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Optical properties of d.c. magneto sputtered tantalum and titanium nanostructure thin film metal hydrides

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Abstract. **Nanostructured thin films of tantalum and titanium were deposited on glass substrate using d.c. magnetron sputtering technique under the argon gas environment at a pressure of 0·1 mbar. Optical transmission and absorption studies were carried out for these samples with pressure of hydrogen. Large changes in both transmission and absorption on loading these films with hydrogen are accompanied by significant phase changes and electronic transformation. Optical photograph shows the colour variation after hydrogenation in case of tantalum film which may be used as decorative mirrors and hydrogen sensors. The hydrogen storage capability of thin films was confirmed by variation in optical properties.**

Keywords. **Optical properties; sputtering; thin films; hydrogen pressure; transmission and absorption.**

1. Introduction

Metal hydrides are projected for many applications including the development of technologies for storage, production and purification of hydrogen for clean energy production (Sandrock 1999). Before that several metal powders including titanium, zirconium, niobium and tantalum were commonly processed by the well known hydride–dehydride (HDH) technique (German 1984). There are many different allotropic forms for titanium hydrides (Numakura *et al* 1984; Woo *et al* 1985) such as α, β and δ-phases given away in the Ti–H phase diagram (Massalski *et al* 1986) depending on the hydrogen concentration, temperature and applied pressure.

According to the phase diagram of the Ta–H system, as reported by Ducastelle *et al* (1970) and later by Schober and Carl (1977), nine ordered phases of tantalum hydride of different stoichiometries were found to exist at low temperatures, but only the disordered α-phase exists at temperatures higher than 350 K. A review concerning the order–disorder transitions in group transition metal hydrides (V, Ni and Ta hydrides) was published by Harabayashi and Anano (1981). The structural investigations were carried out by neutron diffraction and thermal analysis (Ducastelle *et al* 1970; Schober and Carl 1977; Harabayashi *et al* 1981) for tantalum hydrides. The order–disorder transition in metal hydrides is linked to presence of interstitial hydrogen atoms. They were located in either tetrahedral or octahedral interstitial positions in metals.

Since the discovery of the switchable mirrors based on YH_x, LaH_x and rare earth hydride (REH_x) films (Huiberts *et al* 1996), a lot of research has been done on metals and their compositions. The special characteristics of these mirrors is that they can be continuously and reversibly switched between a metallic reflecting state to an insulating transparent state by the absorption of hydrogen. Effect of hydrogen on optical properties used in different applications such as gasochromic (Huiberts *et al* 1996), electrochromic (Notten *et al* 1996; Armitage *et al* 1999) or chemochromic (Vander Sluis *et al* 1999), photochromic (Hoekstra *et al* 2001), piezochromic (Wijngaarden *et al* 2000) and thermochromic (Giebles *et al* 2002). These materials are also interesting for hydrogen storage applications (Schlapbach and Zuttel 2002; Farangis *et al* 2003). Hence, in conclusion, one can say that thin film of metal hydride can be used for many applications as smart windows, switchable mirrors, hydrogen sensors and hydrogen storage. In this paper we are going to present the effect of hydrogen absorption on optical properties of nanostructure thin films.

2. Experimental

Magnetron sputtering has become the process of choice for the deposition of wide range of important coatings, low fraction coatings, wear resistant coatings, corrosion resistant coating, decorative coatings and coating with specific optical and electrical properties (Kelly and Amell 2000). We deposited nanostructured thin films using d.c. magneto sputtering unit (Vacuum Equipment Co, New Delhi) in an argon gas environment at a pressure of

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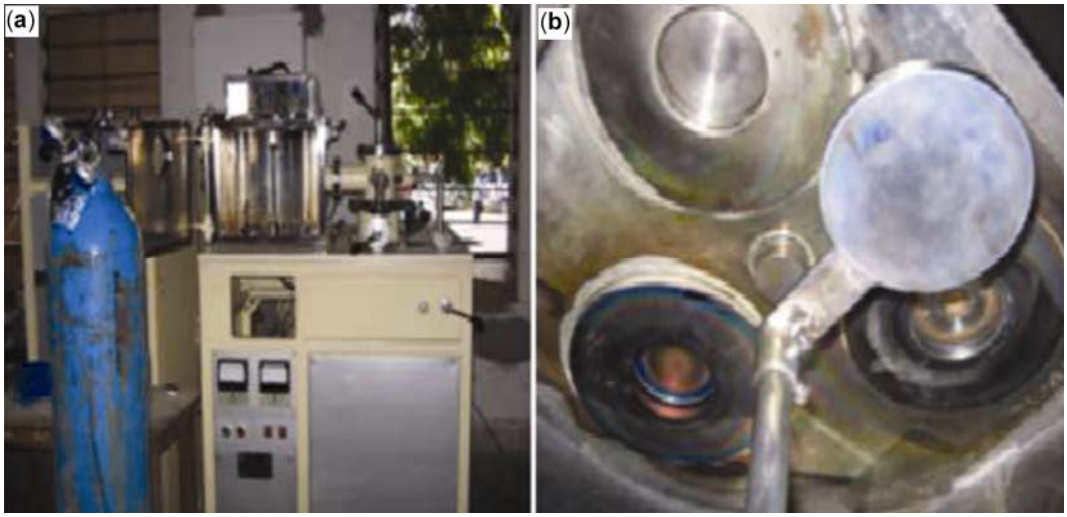

Figure 1. Sputtering unit with multiple targets. (**a**) View of sputtering unit with Argon cylinder and (**b**) direct sputtering with three target and substrate holders.

Figure 2. Ellipsometry with computer.

0·1 mbar. The sputtering unit with sample holder and multiple targets are shown in figure 1. Magnetron sputtering is a powerful and flexible technique to deposit thin films of materials, any metal or alloy or compounds by sputtering of atomized material from a solid due to energetic bombardment on surface layers. We have arranged target at lower position and placed substrate holder above them for thin film deposition. A sheet of pure tantalum and titanium having two inch diameter and thickness, 2 mm, was used as target material. Thin films were deposited on clean glass substrate using argon gas ions to sputtered tantalum and titanium with a deposition rate, 2·5 nm/s. Thickness was measured using ellipsometry as shown in figure 2 for tantalum and titanium thin films. It was found to be 216 nm and 233 nm, respectively. The ellipsometry is a non-destructive optical technique, which deals with the measurement and interpretation state of polarized light undergoing oblique reflection from a sample surface. The ellipsometry is based on measuring the changes of the amplitude and phase of polarized light when reflected on a sample surface. The high sensitivity on phase changes during reflection makes ellipsometry as one of the most precise and accurate methods to measure the thickness of films. Our ellipsometry have polarizer for polarized incident light and analyser for received reflected light from thin film surface. It was well connected with computer program to measure thickness. These films were hydrogenated in gas loading hydrogen absorption chamber with increasing hydrogen pressure at room temperature. The optical transmission and absorption spectra of these films recorded using a Hitachi photo-spectrometer model 330 in the range from 800–300 nm. An optical micrograph was also recorded before and after hydrogenation by using lamobed optical microscope. X-ray fluorescence (XRF) studies were carried out for titanium and tantalum thin films to test the purity of sputtered films. The X-rays were exited by using Am-241 source of 45 mCi placed in a lead collimator, 90 degree scattering geometry was used for excitation of X-rays in different samples in the range of 1·0–30 keV. A silicon drifted peltier cooled 5mm detector was used having a resolution of 150 eV at 6·4 keV. The X-ray emitted from different elements was detected and spectra recorded in computer for analysis.

3. Results and discussion

3.1 *Transmission and optical microscope studies of tantalum thin film*

Figure 3 shows transmission vs energy spectra of tantalum thin film. In this spectra one can observe that after hydrogenation transmission was found to be reduced. The reduced transmission in these films correlated with absorption of hydrogen and residual content of metal with

hydride phase. Similar effect was observed by Schlapbach and Zuttel (2002) for hydrogen storage applications. The optical transmission studies also suggest that there is no significant hydrogen absorption on pressure, 5 Psi, at room temperature, but at pressure, 10 Psi, the transmission was found to be reduced that shows optical properties had been changed with concentration of hydrogen, it also suggested change of phase from one to other state with hydrogenation. Yoshimura *et al* (2002) observed composition dependent transmittance in the hydride state which decreases abruptly for $x < 0{\cdot}1$ ($MgNi_{0{\cdot}1}$) and $x > 0{\cdot}3$ ($Mg_{3{\cdot}3}Ni$) and that decrease was correlated with residual metal content in layers.

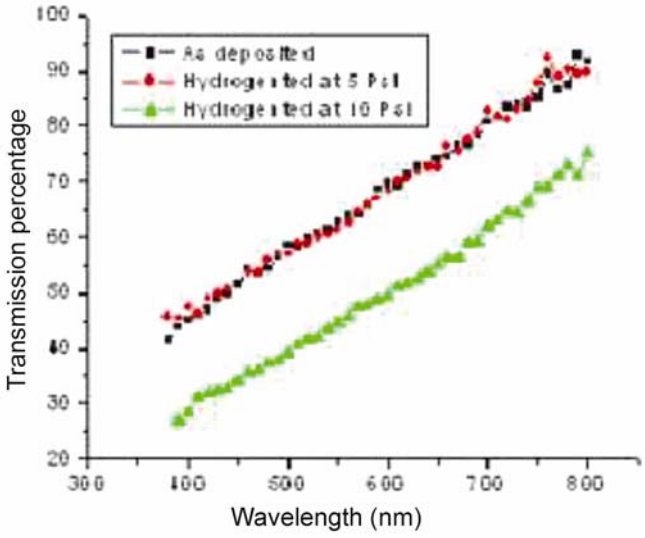

Figure 3. Transmission spectra of tantalum thin films.

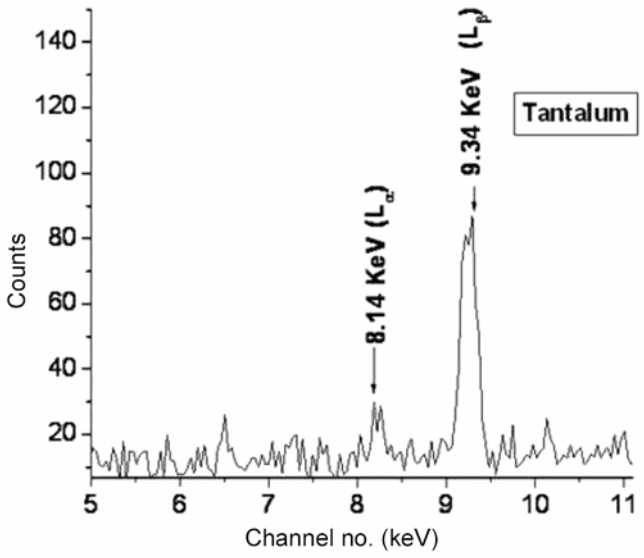

Figure 4. XRF of tantalum thin films.

The absorption of hydrogen did not occur up to 5 Psi pressure, it may be due to the fact that thin film requires high pressure for activation. The optimum or minimum pressure required was 10 Psi for tantalum thin films. Still optimum pressure required more careful studies because we have not taken measurement between 5 Psi and 10 Psi. The XRF of that film carried out to test the purity of films after deposition is shown in figure 4. The L_α and L_β peaks of tantalum appeared at 8·14 keV and 9·34 keV, respectively. The K_α and K_β peaks were not observed due to limitation of detector.

The optical photograph has been taken at a magnification of 40X by using Labomed optical microscope. Figures 5 and 6 show optical photographs for as deposited and hydrogenated tantalum thin films, respectively. One can see a lot of open space on surface, it may be due to order of thickness which was a few nanometer. At the nanometer scale during the growth process, channel formation and percolation take place. Percolation means that grains are connected electrically within metal layer on insulating glass substrate. The irregular morphology was also

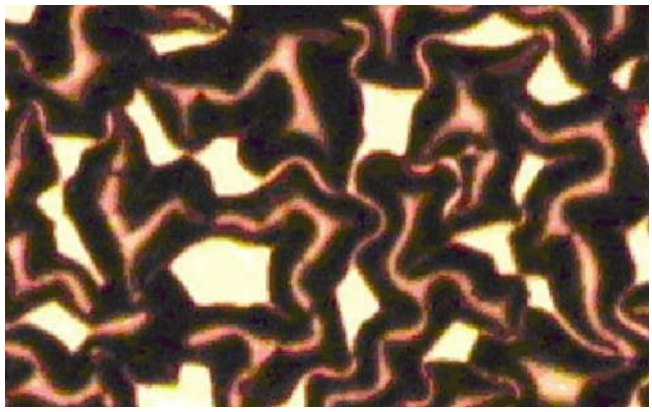

Figure 5. Optical photograph of as deposited thin films in reflectance mode.

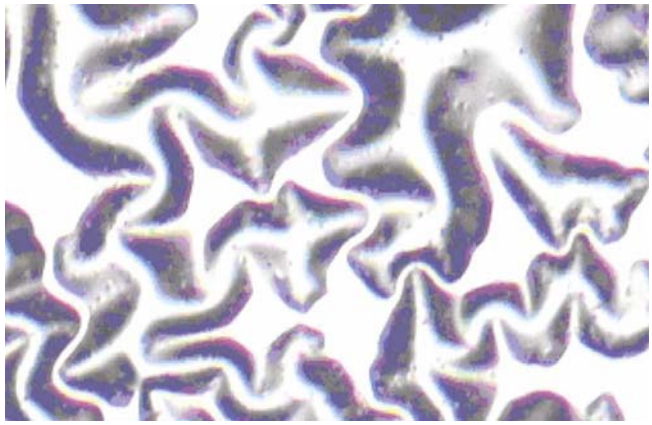

Figure 6. Optical photograph of hydrogenated thin films in reflectance mode.

observed (Kaiser 2002) and is explained on the basis of percolation in thin films.

We have also observed variation of colour from red to gray after hydrogenation. The colour variation correlated with phase change with hydrogenation as well as indication of hydrogen storage in films. It was suggested that tantalum thin film may be used as decorative mirrors for visible light with variation of hydrogen pressure. The variation in colour with hydrogenation in case of YH_x was observed by Huiberts *et al* (1996) that agreed with our present results in tantalum thin films. The colour variation in case of Co–Mg and Ni–Mg was observed by Farangis *et al* (2003).

3.2 *Optical and XRF studies of titanium thin films*

Figure 7 shows the absorption vs wavelength spectra of nanostructure titanium thin film. In the spectra, we saw that absorption increased with increasing hydrogen pressure. Hence one can say that absorption of hydrogen in film decreases the transmission of light. It means that the titanium thin film has the same behaviour as tantalum thin film in transmission mode. Hence we can conclude that titanium and tantalum thin films at nanostructured level do not show switchable behaviour as observed in rare earth and transition metal reported in literature. The optical photograph was taken for this film. It does not show any colour variation with hydrogenation so it cannot be used for decorative mirrors but it can be used as hydrogen sensors. It was also suggested that titanium films absorbed more hydrogen with pressure than tantalum thin films.

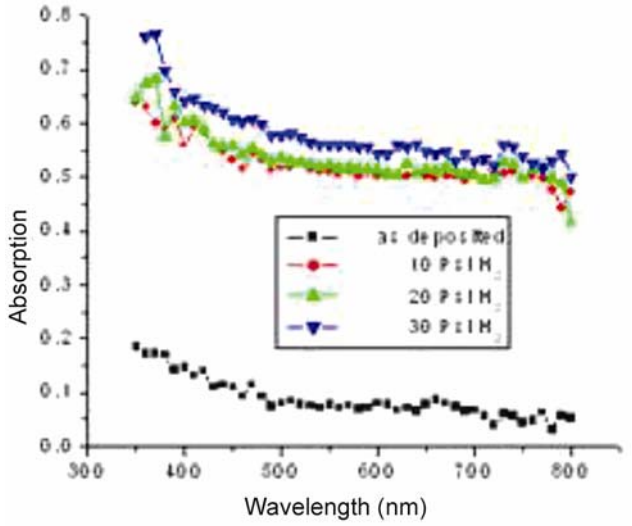

Figure 7. Absorption spectra of titanium thin films.

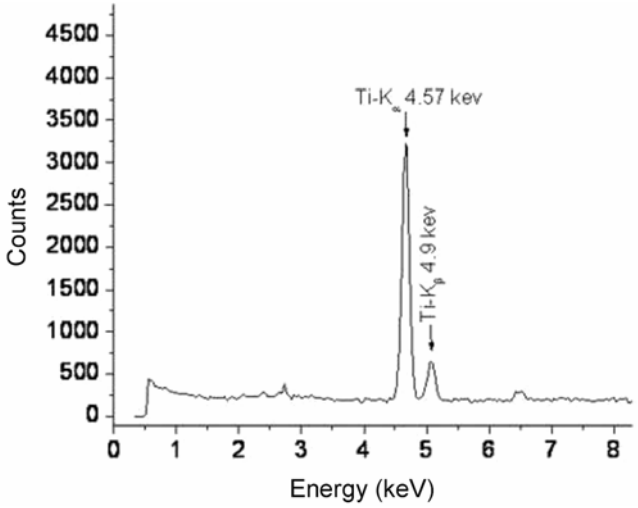

Figure 8. XRF of titanium thin films.

Figure 8 shows X-ray fluorescence (XRF) spectrum of magnetron sputtered nanostructured titanium thin films that contain only pure titanium peaks K_α and K_β at 4·5 keV and 4·9 keV, respectively without any impurity. After deposition, thin film samples bring in atmospheric pressure at room temperature.

4. Conclusions

Thin film of tantalum may be used as hydrogen storage, decorative mirrors and sensors. Thin film of titanium was used only for storage and sensors and not for decorative mirrors and variation of optical properties could be used as an indicator tool for hydrogen storage. The titanium and tantalum thin films at nanostructured level do not show switchable behaviour as observed in rare earth and transition metal reported in literature.

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