

COPPER FILM DEPOSITION WITH $\text{Cu}(\text{dpm})_2$ PRECURSOR

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Copper as interconnections in integrated circuit devices attracts the attention due to high electromigration resistance and low resistivity against aluminum. Different metal organic precursors are used today for copper chemical vapor deposition (CVD). A few copper β -diketonates are investigated for this application. We can notice that copper dipivaloylmethanate (*bis*-(2,2,6,6-Tetramethyl-3,5-Heptanedionato) $\text{Cu}(\text{II})$ – $\text{Cu}(\text{dpm})_2$ has received little attention as the precursor. However, the $\text{Cu}(\text{dpm})_2$ chelate is plausible chelate compound for CVD Cu films. The chelate is volatile enough at temperature higher 150°C and stable relative to decomposition in the vapor phase up to 246°C . The chelate is not toxic and stable for hydrolysis in air atmosphere. The aim this paper is study of kinetics and mechanism copper film CVD with the $\text{Cu}(\text{dpm})_2$ precursor.

The copper films were deposited in the warm-wall, vertical flow reactor. The $\text{Cu}(\text{dpm})_2$ chelate was evaporated from inner sublimator which was heated to temperatures between $150 - 190^\circ\text{C}$. Corresponding partial pressure $p_{\text{Cu}(\text{dpm})_2}$ was in range of $0.03 - 0.09$ Torr. The Cu chelate vapor was mixed with high purity hydrogen and arrived upwards at the horizontal placed sitall (SiO_2) substrate heated to temperature between $270 - 370^\circ\text{C}$. The total pressure in chamber was 1 atm and the flow rate was 12 l/h. The CVD procedure time of every experiment was 15 min. The sitall $20 \times 20 \times 0.4$ mm plates were polished up to surface roughness of $0.03 \mu\text{m}$, washed with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ and $\text{HCl} + \text{H}_2\text{O}_2$ aqueous solutions, deionized water and dried in air.

The film thickness was measured by interferometric microscope (IM, MII-4 LOMO USSR) and ellipsometer LEF-3. The film weight was determined by the Bunge balance (Hanburg) with an accuracy of $\pm 10^{-6}$ g. The X-ray diffraction measurements were performed at the station "Anomalous Scattering" at the second channel of the colliding electron position beam accelerator VEPP-3M of Siberian center of SD (Institute of Nuclear Physics Sd RAS). Scanning electron microscopy (SEM, JEOL-JSM) was carried out to study the microstructure and surface morphology of the Ni films. The resistivity of the films was measured using a four-point probe.

The $\text{Cu}(\text{dpm})_2$ chelate was synthesised and purified by in the Institute of Inorganic Chemistry SD RAS. $\text{H}(\text{dpm})$ (Lancaster, N 1693) was introduced from outer evaporator. CO gas was prepared by the reaction of H_2SO_4 and HCOOH acids at 100°C and dried.

In the paper the temperature dependencies of film deposition rate in surface reaction controlled regime (kinetic regime) and in diffusion regime are presented. The corresponding morphology of the films prepared at 310°C is presented there, too. The kinetic regime was identified as the regime in which the deposition rate at the same temperatures is independent on the linear rate of the gas flow. The effective activation energy is 27 ± 7 kJ/mol. All films have *fcc* Cu structure according to the

synchrotron data. The film thick increases in range of $20 - 120$ nm with temperature increase from 270°C to 370°C . The resistivity of the film in thickness above 100 nm is about $(3 - 5) \times 10^{-6} \Omega \text{ cm}$.

In accordance with the known mass spectrometric study of the Cu β -diketonate decomposition the stable volatile by-products namely $\text{H}(\text{dpm})$, CO and H_2O were registered. It is useful to study their influence on the reaction kinetics and mechanism film formation. The temperature dependence of film deposition rate in the case of $\text{H}(\text{dpm})$ vapor addition with partial pressure of 0.06 Torr is presented. It was shown that the growth rates of the film thickness and mass are larger at the same temperatures against the process without $\text{H}(\text{dpm})$ addition. The effective activation energy decreases up to 10 ± 5 kJ/mol. However, the film thickness increases lower than the film mass with the temperature increase. It means that the $\text{H}(\text{dpm})$ addition leads to the film density increase. The film morphology is shown in the paper. It is similar to the film produced without $\text{H}(\text{dpm})$ addition. The films have *fcc* structure and resistivity equal to $1.1 \times 10^{-4} \Omega \text{ cm}$ (for film 110 nm in thickness).

The temperature dependence of film deposition rate in the case of CO addition with partial pressure of 15 Torr is presented, too. It was shown that the growth rate of the film mass lower at the same temperatures against the process without CO. However, the growth rate of the film thickness loses almost the dependence on the substrate temperature. The effective activation energy increases up to 46 ± 8 kJ/mol. The film morphology study shows that the particle size decrease. All these effects may be explained by poisoning the $\text{Cu}(\text{dpm})_2$ chelate adsorption sites. Nevertheless, the films have *fcc* Cu structure.

Then the temperature dependence of the film deposition rate in the case of H_2O addition at partial pressure of 16 Torr and the same other conditions is discussed. It was shown that the growth rate of the film mass is larger at the same temperatures against the process without H_2O addition. However, the film thickness is not affected by H_2O addition. It means that the film density increase. The effective activation energy decreases up to 10 ± 7 kJ/mol. The reaction order with respect to H_2O in the partial pressure range of $4 - 25$ Torr equal to 0.7. The latter corresponds to the dissociative adsorption of water molecules in part. The morphology study showed that the film microstructure appears to be fractal type. The resistivity of the Cu film 117 nm in thickness is only $5 \times 10^{-3} \Omega \text{ cm}$.

In conclusion it was noticed that the $\text{Cu}(\text{dpm})_2$ chelate was profitably employed as the volatile precursor CVD of the Cu films at relatively low temperature under reduction hydrogen atmosphere. The film resistivity was $3 \times 10^{-6} \Omega \text{ cm}$ and the magnitude of the Cu bulk resistivity may be reached by the film thickness increasing. H_2O and $\text{H}(\text{dpm})$ additions increase the Cu deposition rate but lead to the resistivity increase. Perhaps, H_2O concentration used in this study was surplus but it was determined by effort to increase the deposition rate by film thickness. As the result it was found that the film density was substantially increased. It was shown that CO is the Cu deposition inhibitor.

