

Copper thin films prepared by chemical vapour deposition from copper (II) acetylacetonate

T. MARUYAMA, T. SHIRAI

Department of Chemical Engineering, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Copper thin films were prepared by a low-temperature atmospheric pressure chemical vapour deposition method. The raw material was copper (II) acetylacetonate. 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 close to that for bulk copper.

1. Introduction

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

Various chemical vapour deposition methods [1-9] have been proposed, for example the hydrogen reduction of cuprous chloride [1] at 500-700 °C, copper chloride [2] at 400-1200 °C and copper dipivaloyl-methanate [3], or the decomposition of copper (II) acetylacetonate [4,5] at 260-343 and 300-450 °C, and copper formate [6] at 300 °C. Pauleau and Fasasi [7] proposed the hydrogen reduction of copper (II) acetylacetonate in argon-hydrogen mixtures at temperatures ranging from 225-250 °C. The possibility of using copper (II) acetylacetonate as a metal precursor in argon-hydrogen mixtures for plasma-enhanced CVD of copper films at low substrate temperature has also been explored [8,9].

In the present work, copper (II) acetylacetonate was used as a source material in the low-temperature atmospheric pressure chemical vapour deposition method. The copper films of very low electrical resistivity were deposited with high deposition rates by hydrogen reduction of copper (II) acetylacetonate at a temperature above 220 °C.

2. Experimental procedure

Copper (II) acetylacetonate (Nihon Kagaku Sangyo Co. Ltd) of reagent grade, which is a solid at room temperature, was used as the source material. Fig. 1 shows a schematic representation of the experimental apparatus. Copper (II) acetylacetonate was heated at 220 °C and the generated gas was entrained by nitrogen carrier gas at a flow rate of 300 cm³ 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 cm³ min⁻¹.

A 76 mm × 26 mm borosilicate glass plate was used as the substrate, which 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 measured using a scanning electron microscope. The crystallinity of the film was analysed by the 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 (II) acetylacetonate. 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 from 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 ~40 nm, the film was translucent and was not conductive. The colour of the thin film was sometimes observed to change instantaneously from copper to blue-black, when the film was taken out of the reactor and was exposed to air, indicating oxidation of the thin film by air. It was not until the thickness was increased to above ~40 nm that the film in air kept its copper colour and that the surface had a shiny mirror finish. When the thickness was further increased to above ~200 nm, however, the surface became dull in appearance.

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. 2 shows a typical example of the X-ray diffraction pattern of the copper film. The film was

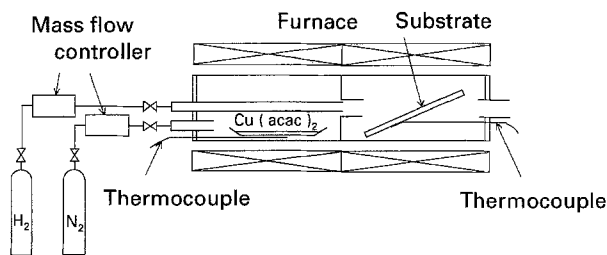


Figure 1 Schematic illustration of the experimental equipment.

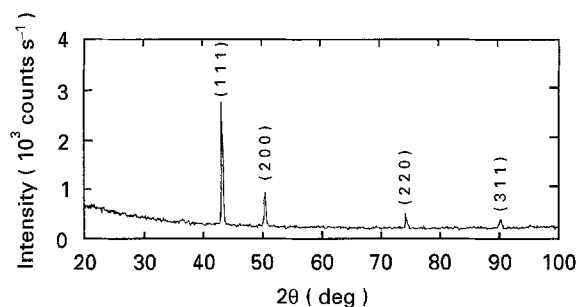


Figure 2 X-ray diffraction pattern of a 610 nm thick copper film for a hydrogen flow rate of $300 \text{ cm}^3 \text{ min}^{-1}$.

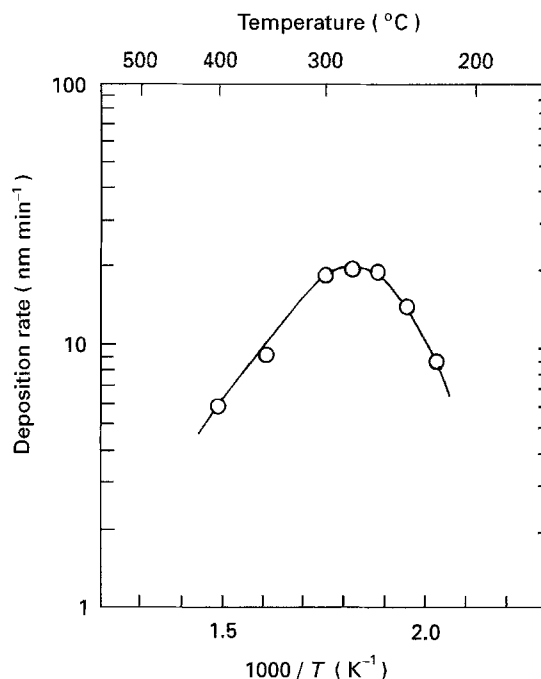


Figure 4 Arrhenius plot of the deposition rate of copper film for a hydrogen flow rate $300 \text{ cm}^3 \text{ min}^{-1}$.

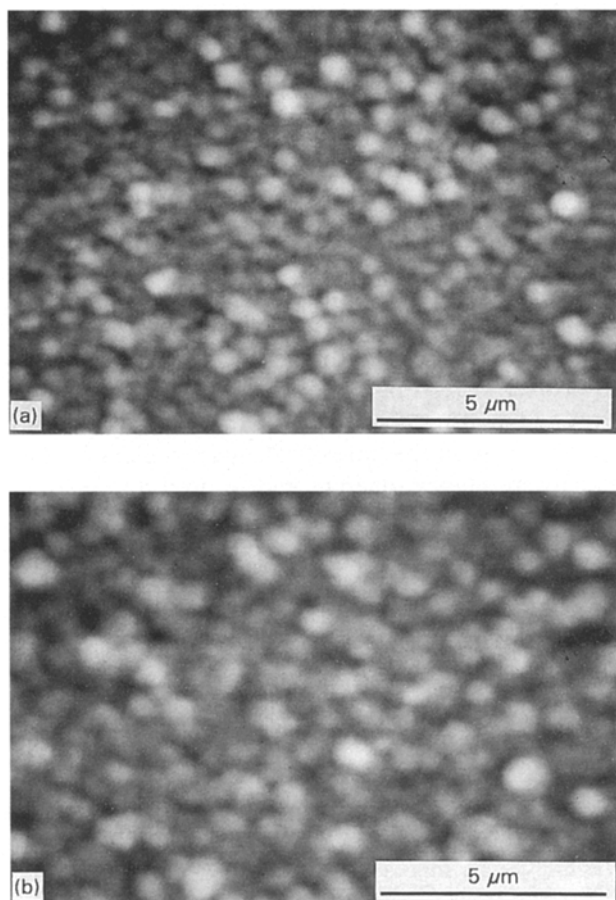


Figure 3 Plane views of scanning electron micrographs of (a) a 300 nm thick copper film, and (b) a 970 nm thick copper film.

610 nm thick and was obtained at a reaction temperature of 280°C and a hydrogen flow rate of $300 \text{ cm}^3 \text{ min}^{-1}$.

Fig. 3 shows plane views of scanning electron micrographs of 300 and 970 nm thick copper films.

The crystallites for the 970 nm thick film are larger in size and had a broader size distribution than those for 300 nm thick film. That is, the surface roughness increases with increasing film thickness, and consequently the surface becomes dull in appearance, when the thickness of the film is over $\sim 200 \text{ nm}$.

Fig. 4 shows an Arrhenius plot of deposition rates, which were obtained at a source temperature of 220°C and a hydrogen flow rate of $300 \text{ cm}^3 \text{ min}^{-1}$. The deposition rate increases with increasing reaction temperature from $220\text{--}260^\circ\text{C}$, then saturates at a temperature in the range $260\text{--}300^\circ\text{C}$ and even decreases at temperature above 300°C . This temperature is close to the thermal decomposition temperature of copper (II) acetylacetonate, which is reported to be 283°C . Therefore, the decrease in deposition rate seems to be associated with the thermal decomposition of copper (II) acetylacetonate. That is, copper (II) acetylacetonate available for hydrogen reduction decreases in concentration with increasing reaction temperature above 300°C , through thermal decomposition in the vapour phase.

Fig. 5 shows the resistivity of copper film as a function of film thickness. The samples were obtained at a reaction temperature of 280°C . At film thicknesses larger than $\sim 300 \text{ nm}$, the films have a constant value ($1.7 \mu\Omega \text{ cm}$) of the resistivity which is very close to that for bulk copper ($1.68 \mu\Omega \text{ cm}$). Thus the surface roughness shown in Fig. 3 does not deteriorate the electrical conductivity of the film. Fig. 6 shows the resistivity of copper film as a function of reaction temperature. The film thickness was larger than 500 nm , and consequently each resistivity is independent of film thickness. At reaction temperatures in the range $260\text{--}300^\circ\text{C}$, the films show a constant value ($1.7 \mu\Omega \text{ cm}$) of resistivity. The slightly larger values at reaction temperatures lower than 260°C are attributable to carbon

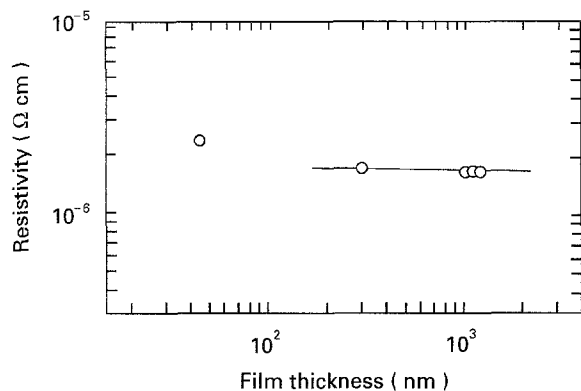


Figure 5 Resistivity of the copper film as a function of film thickness.

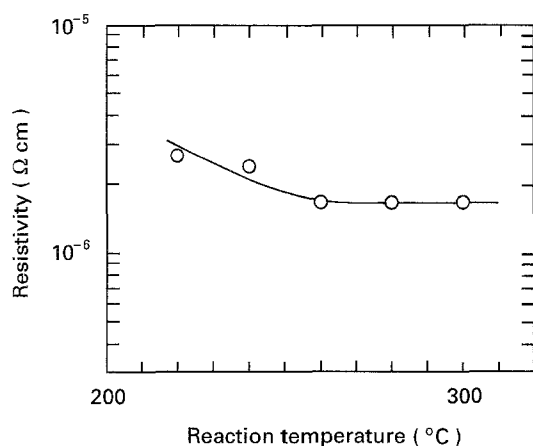


Figure 6 Resistivity of the copper film as a function of reaction temperature.

contamination at reaction temperatures lower than the decomposition temperature of copper (II) acetylacetonate.

The crystallinity and resistivity of the film show no dependence on the 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.

4. Conclusion

Copper thin films were prepared by a low-temperature atmospheric pressure chemical vapour deposition method. The raw material was copper (II) acetylacetonate. 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 close to that for bulk copper.

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