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Effects of the Oxide/Metal Exposed Interface on Hydrogen Permeabilities of V_2O_5/Cu Multilayered Films

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Hydrogen permeabilities of V_2O_5/Cu multilayered films having various lengths of the perimeter of the V_2O_5/Cu interface were investigated. Although the hydrogen permeability of the multilayered film increased with the length of the perimeter, it increased only slowly when the length of the perimeter exceeded 9.6×10^{-2} m since the hydrogen concentration of the V_2O_5 layer is saturated at the region near the V_2O_5/Cu interface.

A transparent amorphous WO_3 (a-WO_3) film has been known to show blue coloration by double injection of protons and electrons due to the formation of tungsten bronze.1) Adachi and coworkers reported that an a-WO_3 film coated with a hydrogen storage alloy such as $LaNi_5$ colored blue when it was held in an atmosphere of hydrogen, and that hydrogen easily permeated through the copper layer in a $LaNi_5$/Cu/a-WO_3 multilayered film whereas the hydrogen injection into the a-WO_3 film hardly occurred when the film was covered with copper alone.2,3) They also revealed that the similar phenomenon was observed in some sandwich-type films using oxides, such as V_2O_5, instead of $LaNi_5$.4)

Recent study5) clarified that the order of hydrogen permeabilities for several multilayered films containing layers of hydrogen-bronze forming oxides, such as V_2O_5, MoO_3 and V-Mo mixed oxide, agreed very well with that of enthalpy changes for dissociating hydrogen molecules on Pt impregnated oxides. The result strongly supports that the ability of dissociation of hydrogen molecules is one of the factors determining the hydrogen permeabilities of the multilayered films. The hydrogen permeabilities, however, may be influenced also by the hydrogen storage abilities of the oxides so that it appears to be difficult to evaluate these two effects separately when the oxide/metal combination is varied.

On the other hand, the hydrogen permeability of multilayered film decreases drastically by hiding the perimeter of the oxide/metal interface, where the interface is exposed to the atmosphere, so that the hydrogen molecules appeared to be dissociated thereat.5) Therefore, the ability of dissociation for hydrogen molecules is expected to be changed depending upon the length of the perimeter of the interface for the same oxide/metal combination. The purpose of this study is to estimate the effect of the ability of dissociation for hydrogen molecules on the hydrogen permeabilities of the metal/oxide multilayered films by using V_2O_5/Cu films having various lengths of the perimeter of the V_2O_5/Cu interface.

Figure 1 presents a schematic representation of the test pieces for estimation of hydrogen permeabilities on

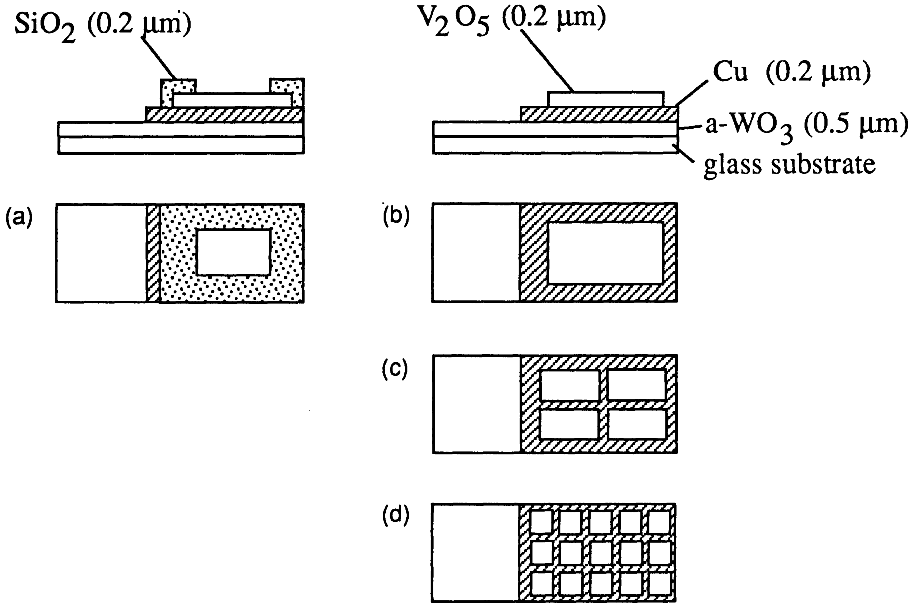

Fig. 1. Schematic representation of the samples.

V_2O_5/Cu multilayered films. Films of a-WO_3 (thickness: 0.5 µm), copper(thickness: 0.2 µm), and V_2O_5 (thickness: 0.2 µm) were successively formed on a glass substrate. The layers of V_2O_5 and a-WO_3 were deposited using a conventional vacuum evaporation method, while the Cu layer was formed by means of an rf sputtering method. The starting materials of V_2O_5, WO_3 were reagent grade of V_2O_5 (99.8 %) and WO_3 (95 %). A 99.99 % of Cu metal disk was used as the target of rf sputtering. By means of an X-ray diffraction method, the V_2O_5 and Cu layers deposited were found to be amorphous and crystal, respectively. For the samples (b) - (d), the V_2O_5 layers were deposited in various morphologies to vary the length of the perimeter of the V_2O_5 layer. At the perimeter, the V_2O_5/Cu interface is terminated and exposed to the atmosphere. The length of the perimeter of the V_2O_5/Cu interface for the samples (b)-(d) were 4.8, 9.6, 18.4 ($\times10^{-2}$ m), respectively, while the areas of the coverage with V_2O_5 were fixed at 1.35×10^{-4} m^2. On the other hand, the perimeter of the V_2O_5/Cu interface for the sample (a) was sealed with SiO_2 (thickness: 0.4 µm) deposited by using an rf sputtering method to hide the exposed interface.

An H_2 pressure of 2.0×10^6 Pa was applied to the test pieces in a stainless steel vessel at 343 K for 1.8×10^4 s. The V_2O_5 and Cu layers were, then, peeled off from the test pieces and the residual hydrogenated a-WO_3 layers were supplied to the measurements of absorption spectra. The amount of hydrogen injected into the a-WO_3 film through the V_2O_5/Cu multilayered films was determined from the spectra according to the method described in the previous study.5) Figure 2 presents the hydrogen contents permeated through the multilayered films as a function of the length of the perimeter of the V_2O_5/Cu interface. The hydrogen content permeated increased with the length of the perimeter. No hydrogen permeation was observed for the specimen (a). The data was plotted on the origin of the coordinate axes. The hydrogen content increased rapidly in the range of the exposed boundary from zero to 9.6×10^{-2} m while it increased slowly beyond 9.6×10^{-2} m.

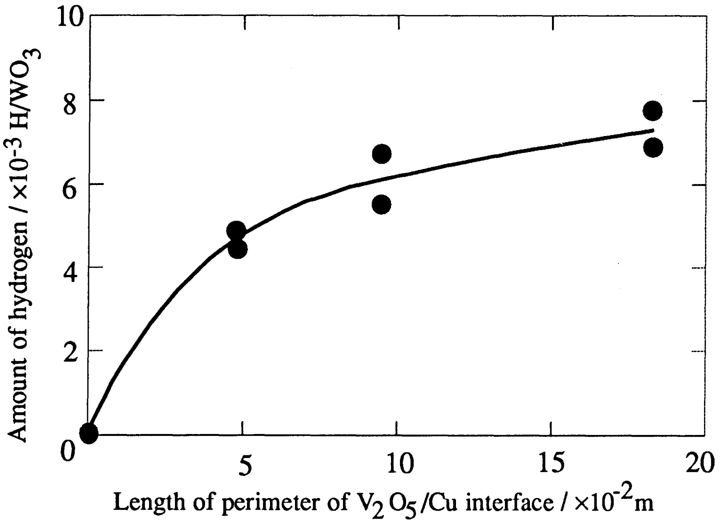

Fig. 2. Hydrogen contents permeated through the multilayered films as a function of the length of the perimeter of the V_2O_5/Cu exposed interface.

All samples had the same area of coverage with the V_2O_5 layer so that the difference in the hydrogenpermeability of each multilayered films was attributed to the difference in the length of the perimeter of the V_2O_5/Cu interface where the hydrogen molecules were considered to be dissociated. The hydrogen atoms dissociated diffuse at the interface and are absorbed by both the V_2O_5 and Cu layers. The amounts of hydrogen to be absorbed, however, may be very different for these layers. V_2O_5 is one of well known hydrogen bronze forming oxides and has been reported that Pt impregnated V_2O_5 absorbs hydrogen with the amount of 4.0 (H/V_2O_5).6) On the other hand, the hydrogen solubility in Cu has been reported to be less than 8.3×10^{-7} (H/Cu)7) and Cu hydride synthesized from an aqueous solution is not thermally stable at 343 K.8) The V_2O_5 layer used was an amorphous film so that the hydrogen storage capability of the V_2O_5 layer may be smaller than that for a crystalline powder. Amorphous V_2O_5 films prepared by vacuum evaporation, however, exhibits significant electrochromism 9, 10) so that, in spite of an amorphous state, still considerable amount of hydrogen appears to be absorbed in V_2O_5. Therefore, the V_2O_5 layer appears to be able to absorb much hydrogen in comparison with the Cu layer. The hydrogen concentration in the V_2O_5 layer increases at the region near the V_2O_5 /Cu interface and a large hydrogen concentration gradient appears to be generated in the Cu layer. The probability of the dissociation of hydrogen molecules increases with the length of perimeter of the V_2O_5/Cu interface and the diffusion of hydrogen into the V_2O_5 layer proceeds remarkably. Subsequently, the hydrogen concentration near the V_2O_5/Cu interface becomes large so that the amount of hydrogen permeated through the Cu layer increases significantly. The hydrogen concentration, however, cannot increase over the saturated value which restricts the hydrogen concentration gradient in the Cu layer. For the above reason, the hydrogen content permeated appears to increase only slowly for the length of the perimeter exceeding 9.6×10^{-2} m.

The large hydrogen permeability of the multilayered film may be partly due to the amorphous structure of the V_2O_5 layer. For crystalline V_2O_5 powders, reversible intercalation and deintercalation of hydrogen occurs only in a small amount of hydrogen up to x = 0.3 of $H_xV_2O_5$ because of the strong interaction between protons and oxygen ions.11) On the other hand, V_2O_5 films prepared by vacuum evaporation have open structures wherein the mobility of protons is expected to be high. Therefore, the hydrogen absorbed in the V_2O_5 layer may easily move into the Cu layer.

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