

Effect of Hydrogenation on the Optical Properties of Cobalt and Tantalum Thin Films

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Abstract

Thin films of cobalt are prepared using thermal evaporation method at pressure 10^{-5} torr. The hydrogen gas is introduced in chamber at different pressure from 0 Psi to 40 Psi to hydrogenate the films. Optical transmission is found to increase and optical absorption decrease with hydrogenation. The optical band gap in Co thin film is found to reduce with increasing of hydrogen pressure. The relative resistance in the Co thin films is also measured at different hydrogen pressures. It is found to vary nonlinear with increase in hydrogen pressure. The Raman Spectroscopy data show that intensity of Raman peaks is decrease with hydrogen pressure. The prepare film after hydrogenation shows the switchable behavior with variable optical band gap. The variation in optical band gap suggests electronic structural phase changes in thin films with hydrogenation. The surface morphology is carrying out for these films with and without hydrogenation by using optical microscope and Scanning Electron Microscope (SEM). Thin films of tantalum also prepared by using DC Sputtering unit and then hydrogenation at pressure 10 Psi. Transmission spectra and surface morphology also carry out for these films before and after hydrogenation. The optimum thickness for switchable mirrors observed was 170.5 nm in case of tantalum.

Key words: Optical absorption; Transmission; Optical energy band gap; Surface Morphology; Resistivity

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INTRODUCTION

The structural and electronic state has intensively been investigated theoretically and experimentally for rare-earth hydrides, which show metal-insulator transitions with the opening of band gap by successive hydrogenation from di- to tri-hydride. The di-hydrides are excellent metals and shiny, while the tri-hydrides are insulators and transparent in the visible part of the optical spectrum [Van der Sluis, Ouwkerk & Duine, 1997; van Gogh et al, 2001]. In 1996, Huiberts et.al was discovered the amazing optical changes of yttrium and lanthanum upon the absorption of hydrogen.

There is an increasing demand for hydrogen in petroleum refining, petrochemical production and semiconductor processing (Ramachandran & Menon 1998), as well as in renewable energy related applications such as clean fuel for vehicles and fuel cells (Veziroglu 1999). This motivates research work towards new methods for hydrogen generation, purification and storage. Hydrogen, the most abundant element on earth in bound state, scores over all renewable fuels regarding reversibility, energy density and compatibility with the environment. The interest in hydrogen as a fuel has grown dramatically. In order to potentially use of hydrogen, hydrogen storage technologies must be significantly improved, if a hydrogen storage based energy system for transport sector is to be established. Many metals and inter-metallic compounds are capable of reversibly absorbing large amounts of hydrogen (Singh, Lototsky & Srivastava, 2007; Singh et al 1985). The behavior of hydrogen in metals has attracted scientific awareness for many decades (Fokai, 1993 and 2005; Wiswall 1978) and is interesting from both basic research and technological points of view. Most of hydrogen's interesting properties relate to the high mobility of the hydrogen atoms, which reaches values similar to those of ions in aqueous solutions. This high mobility exists because the hydrogen atoms occupy interstitial positions in the host lattice

(Richter, Hempelmann & Bowman 1992]. The transition metals are also known to accommodate a great amount of hydrogen and have been studied as promising materials for hydrogen storage (Dam et al 2003). The development in metal hydride technology required a detailed study of hydrogen interaction with metals and alloys. For the fabrication of gradient films Dam et al. 2003 used a sputtering system with several off-axis sources, which can be tilted towards and away from the substrate. Depending on the tilt angle, the thickness of a particular component increased many folds and thin films of Mg_xTM_x (TM=Ni, Co, Fe) show drastic changes in their optical appearance upon hydrogen uptake at room temperature. A lot of work has been performed on cobalt hydride, as a model system, because it possesses one of the highest absorptive capacities among the metal-hydrides. The small size of hydrogen atoms permits dense hydrogen packing in metal hosts that have a high affinity to hydrogen, i.e., a large negative heat of solution for hydrogen. In metal hydrides, hydrogen density can be even greater than in liquid hydrogen [Latroch, 2004; Ekiba1999]. Metal hydride technologies have reached more practical and applied stages in recent years. The hydriding and dehydriding kinetics of metal hydrides is suitable for areas of design and applications of various metal hydride devices, especially in energy conversion devices such as heat pumps, refrigerators, automobiles, power generators, batteries and thermal energy storage units (Suda, 1987; Goodell, Sandrock and Huston, 1980). Raman Effect in solids was due to inelastic scattering of light by the crystal vibrations. (Bergman & Nemanich, 1996; Fukata, Sasaki and Murakami, 1997), an incident light exchanges quanta of energy with the crystal via the creation or annihilation of phonons. As a result, the scattered light loses or gains energy quanta depending on whether a phonon was created or annihilated. In Raman spectroscopy, the shift of the energy of the scattered light is measured, thus a characteristic value of the vibration energy of a given solid may be obtained. The characteristic Raman energy, known as the Raman frequency, may be modified from its ideal value (corresponding to high quality material) among other factors, stress, temperature, structural defects and impurities. Thus Raman spectroscopy may provide valuable information on the material characteristics and quality (Bergman & Nemanich, 1996). An author Adachi et al in 1983 studied the effect of hydrogen absorption on the electrical resistivity of $LaNi_5$ and $MmNi_{4.5}Mn_{0.5}$ films. They had observed that the resistivity increased with hydrogenation. An increase in resistivity of the film was due to the acceptance of electrons from the conduction band of $LaNi_5$ and $MmNi_{4.5}Mn_{0.5}$ films by hydrogen, when hydride anions are formed (Sakaguchi, Yagi, Adachi, & Shiokawa 1987). Metal hydride films with switchable properties are new materials with new physical properties and thus very interesting both from a fundamental

research viewpoint as for technological applications. Devices capable of switching between mirror and transparent states may find applications in architectural and transportation energy conversion, lighting displays, aero-space isolation control and optical communications systems.

Thin film has been attracted great interest in recent years because of the unusual mechanical, electrical, optical, magnetic and surface properties. An incorporation of hydrogen into thin film form is relatively new field of research. The thin films have advantage over bulk hydrides, it provide large surface area with fast charging discharging rate for hydrogen, pulverization is slower, both critical pressure and critical temperature are significantly lower, better heat transfer arrangements, protective surface coating could be done to stop poisoning by oxygen and activation of thin film hydrides is also possible by coating with layer of catalytic material. The high surface area to volume ratio of thin film had significant idea with respect to hydrogen energy storage. Both high surface area and the by birth nano-material are key attributes of this new class of materials for hydrogen storage devices. The interest in hydrogen as energy of the future is due to it being a clean energy, most abundant element in the universe, the lightest fuel, richest in energy per unit mass and unlike electricity. It can be easily store in thin film metal hydrides. We are presenting in this paper effect of hydrogen on transmission spectra of cobalt and tantalum thin films.

1. EXPERIMENTAL

The thin film has been prepared by thermal evaporation method using vacuum coating unit. The HIND HIGH VACUUM unit is used for this purpose and vacuum chamber contains base pressure of the order of 10^{-5} torr. Powder (99.998% pure) of cobalt is placed into boat in the vacuum chamber and glass substrate is placed in the substrate holder, above the boat carrying material. The nano structure thin films of Co (300 nm) were prepared by in situ thermal evaporation. The nano structure of Co film confirms by scanning electron microscope (SEM) by special addition ZEISS model at USIC University of Rajasthan Jaipur. The observed average size of nano particles are around 189- 307nm. Then hydrogen is introduced in chamber at different pressure to see the effect of hydrogen on optical properties and surface morphology of these films. The UV-VIS transmission & absorption spectra of thin films are taken at room temperature in the wavelength range of 300–800 nm with the help of Hitachi-330 spectrophotometer. The thickness of thin films is measured by gravimetric method and confirm by ellipsometry. The D.C. resistance is also measured for these films with help of a digital multi-meter of input impedance of 10 M Ohm. The

optical micrographs of thin films at different pressures of hydrogen in reflection mode are taken with the help of LABOMED optical microscope. In the present work we have used 40 X magnifications of microscope for optical micrographs. Raman spectra of with and without hydrogenated Co thin film is taken by a continuous wave-Green laser with a wavelength of 532 nm at room temperature by help of R-3000 Raman system.

The thin films of tantalum are also prepared by DC Sputtering unit in environment of argon at pressure 0.01 torr. The thickness of thin films is found to be 170.5nm, 177.5nm and 229nm measured by ellipsometry. The hydrogen gas introduces in chamber at pressure 10 Psi to see the effect on optical transmission spectra and surface morphology of films.

2. RESULTS AND DISCUSSIONS

2.1 Transmission Spectra of Cobalt Thin Film

Figure 1 shows the graph between transmissions versus wavelengths for Co thin films at different pressure of hydrogen. The transmission of light is increased with hydrogen pressure for all wavelength compare to without hydrogenated film. The hydrogen uptake in Co thin films is fast and induces a gradual change in optical appearance for thin films. It is observed that optical transmission increase in Co thin film with hydrogen pressure up to 40 psi, Borsa et al 2007 observed in case of Mg-Ti (100nm) thin film that optical transmission increase gradually with increasing amount of hydrogen in samples. Bao et al 2008 were also observed for Mg-Ti alloy drastic change from the metallic state to the transparent state and increase in their transmission with hydrogen absorption.

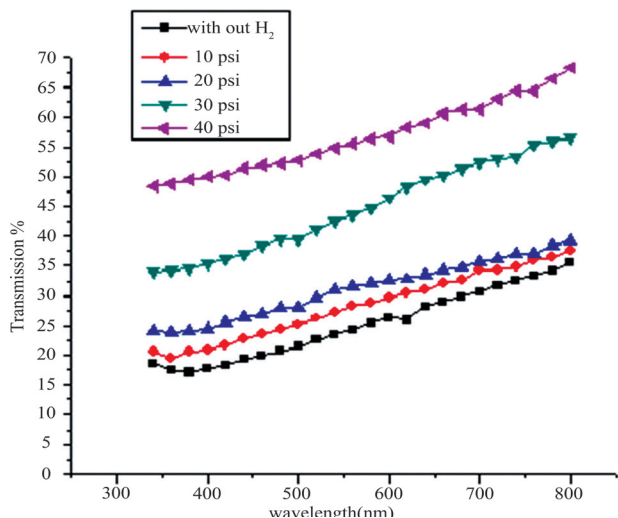


Figure 1
The Optical Transmission Spectra of Co Thin Film with and Without H₂

2.2 Optical Absorption Spectra of Cobalt Thin Film

Figure 2 shows the graph between absorption versus wavelengths of Co thin films at different pressure of hydrogen. The absorption of light is decreased with hydrogen pressure for all wavelength range compare to virgin film. It is also noted that optical absorption decrease in Co thin film with hydrogenation. And suggested that absorbing hydrogen, an electronic phase changes occur and influence the optical band gap. The same behavior was later observed in Mg-alloyed rare-earth hydrides by Van der Sluis et al 1997 and Mg-Ni hydrides Richardson et al 2001. One can say that decrease in absorption and increase in transmission may be due to the change in the occupation of electronic states and shifting of Fermi level in thin films with hydrogen absorption.

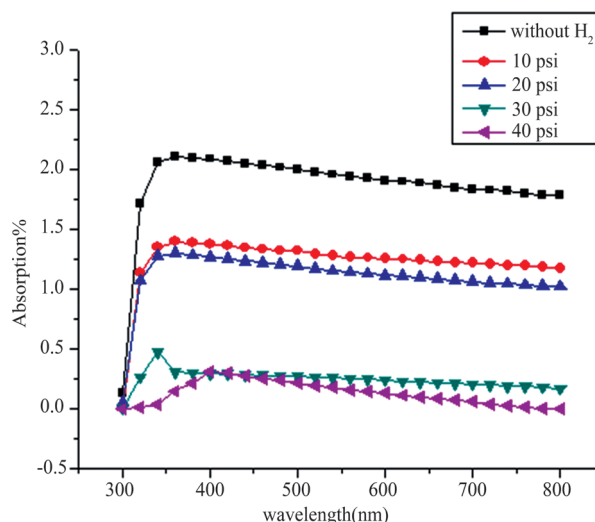


Figure 2
The Optical Absorption Spectra of Co Thin Film with and Without H₂

2.3 Optical Band Gap of Cobalt Thin Film

The optical band gap of films is calculated by using Tauc relation given below.

$$\alpha h\nu = A (E_g - h\nu)^{1/2}$$

Where E_g is the optical band gap; A is constant, and α is absorption coefficient. For investigated samples, the values of optical energy band gap have been calculated using transmission spectra. The determination of E_g from the spectra seems to be more appropriate. According to above relation, the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) dependence is linear. Consequently, the optical band gap, E_g (eV), can be determined by extrapolating the linear portions of mentioned dependence to $(\alpha h\nu)^2=0$. Figure 3, Indicates change in optical band gap with hydrogen pressure. It is observed that optical band gap decrease with hydrogenation in Co thin films. It may due to large accumulation of hydrogen is responsible for it. This variation in optical band due to hydrogenation is

suggested phase changes from metal to semiconductor. The theoretical calculations carried out (Bastide, Bonnetot, Letoffe & Claudy, 1980; Bortz, Bertheville Bottger & Yvon 1999) Suggested that MgH_2 under goes various phase transitions as a function of pressure. The Similar results in case of yttrium hydride measured by Borgschulte et al 2004 and suggested that this system exhibits three thermodynamic phases. The structural phase transitions are accompanied by changes in the electronic structure, which were affecting the optical properties of the material. According them pure yttrium was a shiny metal and di-hydride YH_2 was observed metallic, but has a weak transparency at a photon energy around 1.9 eV, YH_3 was an insulator with an optical band gap of 2.66 eV. The similar result in case of Co thin films is observed by us. The optical band gap of Co thin films with hydrogen pressure vary from 2.32 to 1.97 eV. Hence we can say that Co thin film change electronic phase with hydrogen pressure. The band closing in yttrium hydride at high pressure is measured by Kume et al 2008. We have also measured reduce value of optical band gap in cobalt thin films with hydrogen pressure.

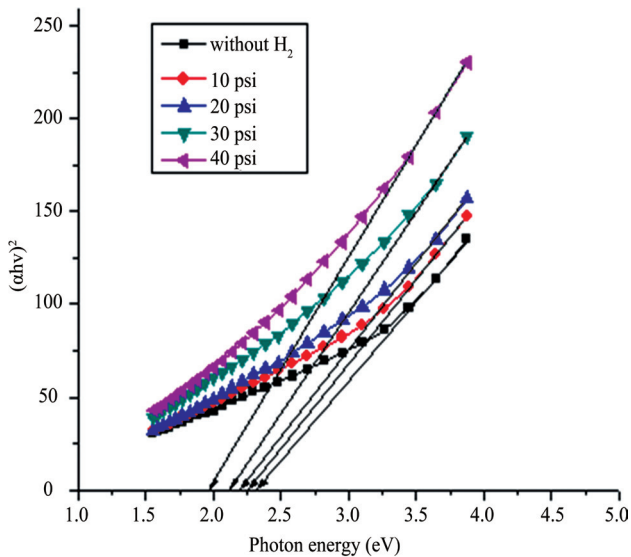


Figure 3
The Optical Band Gap Spectra of Co Thin Film with and Without H_2

2.4 Raman analysis of Cobalt Thin Films

In figure 4 the Raman spectra shows the variation in intensity versus wave number. In these spectra intensity of Raman peaks is decrease with hydrogen pressure and also measured a decrease in broadening of peaks. It is suggesting that hydrogenation may change the phase or make the bonding with metal at interstitial position as well as surface locations. In case of Si crystalline hydrogen absorption peak is observed at 590 cm^{-1} [Fukata, Sasaki, & Murakami 1997]. Raman studies of rare –earth hydrides under high pressure carried out by Kume et al 2008 according them hydrogen related band disappear at

higher pressure in case of YH_3 and ScH_3 . It was suggested strongly by them that there was a common mechanism for the structural transformation from hexagonal to the intermediate phase. In our case we are also relate the decrease in intensity of Raman peak with phase transformation and confirmation of presence of hydrogen in cobalt thin films.

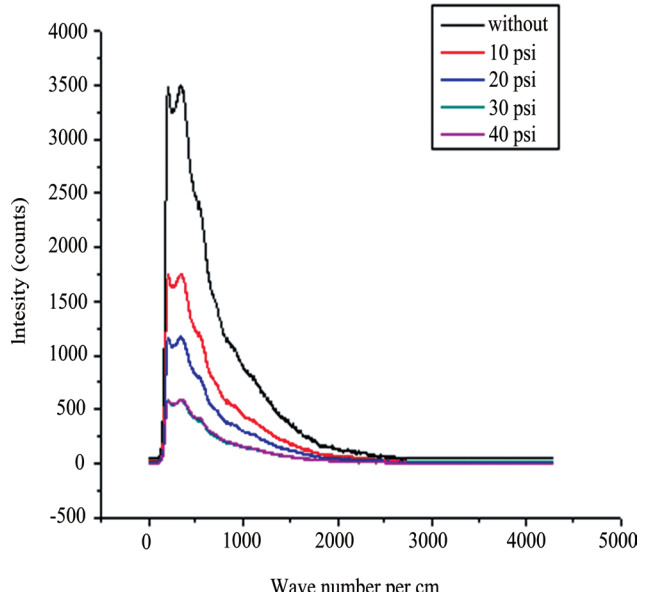


Figure 4
Raman Spectra of Co Thin Film with and Without H_2

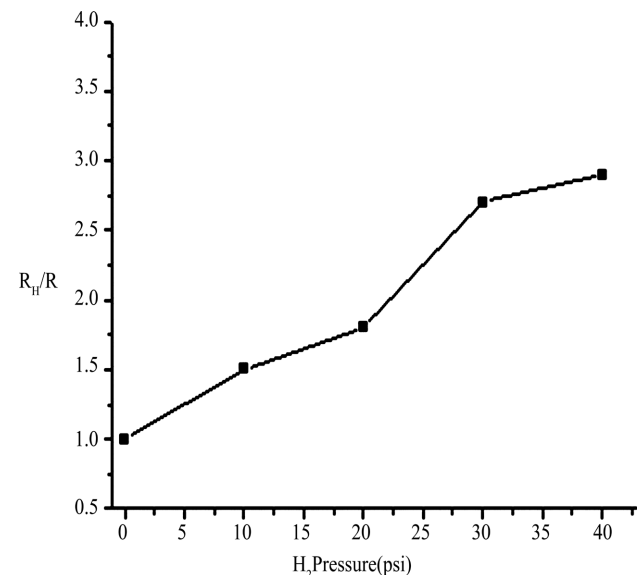


Figure 5
The Variation of Relative Resistance with Hydrogen Pressure in Co Thin Film

2.5 Relative Resistance of Cobalt Thin Films

Figure 5 shows that resistance ratio (R_H/R_0) is increase with hydrogen pressure, due to the net effect of hydrogen absorption by films, where R_0 is the resistance before hydrogen absorption and in R_H is the resistance after hydrogen absorption. The relative resistance ratio is

increases with hydrogen pressure and finally reached the equilibrium position. It is also noted that resistivity increases with hydrogen pressure. It may be suggesting that resistivity increase due to hydrogen takes electrons from the conduction bands of film during the absorption process. This is similar to an earlier work (Singh et al. 1991 & 1992). The increase in resistivity ratio with increasing hydrogen pressure means that hydrogen takes more electrons from the conduction band of the intermetallic compound and accelerates the hydrogen absorption capacity of samples. The increasing behavior of electrical resistivity has been observed (Singh et al. 1985) for rare earth penta-nickelide thin films and it was suggest that the increase in resistivity was due to the enhancement in the absorption of hydrogen due to a large number of voids per unit volume in the amorphous structures. The effect of hydrogen pressure on electrical resistivity is measured in order to analyze the kinetics for hydrogen absorption. Since the resistivity ratio was found to proportional of hydrogen concentration (Singh, Vijay & Jain, 1991). The vacancy creation in Ni and Co metal was depend upon hydrogen concentration in samples (Harada, Yokota, Ishii, Shizuka, Kanazawa & Fukai 2005) and also increased with hydrogen pressure. The vacancy creation during hydrogenation may responsible to increase relative resistance in Cobalt thin films. The increase in resistance in Pd capped Pr nanoparticle layers reported by Kala et al 2008 and suggests the trihydride formation at saturation. The increase in transmission and resistivity with hydrogen concentration were also observed by Azofeifa et al 2005 and suggested that dramatic change in these parameters indicates the formation of a semiconductor phase.

2.6 Surface Morphology of Co Thin Films.

The surface morphology of films shows in figure 6 (a-e) with and without hydrogenation. Morphology indicates the color changes with hydrogenation. The color of thin film is changes from dark yellow to light yellow with hydrogenation. The color changes properties have been observed in Mg-Ti thin film switchable mirrors by Borsa et al 2007 and suggested that hydrogen in thin films induces a gradual change in optical appearance for all nanocrystalline thin films. According them color of fully hydrogenated films changes from dark gray to yellowish with increasing amount of hydrogen. The thin film of cobalt found to change in color with hydrogenation may use as ophthalmic products and also application in chromomeric as smart materials.

In figure 7 shows the size of nano particle in thin film as well as morphology by scanning electron microscope (SEM). The size of particle found in thin is order of 189- 307 nm that is enhancing hydrogen absorption in thin films.

2.7 Thickness Dependence Transmission of Tantalum Thin Films.

The thickness dependence hydrogen absorption carries out in case of tantalum films. In figure 8(a), the transmission is increasing with hydrogenation only for thickness 170.5 nm is showing the switchable mirror effect in thin films. When thickness is being reached up to 177.5 nm see in fig. 8(b), then transmission spectra overlaps to each other or one can say that no increase in transmission observed during hydrogenation process. When we further increase in thickness up to 229 nm than transmission is found to reduce see fig.8(c) with hydrogenation. The reduction in transmission is suggests that hydrogen absorption is a surface phenomenon and could not reach in depth of whole region of higher thickness of film, so it is behavior likes reflecting mirror. Hence one can say that optimum thickness for switchable mirror is 170.5 nm for tantalum films after that switchable effect found to be reversed. We are also examining the surface morphology of films see in fig.9 (a, b, c) for variable thickness of films, with and without hydrogenation. The optical photograph is showing the slight color change after hydrogenation indicates the presence of hydrogen.

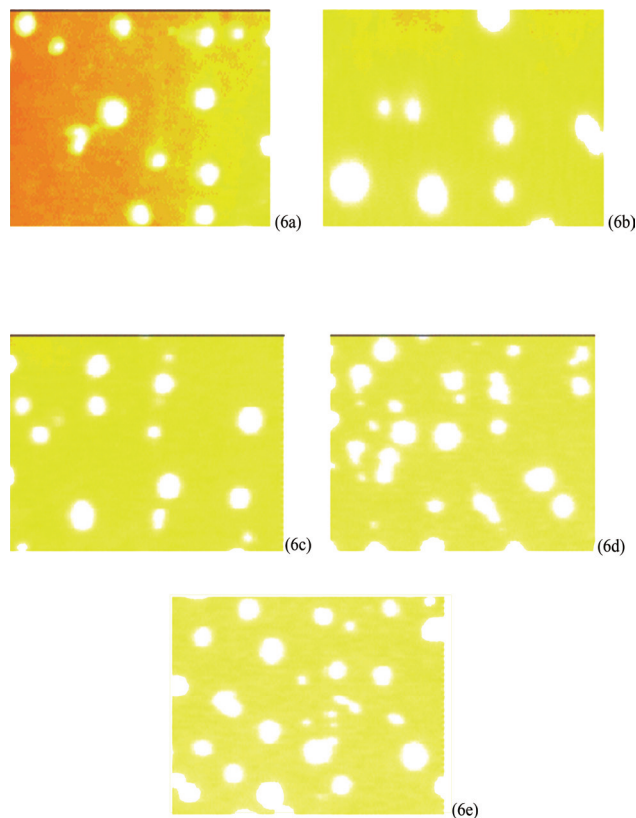


Figure 6
Optical Micrographs of Co Thin Film at Different Pressure (0,10,20,30 and 40Psi) with Hydrogen

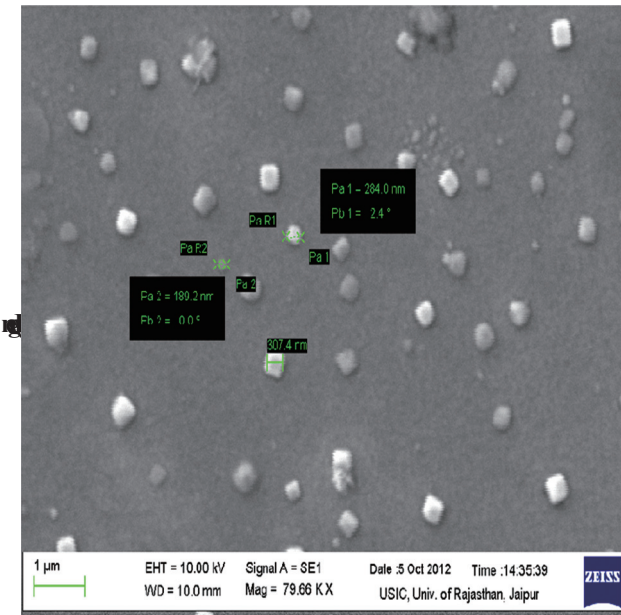


Figure 7
 Scanning Electron Microscope(SEM) Image of Co Thin Film

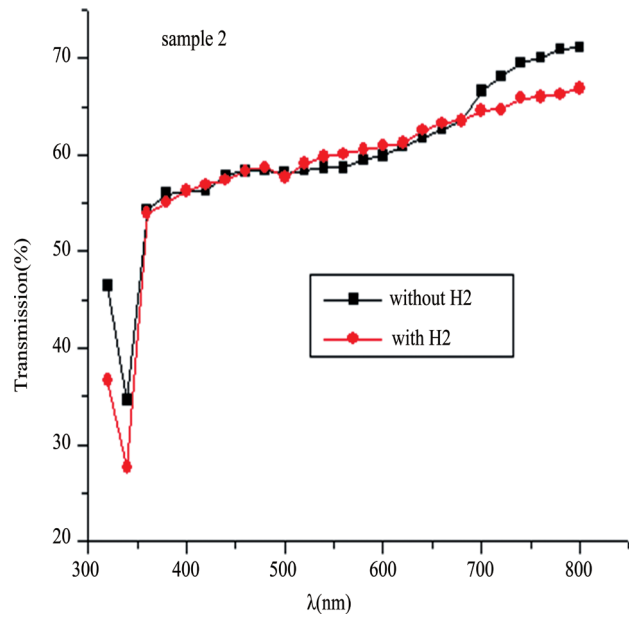


Figure 8 (b)
 D.C Sputtered Titanium Film of Thickness 177.5 nm with and Without Hydrogen

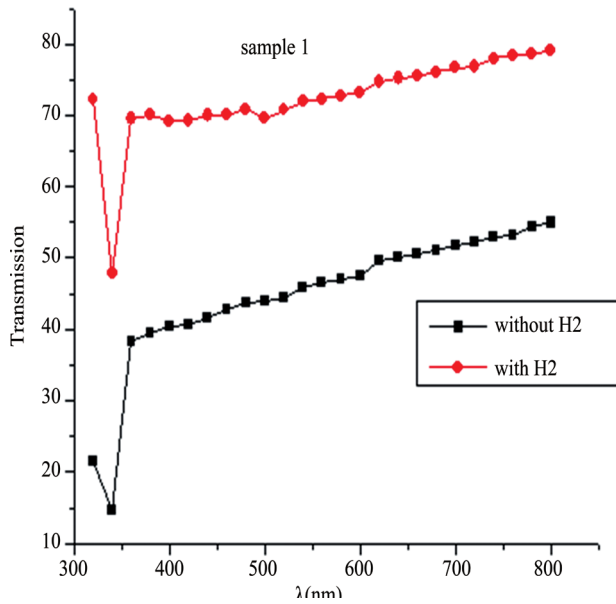


Figure 8 (a)
 D.C Sputtered Titanium Film of Thickness 170.5 nm with and Without Hydrogen

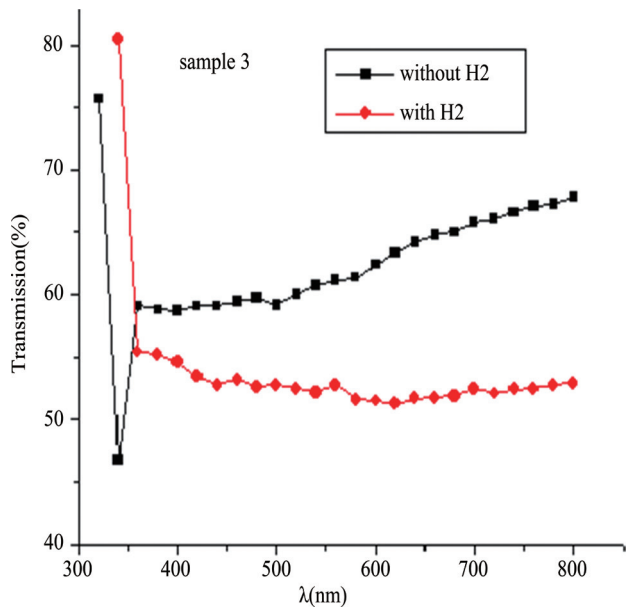


Figure 8 (c)
 D.C Sputtered Titanium Film of Thickness 229 nm with and Without Hydrogen

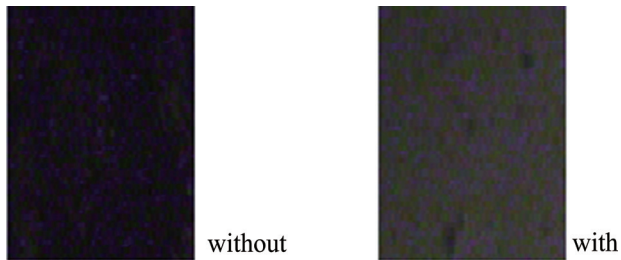


Figure 9 (a)
Optical Photo Graph of D.C Sputtered Tantalum Thin Film (170.5nm) with and Without Hydrogen



Figure 9 (b)
Optical Photo Graph of D.C Sputtered Tantalum Thin Film (177.5nm) with and Without Hydrogen

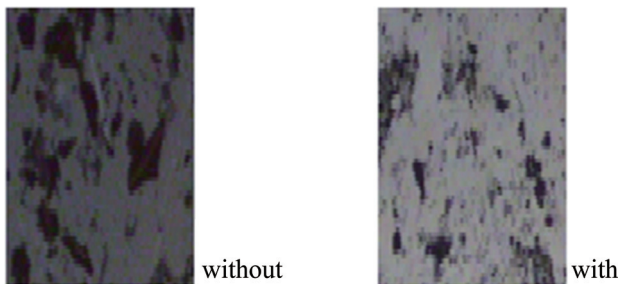


Figure 9 (c)
Optical Photo Graph of D.C Sputtered Tantalum Thin Film (229nm) with and Without Hydrogen

CONCLUSION

Hydrogen is tailored the optical properties of Co thin films. The optical transmission found to increase and optical absorption decrease with hydrogenation. The band gap is found to decrease with hydrogen pressure. The resistance of films is increases with hydrogen pressure, due to the net effect of hydrogen absorption.it is also observed that color of thin film changes from dark yellow to light yellow with hydrogenation. In Raman Spectroscopy intensity of Raman peaks is decreases with hydrogen pressure that suggesting that hydrogenation may change the structural phase. The prepare structure after hydrogenation shows the switchable behavior with variable optical band gap. In case of sputtered tantalum thin films transmission is increased at lower thickness when hydrogen introduced in the thin film but transmission decrease after optimum thickness 170.5nm. Hence one can conclude that thickness and preparation growth of films is play important role in switchable mirrors. The color variation of films covers markets

as chromomeric smart materials for applications in automotive, architectural, aircraft and information display.

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