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Copper thin films prepared by chemical vapour deposition from copper dipivalylmethanate

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Copper thin films were prepared by a low-temperature atmospheric-pressure chemical vapour deposition method. The raw material was copper dipivalylmethanate which is volatile and thermally stable. At a reaction temperature above 220 °C, polycrystalline copper films can be obtained by hydrogen reduction of the raw material. The resistivity of the film was in the range 1.7–2.7 μΩ cm.

1. Introduction

Copper is a promising interconnection material because its electrical resistivity is low and its electro- and stress migration resistances are high. Recently, chemical vapour deposition of copper has attracted much attention for achieving high-density multi-level copper interconnection because it is effective in filling via hole.

Various chemical vapour deposition methods [1–8] have been proposed, for example the hydrogen reduction of cuprous chloride [1] at 500–700 °C or copper chloride [2] at 400–1200 °C, or the decomposition of copper acetylacetonate [3, 4] at 260–343 and 300–450 °C, and copper formate [5] at 300 °C. Van Hemert *et al.* [6] proposed the hydrogen reduction of copper hexafluoroacetylacetonate, which is more volatile than copper acetylacetonate. Copper films of low electric resistivity have been reported to be obtained at 340–390 °C, but the deposition rate must be kept low (4–10 nm min^{-1}) in order to achieve low electrical resistivity [7, 8].

Copper dipivalylmethanate (copper 2,2,6,6-tetramethyl-3,5-heptanedionate) is proposed here as a source material in the low-temperature atmospheric-pressure chemical vapour deposition method. Thermally, copper dipivalylmethanate is more stable than copper acetylacetonate. The copper films were deposited with high deposition rates by hydrogen reduction of copper dipivalylmethanate at a temperature above 220 °C.

2. Experimental procedure

Copper dipivalylmethanate (Nippon Sanso Corporation) of reagent grade was used as the source material. It is a solid at room temperature (melting temperature 199 °C). Fig. 1 shows a schematic representation of the experimental apparatus. Copper dipivalylmethane was heated at 220 °C and the generated gas was entrained by nitrogen carrier gas at a flow rate of 300 $\text{cm}^3\,\text{min}^{-1}$. Hydrogen gas was injected into the nozzle and mixed with the source gas. The flow rate of hydrogen gas ranged from 100–1000 $\text{cm}^3\,\text{min}^{-1}$.

A 76 mm × 26 mm borosilicate glass plate was used as the substrate. The substrate was placed in the closed-tube reactor heated by an external electric furnace. The reaction temperature was in the range 220–400 °C. The total pressure in the reactor was at atmospheric pressure.

The morphology of the film was examined by scanning electron microscopy. The crystallinity of the film was analysed by X-ray diffractometry using CuK_α radiation. The electrical resistivity of the film was measured by the van der Pauw method.

3. Results and discussion

Copper films were grown by the hydrogen reduction of copper dipivalylmethanate. In an inert (nitrogen) atmosphere, no copper film was obtained. At a reaction temperature above 220 °C, smooth copper films were formed on the borosilicate glass substrates. The films were highly adherent and showed no apparent peeling on the glass substrates. The films were very ductile and, when scraped from the substrate, could be folded to a sharp crease without breaking.

The colour and surface morphology of the film changed with film thickness: when the film thickness was less than ~ 50 nm, the film was translucent and was not conductive. The colour of the thin film was sometimes observed to instantaneously change from copper to blue black, when the film was taken out of the reactor and was exposed to air. Thus, the thin film was oxidized by air. It was not until the thickness was increased to above ~ 50 nm that the film in air kept its colour, copper, and that the surface was a shiny mirror. When the thickness was further increased to above ~ 200 nm, however, the surface became dull and milky copper in appearance.

Fig. 2 shows plane views of scanning electron micrographs of a 150 nm thick copper film and a 260 nm thick copper film. A surface pattern is seen to be rather flat in the 150 nm thick film, and it is

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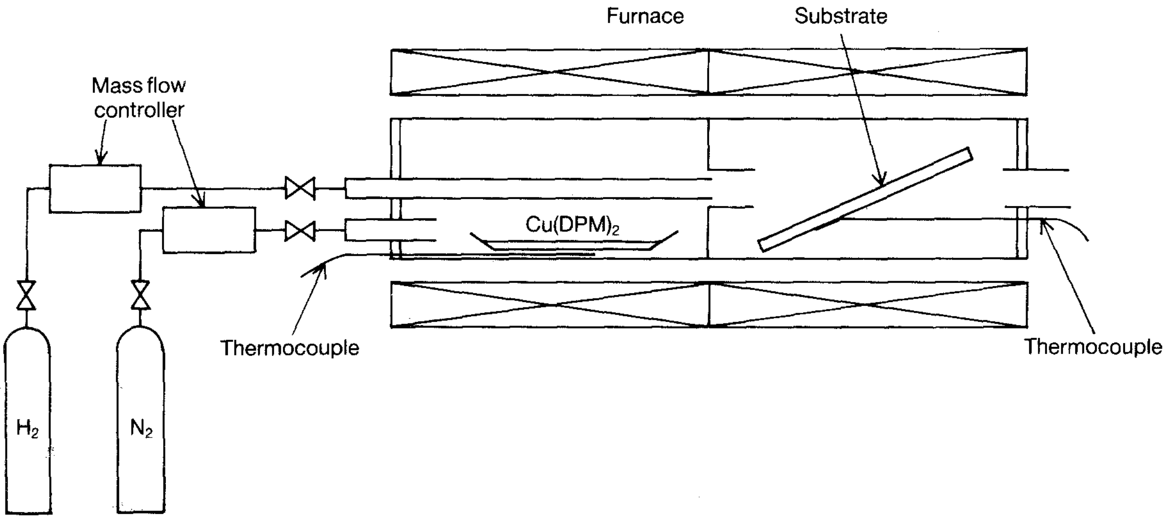

Figure 1 Schematic illustration of the experimental equipment.

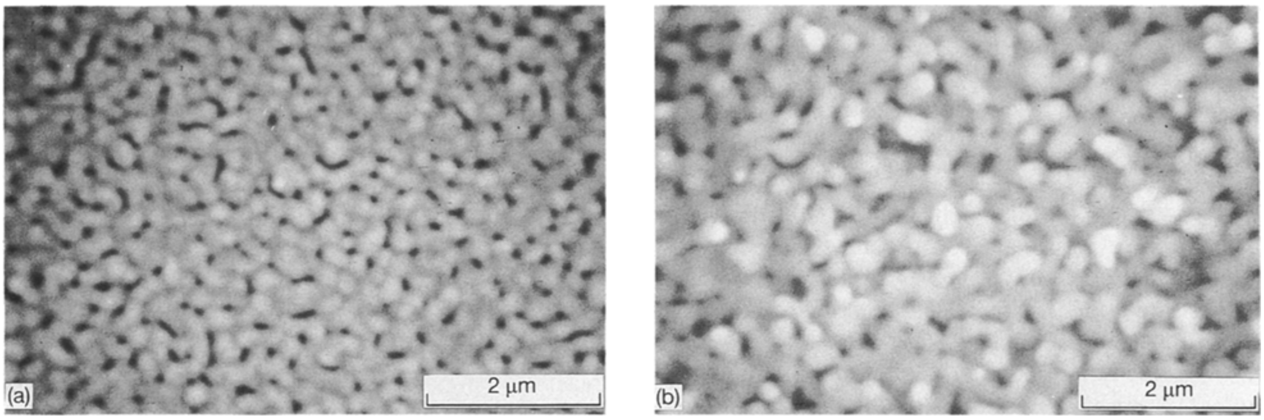

Figure 2 Plane views of scanning electron micrographs of (a) a 150 nm thick copper film and (b) a 250 nm thick copper film.

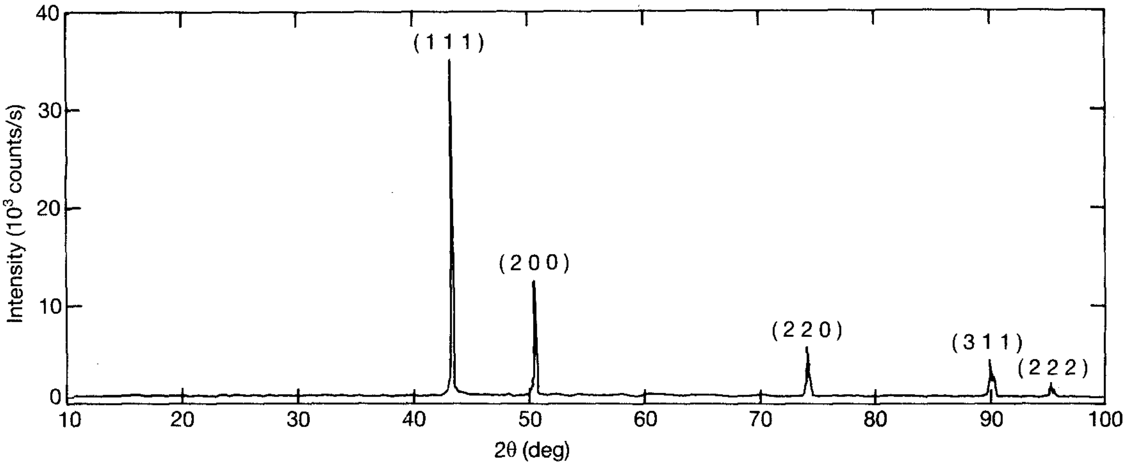

Figure 3 X-ray diffraction pattern of a 2560 nm thick copper film for a hydrogen flow rate of 900 cm^3 min^{-1}.

stereoscopic in the 260 nm thick film. Comparison of the two micrographs suggests that preferred overgrowths occur on the 50–100 nm thick copper film which covers the substrate surface, producing a vertically developing three-dimensional rough and coarse structure, several hundreds of nanometres in height. Thus, the surface becomes dull and milky copper in appearance, when the thickness of the film is over ~ 200 nm.

The X-ray diffraction pattern showed that the copper film was composed of crystallites with a predominant cubic structure and that the structure was not affected by the reaction temperature and hydrogen flow rate. Fig. 3 shows a typical example of the X-ray diffraction pattern of the copper film. The film was 2560 nm thick and was obtained at a reaction temperature of 300 °C and a hydrogen flow rate of 900 cm^3 min^{-1}.

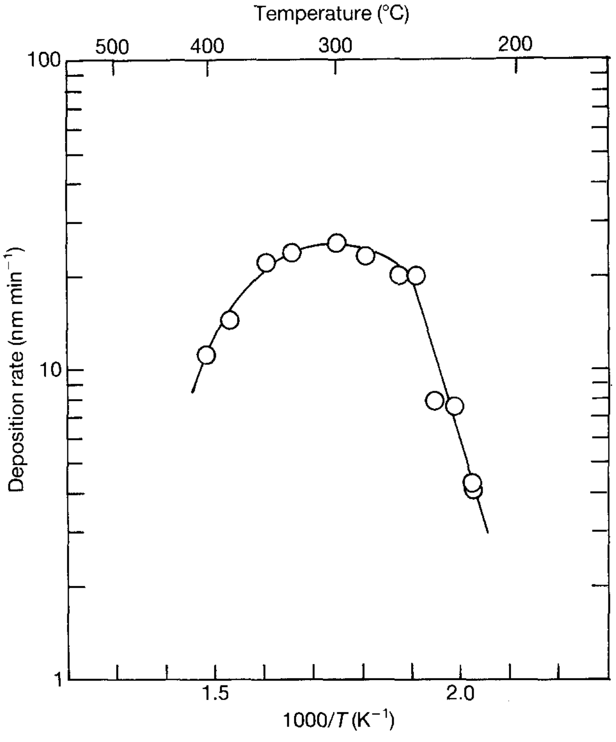

Figure 4 Arrhenius plot of the deposition rate of copper film for a hydrogen flow rate 900 cm^3 min^{-1}.

Fig. 4 shows the Arrhenius plot of deposition rates, which were obtained at a source temperature of 220 °C and a hydrogen flow rate of 900 cm^3 min^{-1}. The deposition rate increases with increasing reaction temperature from 220–260 °C. It saturates at a temperature in the range 260–350 °C and even decreases with temperature above 350 °C. This temperature is close to the thermal decomposition temperature of copper dipivalylmethanate, which is reported to be 338 °C. Therefore, the decrease in deposition rate seems to be associated with the thermal decomposition of copper dipivalylmethanate. That is, the copper dipivalylmethanate available for hydrogen reduction decreases in concentration with increasing reaction temperature above 330 °C, through thermal decomposition in the vapour phase.

The deposition rate increases slightly on increasing the hydrogen flow rate from 100 cm^3 min^{-1} to 900 cm^3 min^{-1}, but the crystallinity and resistivity of the film show no dependence on hydrogen flow rate under the experimental conditions of this study. That is, the hydrogen partial pressure in this study was so large that it did not affect the structure and characteristics of the film.

Fig. 5 shows the resistivity of the copper film as a function of film thickness. The samples were obtained at a reaction temperature of 300 °C and, consequently, at a high rate of deposition, 26 nm min^{-1}. In spite of the deposition at high rate, the films have small values of resistivity which range from 1.7–2.7 μΩ cm, exhibiting low resistivity even in the lower limit of film thickness (~ 50 nm). It is noted that the lowest value is very close to that for bulk copper (1.68 μΩ cm). There is a weak dependence of resistivity on film thickness: resistivity takes a relatively smaller value at a film thickness of ~ 100 nm, and relatively higher values at 300–400 nm. This difference may be attributable to the variation in surface morphology of the film, as follows. While the ~ 100 nm thick film has a smooth surface, the 300–400 nm thick film has a rough surface region (see Fig. 2) which is less electrically conductive than the smooth surface. In the meantime, films of 1000–3000 nm thickness show no further increase in resistivity. This fact suggests that the relative depth of the rough surface region does not increase with film thickness for these thick films.

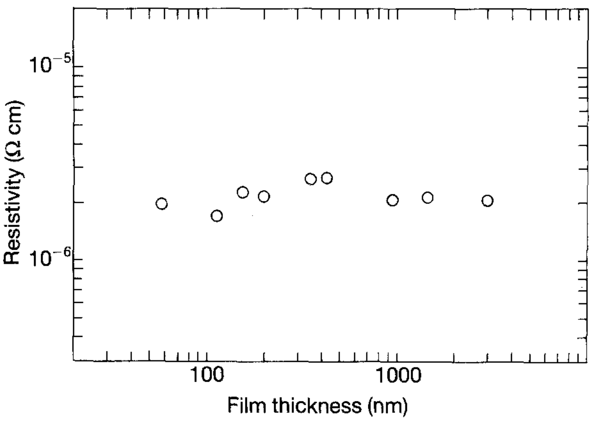

Figure 5 Resistivity of the copper film as a function of film thickness.

4. Conclusion

Copper thin films were prepared by a low-temperature atmospheric-pressure chemical vapour deposition method. The raw material was copper dipivalylmethanate which is volatile and thermally stable. At a reaction temperature above 220 °C, polycrystalline copper films can be obtained by hydrogen reduction of the raw material. The resistivity of the film was in the range 1.7–2.7 μΩ cm.

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