The three optical states of magnesium-containing switchable metal-hydride films

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The first switchable metal-hydride films[1] were made of YH_x or LaH_x protected against oxidation by a thin layer of palladium. With increasing hydrogen concentration these films changed from a metallic shiny mirror to a transparent layer, albeit with characteristic colours: YH_3 is yellow and LaH_3 reddish. Colour neutrality was first realized in Gd-Mg-H films[2]. Later, colour neutrality was also demonstrated[3] in La-Mg-H and Y-Mg-H films. The first rare-earth metal free switchable mirror was recently found by Richardson et al. [4] in Mg_2NiH_x .

All the Mg-containing switchable metal-hydride films, although very different chemically and structurally, have one remarkable characteristic in common: between the metallic mirror-like state and the insulating transparent state they exhibit a black state with little optical transmission and reflection in the visible part of the optical spectrum.

In Fig.1 we give an example for the La-Mg-H system. During hydrogen loading of a 50 nm thick La-Mg alloy film capped with 2.5 nm Pd a point is reached where reflection has dropped to 0.1 before transmission is substantially increasing. At a certain hydrogen concentration (corresponding to ~1000 s loading time) both reflection and transmission are ~0.1 and consequently absorption is about 80 %.

Another example is provided by the Mg_2NiH_x system[5]. Figure 2 shows the variation of the reflectivity and transmission of Mg_2NiH_x during hydrogen loading. Electrical resistivity and X-ray diffraction measured simultaneously indicate that the striking dip in reflectivity occurs in the metallic state of the film (its resistivity being relatively low 0.085 mΩcm) but at the beginning of a disproportionation of the original alloy at a hydrogen concentrations near x~0.7. Since the transmission is ravishingly small the minimum in reflectance corresponds to a “black” state with more than 90 % absorption.

A clue for the origin of the black state is provided by measurements on multilayers of Mg and Y consisting of a stack of 15 blocks of 10 nm Y and 10 nm Mg. The whole stack is capped with 10 nm Pd. Even in this system a black state occurs (near t=4000 s) although YH_x itself does not have a black state. This implies that the key factor is the formation of a mixed Mg-MgH_2 in the Mg sublayer. The coexistence of metallic Mg with insulating MgH_2 (with an energy gap of 5.6 eV) leads to absorption as high as 80 %.

We conclude that a black state can be expected in all systems where the formation of coexisting Mg and MgH_2 is possible (or made possible by a disproportionation process during the first hydrogen loading). This is relevant for further developments of “black” switchable mirrors.

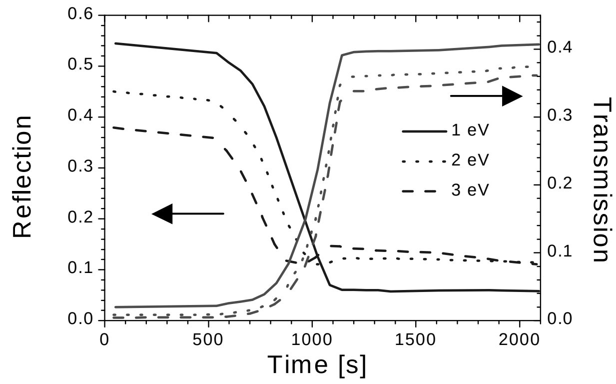

Fig.1: Optical reflection and transmission at three photon energies of a 50 nm thick La-Mg alloy film capped with 2.5 nm Pd during hydrogen uptake.

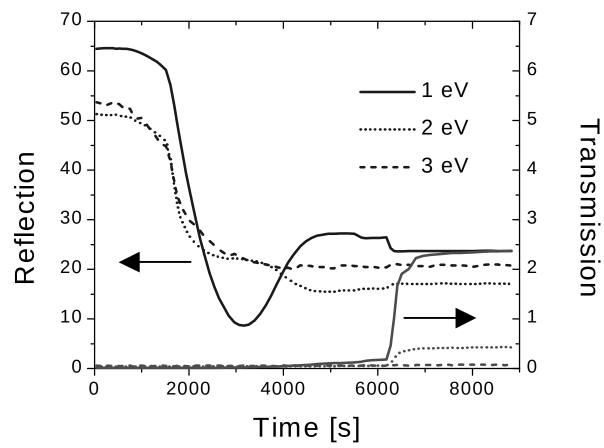

Fig.2: Optical reflection and transmission at three photon energies of a 220 nm thick $Mg_{2.17}Ni$ film capped with 3 nm Pd during hydrogen uptake.

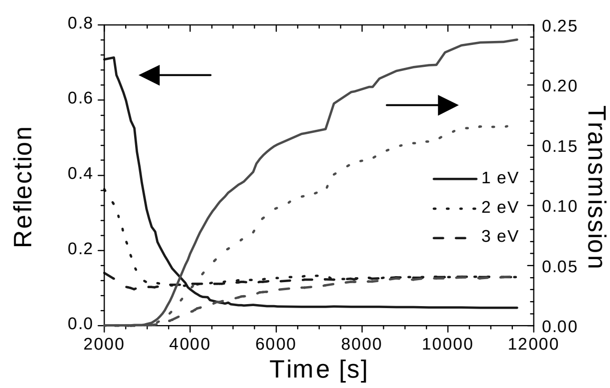

Fig.3: Optical reflection and transmission at three photon energies of a a 15*(10 nm Y+10 nm Mg) multilayer capped with 10 nm Pd. During hydrogen uptake the hydrogen pressure is increased in steps.

[1] J.N. Huiberts, et al. Nature 380 (1996) 231-234
[2] P. Van der Sluis et al. Appl. Phys. Lett. 70 (1997) 3356
[3] J. Isidorsson, et al. Electrochimica Acta 46 (2001) 2179
[4] T.J. Richardson et al. Appl. Phys. Lett. 78 (2001) 3047
[5] J. Isidorsson et al. Appl. Phys. Lett. 80 (2002) 2305