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A Hydrogen Permeation through Metal-oxide Heterojunction

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The hydrogen permeability of dual-layered films of Cu and various oxides was investigated by using the colouring phenomenon of amorphous WO_3 and was found to depend on the difference in work function between Cu and oxides used.

The hydrogen permeation through metal-oxide multi-layered films which have a V_2O_5 layer has been investigated by using the colouration of the amorphous WO_3 (a-WO_3) thin film,[1] which indicates the formation of a tungsten-bronze described by the following reaction:[2]

$$H^+ + e^- + 1/x\ WO_3 \longrightarrow 1/x\ H_xWO_3 \qquad (1)$$

The sandwich-type thin film (V_2O_5/Cu/a-WO_3) was found to exhibit blue shading of a-WO_3 after applying a H_2 pressure. This phenomenon can be regarded as one of the types of the hydrogen spillover. However, the hydrogen injection into a-WO_3 did not occur when the Cu and V_2O_5 layers existed separately and there are some cases that no hydrogen permeation occur even though an oxide layer combined with a metal layer. Therefore, it seems that the formation of the interface between metals and oxides plays an important role for the occurrence of hydrogen permeation through metal layers and that the hydrogen permeation occurs only in the case that the electronic structure of the metal-oxide heterojunction is in a

convenient state for the hydrogen permeation through the boundary in such a type of the dual-layered thin film.

In the present study, the hydrogen permeability of dual-layered films of Cu and various oxides is investigated in order to discuss how electronic work functions of Cu and oxides are concerning with the hydrogen permeability.

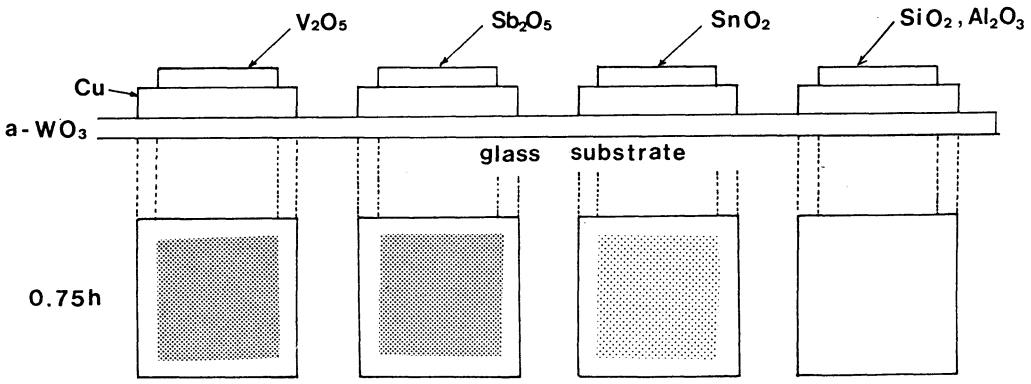

Fig. 1. Schematic illustration of multi-layered specimen and their colouring behaviour under the condition of 343 K, $2x10^6$ Pa H_2.

The schematic presentation of specimens used for the present study is given in Fig. 1. The a-WO_3 thin film which has a thickness of ca. 0.5 μm was coated on a glass substrate using conventional vacuum deposition. A 0.8 μm thick Cu film was formed on the a-WO_3 layer by magnetron-sputtering at an ambient atmosphere of $1.3x10^{-3}$ Pa. V_2O_5, Sb_2O_5, SnO_2, SiO_2, and Al_2O_3 were deposited on the top of the layers. Vacuum evaporation of powder materials was used for the oxides at an ambient pressure of $6.7x10^{-3}$ Pa. The SiO_2 thin film was formed by means of sputtering under the same atmosphere as that for the Cu film. Each film of oxides on the Cu layer has a thickness of ca. 0.5 μm. A hydrogen pressure of $2.0x10^6$ Pa was applied to the specimens in a stainless-steel vessel at 343 K for 0.75 h, and the colouring behaviour of a-WO_3 layer was observed.

Figure 1 shows the coloured state of a-WO_3 after applying H_2 to each

specimen for 0.75 h. A blue shade of a-WO_3 was observed for V_2O_5, Sb_2O_5, and SnO_2. Specimens with SiO_2 or Al_2O_3 exhibited no colouration. The permeability estimated from the colouring decreased in the following order:

$V_2O_5 \simeq Sb_2O_5 > SnO_2 > SiO_2 > Al_2O_3$

This order seems to be related to values of the electronic work function for the oxides. The values of work function for Cu and oxides[3-6] are listed in Table 1. If the work function for a oxide (ϕ_{ox}) is much larger than that for Cu (ϕ_{Cu}), the permeability for the oxide-Cu system is large and no hydrogen permeation is observed for the reverse.

Table 1. Values of work function used

Substance	Work function/eV	$\phi_{Cu} - \phi_{ox}$/eV
Cu[3]	4.9	-
V_2O_5[4]	6.7	-1.8
SnO_2[5]	5.2	-0.3
SiO_2[6]	5.0	-0.1
Al_2O_3[6]	4.7	0.2

It is assumed that protons and electrons electrolytically dissociated at the surface of the oxide penetrate through the oxide layer and that these carriers are injected into the metal layer through the boundary by the hydrogen spillover. In the case of $\phi_{ox} < \phi_{Cu}$, a Shottkey barrier is expected to be formed from the inner side of the oxide layer to the boundary. The electron migration is prevented by the Shottkey barrier, so that the hydrogen permeation through such a type of heterojunction seems to hardly occur. This case corresponds to the combination of Al_2O_3 and Cu. In the case of $\phi_{ox} > \phi_{Cu}$, a gradual potential drop is formed at the boundary region instead of the Shottkey barrier. Electrons migrate into the metal layer along the potential drop and the protons appear to

penetrate the boundary and then slip into the Cu layer because of the attraction by electrons.

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