Published in Surface and Coatings Technology 153, 114-118 (2002).

Hydrogen permeation barrier performance characterization of vapor deposited amorphous aluminum oxide films using coloration of tungsten oxide

Y. Yamada-Takamura*, F. Koch, H. Maier and H. Bolt

Max-Planck-Institut für Plasmaphysik, D-85748 Garching bei München, Germany

*JSPS Research Fellow on leave from Department of Metallurgy and Materials Science, The University of Tokyo, 113-8656 Tokyo, Japan. e-mail: yukiko@plasma.t.u-tokyo.ac.jp

Abstract

Low hydrogen diffusivity and solubility of aluminum oxide make a vapor deposited aluminum oxide (Al_2O_3) film an anticipated hydrogen permeation barrier coating. In this paper, amorphous Al_2O_3 film was deposited using filtered vacuum arc method. As a substrate, vapor deposited amorphous tungsten oxide (WO_3) film was used in order to characterize hydrogen permeation barrier performance of the Al_2O_3 film utilizing coloration of WO_3 when it forms H_xWO_3. The samples were exposed to the flux and angular quantified atomic hydrogen beam, and the degree of coloration was characterized by visible to near infrared range transmission spectroscopy. Using this method, a half-micron thick amorphous Al_2O_3 film reducing atomic hydrogen reaching the underlying WO_3 film to 3×10^{-4} was measured. Furthermore, Al_2O_3 film as thin as 20 nm showed atomic hydrogen reduction of 4×10^{-3}. The results indicate effectiveness of thin vapor deposited Al_2O_3 film as a permeation barrier against atomic hydrogen.

Keywords: C. Filtered arc, D. Hydrogen, D. Aluminum oxide, D. Tungsten oxide

1. Introduction

Preparation of hydrogen permeation barrier coatings and characterizing its hydrogen permeability are of special interest in field of fusion reactor engineering[1]. For hydrogen permeation barrier coatings, some ceramic materials seem promising because of their low hydrogen diffusivity and solubility[2].

The so-called membrane gas permeation technique is often used for characterizing permeability and diffusivity of thin samples[3, 4, 5]. In this technique, two high vacuum chambers are separated by a thin sample, which is often sealed using gold "O"-rings and flanges. Hydrogen gas is introduced in one chamber ("high pressure side" of the sample), and time dependent amount of hydrogen which diffuses through the sample into another chamber ("low pressure side") is detected by pressure increase or by a quadruple mass spectrometer. Thin coatings, where the thickness ranges from a few nm to a few μm, are mostly characterized together with thicker substrates using this technique. Checchetto *et al.*[3, 6] investigated hydrogen barrier performance of ion-beam-assisted deposited TiN-TiC coating (1000nm + 250 nm) on martensitic steel, and found that its hydrogen permeability is at least four orders of magnitude lower than steel itself at temperature interval 470-570K. Serra *et al.*[5] investigated deuterium permeability of sputter deposited alumina films (1.5μm on each side of the substrate material) on martensitic steel over the temperature range 533-733K and the deuterium pressures in the range from 10^3 to 10^5 Pa. They found that the maximum reduction in permeation was around four orders of magnitude.

There is an alternative, although less quantitative, way to measure the permeability of films using vapor deposited amorphous tungsten oxide (WO_3) film. WO_3 is known as an electrochromic material, which is an attractive material for application in displays, intelligent windows and gas sensors[7]. By utilizing its coloration when it reacts with hydrogen, it is possible to characterize hydrogen permeability of thin coatings itself and without any sealing

problem. Adachi *et al.*[8] studied hydrogen permeability of various metal films using WO_3/metal/$LaNi_5$ samples, in which the $LaNi_5$ film acted as an atomic hydrogen source by dissociating hydrogen gas.

In this study, we used a similar new method to characterize hydrogen permeability of filtered arc deposited amorphous aluminum oxide (Al_2O_3) film. Instead of $LaNi_5$ film or Pd film which are difficult to quantify hydrogen fluence to the sample, a flux and angular quantified radical beam was used as an atomic hydrogen source. Degree of coloration of the WO_3 film was characterized by absorption in transmission spectra of the samples.

2. Preparation and characterization of the WO_3 films

The WO_3 films were deposited by electron beam evaporation of 99.99% pure WO_3 (CERAC incorporated) with additional flowing oxygen gas. Substrates were silicate glass for the hydrogen exposure experiments, and a graphite disc for Rutherford backscattering spectroscopy (RBS) measurement.

The measured RBS spectrum, and a simulated RBS spectrum using W:O=0.24:0.76 and thickness 2.83×10^{18} atoms/cm^2 which shows a relatively good fit, are shown in Figure 1. It shows that the film is stoichiometric, and from the additional measurement of the mechanical film thickness (approx. 500 nm) by a surface profilometer (Alpha-Step 200, TENCOR instruments), the density can be evaluated to be 5.6 g/cm^3. The refractive index of the film was estimated to be 2.2 by the film thickness and an interference pattern of a transmission spectrum from 300 nm to 2000 nm. These values for the density and the refractive index correspond well with the previously reported values of an amorphous WO_3 film which showed good electrochemichromic property[9].

3. Filtered vacuum arc deposition of the Al_2O_3 film

Al_2O_3 films were deposited using the filtered vacuum arc method with a toroidal filter[10]. Substrates were WO_3 films deposited on glasses (25mm square) for the hydrogen permeability measurements and a graphite disc (10mm in diameter) for RBS measurement. The cathode material was 99.999% pure aluminum. The arc current was 102.5 A. The base pressure was less than 3.0×10^{-3} Pa, while deposition pressure was 5.4×10^{-2} Pa due to oxygen gas added from the capillary near the substrate. The substrates were not heated. Deposition rate was about 2.2 nm/s, estimated from measured thickness of a deposited film around 1 μm thickness using profilometer.

The Al_2O_3 film for RBS measurement was deposited for 1 minute (about 130 nm). The RBS measurement[11] revealed that the film is stoichiometric and has no heavier metallic impurity. The estimated density of the film was $2.2 g/cm^3$, which is 56% of sapphire. These results suggest that the film is amorphous, which is consistent with the previous grazing incidence X-ray diffraction analysis[10]. For the hydrogen permeability measurement, 10 seconds deposition and 4 minutes deposition were made on the WO_3 film on the glass. From the deposition rate, thicknesses of these films were estimated to be about 22 nm and 530 nm, respectively.

4. Characterization of the coloration of WO_3 films exposed to atomic hydrogen

The WO_3 films on glass substrates were exposed to the atomic hydrogen source using the same system and similar procedure described in detail elsewhere[12]. A sample was fixed into a sample holder with a 20mm square window that allows a part of the sample to be exposed. Then the holder was set into a pre-evacuation chamber, and then transferred in front of the hydrogen source in a main experimental chamber through a vacuum load-lock system. Before hydrogen exposure of the sample, the experimental chamber was evacuated until the residual gas pressure was below 6.0×10^{-4} Pa. The hydrogen gas flow rate was set to 0.33

sccm (which raised the chamber pressure to about 5.7×10^{-2} Pa) and the tungsten capillary temperature was set to about 2100 K, which results in H flux of about 4×10^{15} H/cm^{2}s at the beam center at sample position. There was no additional heating of the sample, but the sample surface was heated by radiation from the hot tungsten capillary. The sample temperature measured at the back of the sample holder was around 60-70˚C.

The atomic hydrogen fluence was varied from 2.4×10^{17} H/cm^2 to 6.2×10^{19} H/cm^2, which corresponds to exposure time of 1 minute to about 260 minutes. The degree of coloration was characterized by transmission spectroscopy in range of 300 nm to 2000 nm. Figure 2(a) shows the transmission spectra of the hydrogen exposed WO_3 films and a transmission spectrum before exposure as a comparison. Since H_xWO_3 can easily react with oxygen in air and turn back to WO_3, the measurement was carried out within 20 minutes after the exposure. The interference pattern of the spectra originated from the thickness of the WO_3 film, which is about 500 nm. When the film was exposed to atomic hydrogen, the transparent film turned blue, and the transmission spectrum exhibited absorption around 800-1600 nm, which is apparent in Fig. 2(a). The absorption increased with hydrogen fluence, but for the samples exposed over 7×10^{18} H/cm^2, the absorption was nearly constant. The degree of absorption was characterized by subtracting a transmission spectrum after the exposure from a transmission spectrum before exposure for each sample, which is shown in Figure 2(b). Then this decrease in transmittance was plotted against hydrogen fluence using a value at the fixed wavelength. Absorption at 1400 nm was chosen because the spectra were less affected by the interference pattern at this wavelength. The result is shown in Figure 3 as filled circles. It is clear from Fig. 3 that the absorption increased rapidly until hydrogen fluence was 5×10^{18} H/cm^2, but then the increase slowed down and became almost saturated. Possible causes for this phenomenon are saturation of hydrogen in the WO_3 film, decrease in hydrogen diffusivity of the film, or achievement of equilibrium between adsorption and desorption of

hydrogen at the film surface.

5. Hydrogen permeation barrier performance of amorphous Al_2O_3 film

The amorphous Al_2O_3 films deposited on the WO_3 films on glass substrates were exposed to the atomic hydrogen beam to characterize their hydrogen barrier performance.

The sample with approximately 20 nm thick Al_2O_3 film was exposed to the atomic hydrogen fluence of 3.6×10^{19} H/cm^2, which corresponds to exposure time of 150 minutes. Transmission spectra before and after atomic hydrogen exposure are shown in Figure 4. The degree of coloration of this sample was lower than that of the least hydrogen exposed bare WO_3 film (fluence: 2.4×10^{17} H/cm^2, exposure time: 1 minute) in this study. In order to estimate the corresponding fluence in case of bare WO_3 film, we performed a curvefit to the data and zero point in Fig. 3, and obtained a solid curve in Fig. 3. According to this curve, the degree of coloration of the Al_2O_3 film coated WO_3 film corresponds to that of the bare WO_3 film exposed to the hydrogen fluence of 1.3×10^{17} H/cm^2 (corresponding exposure time: 0.54 minute). This means that the amount of hydrogen reaching the WO_3 film surface was reduced to about 4×10^{-3} by this extremely thin coating.

The sample with approximately 500 nm thick Al_2O_3 film was exposed to the atomic hydrogen fluence of 8.6×10^{19} H/cm^2, which corresponds to exposure time of 360 minutes. Transmission spectra before and after atomic hydrogen exposure are shown in Figure 5. According to the curve in Fig. 3, the degree of coloration of this sample corresponds to about 2.4×10^{16} H/cm^2 (corresponding exposure time: about 6 seconds) for the bare WO_3 film. This means that the amount of atomic hydrogen reaching the WO_3 surface was reduced to about 3×10^{-4} by this half-micron thick Al_2O_3 film.

The hydrogen permeation through thin Al_2O_3 at low temperature around 60-70˚C estimated from extrapolating reported diffusivity and solubility value of Al_2O_3[2] at high

temperature range, results in an extremely small value. Comparison of this value with above results indicates that the deposited film may not be ideally dense due to its macroscopic and microscopic defects and film structures. However, the results show that the filtered arc deposited Al_2O_3 film works as an efficient permeation barrier even against atomic hydrogen, which is more surface-penetrable compared to molecular hydrogen.

7. Conclusions

Using coloration of a WO_3 film when it reacts with atomic hydrogen, hydrogen permeation barrier performance of amorphous Al_2O_3 film deposited by the filtered vacuum arc method was characterized. This method has advantages compared to the gas permeation technique, such as possibility of characterizing coating itself and no necessity of vacuum sealing. The measured reduction of atomic hydrogen reaching the WO_3 film were 4×10^{-3} and 3×10^{-4} for the Al_2O_3 films with thicknesses as thin as 20nm and 500nm, respectively. The experimental results revealed that even against atomic hydrogen, the filtered arc deposited Al_2O_3 film works as an effective permeation barrier.

Acknowledgment

The authors are grateful to E. Maier and J. Perchermeier for preparing WO_3 films and permitting our use of spectroscopic equipment.

The authors are also grateful to T. Schwarz-Selinger, Dr. A. von Keudell, and Dr. W. Jacob concerning the atomic hydrogen source, and especially grateful to M. Meier for permission and detail instructions on using his atomic hydrogen source.

Figure 1 Measured and simulated RBS spectra of the WO_3 film deposited on a graphite substrate.

Figure 2 (a)Transmittance in range of 300 nm to 2000 nm of the WO_3 films deposited on glass substrates exposed to atomic hydrogen source, and (b)atomic hydrogen fluence dependent decrease in transmittance in range of 300 nm to 2000 nm.

Figure 3 Correlation of atomic hydrogen fluence and decrease in transmittance at 1400 nm.

Figure 4 Transmission spectra of the WO_3 film deposited on glass substrates with 20 nm thick Al_2O_3 film before and after exposure to hydrogen fluence of 3.6×10^{19} H/cm^2.

Figure 5 Transmission spectra of the WO_3 film deposited on glass substrates with 500 nm thick Al_2O_3 film before and after exposure to atomic hydrogen fluence of 8.6×10^{19} H/cm^2.

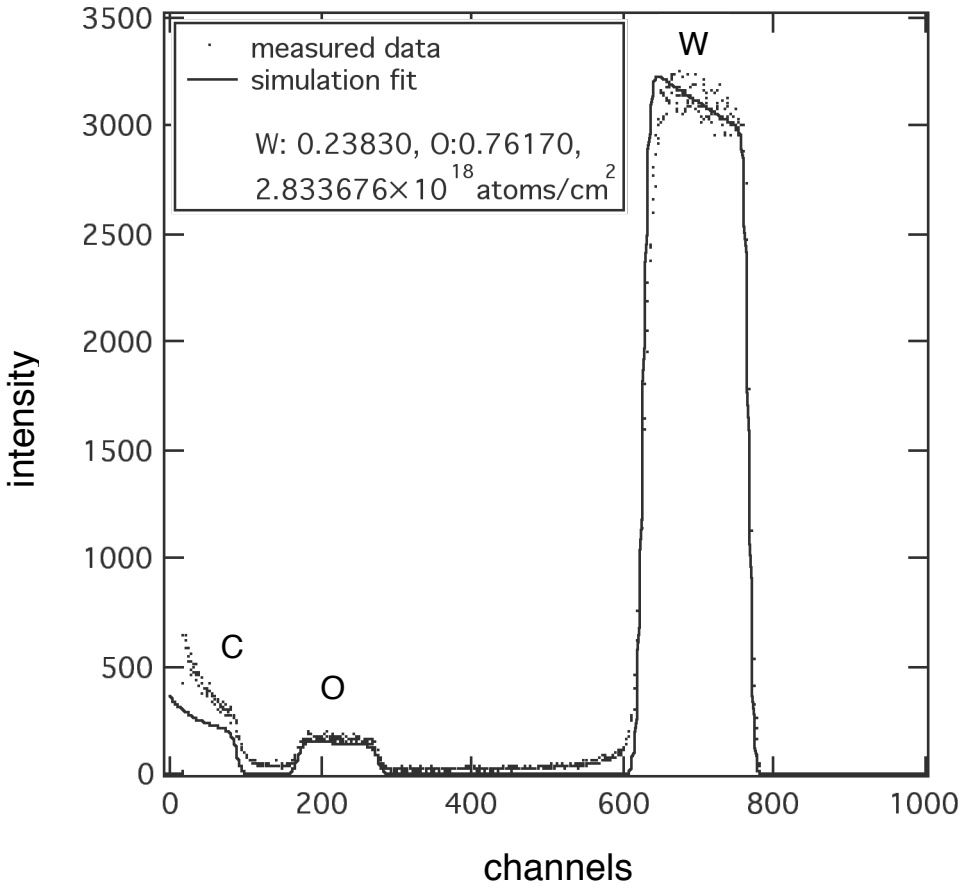
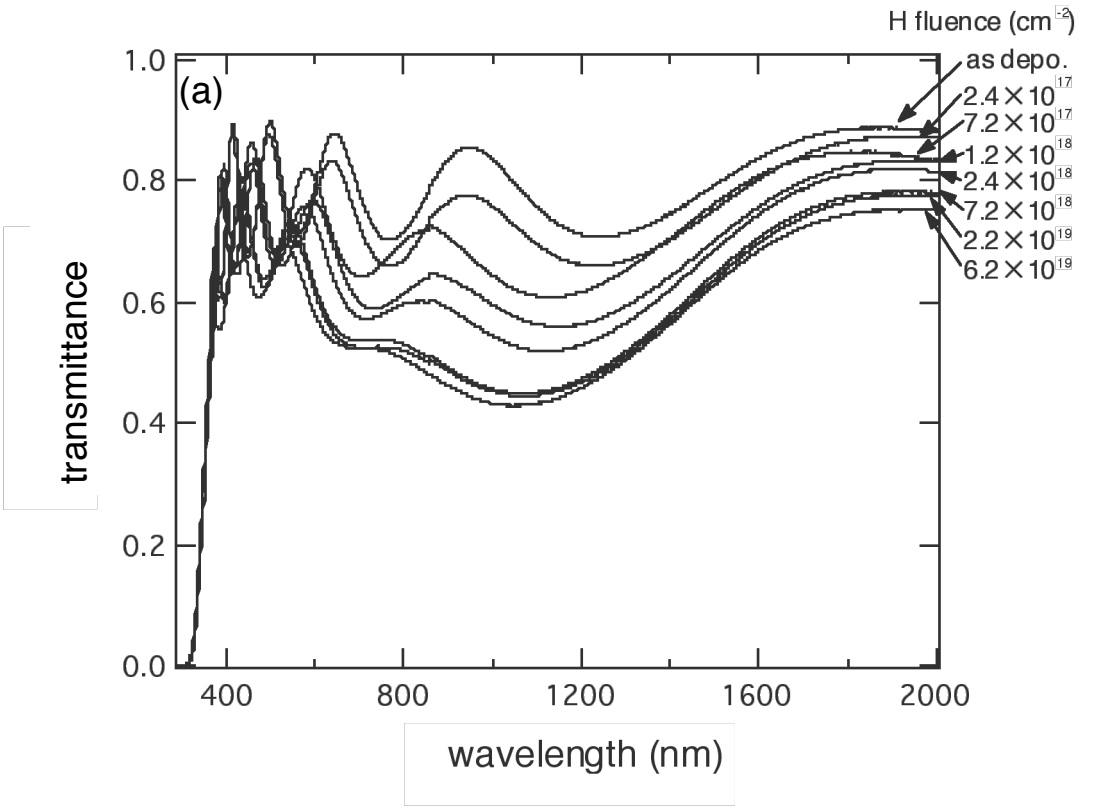

measured data
simulation fit
W: 0.23830, O:0.76170,
2.833676×10^18 atoms/cm^2
W
C
O
intensity
channels
3500
3000
2500
2000
1500
1000
500
0
0
200
400
600
800
1000

Figure 1


H fluence (cm-2)
as depo.
2.4×10^17
7.2×10^17
1.2×10^18
2.4×10^18
7.2×10^18
2.2×10^19
6.2×10^19
(a)
transmittance
1.0
0.8
0.6
0.4
0.2
0.0
400
800
1200
1600
2000
wavelength (nm)

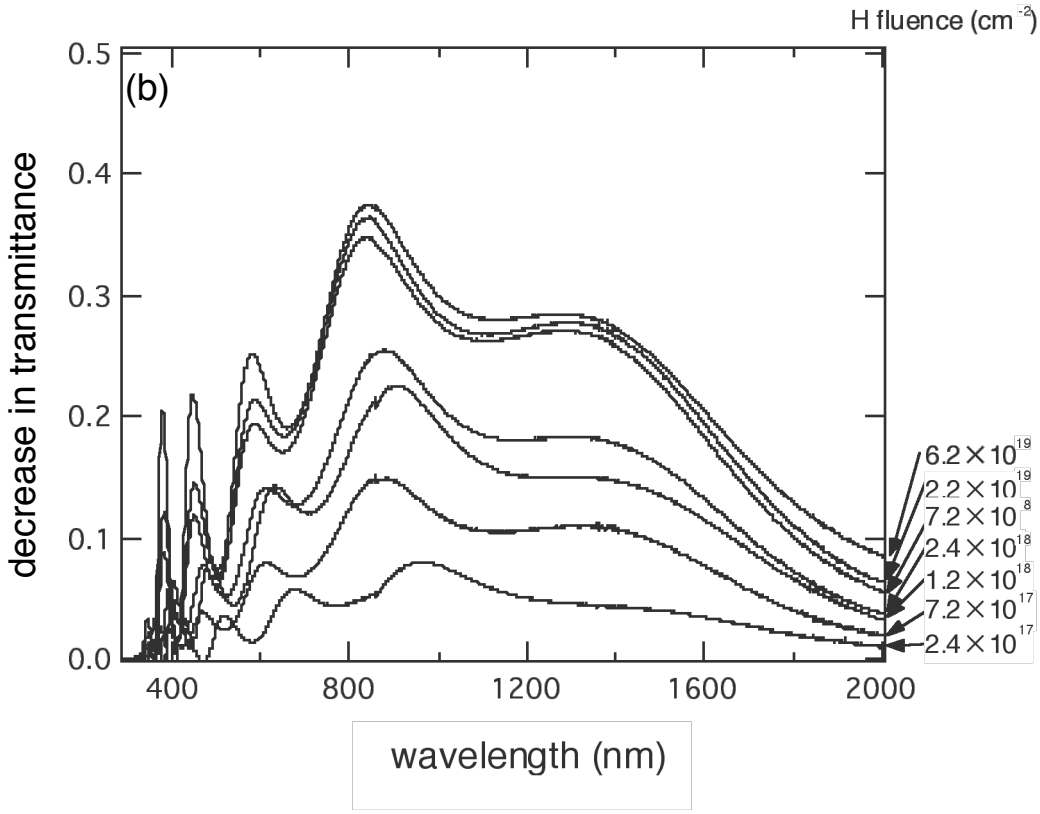

H fluence (cm-2)
(b)
decrease in transmittance
0.5
0.4
0.3
0.2
0.1
0.0
6.2×10^19
2.2×10^19
7.2×10^18
2.4×10^18
1.2×10^18
7.2×10^17
2.4×10^17
400
800
1200
1600
2000
wavelength (nm)

Figure 2

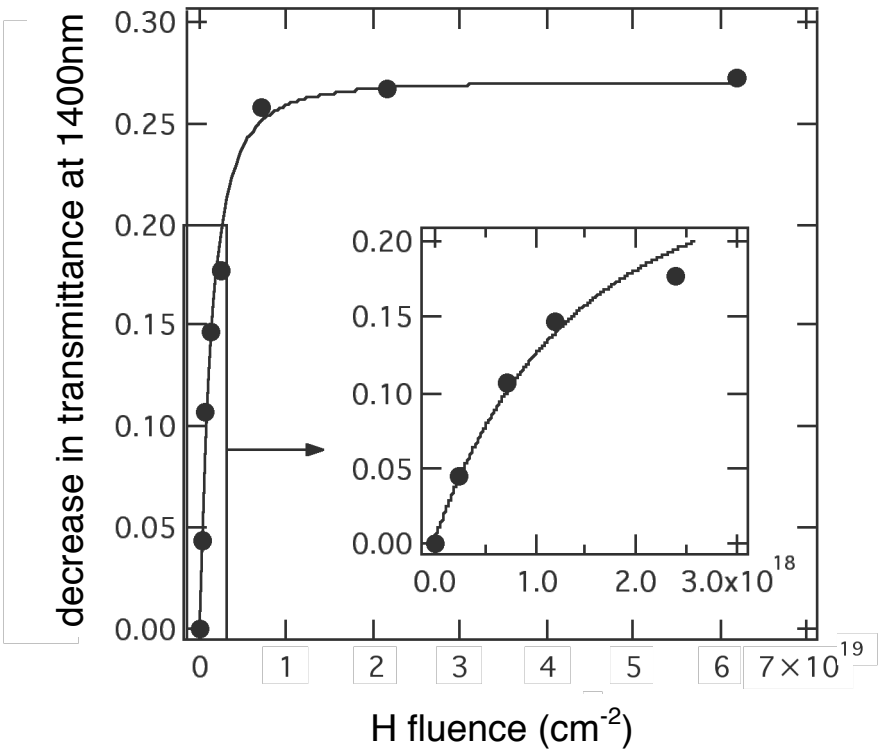

decrease in transmittance at 1400nm
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
7×10^19
H fluence (cm^-2)
0.20
0.15
0.10
0.05
0.00
0.0
1.0
2.0
3.0x10^18

Figure 3

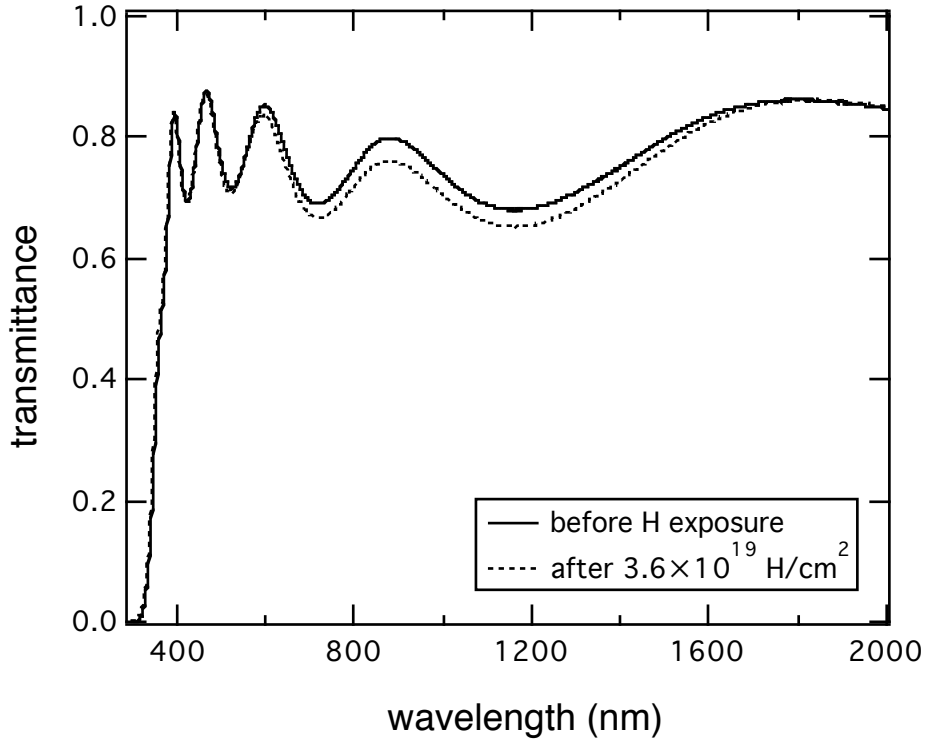

1.0
0.8
0.6
0.4
0.2
0.0
transmittance
400
800
1200
1600
2000
wavelength (nm)
before H exposure
after 3.6×10^19 H/cm^2

Figure 4

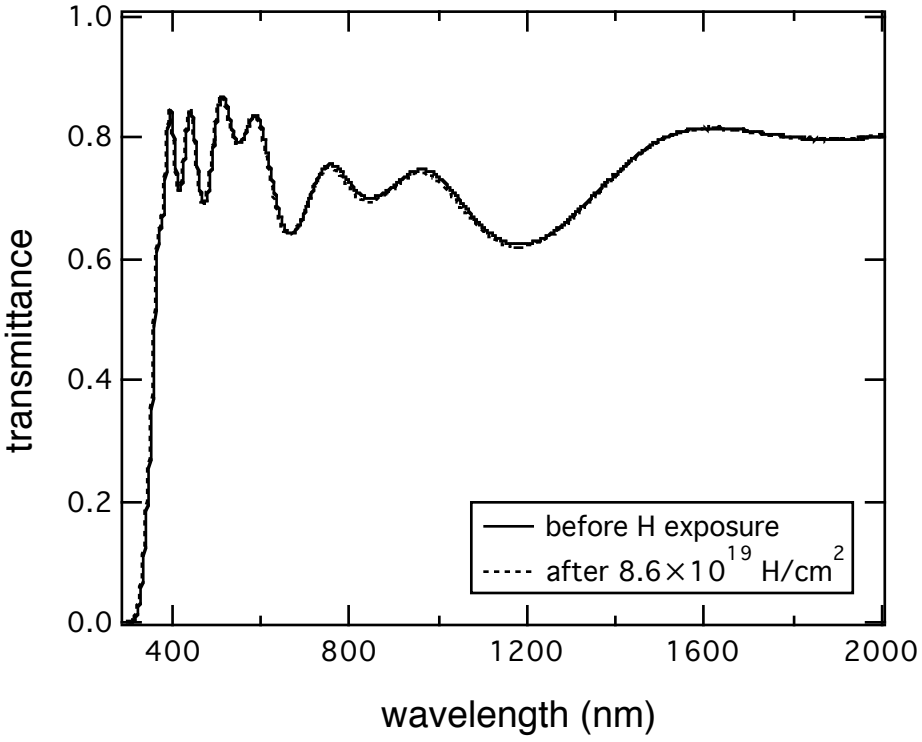

1.0
0.8
0.6
0.4
0.2
0.0
transmittance
400
800
1200
1600
2000
wavelength (nm)
before H exposure
after 8.6×10^19 H/cm^2

Figure 5

References

1 A. Perujo, and K. S. Forcey, Fusion Engineering and Design 28 (1995) 252

2 E. Serra, G. Benamati, and O. V. Ogorodnikova, J. Nucl. Mater. 255 (1998) 105

3 R. Checchetto, L. M. Gratton, A. Miotello, and C. Cestari, Meas. Sci. Technol. 6 (1995) 1605

4 Y. Ishikawa, T. Yoshimura, and M. Arai, Vacuum, 47 (1996) 701

5 E. Serra, P. J. Kelly, D. K. Ross, and R. D. Arnell, J. Nucl. Mater. 257 (1998) 194

6 R. Checchetto, M. Bonelli, L. M. Gratton, A. Miotello, A. Sabbioni, L. Guzman, Y. Horino, and G. Benamati, Surf. Coat. Technol. 83 (1996) 40

7 K. Ito and T. Ohgami, Appl. Phys. Lett., 60 (1992) 938

8 G. Adachi, H. Sakaguchi, T. Shimogohri, and J. Shimokawa, J. Less-Common Metals, 133 (1987) 271

9 K. Miyake, H. Kaneko, M. Sano, and N. Suedomi, J. Appl. Phys. 55 (1984) 2747

10 H. Bolt, F. Koch, J. L. Rodet, D. Karpov, and S. Menzel, Surf. Coat. Technol. 119 (1999) 956

11 Y. Yamada-Takamura, F. Koch, H. Maier, and H. Bolt, Surf. Coat. Technol. 142-144 (2001) 260

12 T. Schwarz-Selinger, A. von Keudell, and W. Jacob, J. Vac. Sci. Technol. A 18 (2000) 995