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Preparation of Cu Thin Films by the Decomposition of Copper Acetylacetonate on Catalytically Active Substrate Surfaces

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A selective CVD system used to deposit the central metal of a volatile complex preferentially on catalytically active substrate surfaces was examined. Copper(II) acetylacetonate was vaporized in a flow of hydrogen and decomposed on Ni, Pd, and Al plates in order to deposit metallic copper. When a Ni plate was used as the substrate, deposition of metallic copper occurred at temperatures in the range 130—180 °C only on the substrate surfaces. The formation of an ultrathin film of Cu of uniform thickness was confirmed. On a Pd substrate, the formation of an ultrathin Cu film of uniform thickness was also observed. On an Al substrate, however, deposition occurred nonselectively at temperatures above 160 °C, not only on the substrate surface, itself, but also on the wall of the glass tube as well as the quartz wool surrounding the Al plate. In addition, the formation of fine particles of Cu, instead of thin film, was found to exist on the substrate. Because the deposition of Cu took place on catalytically active surfaces selectively, the deposition was considered to proceed by a catalytic hydrogenation of the C=O bond of the ligand, thus detaching it from the Cu ion and allowing it to decompose the complex and deposit Cu metal.

A variety of methods have been developed to prepare thin films, some of which have been applied to the manufacture of electronic devices. In addition to conventional evaporation or thermal CVD (Chemical Vapor Deposition), various methods have been attempted in order to lower the temperature of deposition using a laser[1,2] or plasma[3] as the external energy source. It has also been attempted to improve the controllability of the film structure at the atomic range (MOCVD,[4] MBE,[5] ALE,[6] MEE[7] et al.). Such methods are influencing other fields of material preparation, such as the synthesis of inorganic materials.[8,9] Various attempts have also been reported regarding the preparation of heterogeneous catalysts. Niwa et al.[10] as well as Teraoka et al.[11] have reported that the shape selectivity of mordenite could be significantly improved by deposing tetramethylsilane on the outer surface of zeolite. Imizu and Tada[12] tried to form an overlayer of silica on the surface of alumina or magnesia by CVD of $Si(CH_3)_4$, and found a notable improvement in the catalytic activity of olefin isomerization. Okuhara[13] studied both the structure and properties of SiO_2 layers deposited on TiO_2 and ZrO_2.

We reported[14] at ruthenocene ($Ru(cp)_2$; bis(cyclopentadienyl)ruthenium) can be deposited on the surface of Pt gauze in a hydrogen stream to form a thin film at temperatures below 200 °C. This method is unique since the deposition temperature is very low without using any external energy sources; conventional CVD methods require temperatures higher than 800 °C. In addition, deposition occurred only on Pt surfaces selectively, without forming any deposit on the glass wall or silica wool surrounding the substrate. We could apply such a deposition technique to the preparation of supported Pt–Ru and Pd–Cu bimetallic catalysts, in which Ru or Cu is deposited on the surface of Pt particles preferentially using volatile complexes as precursors.[14,15]

In this study we tried to deposit Cu using $Cu(acac)_2$ (acac=acetylacetonate, $CH_3COCHCOCH_3^-$) as the precursor on metal plates, and then characterized the structure of the deposit by means of SEM, EPMA, and XPS in order to clarify the conditions of such selective deposition, in an attempt apply this system to the preparation of supported bimetallic catalysts.

Experimental

Materials. Commercial-grade Ni, Pd, and Al plates (Ichimura Metals Co.) were cut down to 5 mm squares and used as substrates after washing with acetone. $Cu(acac)_2$(Wako Pure Chem. Co., reagent grade) was purified by sublimation in a vacuum. Hydrogen (Showa Denko, 99.99%) was purified by passing through a Pd catalyst in order to remove any trace amounts of oxygen, and then dehydrated by molecular sieve.

Apparatus. Deposition of Cu on each metal plate was carried out using a Pyrex tube reactor heated by two furnaces (Fig. 1) in which a slow flow of hydrogen was passed through at ambient pressure. In the lower part of the reactor, $Cu(acac)_2$ was placed on a plug of quartz wool and heated at 130 °C in order to vaporize the complex slowly. In the upper part, a metal substrate was placed on a plug of quartz wool, the temperature being adjusted so as to control the deposition rate.

Characterization of Deposit. The samples were observed by SEM (JEOL JSM-T100) at magnifications between 500 and 10000. They were then submitted to an EPMA line analysis using a Shimadzu EMX-SM, driving the samples to scan the point of analysis at a rate of 100 μm min^{-1}. The surface structure of the samples was studied by means of XPS (ULVAC-PHY ESCA 558-UP). We tried a wide-range (from 1000 to 0 eV) scan for an overall analysis as well as a narrow-range (20 eV width) scan for analyzing individual elements. The amount of Cu deposited was determined by atomic absorbance spectroscopy after dissolving it by nitric acid.

Hydrogenolysis of Acetylacetone. A fixed-bed flow reactor was used to study the catalytic decomposition of acetylacetone

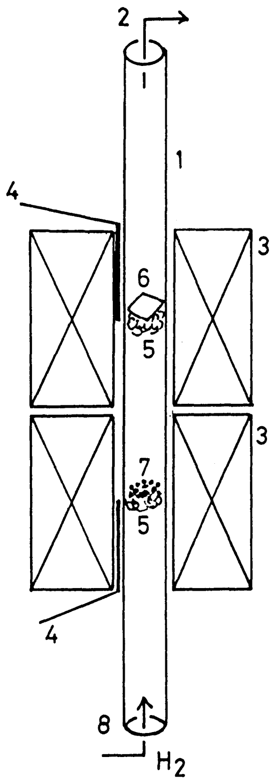

Fig. 1. CVD apparatus. Hydrogen was passed upward, and two furnaces were kept at different temperatures so as to control the rate of vaporization and deposition. 1. pyrex tube, 10 mm o.d., 2. hydrogen outlet, 3. electric furnace, 4. thermocouple, 5. plug of quartz wool, 6. substrate, 7. Cu acetylacetonate, 8. hydrogen inlet.

over a Pd-alumina catalyst. Liquid acetylacetone was evaporated in flowing hydrogen; the reactant gas consisted of H_2/acac=10/1 molar ratio. The products were analyzed by GC-MS (Shimadzu QP-1000).

Results

1. Formation of a Cu Film on a Ni Substrate. We first tried to form a Cu metal film on the surface of a Ni plate by decomposing $Cu(acac)_2$. Because $Cu(acac)_2$ started to sublimate at 120—130 °C, the lower furnace of Fig. 1 was kept at 130 °C and $Cu(acac)_2$ was slowly vaporized in flowing hydrogen. The Ni substrate was kept at temperatures between 110 and 240 °C. When the temperature of the Ni plate was lower than 130 °C, the complex passed through the reactor tube without any chemical change, and then condensed downstream at the cool part of the glass tube. Deposition of Cu was observed at temperatures in the 130—180 °C range. At these temperatures Cu deposition occurred only on the surface of the Ni plate selectively, without any deposition on the quartz wool or glass wall surrounding the substrate. Condensation of unreacted complex was observed downstream, the amount of which decreased as the deposition temperature was increased.

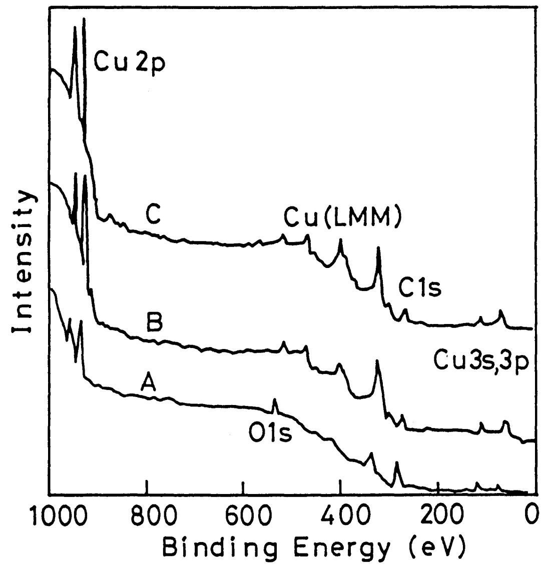

Fig. 2. Wide-range XPS spectra of Cu on Ni plate. Time of argon sputtering: A. 0 min, B. 5 min, C. 10 min.

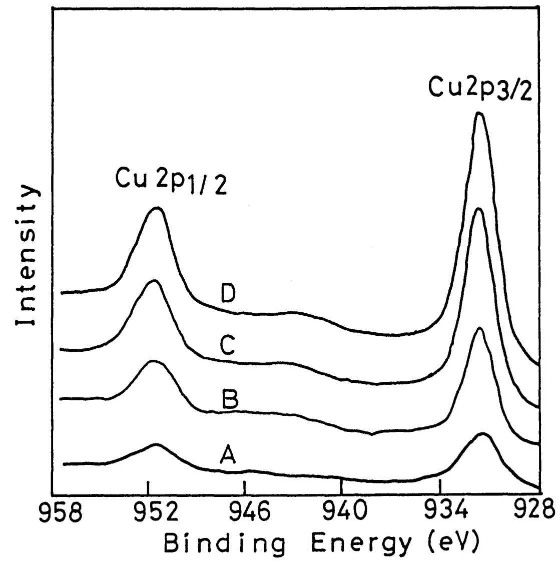

Fig. 3. Narrow-range XPS spectra of Cu on Ni plate. Time of argon sputtering: A. 0 min, B. 1 min, C. 5 min, D. 10 min.

At temperatures higher than 180 °C, the deposition proceeded unselectively, not only on the Ni plate but also on the quartz wool and glass tube surrounding the substrate. The amount of deposition on the wall of glass tube gradually increased as the temperature was increased, together with a decrease in the amount of condensation of unreacted complex. The surface of the sample treated at 160 °C was observed by SEM. The surface was smooth and no particle formation was observed.

The same sample was analyzed by XPS, as shown in Figs. 2 and 3. Before Ar sputtering, significant peaks of

O1s and C1s were observed, though they decreased rapidly upon Ar sputtering. These elements seems to be due to contamination introduced while the sample was exposed to air. Because the signals of Ni were found in trace amounts only after 10 min of Ar sputtering, the sample seems to have been fully covered by a uniform thin film of Cu, without exposing the substrate surface. Figure 3 shows that the film comprised metallic Cu. The adhesion between the substrate and deposit was sufficiently strong and the film could not be removed mechanically by scratching with a nail. The same sample was also analyzed by EPMA. The distribution of Cu was measured by a line analysis over a range of 400 µm. As shown in Fig. 4, the signal intensity of Cu was constant. The heterogeneity of the signal intensity of EPMA was less than 5%. It is clear that deposition occurred at a very uniform thickness. In contrast to XPS, the signal intensity of Ni was much larger than that of Cu. Such a contrast is due to a difference in the analyzing depth of the two machines. Although in the nm depth range, Cu was the main component, in the µm range Ni prevailed to Cu. We thus concluded that the sample was covered by an ultrathin (ca. 50 nm) film of metallic copper of uniform thickness.

2. Deposition of Cu on an Al Plate. The deposition of Cu by the decomposition of Cu(acac)$_2$ was attempted using an Al plate as the substrate, however deposition was not observed at temperatures lower than 160 °C. At temperatures in the 160—200 °C range, although decomposition of Cu(acac)$_2$ took place, deposition of Cu occurred not only on the Al plate, but also on the quartz wool and glass tube. We could not find any selectivity of the substrate during deposition at any temperature.

The surface structure of the sample treated at 160 °C for 15 min was observed by SEM; it was found that ultrafine particles of ca. 200 nm diameter were distributed uniformly on the surface of the substrate. A sample treated at 220 °C for 45 min, Which contained a larger amount of Cu, was also found to be covered by fine particles at a much higher density, showing that particle growth was not the main process of deposition.

The EPMA and XPS results of these samples showed different features from the case of Cu film on a Ni substrate. Figure 5 shows the EPMA of Cu on Al. The signal intensities of Cu and Al changed significantly with the position of analysis. By means of XPS, the signals of both Cu and Al were observed without any sputtering treatment. These results are in consistent with the SEM observations, that the Cu particles were formed on an Al plate and Al surface was not fully covered by Cu.

3. Deposition of Cu on a Pd Plate. The deposition of Cu on a Pd plate occurred in a similar manner as that on a Ni plate. As shown in Fig. 7, the XPS results suggest that the surface was fully covered by metallic

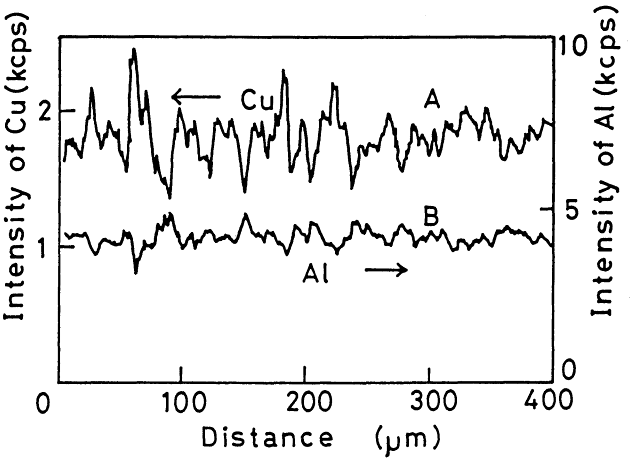

Fig. 5. Distribution of Cu on an Al plate measured by an EPMA line analysis. A. signal intensity of Cu, B. signal intensity of Al substrate.

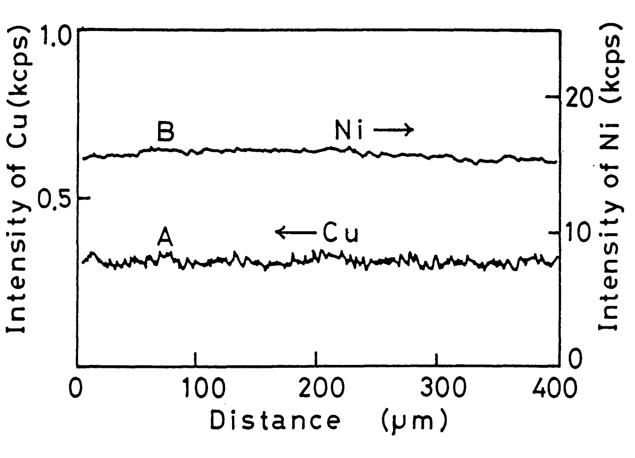

Fig. 4. Distribution of Cu on a Ni plate measured by an EPMA line analysis. A. signal intensity of Cu, B. signal intensity of Ni substrate.

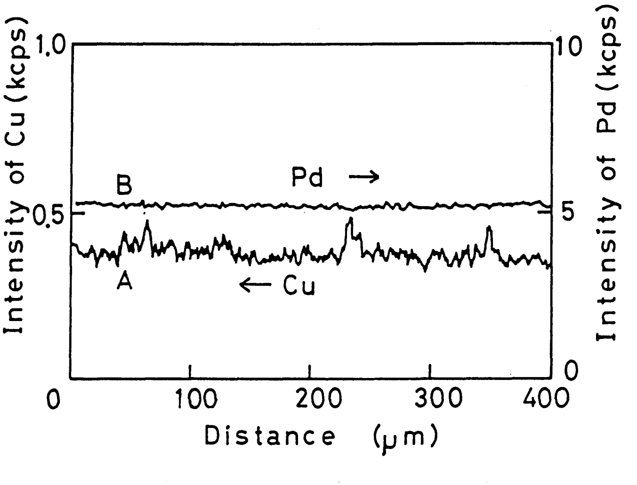

Fig. 6. Distribution of Cu on a Pd plate measured by an EPMA line analysis. A. signal intensity of Cu, B. signal intensity of Pd substrate.

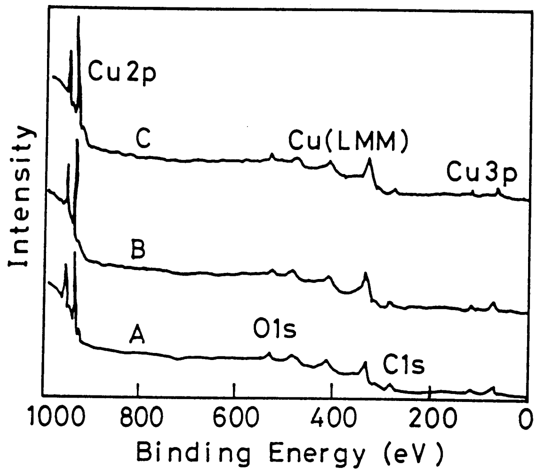

Fig. 7. Wide-range XPS spectra of Cu on a Pd plate. Time of argon sputtering: A. 0 min, B. 5 min, C. 10 min.

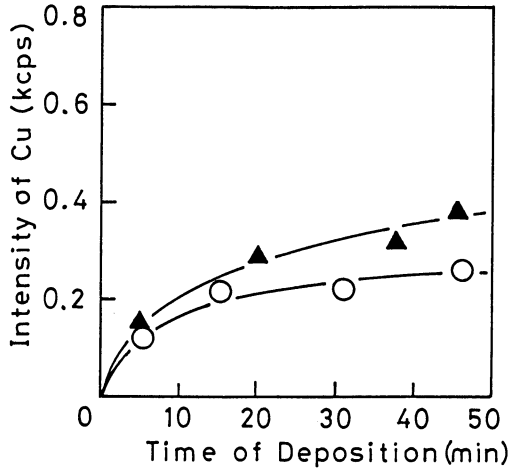

Fig. 9. Change in the intensity of the EPMA signal of Cu deposited on Ni and Pd plates with the time of treatment.
○; Cu on Ni, ▲; Cu on Pd.

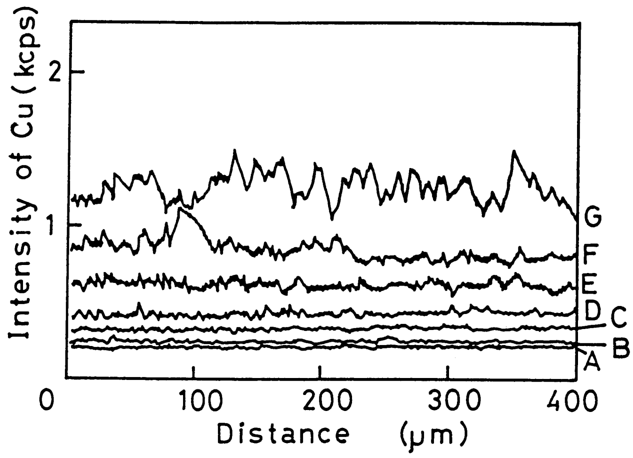

Fig. 8. Distribution of Cu on a Ni plate at different temperature measured by an EPMA line analysis. A. blank (Ni plate), B. substrate temperature 130 °C. 140 °C, D. 150 °C, E. 160 °C, F. 170 °C, G. 180 °C.

Cu, since no signals of Pd were observed. An EPMA line analysis (Fig. 6) showed a flat distribution of the Cu signal intensity, suggesting a uniform distribution of the deposit. We could not observe any particle formation on the surface by means of SEM.

4. Effect of Deposition Conditions. The effect of the flow rate of hydrogen on the deposition rate of Cu(acac)$_2$ on a Ni plate was studied. While the amount of deposition remained constant when the flow rate was lower than 20 ml min^{-1}, it decreased when the flow rate was higher than that. It seemed that a higher flow rate resulted in a shorter contact time between the vapor and the substrate, and that a considerable fraction of the complex passed through unreacted. We therefore controlled the flow rate to be between 5—10 ml min^{-1}.

The effect of the deposition temperature was also studied. Figure 8 shows the results of an EPMA analysis of the Ni plates treated with Cu(acac)$_2$ at different temperatures. Although the amount of deposition increased with temperature at 130—180 °C, the fluctuation of the signal intensity increased, showing that the heterogeneity of deposition became more significant. At temperatures higher than 180 °C the amount of deposition decreased, since the thermal decomposition of the complex took place in advance, so as to contact with the substrate. The deposition process was found to be sensitive to the temperature.

Figure 9 shows the change in the amount of deposition with the treatment time. The initial high rate of deposition on Ni decreased with time. A similar behavior was found on Pd. Monolayer coverage was attained during the initial stage; no change in the deposition rate resulted since the surface was covered by Cu. We suppose that the increase in the film thickness resulted in a reduction of the surface roughness and, thus, decreased the real surface area, which was observed during the slow rate of deposition.

5. Decomposition of Acetylacetone. The reaction of acetylacetone, the ligand molecule of the complex, was attempted in a flowing hydrogen over a Pd/Al$_2$O$_3$ catalyst. The following compounds were found by GC-MS to be liquid products: pentane, 2-pentanone, 2-pentanol. It was clear that the hydrogenation and hydrogenolysis of the C=O bond was the main reaction. Because the thermal decomposition of acetylacetone forms acetone and acetic acid, a catalytic reaction prevailed to the thermal decomposition in the flow of hydrogen.

Discussion

Preparation techniques for thin films using organometallic compounds as precursors, MOCVD,[3] have sometimes been attempted in the production of electronic materials, such as Ca—As semiconductors from alkylgarium and arsin (AsH_3). Acetylacetonato complexes have not yet been widely used in CVD, except for laser-induced CVD.[1] Similar complexes, β-diketonates of Cu, Ba, Y and Sr, were used in the preparation of superconducting oxide films[16,17], in an oxygen atmosphere. The advantage of our present CVD system is the sharp dependence on the chemical nature of the substrate surfaces. It has been discussed that the surface process also participates in a conventional thermal CVD system,[18–19] as well as the homogeneous reactions.[20] In our CVD system the importance of the surface reaction is clear. In the case of an Al substrate, deposition occurred on both the substrate and the glass wall unselectively, and decomposition of the complex seemed to be simply a thermal reaction, instead of a surface reaction. Deposition took place on Ni and Pd plates at lower temperatures than on an Al plate, and the complex passed through in the absence of active substrates. These results suggest that the catalytically active substrate surface accelerated the reaction, thus resulting in substrate selectivity. The product distribution of hydrogenation of acetylacetone, which is the ligand of the complex, suggests that the decomposition of the complex proceeds by hydrogenation of the C=O bond of the ligand, which leads to removal of the ligand from the complex and to deposition of central metal in situ. Because the temperature of deposition was sufficiently low, surface migration of the deposit atoms seemed to be not so significant as in the case of thermal CVD.

The catalytic activity of metals for the hydrogenation of the C=O bond, ex. cyclohexanone, is reported[21] to be $Cu \ll Pd < Ni$; the glass is inactive. Aluminum, the surface of which is covered by alumina (as revealed by an XPS analysis of a fresh Al plate) is also inactive. When the surfaces of Ni and Pd were partly covered by Cu, the catalytic activity of the covered surfaces decreased and the following deposition process took place at the uncovered Pd (or Ni) surface. Thus, covering the substrate surface prevailed to the accumulation of Cu atoms, resulting in thin-film formation, rather than particle formation. In the case of an Al surface, the surface has poor activity to decompose the complex. Once a small number of Cu particles are deposited on the surface by thermal decomposition, the Cu surface shows catalytic activity that is higher than that of an Al surface, and the following decomposition tends to take place on the Cu surface, rather than on the Al surface. Thus, particle formation and particle growth proceeds instead of film formation. However, the activity of the Cu surface is not sufficiently high, as in the case of Ni deposition, which formed large particles of Ni (as we will report in the next paper); particle formation also proceeded and small particles of Cu covered the surface. In this way we could produce thin films of Cu selectively on catalytically active surfaces.

We reported[15] that Cu could be deposited selectively on the Pd surface of a Pd/SiO_2 catalyst when $Cu(acac)_2$ was used as the precursor. This new method of bimetallic catalyst preparation is based on the surface selective deposition process reported here. Our deposition method is effective as a technique which can be used to control the distribution of components over an atomic range in composite materials, such as heterogeneous catalysts.

In order for such deposition of complexes to occur selectively, we should choose precursor complexes which have following characters: (1) They should have low sublimation temperature as well as sufficient stability in the flow of hydrogen to be able to vaporize without decomposition. (2) They should have ligands which can be easily hydrogenated by the help of the catalytic function of the substrate surface at temperatures near to the sublimation temperature. (3) They should be inactive towards surfaces other than the substrate: For example, towards the OH groups of oxide surfaces.

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