with a Pd film.

The amount of studies on Pd-hydrogen and Co-hydrogen systems suggests that a reduction of Co oxide at the interface between Pd and Co has taken place. From XRD and RBS data we conclude that no major structural changes have occurred in these material. Because Co does not absorb hydrogen, the only viable explanation for a clear change in the optical and resistivity data during the first cycle is that a small amount of Co oxide was reduced at the interface with the Pd capping layer.

The reduction of cobalt oxide upon hydrogenation at room temperature is remarkable given that this is normally archived at high temperatures, and this phenomena could be of importance in nanostructured systems that combine palladium and cobalt. The optical and electrical measurements described in this work are a simple method to monitor such phenomena.

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