J. Chem. Sci., Vol. 120, No. 6, November 2008, pp. 573–578.

Two approaches for enhancing the hydrogenation properties of palladium: Metal nanoparticle and thin film over layers†

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Abstract. In the present study, two approaches have been used for enhancing the hydrogenation properties of Pd. In the first approach, metal thin film (Cu, Ag) has been deposited over Pd and hydrogenation properties of bimetal layer Cu (thin film)/Pd(thin film) and Ag(thin film)/Pd(thin film) have been studied. In the second approach, Ag metal nanoparticles have been deposited over Pd and hydrogenation properties of Ag (nanoparticle)/Pd (thin film) have been studied and compared with Ag(thin film)/Pd(thin film) bimetal layer system. The observed hydrogen sensing response is stable and reversible over a number of hydrogen loading and deloading cycles in both bimetallic systems. Alloying between Ag and Pd is suppressed in case of Ag(nanoparticle)/Pd(thin film) bimetallic layer on annealing as compared to Ag (thin film)/Pd(thin film).

Keywords. Cu/Pd bimetal layers; Ag/Pd bimetal layers; nanoparticles; hydrogen sensing; XPS; GAXRD.

1. Introduction

Palladium has several important roles in hydrogen economy, it is used to generate, purify, store and detect hydrogen.[1–4] A multitude of industries use hydrogen as an integral part of the process.[5,6] Hydrogen is highly flammable at concentration $> 4\%$.[1] Being lightest, it disperses rapidly due to low mass and high diffusivity.[1,2] Palladium is chemically selective towards H_2 with a reversible and rapid hydrogen sensing response with high sensitivity.[1] Pd–H is a two phase system with α (low hydrogen concentration H/Pd $\leq 0{\cdot}025$ to $0{\cdot}03$ atomic % at ~ 298 K) and β (high hydrogen concentration H/Pd $\geq 0{\cdot}06$ atomic % at ~ 298 K) phases ($0{\cdot}03 \leq$ Pd/H $\leq 0{\cdot}06$ two phase $\alpha + \beta$ region).[1] This phase transformation from α to β is accompanied by an expansion of the lattice by about 4% which is responsible for mechanical instability in Pd.[1] Pure Pd membrane, however, would be destroyed due to hydrogen embrittlement when it was used at temperatures below 573 K and hydrogen pressures above 2 MPa.[7] Sulphur containing gases like H_2S and SO_2 poison Pd by forming sulphur deposits on its surface.[8–10] The poisoning of Pd with these gases is irreversible. As a result, Pd based hydrogen sensors lose sensitivity to H_2 and have significantly slower response times. 'Nanoparticle route' and 'bimetal layer route' have been employed to maximize the Pd–H interaction and to overcome the above mentioned shortcomings.[11,12] In a bimetallic system, properties of two elements are combined in a synergic manner to yield a surface which is more reactive than either of the two.[12,13] Alloying of Pd with Ni, Cu, Ag or Au enhances the single phase α region.[14] Firstly, the critical temperature of miscibility gap for the α to β phase transition is lowered in Pd alloys. This helps in enhancing their mechanical properties and withstanding repeated temperature cycling. Secondly, hydrogen permeability of many alloys including $PdAg_{23}$, $PdCu_{40}$, PdY_7 and $PdAu_5$ can be improved.[15–17] In the present work, H–Pd interaction in Cu/Pd and Ag/Pd bimetallic layers has been investigated by studying the resistance change on hydrogen loading and deloading. Structural and electronic properties of as-deposited and annealed Cu/Pd and Ag/Pd bimetal layers have been studied.

2. Experimental

Cu/Pd and Ag/Pd bimetal layers were deposited using sequential vacuum deposition at a base pressure

†Dedicated to Prof. C N R Rao on his 75th birthday
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of 1×10^{-6} Torr onto a glass substrate. Film thickness is determined by measuring the frequency shift in a quartz crystal oscillator, which is proportional to the deposited mass and thus will be referred to as 'mass thickness'. The thickness of the Pd film was maintained at 100 Å using a quartz crystal monitor. Cu or Ag layers of 20 Å thickness were deposited onto the Pd films by evaporating high purity Cu or Ag at 1×10^{-6} Torr to form Cu/Pd and Ag/Pd bimetal layer structures, respectively. Ag nanoparticles of effective mass thickness 10 nm have been deposited onto Pd thin film using inert gas deposition technique at argon pressure of 5×10^{-4} Torr. The samples were loaded with hydrogen via gas phase loading. For measuring electrical resistivity in hydrogen, *in situ* electrical measurements were carried out by the four previously deposited aluminum (Al) contacts on glass substrates. For deloading, chamber was evacuated using a mechanical rotary pump. Keithley 224 programmable current source and Keithley 6517A electrometer resistance meter were used during electrical measurements. Structural analysis of the films was done with the help of Philips 'XPert' model glancing angle X-ray diffractometer (GAXRD). XPS measurements were performed in an ultra-high vacuum chamber (PHI 1257) at a base pressure of $5{\cdot}3 \times 10^{-8}$ Pa. The XPS spectrometer is equipped with a high-resolution hemispherical electron analyser (279·4 mm diameter with 25 meV resolution) and AlK_α ($h\nu = 1486{\cdot}6$ eV) X-ray anode as the photon source.

3. Results and discussion

3.1 *Cu(thin film)/Pd(thin film) bimetal layers*

Hydrogen-sensing response of Cu (thin film)/Pd (thin film) bimetal structure is shown in figure 1. Stable and reversible hydrogen sensing response is observed over a number of hydrogen loading and deloading cycles. On hydrogen loading, resistance of bimetal layer increases by about 7·4%. This is because Pd on interaction with hydrogen forms palladium hydride whose resistance is higher than that of Pd. Hydrogen sensing response of annealed Cu/Pd bimetal layer is shown in figure 2. The sensing response decreases in annealed (up to 300°C) Cu/Pd bimetal layers. Percentage change in resistance was observed to be 5·3%, 4·2% and 1·3% in 100°C, 200°C and 300°C annealed Cu/Pd bimetal layers, respectively. However, hydrogen sensing response is higher in 400°C annealed samples. In 350°C, 400°C and 450°C, resistance change is 3·2%, 6·6% and 7·2% respectively. As shown in figure 2, from point A to B, resistance change decreases and from B to C, resistance change increases.

To explain the hydrogen sensing response in terms of electronic and geometric changes that occur during annealing, surface sensitive x-ray photoelectron spectroscopy (XPS) and glancing angle X-ray diffraction (GAXRD) studies have been done.[18] The XPS features of core-electron and valence band (VB) spectra have been recorded for Cu/Pd bimetal

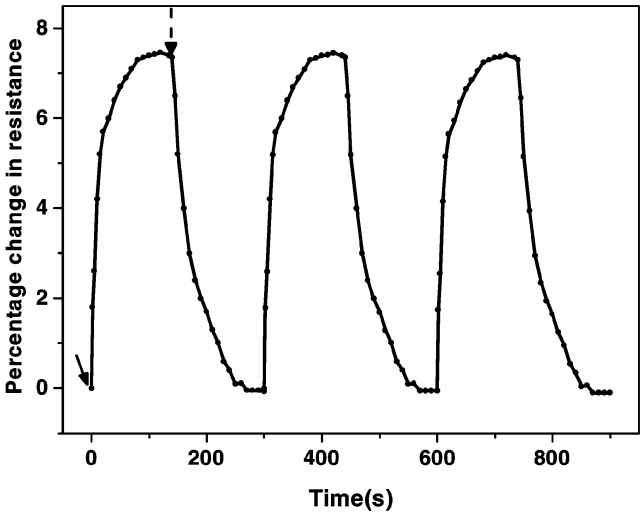

Figure 1. Stable and reversible hydrogen sensing response of Cu/Pd bimetal layers. Solid and dotted arrows show loading and deloading points.

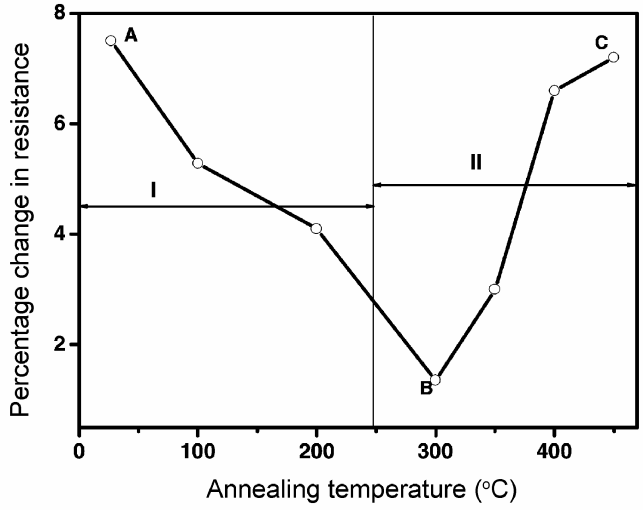

Figure 2. Hydrogen sensing response of Cu/Pd bimetal layer at 100% H_2 concentration and at different annealing temperatures.

layer samples. The intensity of the Pd ($3d_{5/2}$) and Cu ($2p_{3/2}$) XPS core lines was monitored as a function of annealing at different temperatures. It was observed that concentration (intensity ratio: Pd $3d_{5/2}$/ Cu $2p_{3/2}$) composition- profile as a function of temperature can be divided into two regions as shown in figure 3. In the first region (up to 250°C), Pd signal increases whereas Cu signal decreases due to Pd–Cu interdiffusion. In the second region (250°C–600°C), Pd and Cu peak attains a constant value. This region represents Pd–Cu surface alloy formation. Thus with increasing annealing temperature, intermixing occurs between Cu and Pd and a surface alloy is formed at intermediate temperature region. Hydrogen sensing has been observed in temperature range corresponding to regions I and II. Figure 4 shows the Pd ($3d_{5/2}$) core-level spectra of as-deposited and 400°C annealed sample. In sample, annealed at 400°C, there is a clear presence of two Pd peaks. Peak Pd (A) at higher binding energy 337·1 eV is due to alloyed Pd atoms and peak Pd (M) at 335·6 eV is due to metallic Pd atoms. The observed core-level shift is due to charge transfer from Pd to Cu. Cu has a 4*s* conduction band that is only half filled whereas Pd has an almost filled 4*d* valence band. There is a flow of electrons towards the element with the larger fraction of empty states in the valence band.[12] With increasing annealing temperature, area under the alloyed Pd component Pd (A) was observed to increase, whereas that of metallic component Pd (M) keeps on decreasing.

X-ray diffractograms of as-deposited and 400°C annealed Cu/Pd bimetal layers are shown in figure 5.

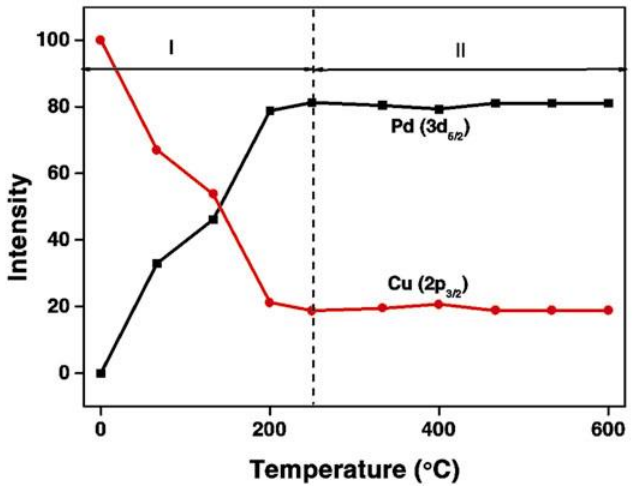

Figure 3. Area of Pd ($3d_{5/2}$) and Cu ($2p_{3/2}$) core level peaks as a function of annealing temperature. Regions I and II corresponding to figure 2 are also shown.

In as deposited Cu(thin film)/Pd(thin film) bimetal layer, there are clear and well separated (111), (200), (220) Cu and Pd peaks. On annealing, Pd (111) and Cu (111), Pd (200) and Cu (200) peaks merge and form Cu–Pd (111) and Cu–Pd (200) peaks. With increased annealing, *d*-values in between to that of Pd and Cu standard ASTM values are attained. The *d*-value for Pd (111) and Cu (111) are 2·25 Å and 2·09 Å respectively. For sample annealed at 400°C, *d* (111) = 2·21 Å. Thus, in case of annealed sample, *d* value lies in between those of pure palladium and copper confirming the surface alloy formation.[18] The *d*-value for the (200) and (220) planes also supports the above observation.

In Cu (thin film)/Pd (thin film) bimetal layer system, valence band (VB) spectra can be divided into three regions; (1) Pd dominance at lower B.E; (2) Cu dominance at higher B.E; (3) intermediate region formed by overlapping of Pd 4*d* and Cu 3*d*.[19] Third region dominates on annealing as formation of new states take place due to the enhanced overlapping of Pd 4*d* and Cu 3*d* bands. In as-deposited Cu/Pd bimetal layer, two effects come into play; (1) electronic effect or ligand effect; (2) geometric effect. Electronic effect arises due to the presence of different kinds of atoms in the surrounding. In Cu/Pd system, due to electronic effect, Pd–H interaction decreases due to electron flow from Pd to Cu. Also due to 7·1% lattice mismatch between Cu and Pd, compressive stress occurs which can also suppress the catalytic activity of Pd towards H_2. However, on annealing, influence of neither electronic nor geometric effect on catalytic interaction of Pd with H_2 is significant. Cu and Pd form common valence band whose catalytic properties are completely different from those of individual Pd and Cu metals. On alloying, compressive stress also reduces, thus catalytic interaction of Cu/Pd bimetal layer increases. Pd/Cu alloy has favourable properties like increased sulphur resistance, good thermal resilience and higher hydrogen permeability as compared to pure Pd.[14] At conditions of H_2S exposure that cause 80% reduction of the hydrogen flux through a pure palladium membrane, it has been reported that there is less than 10% reduction of the hydrogen flux through palladium–copper membrane alloy.[15]

3.2 *Ag(thin film)/Pd(thin film) and Ag(nanoparticle)/Pd(thin film) bimetal layers*

In Ag/Pd bimetal layer system, the effect of converting the metal overlayer from thin film (TF) to metal

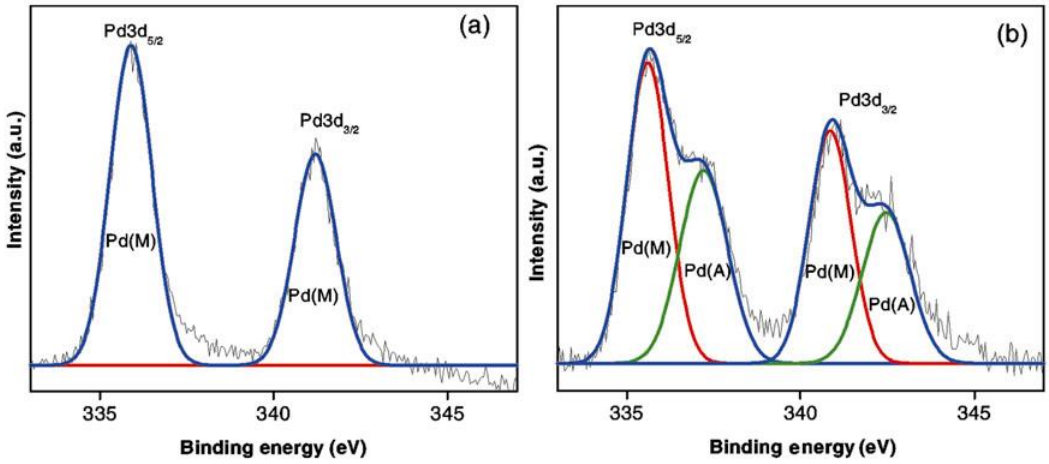

Figure 4. Core level spectra of Pd ($3d_{5/2}$ and $3d_{3/2}$) at temperatures of (**a**) 25°C, (**b**) 400°C, respectively. Peaks Pd (M) and Pd (A) corresponds to Pd metal and Pd alloy.

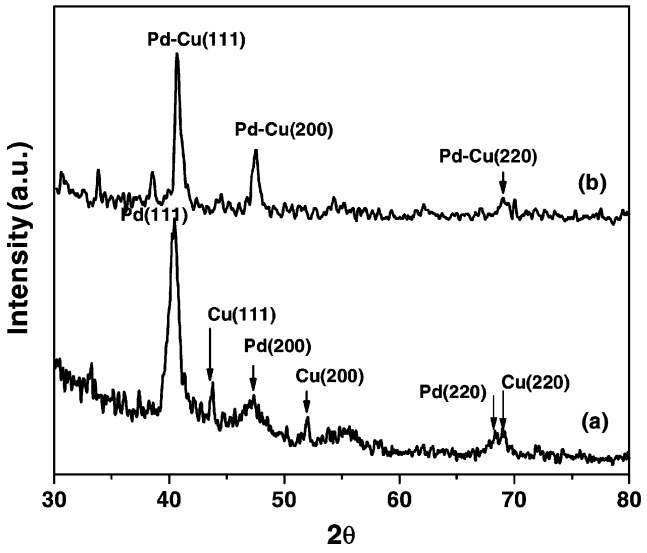

Figure 5. X-ray diffractograms of (**a**) as-deposited and (**b**) 400°C annealed Cu/Pd bimetal layers.

nanoparticle (NP) layers has been investigated. Two types of samples have been studied; (1) Ag(TF)/Pd(TF) and (2) Ag(NP)/Pd(TF). X-ray diffractogram of as deposited and 300°C annealed samples are shown in figure 6. X-ray diffractogram of as-deposited Ag(TF)/Pd(TF) sample show Pd (111) peak at 40·08° and a small shoulder at 38·28° that corresponds to Ag (111) peak. On annealing, Ag (111) and Pd (111) peaks merge and Ag–Pd (111) peak occurs at 39·95°, whereas in Ag(NP)/Pd(TF) sample, peak corresponding to Ag is not observed. However, general XPS scan confirm the presence of Ag on the surface in both Ag(TF)/Pd(TF) and Ag(NP)/Pd(TF) bimetal layers. The absence of Ag (111) peak in XRD studies in Ag(NP)/Pd(TF) is attributed to (1) low intensity due to low mass thickness of Ag and (2) due to broad nature of XRD peak because of nanoparticle nature of Ag. Position of Pd (111) peak remains same even after annealing. This suggests that alloy formation is suppressed in Ag (NP)/Pd (TF) nanoparticle based sample. Valence band spectra of as-deposited and 300°C annealed samples obtained from XPS studies are shown in figure 7. New states emerge on annealing in case of Ag(TF)/Pd (TF) sample, indicating alloying between Ag and Pd. Suppression of alloy formation is also observed at Gd–Pd interface when Gd nanoparticles are used in place of thin films.[20] Thus GAXRD and XPS studies imply that alloying between Ag and Pd is suppressed in Ag(NP)/Pd(TF) bimetal layers.

On hydrogen loading, resistance change of about 2% and 5% is observed in 300°C annealed Ag(TF)/Pd(TF) and Ag(NP)/Pd(TF) samples as shown in figure 8. Along with low sensitivity, large response time has been observed in Ag(TF)/Pd(TF) bimetal layers as compared to Ag(NP)/Pd(TF). Hence, alloying suppresses the hydrogen sensing response in Ag(TF)/Pd(TF) bimetal layer system. This is explained on the basis of d-band centroid positions of Pd and Ag. D-band centroids of these metals are quite far apart, therefore on annealing there is no common valence band formation as occurs in case of Cu/Pd bimetal layer system. Density of states near the Fermi level also reduces on alloy formation between Ag

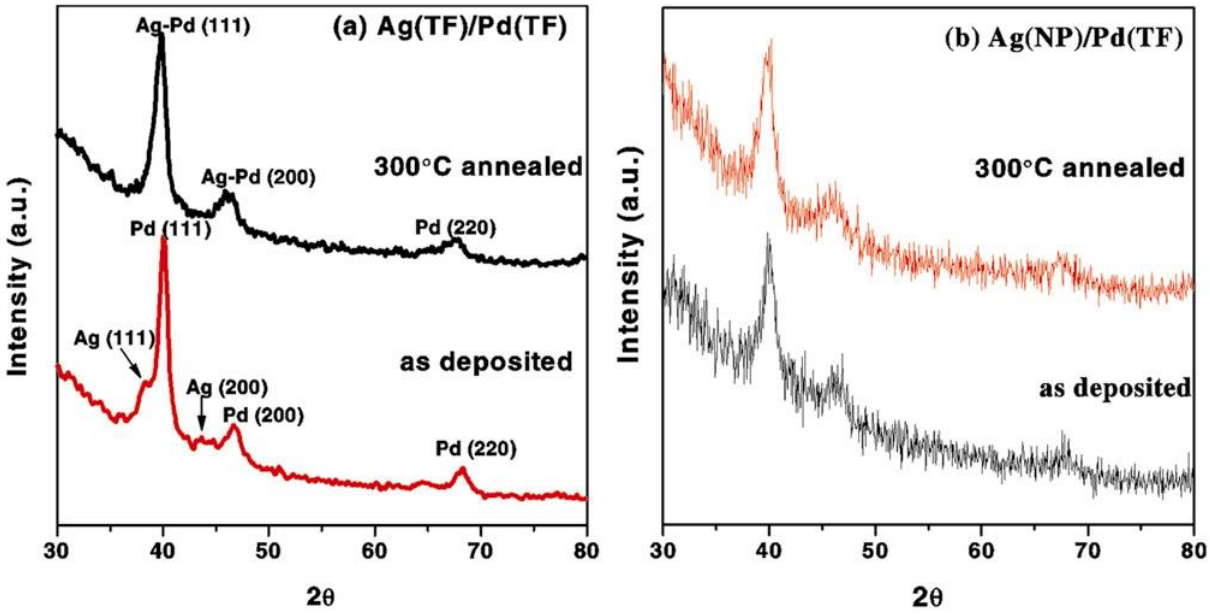

Figure 6. X-ray diffractograms of as-deposited and 300°C annealed (**a**) Ag(TF)/Pd(TF) and (**b**) Ag(NP)/Pd(TF) samples.

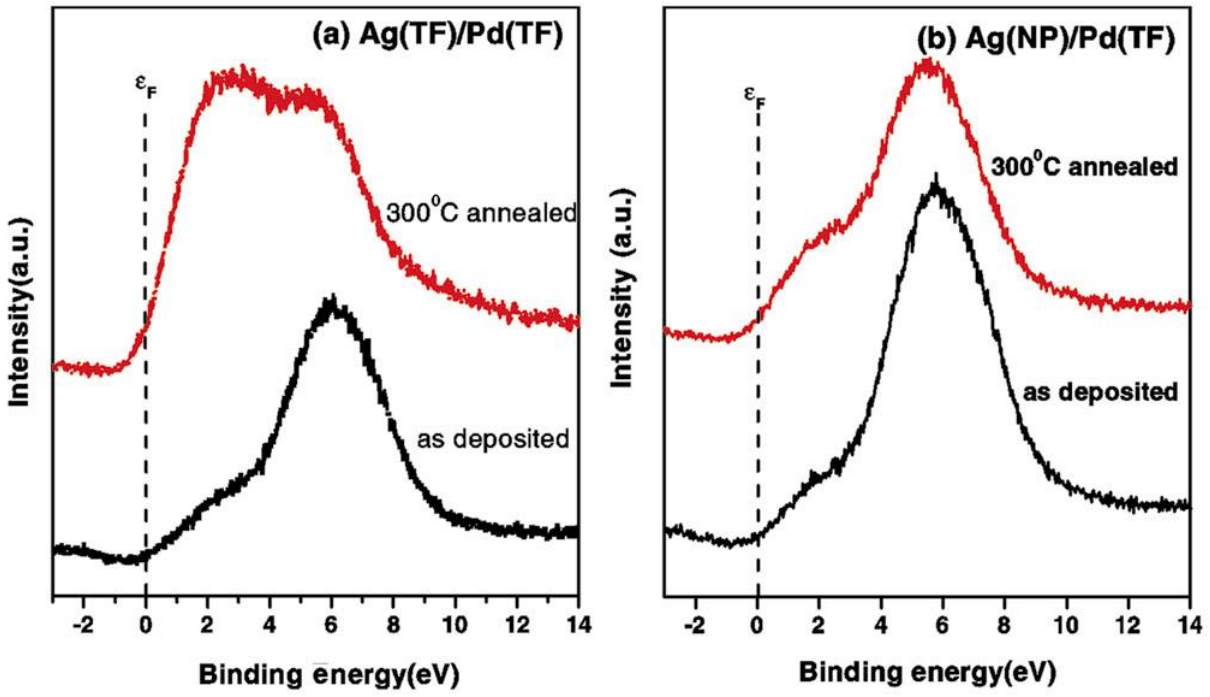

Figure 7. Valence band spectra of as-deposited and 300°C annealed (**a**) Ag(TF)/Pd and (**b**) Ag(NP)/Pd(TF) samples.

and Pd.[21] As a result, interaction of Pd with hydrogen gets reduced on annealing due to alloy formation between Ag and Pd in Ag(TF)/Pd(TF) bimetal layers. This effect can be reduced by using Ag nanoparticles in place of Ag thin films.

4. Conclusions

Cu/Pd and Ag/Pd bimetal layers show reversible and stable hydrogen sensing response. On alloy formation, catalytic activity of Pd towards H_2 gets en-

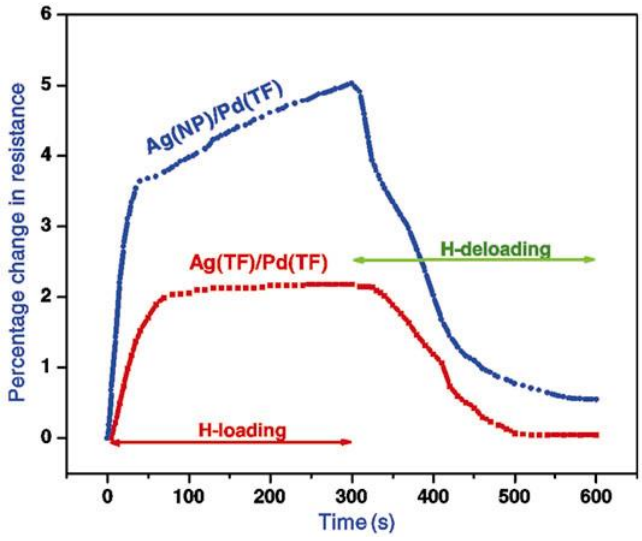

Figure 8. Hydrogen sensing response of 300°C annealed Ag (TF)/Pd(TF) and Ag(NP)/Pd(TF) samples.

hanced in case of Cu(TF)/Pd(TF) bimetal layer structures and decreases in case of Ag(TF)/Pd(TF) bimetal layer structures. Alloying of Ag with Pd is suppressed in case of Ag(NP)/Pd(TF) bimetal layers.

Acknowledgement

One of the authors (MK) thanks Council of Scientific and Industrial Research (CSIR), India for providing Senior Research Fellowship.

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