

Preface

Chemical Vapor Deposition (CVD) is a versatile thin film deposition process, attractive to industry, as it offers advantages like uniform deposition over a large substrate area, conformal coverage into sub-half-micron size trenches, selective area deposition, high degree of compositional control, high throughput, etc. The CVD of Cu has drawn attention recently because of its possible applications in ultra large scale integrated circuits (ULSI) as the interconnect material. This thesis work has been undertaken to understand the effect of different CVD growth parameters on microstructural development of Cu films. For a better understanding of morphological evolution of Cu film, computer simulations of early stages of film growth have been carried out using the Monte Carlo method.

Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) films by CVD has become an important field of investigation especially due to its ability, in contrast with Physical Vapor Deposition (PVD), to provide large area films at a low temperature, and atomically flat surfaces through layer by-layer growth. The major difficulties associated with CVD of YBCO are due to the poor thermal properties of the metalorganic precursors. In this work, an efficient and economical precursor delivery method has been successfully implemented for the in situ growth of superconducting YBCO films with precise control over the deposition process.

In the introductory Chapter 1, an overview of CVD is presented followed by a discussion of the motivation for the present research work.

Chapter 2 deals with the CVD of Cu films. It describes in detail the design and fabrication of a MOCVD system built in house. It comprises a cold wall, vertical flow reactor made of stainless steel. The precursors were evaporated from stainless steel 'bubblers' maintained at well-controlled temperatures. The vapor delivery lines between the 'bubblers' and the inlet of the reactor were heated to avoid condensation of the precursors. A quartz lamp heated graphite block was used as the substrate holder. The reactor pressure was maintained at the desired level using a high capacity 'Roots' pump and a throttle valve placed at the inlet.

of the pump

Growth and microstructure of Cu films obtained from the pyrolysis of the metalorganic precursor bis(dipivaloylmethanato)Cu(II) or $\text{Cu}(\text{dpm})_2$ have been studied as a function of different CVD parameters, such as substrate temperature, 'bubler' temperature, carrier gas flow rate, and reactor pressure. Films were characterized for their resistivity by the van der Pauw method, surface morphology by SEM, optical microscopy, and reflectivity measurements, crystallinity by x-ray diffraction, and for composition by XPS and Auger electron spectroscopy. Growth rate of the films was measured as a function of substrate temperature, showing two distinct growth regimes, (a) kinetically controlled regime at a low temperature where growth rate increases rapidly with the substrate temperature and (b) mass-transport controlled regime where growth rate is largely independent of substrate temperature. Morphological evolution of Cu films has been investigated in different growth regimes. Diffusion of Cu into SiO_2 substrate and formation of silicide at the Cu and SiO_2 interface have been studied. Pyrolysis of $\text{Cu}(\text{dpm})_2$ in pure argon atmosphere at 320°C , leads to the incorporation of Cu_2O into the growing Cu films, whereas at 350°C , formation of pure polycrystalline Cu films takes place. Films deposited at 450°C show isolated crystallites having faceted structure.

An attempt has been made to understand the role of the molecular structure of the metalorganic precursor in determining the growth and microstructure of Cu films. A new precursor, bis(*t*-butylacetoacetato)Cu(II) or $\text{Cu}(\text{tbaaac})_2$ has been synthesised by modifying $\text{Cu}(\text{dpm})_2$. While the threshold temperature for Cu deposition from $\text{Cu}(\text{tbaaac})_2$ is found to be lower (225°C), deposition of Cu film obtained from the pyrolysis of this precursor occurs at a significantly low growth rate compared to $\text{Cu}(\text{dpm})_2$. Films obtained from $\text{Cu}(\text{tbaaac})_2$ show mirror-like reflectivity and dense microstructure, compared to dull and porous Cu films obtained from $\text{Cu}(\text{dpm})_2$. In case of $\text{Cu}(\text{tbaaac})_2$, the Cu films formed have well-connected microstructure with low resistivity at a much lower thickness compared to $\text{Cu}(\text{dpm})_2$ (700 Å vs 4000 Å).

Chapter 3 describes the Monte Carlo simulation technique used to understand aspects of Cu film growth by CVD. A lattice gas model has been considered to study the early stages of film growth. This model has been designed to study the

following processes (a) arrival rate of the precursors on the substrate, and (b) surface diffusion of adatoms on the substrate as well as on the film. Shape and size distribution of clusters have been analysed under different growth conditions. A detailed study has been made in an attempt to understand two intrinsic time scales operational under a given growth condition. One corresponds to the slower arrival rate of precursors to the substrate compared to surface kinetics, where growth rate is controlled by the arrival rate. The other one is related to growth under kinetically controlled regime, where surface kinetics are slower compared to arrival rate. Investigations have also been carried out to understand the energetics responsible for the observed faceted island growth. Despite the unavailability of chemical thermodynamic as well kinetic data needed for a proper simulation of a CVD process, the model works well in explaining some of the experimental results obtained from the CVD of Cu.

Chapter 4 deals with the CVD of YBCO films. The β -diketonate complexes, $\text{Cu}(\text{dpm})_2$, $\text{Ba}(\text{dpm})_2$ and $\text{Y}(\text{dpm})_3$ ($\text{dpm} \rightarrow$ dipivaloylmethanate) have been used as precursor materials. These precursors are solids at room temperature. The Ba precursor, due to the large ionic radius of Ba^{2+} , shows poor volatility, and further, its sublimation temperature is close to the decomposition temperature. Hence, it is extremely difficult to maintain the relative proportions of the input flow rates of the precursors for the repeatability of the deposition process. In this work, an efficient precursor delivery system has been designed and used for in situ deposition of high quality YBCO superconducting films on $\text{MgO}(100)$ substrates. Film deposition has been carried out in a horizontal hot wall quartz reactor. By estimating the input molar flow rates of the precursors, the ratios of evaporated and incorporated mole percents of Cu, Ba and Y cations were investigated. Crystallinity, transition temperature, and surface morphology have been studied as a function of film composition and oxygen partial pressure during film-growth.