Journal of Alloys and Compounds, *185* (1992) 295–300
JALCOM 241

Hydrogen permeability for oxide–metal multilayered films

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(Received January 8, 1992)

Abstract

The hydrogen permeability of multilayered films consisting of various oxide and metal films, *e.g.* V_2O_5/Cu, was investigated using the colouring phenomenon of amorphous WO_3 and was found to be associated with the capability of dissociation of hydrogen molecules and the hydrogen densities of the oxide layers.

Hydrogen separation has been performed using V_2O_5/Cu multilayered films formed on a polyimide membrane. The hydrogen permeability coefficient of the films in the temperature range 343–368 K was found to be about 10 times as large as that of copper films owing to the capability of hydrogen dissociation at the V_2O_5/Cu double layer and owing to the large amount of hydrogen taken up by V_2O_5. Mixtures of H_2–CO and H_2–Ar with 50 mol% H_2 had a concentration of H_2 as high as 97 mol% after permeation through the membrane. When an $LaCu_5$ film was formed between the copper and polyimide film, the hydrogen permeability coefficient of the film increased owing to enhanced recombination of H atoms.

1. Introduction

Blue coloration of a transparent amorphous WO_3 (a-WO_3) film has been known to occur as a result of a double injection of protons and electrons to form a tungsten bronze [1].

Adachi and coworkers reported that a-WO_3 films coated with hydrogen storage alloys such as $LaNi_5$ coloured blue when held in an atmosphere of hydrogen gas, while films covered with copper exhibited no change [2, 3]. They also revealed that V_2O_5/Cu/a-WO_3 multilayered films exhibited blue shading of a-WO_3 after applying an H_2 pressure [4, 5]. These phenomena can be regarded as being due to hydrogen spill-over [6]. Hydrogen injection into a-WO_3, however, did not occur when the copper and V_2O_5 layers existed separately and there were some cases where no coloration was observed even though an oxide layer was combined with a metal layer, *e.g.* SiO_2/Cu.

In the present study the hydrogen permeability of multilayered films consisting of various metals and oxides is investigated by using the coloration of the a-WO_3 film in order to clarify the mechanism of hydrogen permeation

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0925-8388/92/$5.00

through the oxide/metal dual-layered films. Furthermore, the hydrogen separation characteristics were studied using V_2O_5/Cu/polyimide composite films.

2. Experimental details

Figure 1 is a schematic representation of the test piece used to estimate the hydrogen permeabilities of the oxide/metal multilayered films. Films of a-WO_3, copper, various metals (silver, gold, cobalt and copper) and various oxides (V_2O_5, SnO_2 and SiO_2) were successively formed on a glass substrate. These metal and oxide layers were deposited using a conventional vacuum evaporation method, except for copper and SiO_2 layers which were prepared by means of a sputtering method. The copper layer between the a-WO_3 and metal layers was used to contrast the blue shade of a-WO_3 with the colour of copper metal. An H_2 pressure of 2.0×10^6 Pa was applied to the samples in a stainless steel vessel in the temperature range 296–363 K. The progress of coloration of the a-WO_3 film was observed at given intervals of elapsed time.

V_2O_5(0.3 μm)/Cu(1.1 μm) and V_2O_5(0.3 μm)/Cu(1.1 μm)/$LaCu_5$(0.03 μm) multilayered films deposited on a hydrogen-permeable polyimide membrane were used as hydrogen separation membranes. Gas mixtures of H_2(50 mol%)–Ar(50 mol%) and H_2(50 mol%)–CO(50 mol%) with a pressure of 1.5×10^5 Pa at around 318–368 K were applied to the V_2O_5-deposited side of the membranes. The characteristics of hydrogen separation were estimated by a hydrogen separation factor and a hydrogen permeability coefficient [7, 8].

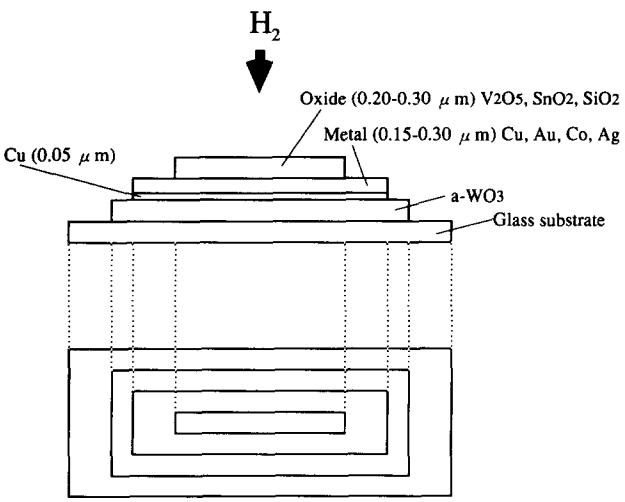


Fig. 1. Schematic representation of test piece.

3. Results and discussion

3.1. Hydrogen permeability

Table 1 shows the colouring behaviour of a-WO_3 on various oxide/metal multilayered films after applying hydrogen for 4.8×10^2 s at 314 K. The colour of a-WO_3 on the V_2O_5/Cu film showed the deepest shade of blue of all the samples. This indicates that the hydrogen permeation rate of the film is the largest of all the multilayered films. The blue shade of a-WO_3 under the area covered with the V_2O_5/Cu layer was found to be deeper than that with the copper layer alone. The colouring behaviour of the V_2O_5/(Au,Co) and SnO_2/(Au,Cu,Ag) films is unlike that of the V_2O_5/Cu film, a uniform blue shading of a-WO_3 being observed under the area coated with the metal layer. In the case of the SiO_2/(Au,Cu,Ag) films no colouring occurred. It was confirmed that the rates at which coloration had proceeded were in the following order:

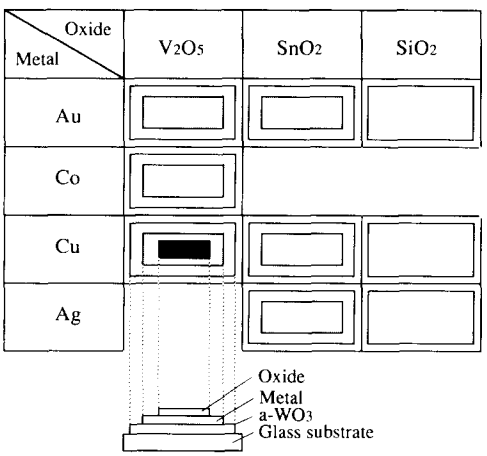
$$V_2O_5/Cu > V_2O_5/Au > V_2O_5/Co = SnO_2/(Au,Cu,Ag) \gg SiO_2/(Au,Cu,Ag)$$

The difference in colouring behaviour of the various oxide/metal multilayered films may be attributed to the capability of dissociation of hydrogen molecules at oxide/metal films and of hydrogen storage in the oxides, both the diffusivity and solubility of hydrogen in the metals being important.

V_2O_5 exhibits a phenomenon of electrochromism similar to WO_3 [9] and SnO_2 [10]. When hydrogen gas was applied to the Cu/V_2O_5 and Cu/SnO_2 films, a colour change of V_2O_5 and SnO_2 was observed, though no colouring

TABLE 1

Schematic illustration of multilayered specimens and their colouring behaviour at 314 K and 2×10^6 Pa



occurred when these oxide films existed separately. This fact indicates that these two oxides were reduced by the spilt-over hydrogen. Consequently, it is confirmed that the Cu/V_2O_5 and Cu/SnO_2 films can dissociate hydrogen molecules into atoms or ions.

V_2O_5 is known to absorb hydrogen at high densities comparable to that of liquid hydrogen [11]. The spilt-over hydrogen dissolves into the V_2O_5 layer and the hydrogen concentration between the V_2O_5 and copper layers becomes adequately high, so that the concentration gradient of hydrogen reaches a critical value needed for the diffusion of hydrogen in the copper layer. Therefore the blue colour of the area covered with V_2O_5/Cu has become sufficiently deep before colouring of the surroundings.

Since the capability of hydrogen storage in SnO_2 is very poor in comparison with that in V_2O_5, the dissociated hydrogen appears to spill over the surface of the copper layer and permeates through the copper layer into the SnO_2/Cu film. Consequently, the colouring of a-WO_3 was observed uniformly under the copper layer.

The SiO_2/Cu film does not seem to be able to dissociate hydrogen molecules because no colouring occurred.

There is a difference in the colouring behaviour of the metal layers formed under the same oxide layer, *e.g.* V_2O_5/Cu *vs.* V_2O_5/Au. For the V_2O_5/Au film the colouring of a-WO_3 occurred uniformly under the region covered with the gold layer. The diffusivity of hydrogen (D_H) in copper and the solubility of hydrogen (S_H) in copper at 773 K are 2.7×10^{-9} m^2 s^{-1} and 2×10^{-1} at.% H respectively [12, 13]. Both D_H and S_H for copper are larger than for gold ($D_H=1.4\times10^{-9}$ m^2 s^{-1}, $S_H=3\times10^{-2}$ at.% H) [12, 13]. Since the permeation rate of hydrogen is dominated by the product of D_H and S_H, copper exhibits a large permeation rate in comparison with gold. Therefore it appears that the large amount of hydrogen stored in the V_2O_5 layer was transported to the copper layer immediately, permeated through the copper layer and was injected into the a-WO_3 layer. However, since the gold layer hardly absorbs the hydrogen supplied from the V_2O_5 layer, most of the hydrogen did not dissolve into the gold layers directly but spilt from the interface between the V_2O_5 and gold layers. After spreading over the surface of the gold layer, the hydrogen dissolved into the gold layer.

3.2. Hydrogen separation characteristics

Since the permeation rate of hydrogen for the V_2O_5/Cu multilayered film was largest of all the samples, the hydrogen separation characteristics, such as the separation factor and permeability coefficient, were investigated using the film formed on the hydrogen-permeable polyimide membrane. Figure 2 reveals the temperature dependence of the hydrogen permeability coefficient for the V_2O_5/Cu and copper films. The coefficient for the copper film at 343 K was 5×10^{-18} m^2 s^{-1} Pa$^{-1/2}$. However, it was found that the permeation rate of the V_2O_5/Cu film became more than 10 times as large. This can be attributed to the fact that the V_2O_5/Cu film dissociates hydrogen molecules easily and the surface of V_2O_5 absorbs much hydrogen.

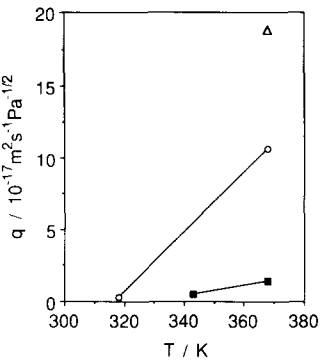


Fig. 2. Temperature dependence of hydrogen permeability coefficient for V_2O_5/Cu and V_2O_5/Cu/$LaCu_5$ multilayered films: ○, V_2O_5/Cu; △, V_2O_5/Cu/$LaCu_5$; ■, copper. Applied gas 99.999% H_2.

TABLE 2

Hydrogen separation characteristics of V_2O_5/Cu/polyimide films

Composition of applied gas (mol%)	Composition of film	Hydrogen permeability coefficient (10^{-17} m^2 s^{-1} $Pa^{-1/2}$)	Hydrogen concentration in permeated gas (mol%)	Hydrogen separation factor
H_2(50) – Ar(50)	V_2O_5/Cu	6.6	97.7	42.5
	V_2O_5/Cu/$LaCu_5$	14.4	> 99	> 99
H_2(50) – CO(50)	V_2O_5/Cu	6.2	> 99	> 99

In order to accelerate the recombination of H atoms, a thin $LaCu_5$ film was formed between the copper film and the polyimide membrane. The hydrogen permeability coefficient of the V_2O_5/Cu/$LaCu_5$ multilayered film obviously increased in comparison with that of the multilayered film without an $LaCu_5$ film.

Table 2 shows the hydrogen separation characteristics of the V_2O_5/Cu and V_2O_5/Cu/$LaCu_5$ films deposited on the polyimide membrane. A mixture containing 50 mol% H_2 was concentrated to 94.6 mol% H_2 using the polyimide membrane. The hydrogen concentration in the permeated gas increased to 97.7 mol% H_2 or more (as high as 99 mol% H_2) when the V_2O_5/Cu and V_2O_5/Cu/$LaCu_5$ layers were formed on the polyimide membrane. It is worth noting that there was no difference in separation factor between the H_2–Ar and H_2–CO gas mixtures used as the applied gas. The V_2O_5/Cu film appears to have a large resistance to harmful CO as an impurity in the hydrogen gas.

Acknowledgment

This work was partially supported by a Grant-in-Aid for Developmental Scientific Research (03750581) from the Ministry of Education, Science and Culture.

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