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Stability of hydrogen-induced optical switching properties of palladium-coated magnesium–nickel films

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ABSTRACT

Hydrogen (H_2)-induced optical switching properties of palladium-coated magnesium–nickel films were investigated. When the H content increased, the film started with an amorphous α-phase solution of H, and then became a mixture of amorphous α- and β-phase, and finally an amorphous β-phase solution of H. The film experienced volume changes, leading to damage of the Pd layer, followed by oxidation of the alloy layer and failure of the switching properties. If the Pd cover layer is made to have an appropriate thickness, the cyclic lifetime can be substantially extended to over 1000 cyclic exposures to 4% H_2 (in argon) and air.

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1. Introduction

More advanced hydrogen (H_2) sensors are desired to ensure the safe use and storage of H_2, associated with its increasing technological importance [1]. The optical transmittance of palladium capped magnesium–nickel (Pd/Mg–Ni) films is found to be markedly switchable during hydrogenation and dehydrogenation [2–14], and hence is claimed to be useful in detection of H_2 [9,15]. A Pd/Mg–Ni film is applicable at a much lower temperature compared with a conventional metal-oxide sensor (>500 °C), such that material instability caused by high operation temperature, and subsequent drift of the sensing properties can be diminished [16–18]. However, not unlike many other studies on gas sensor materials, reports on the hydrogen sensing properties of Pd/Mg–Ni films mainly concentrate on their sensitivity and response time. Information on the stability of detection, though of great practical importance, is much less presented and discussed. [12,13,15,19].

This study started with investigating the H-induced response of optical transmittance (T) of Pd/Mg–Ni films. Measurements were performed at 60 °C in a quasi-static mode first, where the change of T was recorded with H_2 partial pressure (P_{H2}) rising with a very low rate. The plot of T versus P_{H2} is defined as the optical transmittance–pressure isotherm (TPI). Measurements were also performed in an accelerated aging testing mode at 60 °C (or cyclic test), where the sample was exposed alternatively to H_2 at a certain P_{H2} and air. Combining the results of optical measurements and compositional/structural analyses, one expected to gain insights on the mechanisms affecting the stability of the optical switching response. Based on the findings, we were inspired to adjust the thickness of the Pd cover layer for improving the cyclic lifetime of the H-sensing properties of Pd/Mg–Ni films.

2. Experimental techniques and characterization

Pd/Mg–Ni films were prepared by using a 3-head sputtering system with a background pressure of 2×10^{-6} Torr. Corning 7059 glass substrates were cleaned in acetone followed by ethanol in an ultrasonic bath, each for 5 min. They were then mounted to the substrate holder which remained unheated during deposition. 2-in Mg, Ni and Pd discs (purity 99.95%) were used as targets. They were first pre-sputtered to remove surface oxide. The Mg and Ni targets were then co-sputtered in argon (Ar) at 10 mTorr, and power levels of 104 and 60 W respectively, to deposit a 30-nm Mg–Ni alloy layer. A 5- or 10-nm Pd cover layer was then added. The thickness of the bi-layer film was measured with a surface profiler (Tencor 10). The thickness of the Pd cover layer was derived from the calibration data of the coating rate of Pd.

A Philips X'Pert X-ray diffractometer (XRD) was used to record XRD patterns. A NanoScope IV (Digital Instruments) atomic force microscope (AFM) was used to observe their surface morphology and derive the root-mean-square roughness (z_{rms}). A Phi 5600 system X-ray photoelectron spectrometer (XPS) was used to analyze the composition and chemical states of Mg, Ni, Pd and oxygen as functions of depth. With the use of a standard software, a Shirley background was removed from the spectra to get a photoelectron peak, which was either fitted to a single- or multi-peak model depending on the peak shape. Identification of the composition of a Mg–Ni film is not straightforward, because the relative contents of the elements are not constant with depth, and are also

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changed by the switching processes. Therefore, the average of the Mg-to-Ni ratio over 13 to 20 nm of depth in the as-deposited films is used to represent the nominal film composition, because in this range the ratio varies very little and the contents of Pd and O are negligibly small. This ratio is 1.8 for the films used in this study.

The value *T* of a film for a 632.8-nm He–Ne laser was measured to represent the detection signal of H_2. A film sample was placed in a measurement chamber and heated up to 60 °C. This measurement temperature was chosen, because the results of an exploratory test showed that the response and recovery rates were faster for the temperature increasing from 20 to 100 °C, but the sensitivity dropped. A measurement temperature of 60 °C gave a fairly good combination of these performance indexes. In a quasi-static test, the measurement chamber was first pumped down to rough vacuum, and then a 4%H_2–96%Ar gas was admitted stepwise with a very low effective rate. P_{H2} was increased very slowly from 70 to 3000 Pa. For the sake of discussion, P_{H2} was further converted into a nominal H_2 concentration per atmospheric pressure (C_{H2}). The measured values of *T* were plotted against P_{H2} (or C_{H2}) to produce a TPI. In a cyclic test, the sample was exposed alternatively to 4%H_2–96%Ar gas at a certain P_{H2} and dry air at 1 atmosphere pressure, each for 10 min. Meanwhile, the change of *T* was recorded.

3. Results and discussions

3.1. H-induced optical transmission response and cyclic instability

The TPI of a film with a 5-nm Pd cover layer shows a 3-stage feature (Fig. 1), which is analogous to that observed in the pressure–composition isotherm (PCI) of crystalline Mg_2Ni–hydride system [20,21]. The three stages in the PCI of a crystal are associated with the following transitions. The crystal starts with a hexagonal α-Mg_2NiH_x phase containing interstitial H atoms. When *x* increases from 0 to 0.3, the lattice constants *a* and *c* change from 0.516 and 1.320 nm to 0.523 and 1.343 nm respectively, corresponding to a 4.52% expansion in volume. Further hydrogenation initiates transition from the α-$Mg_2NiH_{0.3}$ phase to a β-Mg_2NiH_4 phase, resulting in a solid admixture. The β-phase has a monoclinic lattice with *a, b* and *c* equal to 0.6503, 0.6426, and 1.3209 nm [22]. The α- and β-phases contain 6 and 8 molecules in the respective unit cells, so that complete transition involves a 32% expansion in volume. Afterwards, the β-phase dominates. Its volume can only slightly expand with increasing interstitial incorporation of H atoms.

Our films were identified to be X-ray amorphous. The appearance of the 3-stage feature in their TPI implies that their structures at various stages should exhibit similar short-range orders as those of the crystalline phases appearing at the corresponding stages. In particular, a film starts with an amorphous α-phase solution of H atoms, and then becomes a mixture of the amorphous α-phase and a β-phase mixture, and finally the amorphous β-phase containing interstitial H atoms. The thickness of the film at the dehydrogenated state after 30 switching cycles was found to be 54 nm, showing a 54.3% increase from that of the as-deposited metal film, i.e. 35 nm.

Fig. 2(a)–(c) shows the cyclic response of *T* of a film with a 5-nm Pd cover layer measured at 60 °C. Detection sensitivity (*S*) is defined as the percentage change of *T*, which is shown in Fig. 2(d). Three tests were performed by using different C_{H2} values. In the test with $C_{H2} = 6400$ ppm within Stage I, the film remained in the amorphous α-phase. The H content and hence the volume of the film varied only mildly during switching. The bi-layer structure remained intact throughout the process. The H-induced optical switching response is highly repeatable. This is further illustrated by the consistency between the plot of the cyclic test results and the TPI in Stage I as shown in Fig. 1 (also see the inset). In the cyclic test with $C_{H2} = 12{,}800$ ppm in Stage II, the optical sensing response increased to the maximum at the 5th cycle. At this C_{H2} level, the Mg–Ni layer tends to perform reciprocating transitions between the amorphous α- and β-phases, but the accompanying deformation was restricted by the integrity of the film material when it was first exposed to H_2. Along with the evolution of deformation in successive exposures to H_2, the sensitivity grew. This is supported by the observed surface roughening and thickening of the film after performing many switching cycles as presented in the next Section. In the ensuing cycles, the sensitivity dropped from the maximum and deterioration persisted. In the cyclic test with $C_{H2} = 40{,}000$ ppm in Stage III, the optical response of the first cycle was the strongest, because at this C_{H2} level, the α-to-β transition had fully commenced in the first H_2 charging process. Degradation of sensitivity continued in all the following cycles. In addition, Fig. 1 shows that the TPI measured after 30 switching cycles deviates significantly from that measured immediately after deposition, further confirming that the film structure and the H-sensing response have been altered irreversibly.

3.2. Mechanisms responsible for the instability of sensitivity

To explain the degradation of the H_2 sensing properties observed in Stage II and III, we refer to the AFM images and XPS data of the film with a 5-nm Pd cover layer recorded immediately after deposition [Fig. 3(a)] and after 30 switching cycles performed with $C_{H2} = 40{,}000$ ppm [Fig. 3

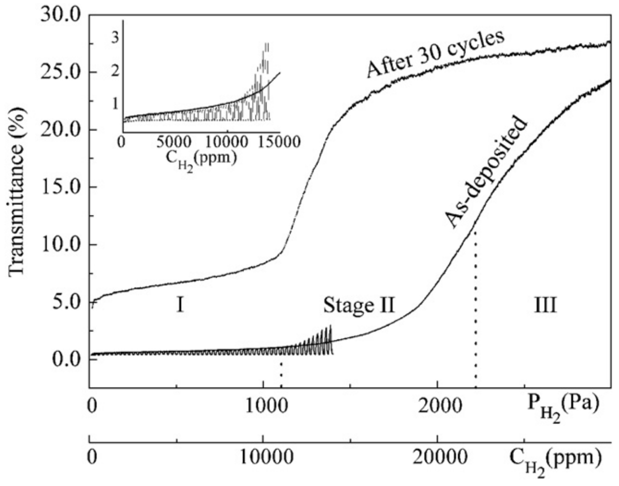

Fig. 1. TPI of a Mg-Ni film with a 5-nm Pd cover layer measured at 60 °C, immediately after deposition and after 30 switching cycles; and the cyclic response of *T* at low C_{H2}. Inset: Magnified TPI (as-deposited) and cyclic response in Stage I.

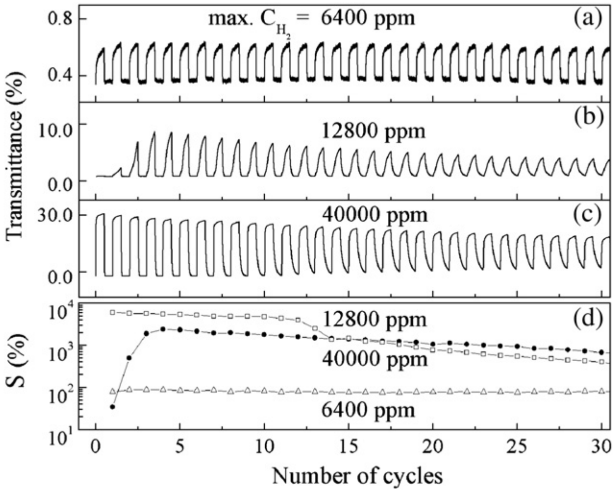

Fig. 2. H-induced cyclic optical transmission response and sensitivity *S* (percentage change in *T*) of a film with a 5-nm Pd cover layer measured at 60 °C, with $C_{H2} = 6400$, 12,800 and 40,000 ppm.

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