Hydrogenation and Dehydrogenation Properties of [AlN-Pd]/Y and [AlOx-Pd]/[AlN-Pd]/Y Films

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We report hydrogenation and dehydrogenation properties of the [AlN-Pd]/Y and [AlOx-Pd]/[AlN-Pd]/Y films. The [AlN-Pd] and [AlOx-Pd]/[AlN-Pd] composite cap layers were deposited on yttrium layers by a rf-magnetron sputtering method. The cap layers were used to protect the Y layers from oxidation. Electrical resistivity of the films was measured during a few cycles of hydrogen loading and unloading in order to monitor the hydrogenation and dehydrogenation of the Y layers. As repeating the cycles, the amplitude of resistivity change was gradually reduced for the [AlOx-Pd]/[AlN-Pd]/Y film. On the other hand, the [AlOx-Pd]/[AlN-Pd] protective layer showed much better stability against the high temperature steam than the [AlN-Pd] layer. [doi:10.2320/matertrans.48.635]

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It is well known that the rare-earth thin films cause a metal-semiconductor transition due to hydrogenation and dehydrogenation.¹⁻³⁾ Simultaneously, visible light transmissivity and electric resistivity of the films change reversely.^{2,4-6)} The rare-earth films were usually capped with thin palladium layers to protect the chemically reactive rare-earth layer against oxidation and catalyze the dissociation of H₂ molecules.

Recently, we have found composite materials composed of ceramics and metals, which can be synthesized easily, permeate the hydrogen quickly and also prevent rare-earth layers from oxidation. Moreover, the Pd cap layer shall be replaced by them because the stability of the rare earth layers was significantly improved.

In this paper, we report the hydrogenation and dehydrogenation properties of composite materials/yttrium layered films. These micro-structures of two composite materials : AlN-Pd and AlOx-Pd were also investigated.

The [AlN-Pd](7 nm)/Y(300 nm) and [AlOx-Pd](3.5 nm)/[AlN-Pd](3.5 nm)/Y(300 nm) films were prepared by radio r.f.-magnetron sputtering equipment. The vacuum system provides a residual pressure near 0.933×10^{-4} Pa. Ar, Ar/N₂(15%), Ar/O₂(40%) with the purity of 99.99%, were used as sputtering gases, the gas flow rate was adjusted with a mass flow controller to obtain a pressure of 0.933 Pa. The sputtering rate was Y = 0.51 nm/s, and AlN-Pd = 0.31 nm/s, AlOx-Pd = 0.24 nm/sec respectively. The Pd concentrations were about 25 at% for both composites. Pd concentration was measured by Electron Probe Micro-Analysis (EPMA). A typical HR-TEM plain-view image of the composite layer is shown in Fig. 1. The electron diffraction patterns for the composite layers showed only the ring corresponding to the Pd lattice plane distance. These results indicate Pd clusters with less than 5 nm diameter are distributed in the amorphous-like AlN host matrix.

To investigate the characteristics of [AlOx-Pd] composite layers, we synthesized [AlOx-Pd]/[AlN-Pd]/Y films. We have deposited a few kinds of composite layers consisted of

Fig. 1 HR-TEM plain-view image of the [AlN-Pd] composite material. The black spherical clusters were Pd with less than 5 nm diameter. Similar structures were observed also for the [AlOx-Pd] composite.

Pd and oxide based host matrix, including aluminum oxide, as the topmost layers on Y layers. But we found that the Y layers did not absorb hydrogen for these samples. According to literature,⁷⁾ thin rare earth oxide layer might be formed between the metallic rare earth and oxide-base layers and block the hydrogen migration. The hydrogen permeation through the composite layers was examined by the electrical resistivity behaviors¹⁾ accompanying with hydrogenation and dehydrogenation of the rare earth layers. The changes of electrical resistivity for the composite films in alternating hydrogen pressure, which were examined with composite single layered films, were much smaller than those of Y layers. By use of X-ray diffraction, it was confirmed that the YH₃ phase just after the hydrogenation and only YH₂ phase after the dehydrogenation existed. Moreover, the visual light transmissivity changed considerably, which was consistent with the earlier literature.¹⁾ No micro-cracks or exfoliations were found by optical microscopy, secondary electron microscopy (SEM) and atomic force microscopy (AFM) surface observations. These results indicate that the hydrogen permeated through the composite layers and induced the phase changes in Y layers.

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Fig. 2 Time dependences of electrical resistivity of the films during hydrogenation. X-axis is elapsed time after the introduction of hydrogen gas. (a) [AlN-Pd]/Y, (b) [AlOx-Pd]/[AlN-Pd]/Y

The hydrogenation was performed by introducing hydrogen gas into a vacuum container up to about 0.1 MPa and dehydrogenation was done by evacuating the container at room temperature. The hydrogenation and dehydrogenation cycle was repeated at least 3 times. The time dependences of the electrical resistivity of these films during hydrogenation and during dehydrogenation are shown in Fig. 2 and Fig. 3, respectively.

As shown in Fig. 2, the resistivity of [AlN-Pd]/Y and [AlOx-Pd]/[AlN-Pd]/Y films was increased by more than 100 times by hydrogenation and the required times for the onset of the resistivity increase were significantly reduced after the first dehydrogenation. Some reasons for the accelerated resistivity response of these once hydrogenated films may be enumerated. The most possible reason would be the difference of initial phase of Y layers. The XRD measurements showed that if the Y layers were hydrogenated once, they did not return to h.c.p Y phase and terminated at f.c.c YH₂ phase even in vacuum or air atmosphere. It is known that the YH₂ phase is quite stable at room temperature.¹⁾ During the first hydrogenation, the Y layers must pass through the phase transition: Y to YH₂ initially. On the contrary, this phase transition is not necessary in the second and later hydrogenation processes.

To examine the durability against the high temperature steam, the [AlN-Pd]/Y and [AlOx-Pd]/[AlN-Pd]/Y films were exposed to 100% steam at 373 K for 10 minutes. The [AlOx-Pd]/[AlN-Pd]/Y film after the exposure showed no visible changes and could be hydrogenated by being placed in

Fig. 3 Time dependences of electrical resistivity of the films during dehydrogenation. X-axis is elapsed time after evacuation started. (a) [AlN-Pd]/Y, (b) [AlOx-Pd]/[AlN-Pd]/Y

H₂ atmosphere. On the other hand, the [AlN-Pd]/Y films flaked off thoroughly after the exposure.

As the conclusion, the [AlOx-Pd]/[AlN-Pd] and [AlN-Pd] layers permeate hydrogen quickly and Y underlayer can be hydrogenated easily. The durability against the high temperature steam was improved by depositing the [AlOx-Pd] as the topmost layer.

If the composite materials are employed as industrial applications, for example, as the hydrogen leak sensor, they have many advantages: lower cost, higher mechanical and chemical stabilities, higher electrical resistivity, which enables us to detect the electrical resistivity changes of rare earth layer more sensitive, and soon.

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