CHEMISTRY LETTERS, pp. 1839-1842, 1987.

Structure Dependence in Hydrogenation of 1,3-Butadiene over Ru Thin Film Prepared by RF Sputtering Method

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The structure of the Ru film prepared by the RF sputtering method changed with film growth. This influenced the activity and the selectivity in the hydrogenation of 1,3-butadiene. It has been found that the partial hydrogenation of 1,3-butadiene proceeds preferably over (002) face of Ru.

It is well known that a structure of a metal film prepared by a vacuum evaporation changes from an island structure to a channel structure up to a continuous film with film growth. Wilman et al.[1-3] observed a preferred orientation of Ib metal films condensed in a vacuum. The most densely populated face, (111) for the fcc metal, was initially parallel to the substrate surface. Thornton observed a tapered columnar structure of a film prepared by a sputtering method.[4] This columnar structure was found to be affected by a substrate temperature.

In this investigation, Ru thin films were prepared by an RF sputtering method using a glow discharge, by the similar procedure described previously.[5,6] A Ru ingot (6 x 20 x 3.5 mm^3) was employed as a target. It was made of Ru powder (99.99%) using a sintering technique. A sputtering gas was a high purity of Ar (99.9995%) at a pressure of 0.05 Torr. Under this condition, a Ru thin film was deposited on a glass substrate at a rate of 3 nm/min. The thickness of the films was controlled by changing the discharge time. The hydrogenation of 1,3-butadiene was carried out over the Ru thin films with various thickness using a closed circulation system at 323 K and 423 K. The structures of the Ru films were investigated by X-ray diffraction analysis (XRD).

Figure 1 shows the XRD patterns of the Ru thin films with various thickness. Three peaks due to Miller indices (101), (002), and (100) of Ru hcp structure appeared at 44.4, 42.4, and 38.8 degree. The peak intensity of (101) increased and (002) decreased with increasing the film thickness. It was found that the microstructures of the Ru thin films was evidently altered with the film thickness, viz., the film growth. The (002) face is the most densely populated face in the Ru hcp structure. In the initial stage of the film growth, the (002) face is assumed to preferentially grow and to be parallel to the substrate surface. Then, the preferred orientation of the Ru film changes from the (002) orientation to the (101) orientation.

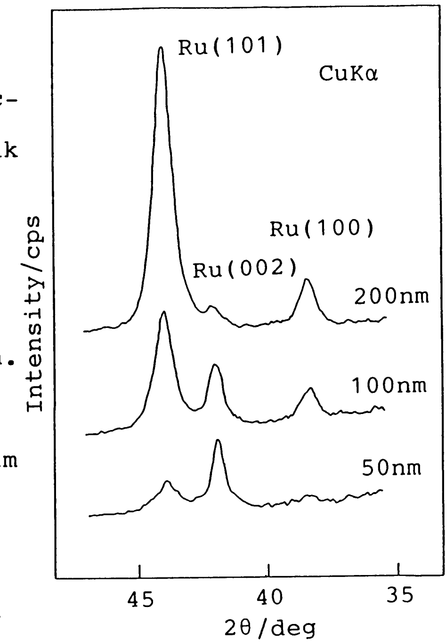

Fig.1. XRD Patterns of Ru films with various thickness.

It was examined how these alterations in the microstructure of the Ru film influence the activity and the selectivity in the hydrogenation of 1,3-butadiene. The selectivity in the hydrogenation of 1,3-butadiene was evaluated by the extrapolation to 0% conversion of the product distribution curve. Figures 2 and 3 show the selectivities for butane and 1-butene at 323 K and 423 K, respectively, as a function of the relative intensity of the (002)

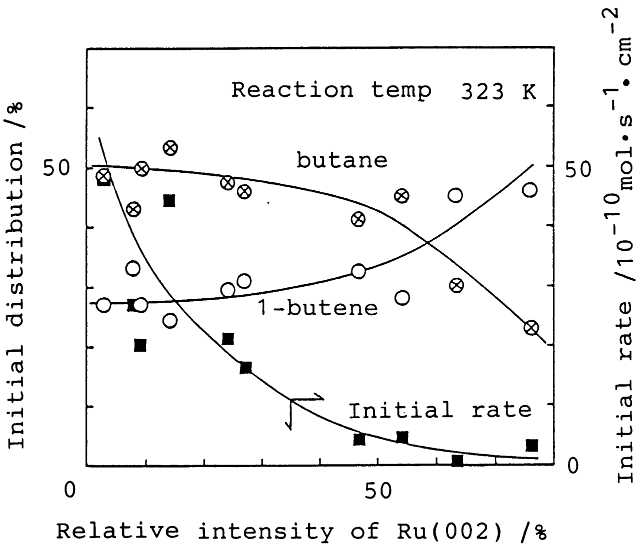

Fig.2. Initial product distribution and initial rate in the hydrogenation of 1,3-butadiene over Ru films at 323 K as a function of the XRD relative intensity of Ru(002).

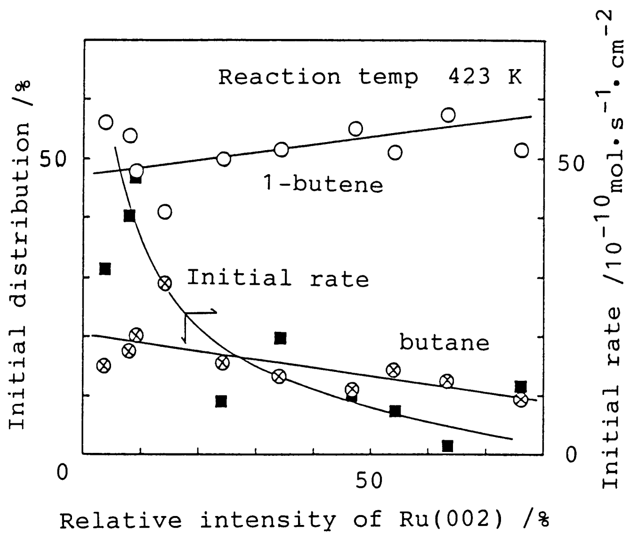

Fig.3. Initial product distribution and initial rate in the hydrogenation of 1,3-butadiene over Ru films at 423 K as a function of the XRD relative intensity of Ru(002).

face which was a proportion of (002) peak in all the XRD peaks. In both cases, the hydrogenation activity decreased with increasing the (002) intensity. In other words, the activity increased with increasing the film thickness. If the structure of the Ru film is the columnar structure which is characteristic to sputtered films, the surface area of the film increases with increasing the film thickness. On the other hand, the selectivity for 1-butene increased and that for butane decreased with increasing the (002) intensity. The selectivity to trans- and cis-2-butene was independent on the (002) intensity. It was found that the (002) face of Ru was preferred for the formation of 1-butene, viz., the partial hydrogenation of 1,3-butadiene. When the reaction temperature was elevated from 323 K to 423 K, the selectivity to 1-butene was much enhanced. It was reported that there were two types of a hydrogen adsorptive site on a Ru(002) face,[7] that is, a hcp site and a fcc site. The hcp sites are defined as threefold hollow sites such that directly below there is Ru atom in the second Ru layer. The fcc sites have no Ru atom in the second underlying layer. TPD spectra of hydrogen on a Ru(002) face showed two desorption peaks around 320 K and 430 K. An adsorption energy was larger at the fcc site than at the hcp site.[8] Therefore, the site due to the higher desorption peak was found to be the fcc site. At the reaction temperature of 423 K, hydrogen is not assumed to adsorb on the hcp site. The reduced surface hydrogen concentration brings about the increase in the selectivity for 1-butene. The extent of increase in 1-butene was pronounced in the low (002) intensity range. The surface structure of the Ru film is naturally presumed to be changed by elevating the reaction temperature. The selectivity in the hydrogenation would be affected by not only the adsorptive property of hydrogen but also the surface structure of the Ru film.

The change in the film structure at high substrate temperature was examined as well. Figure 4 shows XRD patterns of the Ru films with the same thickness prepared at room temperature and 573 K. The (002) intensity obviously increased by elevating the substrate temperature. The Ru film prepared at high substrate temperature is expected

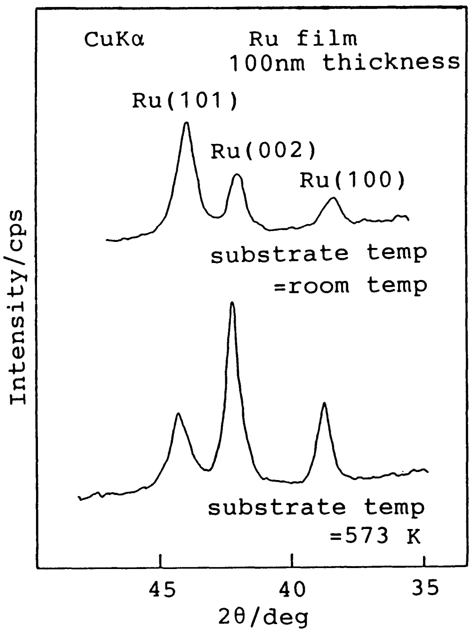

Fig.4.XRD patterns of Ru films with the same thickness prepared at different substrate temperature.

Table 1. Product distribution and initial activity in the hydrogenation of 1,3-butadiene over Ru films[a)] prepared at different substrate temperature

Substrate temp / K	Reaction temp / K	Distribution / % n-b	1-b	t-2-b	c-2-b	Initial activity / $10^{-10}mol\cdot s^{-1}\cdot cm^{-2}$
Room temp	323	52.0	27.0	12.0	9.0	31.5
573		35.6	36.4	16.7	11.3	3.80
Room temp	423	30.2	43.0	14.3	12.5	30.5
573		11.3	50.8	22.2	15.7	11.4

a) Film thickness = 100 nm.

to show the higher selectivity for 1-butene. The activity and the selectivity in the hydrogenation of 1,3-butadiene over the Ru films prepared at different substrate temperature were tabulated in Table 1. The selectivity for 1-butene was indeed higher and that for butane was lower over the Ru film prepared at 573 K than over the Ru film prepared at room temperature. However, the hydrogenation activity was decreased on the film prepared at high substrate temperature. The unevenness due to the columnar structure is supposed to be reduced at high substrate temperature. The decrease in the activity was attributable to the reduction of the surface area of the film.

In conclusion, the microstructure of the Ru film prepared by the RF sputtering method changed with the film thickness, viz., the film growth. The alterations in the film structure influenced the activity and the selectivity in the hydrogenation of 1,3-butadiene. It was found that the Ru(002) face was favorable to the formation of 1-butene, viz., the partial hydrogenation of 1,3-butadiene.

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(Received June 29, 1987)