Structure Dependence in the Hydrogenation of Acetylene over Columnar Pd Film

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Synopsis. Pd films prepared by the UHV RF sputtering system had the tapered columnar structure as observed using SEM. The microstructure of the films changed with the film thickness. This affected the hydrogenation of acetylene. The Pd films which showed the strong (220) intensity in XRD exhibited the high ethylene selectivity.

It is known that a preferred orientation of evaporated metal films on glass substrates alters with the film growth.[1] The changes in the microstructure of metal films are expected to influence their catalytic properties. Previously, structure dependence was observed in the hydrogenation of 1,3-butadiene over Ru thin films[2] prepared by an RF sputtering method.[3] The microstructure of the Ru films changed with the film thickness, that is, the (101) peak increased and the (002) peak decreased with increasing film thickness in X-ray diffraction patterns (XRD). The partial hydrogenation of 1,3-butadiene was found to proceed preferably over the (002) face of Ru.

In this investigation, similar structure dependence is examined on Pd films prepared using the new RF sputtering system equipped with a ultra high vacuum (UHV) chamber.

Experimental

A schematic drawing of the experimental apparatus is shown in Fig. 1. The UHV chamber is 200 mm in diameter and 175 mm in height in inside dimensions and evacuated up to 10^{-8} Torr (1 Torr=133.322 Pa) using a turbo molecular pump (Shimadzu TMP-150, 160 l/s). The target (70 mm in diameter) and the substrate (70 mm in diameter) are at floating and at ground potential, respectively, and placed with their distance of 60 mm at the center of the UHV chamber. A high purity gas of Ar (99.9995%) at a pressure of 0.02 Torr was introduced into the chamber through a variable leak valve. The purity of Ar was confirmed using a quadrupole mass filter (ULVAC MSQ-150A) in advance of the glow discharge. RF power (13.56 MHz) of 100 W was supplied to the target on which a Pd plate (99.95%) was mounted. The glow discharge was generated between the target and the substrate because the shield (ground potential) around the target prevented the discharge which occurred at the undesirable place. Sputtered Pd atoms were deposited on a Pyrex glass substrate. The film thickness was simultaneously measured using a film thickness monitor with a quartz oscillator (Inficon XTM) which was set in the neighborhood of the substrate. Under this condition (Ar: 0.02 Torr, RF power: 100 W), the Pd film was deposited at a rate of 13 nm min^{-1}. The target, the substrate, and the sensor head of the film thickness monitor were water-cooled and maintained at room temperature.

The structure of the Pd films with various thickness was investigated by XRD and scanning electron microscopy (SEM). These investigations were performed by using

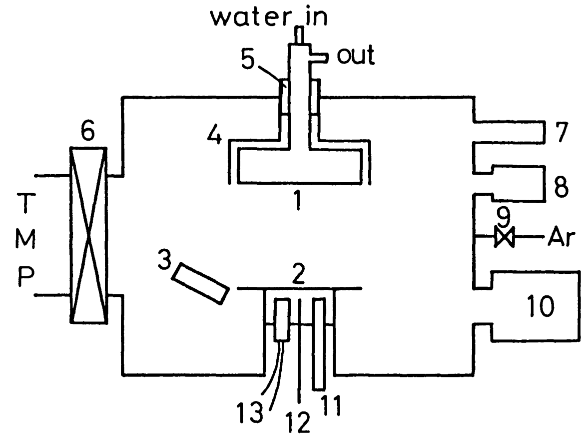

Fig. 1. Schematic drawing of the UHV RF sputtering apparatus. 1: target, 2: substrate, 3: sensor head of film thickness monitor, 4: shield, 5: insulator, 6: bellows stop valve, 7: low vacuum gauge, 8: high vacuum gauge, 9: variable leak valve, 10: mass filter, 11: cooling water tube, 12: thermocouple, 13: heater.

Shimadzu VD-1 X-ray diffractometer and Akashi ALPHA-30A scanning electron microscope.

The hydrogenation of acetylene was carried out over the Pd films with various thickness at 273 K using a closed circulation system. A ratio of H_2/acetylene and a total pressure in the system were controlled to 6 and 140 Torr, respectively. The products of the hydrogenation were analysed by the gas chromatograph (Shimadzu GC-8A) with the thermal conductivity detector. A column used was an activated charcoal 3 m column.

Results and Discussion

In the XRD patterns of the Pd films, three peaks due to Miller indices (111), (200), and (220) of Pd fcc structure appeared at 40.3, 46.5, and 68.0 degree of 2θ. Figure 2 shows the changes in the relative intensity of these peaks with the film thickness. The (220) intensity steeply increased and the (111) intensity decreased with increasing film thickness. This indicates that the Pd film above 1 μm in thickness practically has the (220) oriented structure and that the microstructure of the Pd films is obviously changed with the film thickness. The (111) face is the most densely populated face in Pd fcc structure. The (111) face was preferentially oriented in the Pd films at the initial stage of the film growth. Then, the preferred orientation altered from the (111) orientation to the (220) orientation with the film growth. These results are agreed with the previous reports.[1,4]

Figure 3 is the SEM images of the surface view and the fracture cross section of the Pd film with 1 μm in

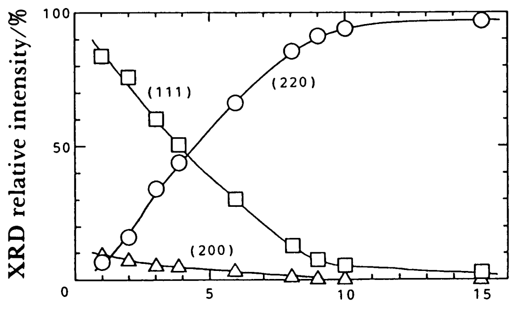

Fig. 2. Dependence of XRD relative intensity for the Pd films on film thickness.

thickness. The Pd film evidently had the tapered columnar structure as observed by Thornton.[5] The surface was not flat and the intercolumn boundaries were obviously voids. At the bottom of the Pd film, the columns were fine (about 40 nm). The diameter of the columns increased toward the top of the film. It was found that both the diameter and the length of the column increased with increasing film thickness. This was also observed in the surface view SEM images of the Pd films with various thickness. The average diameter of the columns was 200 nm in the Pd film with 1 μm in thickness. The column diameter was generally uniform except for some fine columns which had not yet grown. The SEM images elucidated the microstructure of the Pd film prepared by the RF sputtering method. XRD offers the relative composition of the crystal faces which are parallel to the substrate surface. Since the surface of the film is not flat, the (220) face, which is preferentially oriented in the Pd film with 1 μm in thickness, would not be exposed on the column surface in the SEM image. However, it is considered that each column in the SEM image has the same orientation.

The catalytic property of the microstructure of the Pd films with various thickness was evaluated in the hydrogenation of acetylene. Figure 4 shows the dependence of the activity and the initial selectivity for ethylene on the film thickness. The activity was estimated on the basis of the geometrical surface area of the substrate. The activity increased with increasing film thickness. The activity of the 1.5 μm Pd film was 5 times as great as that of the 100 nm Pd film. As observed in the SEM images, the columns grow with the film thickness and the intercolumn boundaries are voids. Therefore, the side of the column is considered to effectively participate in the hydrogenation of acetylene. The increase in the film thickness brings about the enhancement of the true Pd surface area, resulting in the high hydrogenation activity. On the other hand, the selectivity for ethylene in the hydrogenation of acetylene increased with increasing film thickness as well as the activity. The selectivity reached 96% on the Pd films above 800 nm in thickness. The Pd films which showed the stronger (220) intensity in its XRD pattern was found to exhibit the higher selectivity to ethylene. With the

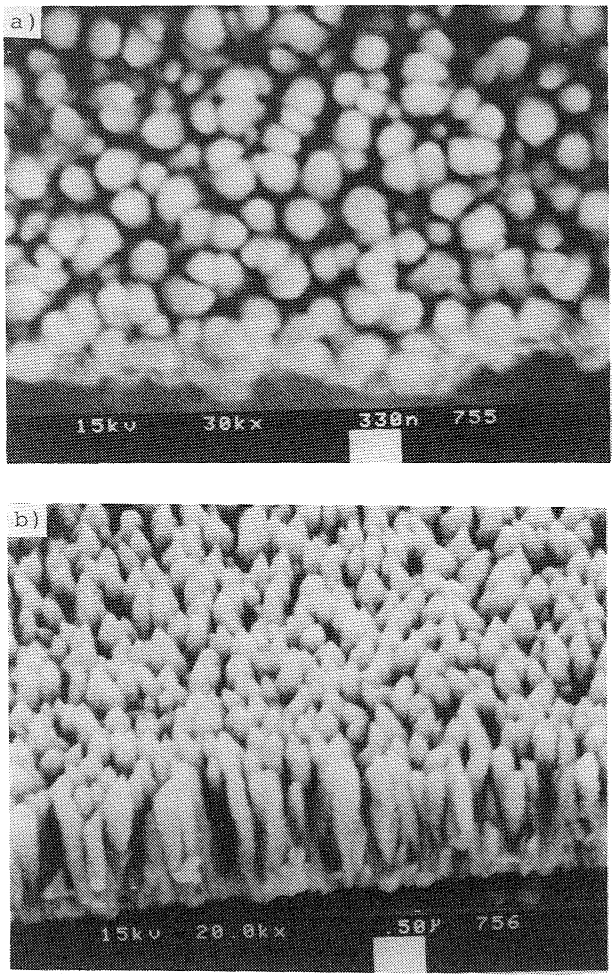

Fig. 3. Scanning electron micrographs of the Pd film with 1 μm in thickness. a) surface view, b) fracture cross section.

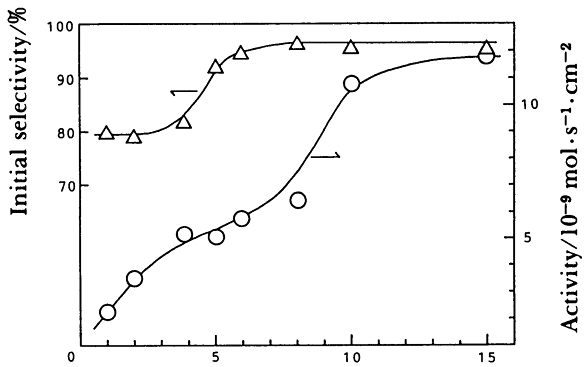

Fig. 4. Dependence of the activity and the initial selectivity for ethylene in the hydrogenation of acetylene on film thickness.

Ru film,[2] the (002) face, which was the most densely populated face of Ru hcp structure, was favorable for the partial hydrogenation of 1,3-butadiene. Although the (111) face of Pd is the same arrangement of the atom as the (002) face of Ru, the (111) face of Pd does not seem to be suitable for the partial hydrogenation of acetylene.

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