Thermodynamic investigation of the MOCVD of copper films from *bis*(2,2,6,6-tetramethyl-3,5-heptadionato)copper(II)

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Abstract. Equilibrium concentrations of various condensed and gaseous phases have been thermodynamically calculated, using the free energy minimization criterion, for the metalorganic chemical vapour deposition (MOCVD) of copper films using *bis*(2,2,6,6-tetramethyl-3,5-heptadionato)copper(II) as the precursor material. From among the many chemical species that may possibly result from the CVD process, only those expected on the basis of mass spectrometric analysis and chemical reasoning to be present at equilibrium, under different CVD conditions, are used in the thermodynamic calculations. The study predicts the deposition of pure, carbon-free copper in the inert atmosphere of argon as well as in the reactive hydrogen atmosphere, over a wide range of substrate temperatures and total reactor pressures. Thin films of copper, grown on SiO₂/Si(100) substrates from this metalorganic precursor by low pressure CVD have been characterized by XRD and AES. The experimentally determined composition of CVD-grown copper films is in reasonable agreement with that predicted by thermodynamic analysis.

1. Introduction

Chemical vapour deposition (CVD) is a versatile process for the preparation of thin films of a variety of materials, such as metals, semiconductors, oxide superconductors, and oxide ferroelectrics (Kern and Ban 1978). CVD conditions can be tailored to yield microcrystalline and amorphous films, uniform deposition over large areas, and good step coverage of high aspect-ratio features. The mechanisms of film synthesis by CVD are not always clear, and a significant number of preliminary experiments are often necessary to determine the optimum operating conditions. A better understanding of the fundamental aspects of this deposition technique is needed for a more efficient approach to CVD process development, and to grow, for example, metal films with low impurity levels (and thus with resistivity close to that of the bulk) and with desirable morphology, at lower temperatures. In general, both thermodynamics and kinetics play essential roles in the process of thin film growth by CVD. While thermodynamics govern the behaviour of the system at equilibrium, kinetics control the tendency of the system to move towards the equilibrium state under a given growth condition. The extent the system is away from equilibrium depends upon the time scales of various atomic level processes (Goswami *et al* 1997). For a given chemical system, a thermodynamic simulation of the CVD process may provide valuable information on the composition of the resulting gaseous and condensed phases at equilibrium as a function of the process parameters, and has been found helpful in several systems (Fredriksson and Forsgren 1996; Bernard *et al* 1999; Sourdiaucourt *et al* 1999; Kang *et al* 2000).

In thermodynamic modelling, it is assumed that the substrate is in equilibrium with the vapour phase. As the films were grown in the present study at a low growth rate in the mass-flow-limited CVD regime, the deposition may be considered an equilibrium process. The modelling is based on the minimization of the total Gibbs free energy of the system, obeying the mass balance conditions, as originally described by Eriksson (1971). This method can be used for predicting the trends in the CVD process as a function of experimental thermodynamic parameters, thereby helping in the selection of suitable operating conditions as well as in predicting the possible impurities in the deposited films.

The CVD of an elemental metal such as copper is likely to be simple and illustrative enough as a model system for the study of the fundamental aspects of CVD. Furthermore, copper has already been employed in the metallization of ultra-large-scale integrated (ULSI) circuits, owing to its low resistivity and high resistance against electromigration (Murarka *et al* 1993). It is surmised that,

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as feature sizes of ULSI devices continue to shrink, CVD would become the process of choice for the deposition of copper in ULSI circuits. As in any CVD process, the choice of precursors, together with the process parameters, determines the microstructure and related properties of Cu films. Thermodynamic modelling can be a useful tool in making the proper choice of growth conditions. Specifically, such calculations may be used to predict the range of CVD parameters where the co-deposition of carbon, a problem often encountered in MOCVD, is a minimum. A considerable amount of experimental work has been reported on the effect of MOCVD processing conditions on film purity, resistivity, morphology, selectivity, and growth rate of the Cu films (Griffin and Maverick 1995; Kim *et al* 1998). But there is no report in the open literature of an effort, based on thermodynamic modelling, to predict the effect of processing conditions on the deposition of copper films produced by thermal MOCVD, though the formation of the oxides of copper has been investigated by this method (Ottosson and Carlsson 1996).

As part of a systematic investigation of the thermodynamic aspect of the MOCVD growth of copper films, we have reported a detailed calculation and experimental verification on Cu films grown using *bis*(*t*-butyl-3-oxobutanoato)copper(II) [Cu($C_8H_{13}O_3$)$_2$, abbreviated Cu(*t*bob)$_2$], as the precursor material (Sukanya *et al* 2002). In the present study, the reliability of the above approach to MOCVD of Cu films has been investigated using another precursor of the ***b***-diketonate class. We have employed as precursor the Cu(II) ***b***-diketonate complex, *bis*(2,2,6,6-tetramethyl-3,5-heptadionato)copper(II), abbreviated hereafter as Cu(thd)$_2$ (referred to also as copper dipivaloylmethanate). Though fluorinated ***b***-diketonate copper complexes have been developed in recent years for achieving high-rate copper deposition, Cu(thd)$_2$ is illustrative of the chemistry of the MOCVD of copper. The Cu(thd)$_2$ complex, which has previously been studied (Maruyama and Ikuta 1993) as a precursor for the CVD of copper, is chemically stable, and sublimes at relatively low temperatures (~ 100°C). As the experimental part of this effort, copper films have been grown from Cu(thd)$_2$ by low pressure CVD on SiO$_2$/Si(100) substrate under (i) the inert atmosphere of argon and (ii) a highly reactive hydrogen atmosphere, over a wide range of deposition conditions. Our thermodynamic calculations are corroborated by experimental results, as reported below.

1.1 *The principle of the thermodynamic approach*

The method of equilibrium calculations is based on the minimization of the Gibbs free energy of the system under consideration, and follows an approach outlined by Eriksson (1971). For calculating the equilibrium composition, i.e. the non-negative set of mole numbers which gives the lowest possible value of the total free energy of the system, and which satisfies the mass balance conditions, an iterative procedure is used. For a system of known initial composition, studied at a given temperature and total pressure, this method gives the relative compositions of the species present both in the vapour phase and in the deposit, when equilibrium is reached. Its application to a given CVD system supposes that the deposit can be considered to be in equilibrium with the vapour phase, and that all the chemical species present at equilibrium can be enumerated and taken into account in the calculations.

As noted above, for the MOCVD of copper thin films carried out in this study, Cu(thd)$_2$, whose structure is shown in figure 1, was used as the precursor. (The ligand will be denoted by *thd*.) Therefore, any product of the chemical reactions occurring during the CVD process should comprise one or more of the elements Cu, O, C, and H. This would be true regardless of whether argon or hydrogen is used as the carrier gas, as argon is inert. It is very important to choose correctly the chemical species that can be present at equilibrium as a result of the chemical reactions that occur. Otherwise, thermodynamic calculations may yield a combination of phases that is far from experimental reality. In the absence of a mass spectrometric analysis of the species present in the CVD reactor (such as through a residual gas analyser), an informed and careful enumeration of the species that can result from the CVD process is an important step in thermodynamic modelling. The –C(CH$_3$)$_3$ moiety, being labile, is expected to be detached first from the precursor (figure 1). This group, depending on the reactor ambient, can possibly produce hydrocarbons that contain up to four carbon atoms per formula unit. After the removal of the two –C(CH$_3$)$_3$ moieties in it, the *thd* ligand is left with three carbon atoms, which can potentially produce different chemical species, such as, aldehydes, ketones, ketenes, alcohols etc containing a maximum of three carbon atoms per formula unit. Based on such considerations, all the various inorganic and organic compounds, in condensed and gaseous phases, which can result from the pyrolysis
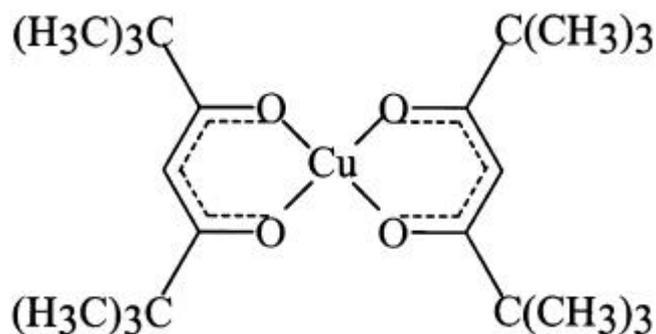

Figure 1. Molecular structure of the metalorganic precursor Cu(thd)$_2$.

of this precursor, are listed in table 1. Mass spectrometric analysis of the precursor (figure 2) has been consulted in choosing the gaseous compounds included in the modelling, from among all those listed in table 1.

The partial pressure of the precursor in the reaction chamber in the depositions reported here is very low (~ 0·1 Pa); the total reactor pressure, almost entirely due to the carrier gas, is 1·33 kPa (10 Torr). Therefore, the probability of interaction between the decomposed fragments of the precursor is low, i.e. these primary fragments can undergo collisions only with the atoms/molecules of the carrier gas. Such collisions, leading to further fragmentation and reaction(s), become important when a reactive gas like hydrogen or oxygen is used as the carrier or added to the carrier gas flow. Reactions of this kind are not expected when an inert gas is used as the carrier, implying that the relative mole ratio of the elements Cu, H, O, and H is not altered by the CVD process.

In the modelling of the CVD process conducted in the inert ambient of argon, the data obtained from mass spectrometric analysis were used directly. The fragments of higher molecular weight are not included in the calculations as they are expected to undergo further fragmentation to produce $-C(CH_3)_3$ ($m/z = 57$), $CHCO$ ($m/z = 41$), and CH_3CO ($m/z = 43$), which are indeed seen in the spectrum. The corresponding stable gaseous species are C_4H_8 (isobutene), CH_3CHO (acetaldehyde), and C_2H_2O

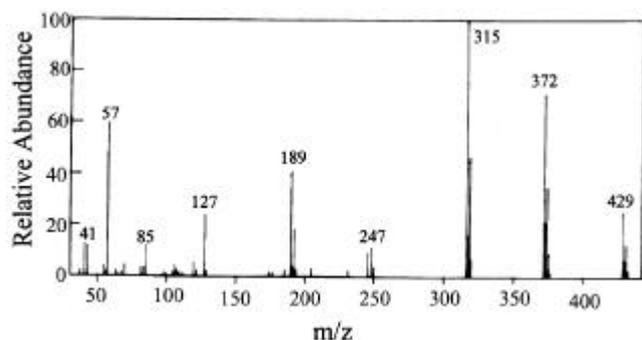**Figure 2.** Mass spectrum of Cu(thd)$_2$ recorded in the electron impact mode.

(ketene). CO has also been considered in our calculations, as the molecular structure of the precursor (figure 1) suggests that it is a probable reaction product, though its m/z value (28) is too low to be detected by mass spectral analysis employed in the present study. The probable solid products of the reactions involved are metallic copper, its oxides, hydroxide, and carbonate. For several of the inorganic and organic compounds listed in table 1, such as Cu(g), CuH(g), O(g), H(g), C(g), CH(g), CH$_2$(g), CH$_3$(g) etc, the Gibbs free energy of formation has a positive value in the range of conditions used in this study. These are therefore, unstable, and are not considered to be present at equilibrium—a premise ascertained by a few trial calculations that included these species. The list of compounds, predicted on the basis of these considerations to be present at equilibrium during the CVD process carried out in an argon atmosphere, is given in table 2a.

When a highly reactive gas like hydrogen is used as the carrier, not only is the mole ratio of the elements affected, but the list of stable compounds to be considered in the thermodynamic analysis also changes drastically. The unsaturated hydrocarbon C_4H_8, enumerated in the previous case, is expected to become saturated to give C_4H_{10}, and to produce three other saturated hydrocarbons, CH_4, C_2H_6, and C_3H_8, in the presence of the reactive hydrogen gas. Saturated alcohols are expected to be formed, which can produce water vapour and CO. The entire list of compounds to be considered in the thermodynamic analysis of the CVD process conducted using hydrogen as the carrier gas is given in table 2b. Hydrogen is not included separately in the list, as the extra amount of hydrogen that can be consumed by the precursor to produce different condensed and gaseous species [such as Cu(OH)$_2$ in the solid phase, and CH$_4$, H$_2$O etc in the gas phase] is already considered. However, in the experimental work carried out here, the partial pressure of Cu(thd)$_2$ is of the order of 0·1 Pa, while the total reactor pressure is 1·33 kPa. It may, therefore, be assumed that the 'excess' hydrogen present in the chamber, over and above that required for the formation of the species listed above, does not affect the CVD reactions.

Table 1. List of all possible condensed and gaseous phases which may be formed during Cu–MOCVD from Cu(thd)$_2$ in argon and hydrogen atmospheres.

Condensed phases				Gaseous phases		
Cu	Cu	H	CO	C_2H_6	HCHO	CH_3OH
CuO	Cu_2	H_2	CO_2	C_3H_4 (propadiene)	CH_3CHO	C_2H_5OH
Cu_2O	CuO	H_2O	CH	C_3H_4 (propylene)	C_2H_5CHO	C_3H_5OH
CuH_3	CuH	H_2O_2	CH_2	C_3H_6	CH_3COCH_3	C_3H_7OH
$Cu(OH)_2$	O	C	CH_3	C_3H_8	$C_2H_5COCH_3$	
$CuCO_3$	O_2	C_2	CH_4	C_4H_8 (isobutane)	C_2H_2O	
C	O_3	C_3	C_2H_2	C_4H_{10} (isobutane)		
		C_4	C_2H_4			

Table 2. The phases considered for the thermodynamic analysis of Cu–MOCVD in argon and hydrogen atmospheres.

(a) In argon atmosphere		(b) In hydrogen atmosphere	
Condensed phases	Gaseous phases	Condensed phases	Gaseous phases
Cu	CO	Cu	H_2O
CuO	C_4H_8	CuO	CO
Cu_2O	CH_3CHO	Cu_2O	CH_4
$Cu(OH)_2$	C_2H_2O	$Cu(OH)_2$	C_2H_6
$CuCO_3$		$CuCO_3$	C_3H_8
C		C	C_4H_{10}
			HCHO
			CH_3CHO
			C_2H_2O
			CH_3OH
			C_2H_5OH
			C_3H_7OH

Thus, instead of including all the compounds that may possibly be formed, the compounds likely to be found at equilibrium are short-listed, based on mass spectral studies and on chemical reasoning. It is seen that such an approach helps to pare down the list of species to be included in any calculation considerably, making the calculations computationally more efficient. Calculations were then performed, as described earlier (Sukanya *et al* 2002), to predict the concentrations of the various solid and gaseous phases resulting from the CVD process, as a function of temperature and pressure. The required standard free energies of formation of the inorganic compounds in table 2 were obtained from the JANAF thermodynamic tables (Chase *et al* 1985), and those for the organic compounds from a recent compilation by Yaws *et al* (1992).

2. Experimental

The metalorganic precursor, $Cu(thd)_2$, which is a crystalline solid at room temperature was synthesized, purified, and characterized in our laboratory. The mass spectrum of the complex, $Cu(thd)_2$ was recorded in the electron impact mode with a beam energy of 70 eV. Thin film deposition was carried out in a low-pressure, cold-wall, CVD reactor with vertical flow built in house (Goswami 1995), in which the total pressure, gas flow rate, and substrate temperature could be varied and controlled. Deposition conditions are summarized in table 3. The substrates were 20×20 mm pieces of Si(100) on which a thermal oxide (~ 1 μm thick) had been grown. These were placed about 30 mm from the 'shower-type' manifold through which the precursor vapours were carried into the reactor. This arrangement resulted in films with a uniform thickness (to within 20%) over the substrate area. (For each film, the average thickness was estimated by measuring the substrate weight gain using a semi-microbalance. The uniformity of deposition was verified by profilometric measurements on selected samples at

Table 3. Range of deposition conditions.

Precursor	$Cu(thd)_2$
Substrate temperature (T_{sub})	250–450°C
Vapourizer temperature	120°C
Carrier gas	Ar, H_2
Carrier gas flow rate	50–200 sccm
Total reactor pressure (P)	1–100 Torr
Deposition time	15–120 min
Substrate	SiO_2/Si(100)

different spots of the surface of the film.) The as-deposited films were characterized by X-ray diffraction (XRD) for the identification of the crystalline phases, and Auger electron spectroscopy (AES) for quantitative elemental analysis. Film resistivity was measured by the van der Pauw method. Film growth was studied experimentally as a function of substrate temperature and reactor pressure to find the conditions required for a good growth rate, though no attempt was made to design the reactor for high growth rates. Films grown under these conditions have been used in the present study to compare the theoretically simulated data with experimental observations. A substrate temperature of 350°C and a total reactor pressure of 1·33 kPa (10 Torr) were found to give reasonable growth rates for depositions under argon (Goswami 1995), as well as under hydrogen ambient. Thermodynamic calculations have been carried out and reported here for these conditions, as well as for a wide range of conditions indicated in table 3.

3. Results and discussion

Figure 3 shows the calculated equilibrium molar concentrations of various condensed and gaseous phases as a function of temperature when argon is used as the carrier gas and the total reactor pressure is 1·33 kPa. The calculations have been performed assuming that one mole of

the precursor is consumed. If a different amount of precursor is considered, there will be a multiplication factor to the *y*-axis of figure 3, relative proportions of the resulting compounds remaining the same. Phases other than the ones shown in this figure have been disregarded as they are formed in negligible and experimentally undetectable quantities ($< 10^{-4}$ mole). It can be inferred from the figure that pure, carbon-free copper is formed over the entire temperature range considered, even in the inert atmosphere of argon, though the oxides of copper are thermodynamically much more stable than the metal. The formation of carbon monoxide and the organic compounds, with stabilities comparable to or higher than those of the oxides of copper (Chase *et al* 1985; Yaws *et al* 1992), is found to be preferred under equilibrium conditions. This may be the consequence of the constraint that, in the inert argon ambient, the mole ratio of the elements is fixed by the precursor molecular formula. Compositions of the different gases obtained from the calculation also remain constant over this range.

A similar study has been carried out as a function of pressure, keeping the temperature constant at 350°C. The results are presented in figure 4, which indicate no change in composition of the condensed and the gaseous phases as a function of pressure. The thermodynamic calculations thus predict the formation of carbon-free, pure copper in the solid phase, and carbon monoxide, isobutene, and acetaldehyde in the gaseous phase, the compositions of all these species being constant in this range of temperature and pressure. It appears from these calculations that the carbon present in the system is consumed fully by the formation of the monoxide and the stable organic compounds, leaving carbon-free 'clean' copper as the solid deposit.
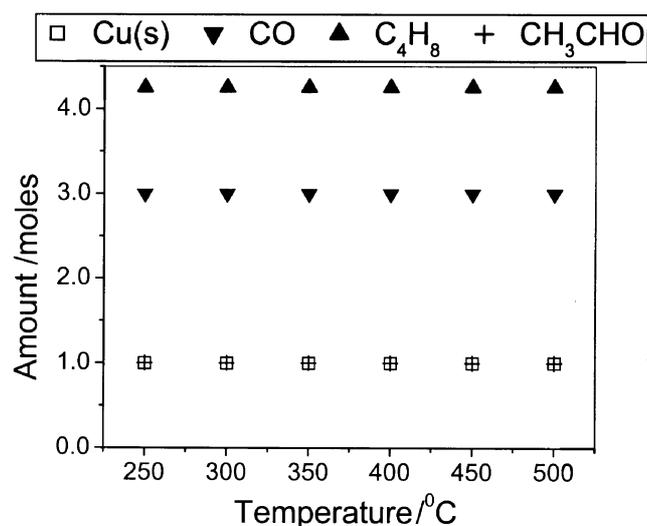
The results of similar calculations for CVD in hydrogen atmosphere, shown in figures 5 and 6, differ significantly from those obtained for CVD in argon. When the total pressure is maintained constant at 1·33 kPa (figure 5), the Cu-film is not totally carbon-free at lower temperatures (< 347°C), with the amount of carbon increasing slowly as the temperature decreases. These results are presented on a logarithmic scale to show clearly the variations in the amount of different compounds formed as the CVD parameters change. Carbon-free pure copper appears at higher temperatures where the compositions of the condensed phase (copper), and the gaseous phase (water vapour, carbon monoxide, and methane) remain
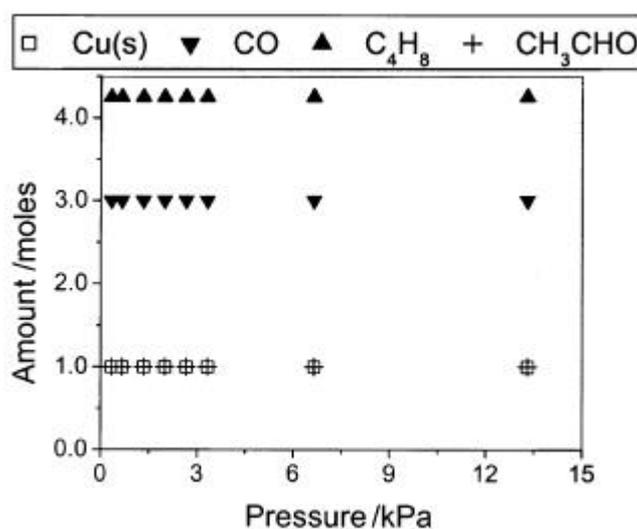

Figure 4. Equilibrium molar concentration of various phases in argon atmosphere as a function of pressure, when the substrate temperature is constant at 350°C.
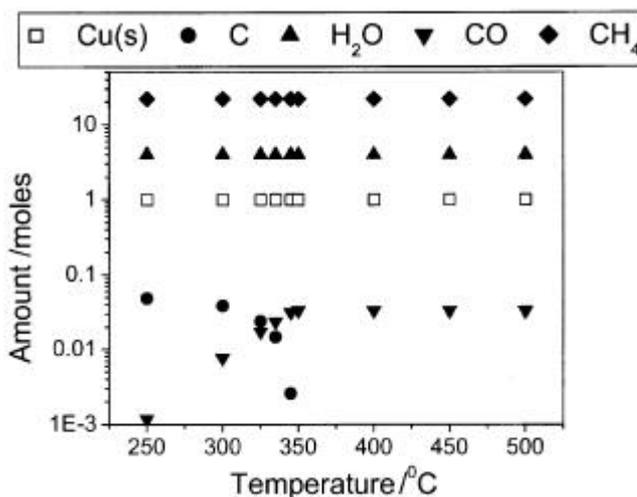

Figure 3. Equilibrium molar concentration of various phases in argon atmosphere as a function of temperature, when the total reactor pressure is constant at 1·33 kPa (10 Torr).

Figure 5. Equilibrium molar concentration of different phases in hydrogen atmosphere as a function of temperature, the total reactor pressure being constant at 1·33 kPa (10 Torr).

constant. The results of thermodynamic calculations carried out for deposition at 350°C (figure 6) predict the possibility of a small percentage of carbon in copper films deposited at higher pressures (> 1·73 kPa or 13 Torr), the percentage increasing slowly as pressure increases. Up to about 1·6 kPa (12 Torr), the amounts of carbon-free copper and the gaseous phases remain constant as the pressure varies. The results of our thermodynamic modelling, both in argon and hydrogen atmosphere, may be summarized as predicting the
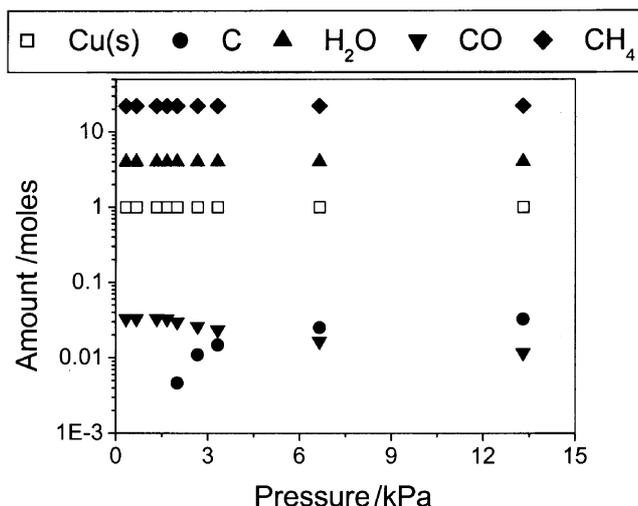
deposition of pure and carbon-free copper, except for a very small amount of carbon predicted to be present when deposition is carried out at relatively low temperatures and high pressures.

The experimental results of Cu film deposition using $Cu(thd)_2$ may now be compared with thermodynamic simulations. As thermodynamic calculations take no account of reaction kinetics, reaction rate constants, and activation energies, errors in the list of species predicted to be present at equilibrium are possible. However, if CVD is performed in the mass transport-limited regime at a low growth rate, these errors can be minimized (Kang *et al* 2000). The Arrhenius plot for the MOCVD growth of Cu films in hydrogen atmosphere is shown in figure 7. The deposition rate reaches its peak at ~ 350°C, indicating that deposition around and above this temperature is mass transport-limited. When argon is used as the carrier gas, the deposition rate is reasonably saturated at ~ 350°C, within the mass transport limited regime, although the maximum is at ~ 370°C. Thus, the reliability

Figure 6. Equilibrium molar concentration of different phases in hydrogen atmosphere as a function of pressure, the substrate temperature being constant at 350°C.
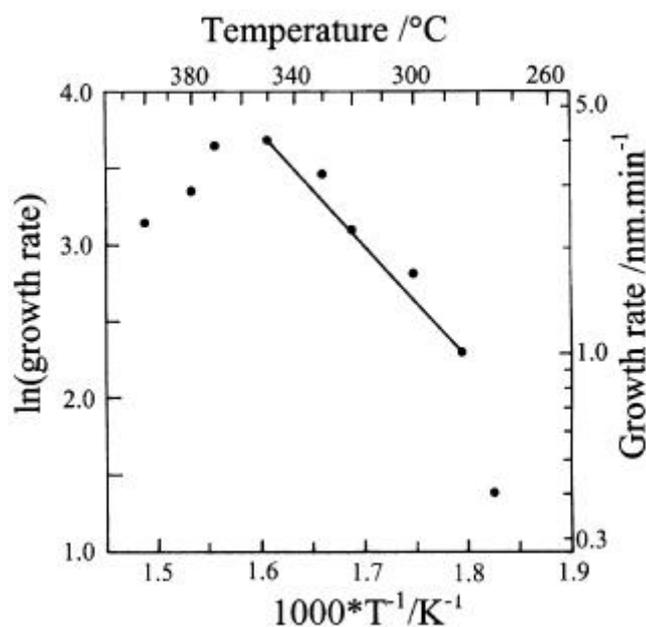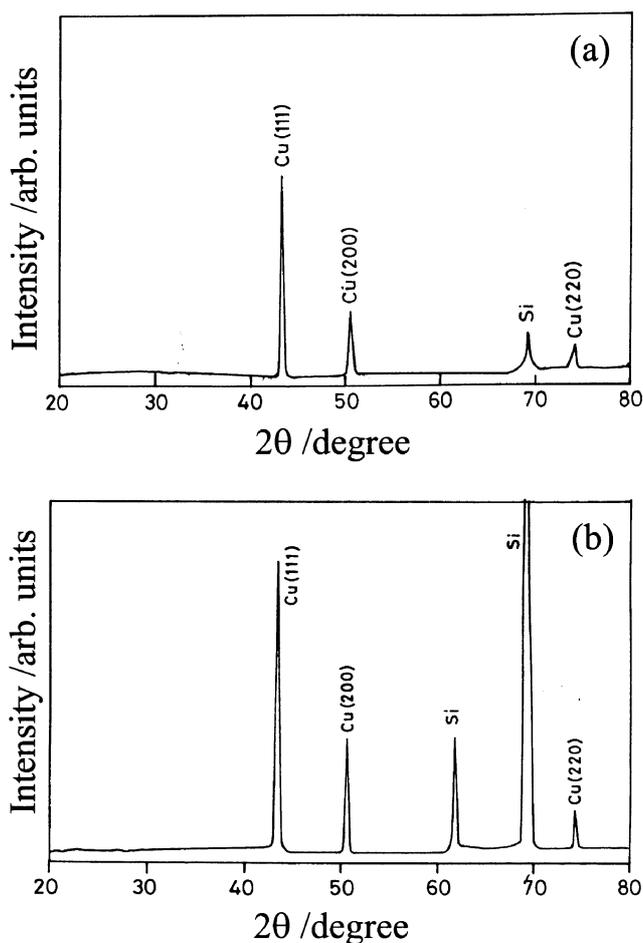

Figure 7. Arrhenius plot of growth rates of Cu films from $Cu(thd)_2$ on $SiO_2/Si(100)$ under hydrogen atmosphere at $P = 1·33$ kPa (10 Torr).

Figure 8. X-ray diffraction patterns of Cu films deposited on $SiO_2/Si(100)$ from **(a)** $Cu(thd)_2$ in Ar, and **(b)** $Cu(thd)_2$ in H_2 at $T_{sub} = 350$°C and $P = 1·33$ kPa (10 Torr).
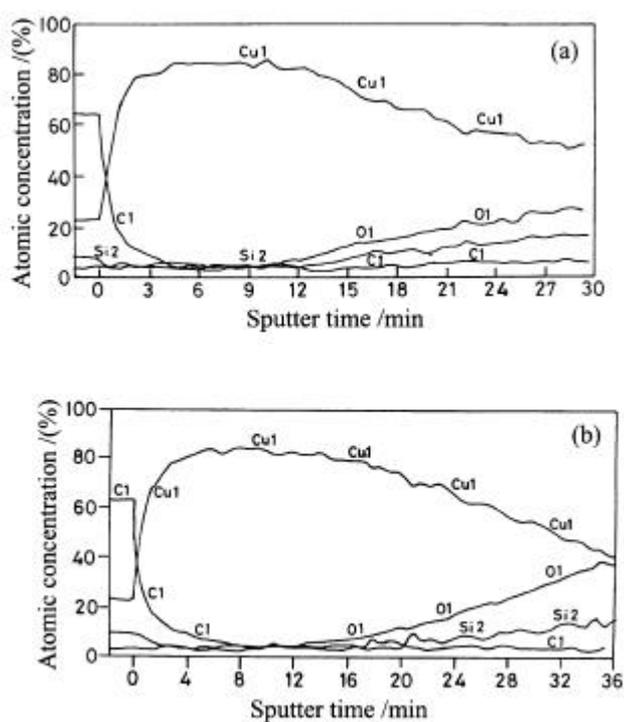
Figure 9. Auger compositional depth profile for Cu films grown on $SiO_2/Si(100)$ from **(a)** $Cu(thd)_2$ in Ar, and **(b)** $Cu(thd)_2$ in H_2 at $T_{sub} = 350°C$ and $P = 1·33$ kPa (10 Torr).

of thermodynamic predictions is limited to depositions carried out at ~ 350°C and above.

Figures 8(a) and (b) show the XRD patterns of thin films deposited at 350°C and a reactor pressure of 1·33 kPa in argon (Goswami 1995) and in hydrogen, respectively. Within the detection limits of XRD, pure Cu is present in both the cases, to the exclusion of any copper oxide, in agreement with the thermodynamic calculations. XRD patterns for films deposited under other CVD conditions, in the range of temperature and pressure given in table 3, also present the same result.

The purity of the copper films predicted by the thermodynamic modelling can also be verified from room temperature electrical resistivity measurements. The resistivity of a high-purity film is expected to be close to its bulk value, provided that the film is continuous and its grains are not too small, and that the film is sufficiently thick that surface scattering of carriers does not dominate electrical resistivity. The films grown in hydrogen atmosphere show a minimum resistivity of 2·15 $\mu\Omega$-cm (120 nm thick), while the value is higher (2·5 $\mu\Omega$-cm) for a film grown in argon (Goswami 1995), the difference likely being the result of the difference in the grain structures of the films in the two cases. But the measured value of the minimum resistivity in each case is not far from the resistivity of bulk copper (1·7 $\mu\Omega$-cm). This may be attributed to the 'clean' pyrolysis of the precursor

occurring during the CVD process, as predicted by thermodynamic modelling.

The Auger electron spectroscopy (AES) depth profiles of the Cu films grown in argon (Goswami 1995) and hydrogen ambient are shown, respectively, in figures 9(a) and (b). From the elemental composition obtained from AES, it is apparent that the Cu films are slightly (< 4 at.%) contaminated by carbon, oxygen, and silicon. Chemical interactions at the Cu–Si interface are also apparent. It has been established previously (Baum and Larson 1993) by Auger analysis that, even in electron beam-evaporated high purity copper films, the typical oxygen content is about 5 at.%, which can only be eliminated if copper is passivated against oxidation by suitable means (Murarka *et al* 1993). Because of the presence of hydrogen in the reactor (figure 9(b)), the likelihood of oxygen incorporation in the copper films during film growth is greatly minimized. It may, therefore, be inferred that the oxygen present in the copper films grown in this study is due to post-deposition oxidation, and not due to contamination during the CVD process. The presence of the small amount of residual carbon observed may be interpreted as reflecting the inability of thermodynamic modelling to take reaction kinetics—in particular, the nature of the surface which determines the adsorption and desorption processes basic to CVD—into account.

4. Conclusions

Thermodynamic modelling of the MOCVD growth of copper films using $Cu(thd)_2$ as the precursor material has been carried out. As such modelling cannot take into account either reaction kinetics or mass transfer in the vapour, it gives a simplified representation of the metal deposition process. Nevertheless, this type of modelling can be useful in predicting trends in a thermal CVD process as the process parameters change. Mass spectral analysis of the precursor, together with chemical reasoning, was employed to select, from among the many chemical species possible, those likely to be present at equilibrium in the CVD process conducted in two different atmospheres. Different combinations of probable reaction products have to be considered for CVD conducted in inert (argon) and reactive (hydrogen) ambients. The thermodynamic modelling carried out here shows that pure and carbon-free copper can be deposited from $Cu(thd)_2$ under both the ambients, over a wide range of substrate temperatures and reactor pressures. The thermodynamic yield is in reasonable agreement with experimental observations.

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