Hydrogenation induced reversible modulation of perpendicular magnetic coercivity in Pd/Co/Pd films

Wen-Chin Lin, Cheng-Jui Tsai, Bo-Yao Wang, Chao-Hung Kao, and Way-Faung Pong

Citation: Appl. Phys. Lett. 102, 252404 (2013); doi: 10.1063/1.4812664
View online: http://dx.doi.org/10.1063/1.4812664
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i25
Published by the AIP Publishing LLC.

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors
Hydrogenation induced reversible modulation of perpendicular magnetic coercivity in Pd/Co/Pd films

Wen-Chin Lin,1,a) Cheng-Jui Tsai,1 Bo-Yao Wang,2 Chao-Hung Kao,2 and Way-Faung Pong2
1Department of Physics, National Taiwan Normal University, Taipei 116, Taiwan
2Department of Physics, Tamkang University, Tamsui 251, Taiwan

(Received 18 April 2013; accepted 14 June 2013; published online 27 June 2013)

In perpendicularly magnetized Pd/Co/Pd trilayers, the hydrogenation not only increased Kerr signal but also significantly enhanced the magnetic coercivity ($H_C$) by 17%. The reversibility was demonstrated by cyclic $H_2$ exposure. The time constants of hydrogen absorption and desorption effect on $H_C$ range from tens to hundreds seconds, depending on the $H_2$ gas pressure. The magnetooptical Kerr signal and magnetic coercivity was simultaneously recorded during $H_2$ absorption and desorption. These multifarious signals respond differently and provide a detailed understanding of hydrogenation effect on the functional Pd/Co/Pd trilayers. © 2013 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4812664]

Metal-hydride systems have been widely studied in the last decades due to the potential of hydrogen storage and sensing. Hydrogen is able to modify the crystalline structure, morphology, and especially the electronic structures; meanwhile, the optical and magnetic properties are modulated.1,2 Based on this idea, hydrogenated metallic films are considered as functional materials in high tech application.2 Pd is usually used as a catalyst for hydrogen dissociation and absorption.2–6 In the initial stage, H atoms occupy the interstitial sites of the Pd crystalline lattice ($\alpha$ phase). With increasing hydrogen absorption, the Pd lattice is expanded by 2–3% ($\beta$ phase).7–9 Therefore, Pd thin films of few nm thickness are widely used in metal-hydride systems.10 Many studies have been devoted to the combination of Pd layers with other functional thin films for the investigation of hydrogenation effect.7,11,12 The hydrogenation of Pd capping layer may induce proximity effect upon the underneath functional thin films. This effect is important from fundamental point of view and also applicable in future techniques. Especially, some studies have focused on the combination of hydride-metal with magnetic materials. For example, long range magnetic interlayer coupling in Fe/V and Fe/Nb multilayers change signs, because hydrogen adsorption changes the electronic structures of V and Nb intermediate layers.13–15 Recently, Chang et al. reported on the metallic spintronic thin film as a hydrogen sensor.16 Lederman et al. reported on 50% magnetooptical (MO) enhancement in a hydrogenated Pd/Fe bilayer sample.5 Our previous studies also investigated the reversible MO enhancement with the variation of Pd thickness and different magnetic underlayers.17,18 However, in all of these Pd/Fe, Co, and Ni bilayers, only the MO enhancement was observed. The intrinsic magnetic behavior, like magnetic coercivity and magnetic anisotropy, was invariant with hydrogenation. In magnetism, Pd is also a particular element for the promotion of perpendicular magnetic anisotropy, which is a key issue in magnetic storage and sensor.19,20 Pd/Co/Pd trilayers were used in this study. Post-annealing promoted the alloy formation at the Pd/Co interface and led to the enhanced surface magnetic anisotropy, which dominated the perpendicular magnetization.20 The hydrogenation effect on perpendicularly magnetized Pd/Co/Pd thus is an interesting system to explore. Okamoto et al. first reported on the reduction of magnetization and the enhancement of magnetic anisotropy in hydrogenated Pd/Co/Pd trilayers with hydrogen gas pressure from 1.3 atm to 3 atm.21 The hydrogen absorption in Pd/Co/Pd caused irreversible enhancement of Pd(111) orientation along with the significant increase in perpendicular magnetic anisotropy. After dehydrogenation, the magnetic anisotropy did not recover the initial value of un-hydrogenated state. In 2011, K. Munbodh et al. reported another experiment of Pd/Co/Pd using polarized neutron reflectivity.7,22 The observed hydrogen effects on magnetization and magnetic anisotropy were similar to the results of Okamoto et al. However, until now, no well reversible control of magnetic anisotropy was achieved through hydrogenation. The detailed studies of response time and the sensitivity to the different hydrogen gas pressure are still lacking. Thus, in this experiment, we thoroughly investigate the reversible hydrogenation effect on perpendicular magnetic anisotropy of Pd/Co/Pd trilayers using the hydrogen gas pressure from 10 to 1000 mbar. The optical, magneto-optical, and magnetic properties were simultaneously recorded for the understanding of the detailed mechanism in hydrogenation and dehydrogenation.

The 5 nm Pd/4 nm Co/5 nm Pd thin trilayers were deposited on $\text{Al}_2\text{O}_3(0001)$ substrate by e-beam heated evaporators in an ultra-high vacuum (UHV) chamber with a base pressure of $3 \times 10^{-9}$ torr.17 Post-annealing at 700 K was in situ carried out right after deposition. The magnetic properties were investigated at room temperature (RT) using magneto-optical Kerr effect (MOKE). The MOKE measurement system was composed of four electromagnet poles installed in a vacuum chamber. The MOKE hysteresis loops were measured in both perpendicular and in-plane geometry by simply switching the polarity of electromagnet without changing the optical setup. The MOKE chamber was either in air or pumped to a vacuum of $5 \times 10^{-2}$ Torr. Afterward the MOKE chamber was filled

---

a)E-mail: wclin@ntnu.edu.tw
with different hydrogen pressure in order to investigate the hydrogenation-induced effect on the magneto-optical and magnetic properties.

Fig. 1(a) shows the in-plane MOKE hysteresis loops of the as-deposited (non-annealed) Pd/Co/Pd measured in air, vacuum, and 1 atm hydrogen gas pressure. The as-deposited Pd/Co/Pd trilayers on Al2O3(0001) exhibited only in-plane magnetism. The Kerr signal is clearly enhanced, but the magnetic coercivity (Hc) is always invariant, like our previous studies on Pd/Fe, Co, Ni bilayers. This indicates H2 adsorption does not affect the magnetization processes of magnetic films, and the MO enhancement should originate from H2-induced change of Pd optical properties. On the other hand, the post-annealed Pd/Co/Pd preferred an oblique magnetic easy axis. Magnetic hysteresis loops of comparable Hc were observable in both perpendicular and in-plane MOKE geometry. Fig. 1(b) shows the perpendicular MOKE hysteresis loops of the post-annealed Pd/Co/Pd measured in air, vacuum, and 1 atm hydrogen gas pressure. After exposure to 1 atm hydrogen gas, not only the magneto-optical Kerr signal but also the magnetic coercivity Hc was increased.

The samples of Figs. 1(a) and 1(b) were grown with the same conditions. Post-annealing promoted the alloy formation at Co/Pd interface, which resulted in the perpendicular anisotropy. The interface properties of the Pd/Co/Pd films were also characterized via surface sensitive Co L-edge X-ray absorption near edge structure (XANES) in total energy yield (TEY) mode, in which the XANES signal is known to be exponentially damped with increasing distance of elements away from the surface. Our measurements show that the intensity of Co L-edge XANES significantly increased for the Pd/Co/Pd films after annealing at 700 K. The non-annealed film showed only about 1/10 intensity of Co L-edge XANES as compared with the annealed film. Since both films were prepared in identical condition, the significant enhancement of Co XANES signal can be attributed to a diffusion of Co atoms from middle Co layer into the top Pd layer. Intuitively the significant contrast of Hc enhancement between the post-annealed and non-annealed Pd/Co/Pd might result from the hydrogenation of the Pd/Co alloy interface, since the interface anisotropy dominated the magnetic behavior. Because hydrogen absorption has been reported to change the electronic structure of Pd significantly, the hydrogen-induced modulation of magnetic coercivity observed in Fig. 1(b) could be due to the fact that hydrogen changes the spin-orbit coupling of Pd, especially at the Pd-Co alloy interface.

In our MOKE measurement, a p-polarized 670 nm laser was shone on the sample with an incident angle of 45°. The reflected beam was detected by an analyzer, which was composed of a linear polarizer at a small angle φ from the s-axis and a photodiode. When the sample is magnetic, the reflected beam is no more purely p-polarized. Instead, it is composed of a p-component (Ep) and an s-component (Es). The ratio of Ep/Ep is expressed as θ + εs, where θ is the Kerr rotation, and ε is the Kerr ellipticity. When φ is very small, the measured light intensity I can be expressed as a parabolic function of φ, like Eq. (1) and the data curves in Fig. 1(c).

\[ I_{\pm m} = |E_p|^2 (\theta_{\pm m}^2 + 2\theta_{\pm m}\phi + \theta_{\pm m}^2 + \varepsilon_{\pm m}^2) \]  

(1)

The indexes of ±m indicate the values corresponding to the positively/negatively magnetization state. The saturation Kerr rotation, defined as \( \Delta\theta = (\theta_{+m} - \theta_{-m})/2 \), is obtained from the shift of the extinction (minimum) angle of the two parabolas of the positively and negatively magnetized sample, i.e., \( \pm m \). When the magnetization is switched, the change of intensity \( \Delta I = I_{+m} - I_{-m} \), named Kerr intensity, is a linear function of analyzer angle φ, as shown in

![Fig. 1. MOKE hysteresis loops measured in air, vacuum, and 1 atm H2 gas for (a) as-deposited and (b) post-annealed 5 nm Pd/4 nm Co/5 nm Pd trilayers. (c) Light intensity \( I_{\pm m} \) (upper part, left axis) and Kerr intensity \( \Delta I = I_{+m} - I_{-m} \) (lower part, right axis) measured in vacuum and 1 atm H2 gas, respectively.](image-url)
Eq. (2). The slope of Kerr intensity $\Delta I$ is proportional to $|E_p|^2$ and $\Delta \theta$. The lower panel of Fig. 1(c) shows the Kerr intensity $\Delta I$ deduced from the difference between experimental curves of the parabolic functions $I_{\pm m}(\phi)$. The solid lines are obtained by the linear fitting. The reflectivity $|E_p|^2$ and the saturation Kerr rotation $\Delta \theta$ are deduced from fitting the parabolic curves $I_{\pm m}(\phi)$ and the linear functions $\Delta I(\phi)$ in Fig. 1(c). $|E_p|^2$ determines the curvature of parabolic function and corresponds to the reflectivity of sample, especially the top layer of Pd. According to our fitting results, the reflectivity $|E_p|^2$ is decreased by 7% after hydrogen exposure. This is consistent with previous studies. Matelon et al. reported the hydrogenation-induced reduction of reflectivity reached 8% for 7.6 nm Pd/Si(111) and 16% for 7.6 nm Pd/Al$_2$O$_3$(110). Besides, our fitting also shows that after hydrogenation, the saturation Kerr rotation $\Delta \theta$ is significantly enhanced by 45%, from $9 \times 10^{-3}$ to $13 \times 10^{-3}$ degree. As shown in Fig. 1(c), the extinction (minimum) angles of $I_{\pm m}$ parabolas is shifted by 0.16 degree, because hydrogenation changes the optical properties of Pd cover layer. Since the MOKE measurement provided the intrinsic magnetic property of $H_C$ and the MO signals, the different responses of $H_C$ and MO signals to hydrogenation will be compared for discussion later in the text.

$$\Delta I = 4 \Delta \theta |E_p|^2 \phi + \text{constant.} \quad (2)$$

Fig. 2 shows the reversibility of the hydrogenation effect. Both the $H_C$ and Kerr intensity were simultaneously recorded in cyclic hydrogenation in 1 atm hydrogen gas. The magnetic coercivity repeatedly increased from $20.4 \pm 0.1$ Oe to $23.8 \pm 0.1$ Oe after hydrogenation, and decreased to the original $H_C$ after dehydrogenation by simply pumping out the hydrogen gas from the MOKE chamber and keeping the sample in a vacuum. The magneto-optical Kerr signal was also cyclically enhanced by $17 \pm 3\%$ after hydrogenation. But the dehydrogenation did not fully recover the initial value of Kerr intensity, because the 8 min of waiting time after pumping of hydrogen gas is not long enough to recover the initial condition. Our previous studies also reported that the recovering time of MO signals in Pd/Fe, Co, and Ni bilayers actually took 50–200 min, depending on the Pd thickness and surface morphology, since some of the hydrogen atoms in the Pd lattice are hard to desorb.

In order to investigate the time constant and the correlation between $H_C$ enhancement and hydrogen gas pressure $P_{H_2}$, the hydrogenation effect on $H_C$ was monitored as a function of reaction time under the various hydrogen gas pressure from 10 to 1000 mbar. Fig. 3(a) shows the measured $H_C$ as a function of reaction time after hydrogen exposure. For 10 mbar hydrogen, the $H_C$ slowly increased only $\sim 0.2$ Oe. After exposure to 30 mbar hydrogen gas for 10 min, the $H_C$ enhancement reached 1.0 Oe. The higher hydrogen gas pressure led to the larger $H_C$ enhancement. When the hydrogen gas pressure reached 400 mbar or even higher up to 1000 mbar, the $H_C$ increased to $23.8 \pm 0.1$ Oe and the enhancement saturated at $\Delta H_C = 3.4 \pm 0.1$ Oe. In Fig. 3(a), the solid curves are obtained by fitting the experimental data with a exponential function: $\Delta H_C(t) = (1-e^{-t/\tau}) \cdot \tau$ is the time constant of hydrogenation effect on $H_C$. The fitting curves match the experimental data very well, indicating that the hydrogenation effect of $H_C$ enhancement follows the exponential function. The fitted time constants $\tau$ and the measured $\Delta H_C$ are plotted in Fig. 3(b) as a function of hydrogen gas pressure. When $P_{H_2}$ is below 100 mbar, the $\Delta H_C$ drastically increases with $P_{H_2}$, and the time constant ranges hundreds seconds. While $P_{H_2}$ is above 400 mbar, the hydrogenation effect on $H_C$ completed within 50 s and the $\Delta H_C$ saturates at $3.4 \pm 0.1$ Oe.

In contrast to the quick absorption, the hydrogen desorption took a longer time. The magnetic coercivity $H_C$ was recorded as a function of time after pumping out the hydrogen gas from MOKE chamber and keeping the sample in a vacuum of 5 × 10$^{-2}$ mbar. The time-dependent $H_C$ is plotted in Fig. 3(c) for the samples previously exposed to 10–1000 mbar hydrogen gas. After exposure to 30 mbar hydrogen gas, the recovery of $H_C$ takes $\sim 100$ s. For samples exposed to 60–1000 mbar hydrogen gas, the recovery time constant gradually increased to 200–300 s. Besides, as shown in Fig. 3(c), the decay of $\Delta H_C$ does not behave like a simple exponential decay. There is always a small kink appearing at $H_C \approx 21.3$ Oe ($\Delta H_C \approx 0.9$ Oe) of the monotonically decreasing curves. At this kink, the slope, $\Delta H_C/\Delta t$, is nearly zero, and afterward the $\Delta H_C$ drops down again. Previous studies focus more on the hydrogenation process, including hydrogen dissociation and absorption. Fig. 3(a) shows that when hydrogen gas pressure is above 400 mbar, the hydrogenation effect on $H_C$ saturated within 50 s. However, the dehydrogenation, including hydrogen diffusion toward the surface and then desorption, actually takes a longer time up to hundreds seconds.

We take a closer look on the detailed dehydrogenation processes by simultaneous recording of magneto-optical and magnetic signals. The intrinsic magnetic properties of Pd/Co/Pd trilayers were monitored by continuous measurement of $H_C$. Besides, the MOKE measurement brings in other two important messages. One is $I_{\text{sum}} = I_{\pm m} + I_{-m}$ and the other one is the Kerr intensity $\Delta I = I_{\pm m} - I_{-m}$. $I_{\text{sum}}$ mainly signifies...
the optical properties of Pd overlayer, while the Kerr intensity $I$ denotes the magneto-optical properties dominated by both the magnetic underlayer and Pd capping layer. The analyzer angle $\phi$ was set at $\sim 2$ degree during the MOKE measurement. According to Fig. 1(c), $I_{\text{sum}}$ and $\Delta I$ increased after hydrogenation. Fig. 4 shows the time dependent measurement of $H_C$, $I_{\text{sum}}$, and $\Delta I$, while the sample undergoes hydrogenation and then dehydrogenation in sequence. For the ease of comparison, the variations of the three signals are normalized. After exposure to 200 mbar hydrogen gas, as shown in Fig. 4(a), the $I_{\text{sum}}$ value increased and saturated faster than $H_C$ did. This is straightforward because $I_{\text{sum}}$ variation is mainly due to the Pd-hydride, while $\Delta H_C$ originated from hydrogenation of Pd/Co interface, which is apparently deeper than the Pd capping layer and takes a longer time to achieve. While the hydrogen gas pressure is higher, i.e., 800 mbar as shown in Fig. 4(b), the $H_C$ and $I_{\text{sum}}$ increased almost simultaneously. Due to the unstable optical properties and the very small signal, Kerr intensity seriously fluctuated until both the $H_C$ and $I_{\text{sum}}$ became stable. Considering the dehydrogenation, right after removing out the hydrogen atmosphere, the $I_{\text{sum}}$ significantly dropped down, followed by a moderately decreasing curve. With the higher hydrogen gas exposure, the $I_{\text{sum}}$ dropped more seriously at the moment of hydrogen pumping. This indicates that the quick drop of $I_{\text{sum}}$ might be due to the fast desorption of $\beta$ phase hydrogen or the physically absorbed hydrogen on Pd surface. Afterward the $\alpha$ phase hydrogen, which occupied the interstitial sites of the Pd crystalline lattice, gradually desorbed with a relatively slow rate. The microscopic picture of $\alpha$ phase dehydrogenation can be considered as that the hydrogen atoms diffused between the interstitial sites of the crystalline lattice from the underlayer toward the Pd top layer. Therefore, it is intuitive to have first the dehydrogenation of Pd/Co interface and then later the dehydrogenation of Pd cover layer. Fig. 4 shows us the clear experimental result of that $H_C$ decreased.
and recovers the initial conditions more quickly than $I_{sum}$ did. Since the magneto-optical Kerr intensity originated from the combination of top Pd layer and underline Co layer, the decay speed of $\Delta I$ enhancement is in between of $H_C$ and $I_{sum}$. One noticeable observation is that $I_{sum}$ keeps nearly invariant for a while until $H_C$ recovered the initial value. After the $\Delta H_C$ recovery completed, $I_{sum}$ started to decreased again. This coincidence might be because during the desorption of $z$-phase hydrogen, the diffusion rate of hydrogen atoms from underlayers into Pd top layer equals the desorption rate of hydrogen atoms from Pd surface. There is a period of time, in which the density of hydrogen atoms in Pd top layer is nearly invariant. Until in the Co underlayer the hydrogen is fully removed, the hydrogen density in Pd starts to decrease and thus $I_{sum}$ is reduced again. Besides, the kink appearing during the decay of $\Delta H_C$ is coincident with the invariant period of $I_{sum}$. The appearance of this kink in $\Delta H_C$ decay might be another indication of $\beta$ to $z$ phase transition in the magnetic metal-hydride.

In summary, we demonstrated a reversible modulation of magnetic coercivity $H_C$ in the perpendicularly magnetized Pd/Co/Pd/Al$_2$O$_3$(0001) system by cyclic hydrogenation and dehydrogenation. The $H_C$ enhancement was sensitive to the hydrogen gas pressure $P_H$, and saturated at $\Delta H_C = 3.4$ Oe when $P_H$ was above 400 mbar. The response time of $H_C$ enhancement and recovery ranges between tens to hundreds seconds, strongly depending on $P_H$. The MO signals reacted faster (slower) than the $H_C$ after hydrogenation (dehydrogenation). The time-dependent evolution of $H_C$ and MO signals indicates that the significant $H_C$ enhancement originates from the hydrogenation of magnetic layer or interface and provided valuable information for the application of magnetic metal-hydride system.

This work was supported by the National Science Council of Taiwan under Grant Nos. NSC 99-2112-M-003-009-MY3.


