## MOCVD OF COPPER FILMS FROM BIS(ETHYL-3-OXO-BUTANOATO)COPPER(II): EXPERIMENT AND THERMODYNAMIC ANALYSIS

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The chemical vapour deposition of the interconnection material, copper, in VLSI (very large scale integrated) circuits, is expected to result in excellent coverage of the inner surfaces of holes and trenches of high aspect ratios, making it a preferred process for the metallization of the coming generations. Thermodynamic analysis of the CVD process can predict trends as a function of various experimental parameters, thereby helping in a more systematic development of the process. It can also predict the possible impurities and undesired phases in the deposit. In this paper, we report on the thermodynamic investigation of the CVD of copper from the precursor bis(ethyl-3-oxo-butanoato)copper(II), Cu(etob)<sub>2</sub>, in argon and hydrogen ambients.

Although CVD is a nonequilibrium process controlled by kinetics and transport phenomena, equilibrium analysis is useful in understanding and developing the CVD process. In thermodynamic modeling, it is assumed that the substrate is in equilibrium with the vapour phase (1). The calculations are based on the minimization of the total Gibbs free energy of the system, while simultaneously satisfying the mass balance conditions (2). To arrive at the list of probable reaction products to be present at equilibrium, we have employed 'chemical reasoning', in addition to consulting the mass spectrum of the precursor.

Variations in the equilibrium molar concentration of various chemical species that can result during the CVD process using the above precursor in Ar atmosphere, as a function of temperature [Fig. 1] shows that only copper (and no copper oxide) is formed; the amount of carbon deposited decreases with increasing temperature. The temperature required for obtaining carbon-free copper films increases with increase in total reactor pressure (P). In hydrogen ambient, *pure copper* is obtained in the solid phase [Fig. 2]. What is noteworthy is that there is no trace of carbon under any of the deposition conditions considered.

Thin films of copper have been grown by MOCVD on  $SiO_2/Si(100)$  substrate from  $Cu(etob)_2$  in hydrogen ambient at different substrate temperatures and total reactor pressures. The X-ray diffraction pattern of the film grown at 300°C shows that pure copper (and no oxide) is formed under the deposition conditions employed. Auger electron spectroscopy (AES) depth profile [Fig. 3] also indicates the formation of pure copper with the concentration of carbon and oxygen being  $\leq 5$  at%. The presence of C and O in the films is likely due to post-deposition contamination (3).

The near-bulk value of resistivity (1.99  $\mu\Omega$ -cm vs. 1.67  $\mu\Omega$ -cm) and low carbon content of copper films grown from Cu(etob)<sub>2</sub> support the prediction by thermodynamic analysis that films prepared under these conditions would be oxide- and carbon-free. Thus, we infer that the methodology adopted here to predict the equilibrium molar concentrations of the products of the MOCVD reactions can be a useful guide to the understanding and development of practical CVD processes.

## ACKNOWLEDGMENTS

The authors are grateful to D. Cahen, Weizmann Institute of Science, Israel, for the AES analysis.

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Fig. 1. The equilibrium molar concentration of various species in argon atmosphere as a function of temperature at P = 1 Torr.



Fig. 2. The equilibrium molar concentration of various species in hydrogen atmosphere as a function of temperature at P = 25 Torr.



Fig. 3. AES depth profile of Cu films deposited in hydrogen atmosphere at  $300^{\circ}$ C and P = 25 Torr.