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EFFECT OF HYDROGEN ON THE STRUCTURAL AND MAGNETIC PROPERTIES OF Pd-capped Nb/Co tri-layer

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Abstract.
Metallic multilayers have attracted much interest due to their interesting magnetic properties. In present investigation, Pd/Nb/Co tri-layers were deposited on Si (100) substrate by DC magnetron sputtering. The tri-layer samples were hydrogenated in hydrogen atmosphere of one bar for different time durations. The samples have been analysed by XRD, AFM, and FE-SEM for their structural and morphological studies, respectively. Nb-hydride formation has been observed after hydrogenation as confirmed by XRD data. The magnetic properties of as-deposited and hydrogenated Pd/Nb/Co tri-layer have been tested at low temperature (5K) using superconducting quantum interference device (SQUID) magnetometer. Insertion of hydrogen in Pd/Nb/Co tri-layer system increases the remanent magnetic moment but reduces the saturation magnetic field. Hydrogenated try-layer system possesses ferromagnetic nature, while an anti-ferromagnetic nature has been observed for as-deposited Pd/Nb/Co tri-layer.
Keywords: Hydrogen, SQUID, XRD, Sputtering, Magnetic materials, thin films.

1. INTRODUCTION

Hydrogen can be easily introduced into metals to modify the interface structure of multilayers [1-2]. Study of hydrogen effect on the magnetic properties of metallic thin films/multilayers is very important for technological and basic research. [3]. In spite of this, very little is known about the behavior of hydrogen in multilayered structures. Hydrogen occupies interstitial sites in metal lattices and usually expands them. Such expansion of lattices can alter the Fermi momentum and density of states at the Fermi level. Therefore, changes in the magnetic properties are expected on the hydrogenation of multilayers. On hydrogenation, antiferromagnetic ordering in niobium–iron multi-layers has been

reported by Nagengast *et al.* [2]. Hydrogen effect on magnetic properties on Co/ Pd, Co/Pt, Co/Au and other multilayers have been reported by various groups [4-6].

2. EXPERIMENTAL DETAILS

2.1 Synthesis of Pd/Nb/Co Tri-Layer

Pd/Nb/Co tri-layer was prepared on Si (100) substrate using Pd (99.95 % purity), Co (99.95 %) and Nb (99.95) target, by DC magnetron sputtering. A custom built 12″ diameter chamber (Excel Instruments, Mumbai) was used for sputtering. Chamber was evacuated to high vacuum (2.0 $\times 10^{-6}$ Torr) by turbo molecular pump backed by a rotary pump. High purity (99.99%) inert gas (Ar) was used as sputtering gas during deposition. The substrates were etched in HF and then cleaned by rinsing in ultrasonic bath of acetone. The distance between substrate to target was kept constant at 45 mm. Pre-sputtering of the targets for 5 min was carried out before starting deposition. The sputtering parameters for Pd/Nb/Co tri-layer samples are shown in Table 1.

TABLE 1: Sputtering Parameters for Pd/Nb/Co Tri-Layer

Target	Base Pressu	Gas Us	Sputter Pressur	Sputtering Power	Deposition Time	Substra Used	Substrate Temperatu
Pd, Nb, (	2.0 × 10-6 T	Ar	10 mTor	15W(Pd), 50W(Co), 15W(Nb),	30 sec (Pd), 5min (Nb),5min(Co)	Si (100)	100°C

2.2 Hydrogenation of Pd/Nb/Co tri-layer

Because of technical difficulties, it was not possible to hydrogenate the Pd/Nb/Co tri-layer samples inside the SQUID magnetometer for magnetic measurements under hydrogen atmosphere. Therefore, the Pd/Nb/Co tri-layer was hydrogenated into a custom built stainless steel thin film hydrogenation set-up (Excel Instruments, India). The samples were exposed to hydrogen gas (purity: 99.999%) at 1 bar pressure and 200°C temperatures for 2-12 hrs duration. Samples were, then, cooled down to

room temperature in H_2 atmosphere, and transferred to the SQUID magnetometer for magnetization measurements.

2.3 Characterization

Grazing angle X-ray diffractometer (Bruker AXS, D8 advance model), using CuK_α radiation in $(\theta - \theta)$ geometry, was used to study crystallinity and phase formation**.** FE-SEM (FEI, Quanta 200F) was used to measure film thickness of the as-deposited and hydrogenated samples. Surface topography and grain size were analyzed using AFM (NT-MDT, Ntegra), operated in semi contact (tapping) mode. The magnetic behavior of the tri-layer samples was investigated by measuring the hysteresis loops at temperature 5K using superconducting quantum interference device (SQUID) magnetometer.

3. RESULTS AND DISCUSSION

XRD patterns of as-deposited and hydrogenated samples are shown in Figure 1. XRD pattern of the as-deposited Pd/Nb/Co tri-layer contains XRD peaks corresponding to bcc-Nb along (110) and (200) orientation at 37.58° and 54.30°, respectively. XRD pattern also shows the mixed phases of cobalt corresponding to fcc-Co (111) and hcp-Co (002) orientation at 44.23° and 47.48°, respectively. Numerous experimental studies have reported the presence of the FCC and HCP Co phases [7-8]. XRD patterns of all hydrogenated (2-12hrs duration) samples reveal the reflections for cubic-NbO corresponding to (110), (200) and (210) orientation at 29.45°, 43.07° and 48.57°, respectively. The reason of NbO formation may be due to the reaction of Nb with small amount of oxygen, available inside the chamber during hydrogenation process. XRD patterns for hydrogenated sample also show the Niobium hydride (NbH_2) formation: cubic NbH_2 (111) and NbH_2 (200) corresponding to 36.03° and 39.43° angles, respectively. From the XRD pattern of hydrogenated samples, it has been observed that Nb absorbed hydrogen and formed NbH_2 and there is no sign of hydrogen absorption or hydride formation for Co. This is because of the fact that Nb layer has a high solubility for

hydrogen than Co [2]. The Pd/Nb/Co tri-layer system consisted of very thin Pd cap on the top of the Nb/Co bilayer to facilitate hydrogen absorption. In XRD pattern, there is no detectable peak for Pd because it was deposited for short time (30 sec).

The cross-sectional view of as-deposited and hydrogenated (at 100°C for 6 hrs) Pd/Nb/Co tri-layer are shown in Figure 2. The thickness of as-deposited Co and Nb has been measured from Figure 2 (a) and it comes out to be ~130 and 320nm respectively. Similarly, thickness of hydrogenated sample has been measured using cross-sectional view shown in Figure 2 (b). For hydrogenated sample, thickness of Co is found to be the same as for the as-deposited one, while thickness of NbH_2 comes out to be ~ 345 nm. It is observed that the formation of NbH_2 increases the film thickness of the hydrogenated sample by 7.81 % as compared to the as-deposited one.

This result may be due to plane expansion following hydride formation. The peaks in the XRD pattern are shifted to lower angles by hydrogen absorption. This also suggests an increase of the tri-layer thickness on hydrogenation.

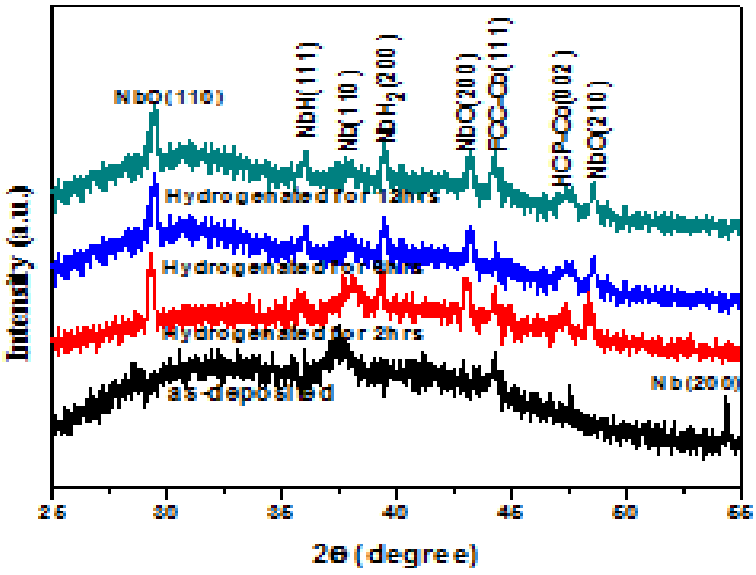


FIGURE 1: XRD patterns of as-deposited and hydrogenated Pd/Nb/Co tri-layer

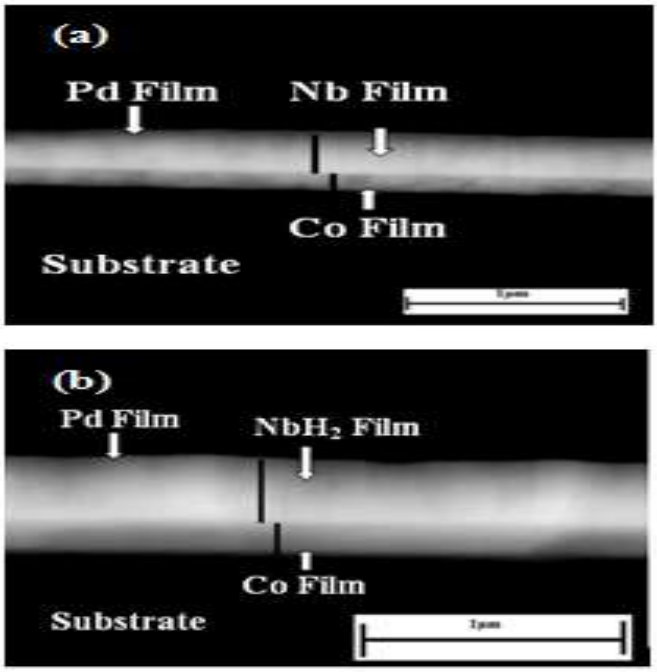
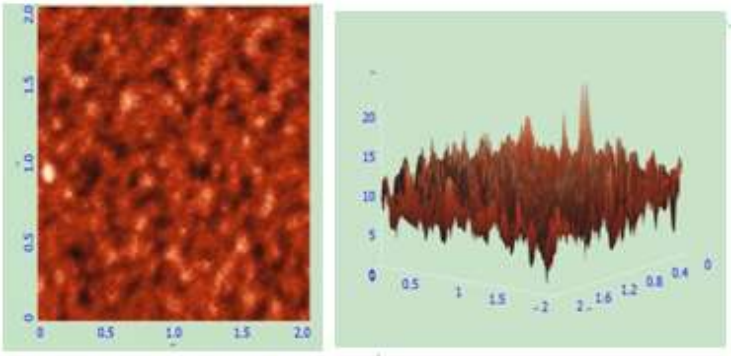
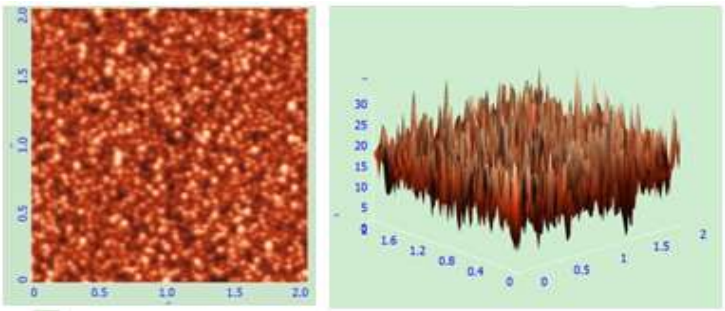


FIGURE 2: FE-SEM cross-sectional view of **(a)** as-deposited and **(b)** Hydrogenated Pd/Nb/Co tri-layer at 100°C for 6 hrs



(a)



(b)

FIGURE 3: 2D &3D AFM images of **(a)** as-deposited and **(b)** hydrogenated Pd/Nb/Co tri-layer

There is no increment in thickness of Co after hydrogenation because there is no hydride formation for cobalt after hydrogenation. The results, observed from thickness measurements, have complete agreement with the XRD pattern shown in Figure 1.

The 2D and 3D AFM images (scan area 2×2μm) of the topography of as-deposited and hydrogenated (6 hrs) samples are shown in Figure 3 (a) and Figure 3 (b), respectively. The measured values of grain size for as-deposited and hydrogenated sample are ~10nm and 62nm respectively. The height of the grains is also shown in 3D AFM images. Larger height for hydrogenated sample has been observed in comparison to as-deposited one. This result is due to the volume expansion of sample that leads to increment in grain size after hydrogenation [2]. The rms surface roughness of as-deposited and hydrogenated samples, imaged in Figure 3 (a) and (b) are 3 and 5 nm, respectively. This shows that the hydrogen absorption makes a smoother surface rough.

Magnetization versus in-plane magnetic field loops of Pd/Nb/Co tri-layer has been recorded before and after hydrogenation by SQUID magnetometer. Figure 4 (a) exhibit antiferromagnetic character, such as small remanent magnetic moment and large saturation field (~1T). Therefore, this tri-layer possesses antiferromagnetic nature before hydrogenation. The loops as shown in Figure 4 (b), (c) and (d) exhibit ferromagnetic character, such as square shape, small saturation field (~ 250 Oe) and large remanent magnetic moment. Antiferromagnetic ordering has been removed on introducing hydrogen in the Nb spacer layer but it does not necessarily mean that the sign of the coupling has been changed to ferromagnetic. However, Klose *et al*, reported, an indirect argument, that the coupling has switched to ferromagnetic [9]. The reason is the pinning of the magnetic domains which is most likely

caused by defects due to the large lattice mismatch of the Co and Nb layers after hydrogenation. In magnetic system, a magnetic structure persists until a force surmounting the pinning strength reverses the ordering. As shown above, the magnetic coupling of the Pd/Nb/Co tri-layer system becomes ferromagnetic upon hydrogenation. After hydrogenation, expansion of Nb layer (confirmed by thickness) affects the Fermi wave vector of Nb and also the magnetic pinning [9]. The coercivity of as-deposited sample is found to be 65 Oe and it is 305, 338 and 350 Oe For hydrogenated samples for 2, 6 and 12 hrs, respectively. Coercivity of as-deposited sample is smaller than that of the all hydrogenated samples because it shows antiferromagnetic nature.

The value of coercivity of hydrogenated samples (ferromagnetic nature) for 6 hrs and 12 hrs hydrogenation is almost the same, which means tri-layer system reaches saturation for hydrogen absorption in 6-12 hr duration. It is also confirmed from the Figure 1, as there is no big difference in XRD patterns for hydrogenated samples for 6 and 12hrs hydrogenation. The results from the Figure 4 also show an increase in the remanent magnetic moment and a decrease in the saturation magnetic field for hydrogenated sample as compared to as-deposited (before hydrogenation). The reason for these changes is not clear so far in the literature. But the reason behind the increase of the remanent magnetic moment and the decrease in the saturation magnetic field after hydrogenation may be due to the presence of hydrogen in the metal lattice [10] as well as structural changes, created in the tri-layer by the hydrogenation. During hydrogenation, metal vacancies are created and hydrogen atoms are occupied in interstitial sites of the metal. The subsequent atomic mixing at the interfaces due to vacancy diffusion and redistribution of hydrogen to energetically favorable interfacial sites, are possible explanation of this magnetic change [11].

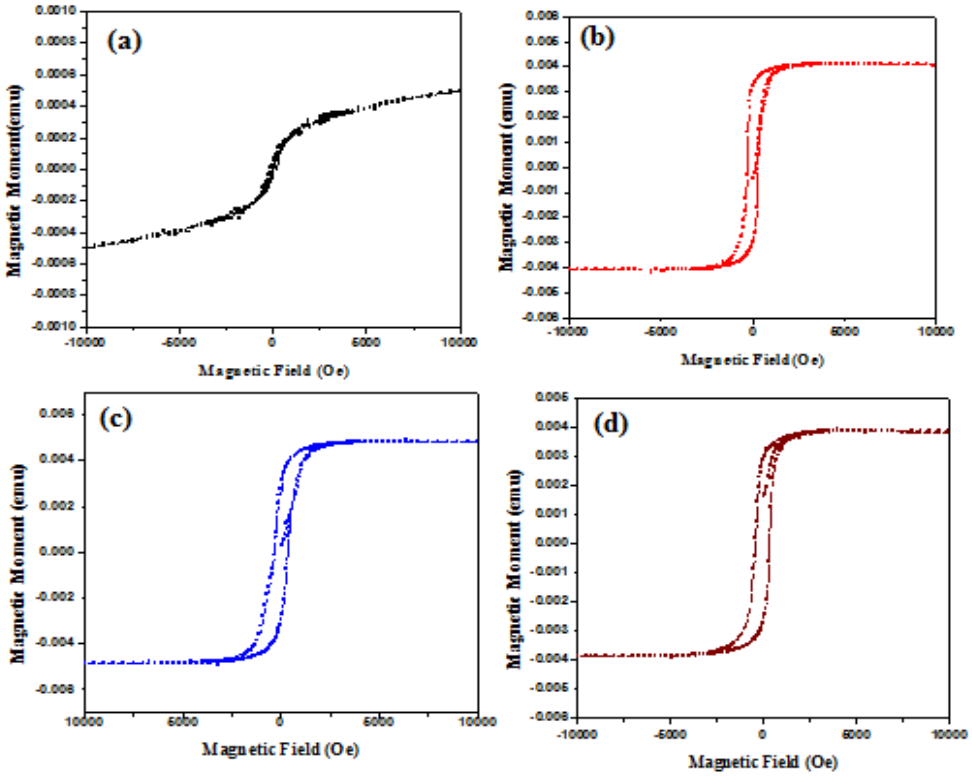


FIGURE 4: Magnetic moment versus in-plane magnetic field loops of Pd/Nb/Co tri-layer of: **(a)** as-deposited, **(b)** hydrogenated for 2 hrs, **(c)** hydrogenated for 6 hrs and **(d)** hydrogenated for 12 hrs

4. CONCLUSION

This study shows that introducing hydrogen into multilayer structure of metals alters the magnetic ordering. After hydrogen exposure, tri-layer thickness increases due to inclusion of hydrogen in the lattice of tri-layers. Nb hydride formation has been observed in the XRD, after hydrogenation. Hydrogen exposure also changes the surface roughness of the tri-layer.

The magnetization behavior of the Pd/Nb/Co tri-layer has been studied by SQUID magnetometer measurement. The effect of hydrogen on magnetic properties of the tri-layer system has been observed. Hydrogenated Pd/Nb/Co tri-layer samples presented a ferromagnetic nature, while antiferromagnetic nature has been observed for as-

deposited Pd/Nb/Co tri-layer. Therefore, a switching from antiferromagnetic nature to ferromagnetic nature has been observed for Pd/Nb/Co tri-layer. The hydrogen exposure increases the remanent magnetic moment but reduces the saturation magnetic field. These changes are due to the formation of metal atom vacancies and lattice mismatch at the interfaces.

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