

Binary Phase Diagram and Thin Film Coatings of Bimetallic Oxides using Bis(N-isopropylsalicylaldimine)M(II) M = Co, Ni and Zn as a Single Source Precursor for Thermal Chemical Vapor Deposition

C. CHANDRAKALA, P. SRAVANTHI, K. S. NAGARAJA, B. JEYARAJ

Department of Chemistry, Loyola Institute of Frontier Energy (LIFE)
Loyola College, Chennai-600 034. India. Fax: +91 44 28175566
E.mail: bchandru8484@gmail.com; bjlifchemistry@gmail.com

Abstract

The metal Schiff base complexes of bis(N-isopropylsalicylaldimine)cobalt(II), bis(N-isopropylsalicylaldimine)nickel(II) and bis(N-isopropylsalicylaldimine)zinc(II) were prepared by simple combination of the metal salts with the ligands in the right proportions via a condensation reaction. These complexes were characterized by various spectroscopic techniques. Formations of the nitrogen coordination with metal and the wavelengths of maximum adsorption complexes were confirmed by FT-IR and UV-visible spectroscopy respectively. Determination of the melting points and the volatility of the complexes were studied by TGA/DTA analysis. The complexes were found to be volatile based on the TG/DTA study. The volatile complexes would also be studied by (EI-MS) to determine the molecular formulae and the corresponding molecular weight. The binary phase diagrams of Co(salisopropylamine)₂ - Ni(salisopropylamine)₂; Ni(salisopropylamine)₂ - Zn(salisopropylamine)₂ and Co(salisopropylamine)₂ - Zn(salisopropylamine)₂ were constructed by taking different mole ratios the corresponding parent complexes. These binary eutectics were used for the bimetallic deposition of the metal oxide thin films over silica by TCVD method. These bimetallic thin films can be used for carbon nano tubes (CNT) and sensors applications.

Keywords: Volatile Schiff base complexes, Thermal Chemical Vapor Deposition (TCVD), Binary phase diagram, Metal oxide thin films, SEM/EDAX

Introduction

The searches for new composite and multiphase composition have been a matter of interest in the recent years because of the enormous technological implications of these processes. In this sense, several studies with transition metal compounds with doped-metals [1] have been reported in recent years. Systems in which conditions are present in two or more phases are called heterogeneous system. The study of heterogeneous equilibria can be made with the help of phase rule. It predicts qualitatively the effect of temperature, pressure and concentration on poly phase equilibria. For preparing thin films of mixed metal oxides using CVD techniques, it would be important to study the phase diagrams of these mixed metal oxides. The knowledge of these phase diagrams are important to understand the mechanisms of the reactions that occur during metallization and future heat treatment of semiconductor devices [2-5]. These metal oxide thin films were obtained by the lowering melting point composition. The objective of this work is to investigate mixed metal precursors from the metallo-organic complexes using phase rule. Bis(N-isopropylsalicylaldimine)cobalt(II), bis(N-isopropylsalicylaldimine)nickel(II) and bis(N-isopropylsalicylaldimine)zinc(II) complexes would be prepared and characterized by using FT-IR, UV-Vis, EI-Mass and TG-DTA techniques. Then the phase diagrams of Co(salisopropylamine)₂ - Ni(salisopropylamine)₂; Ni(salisopropylamine)₂ - Zn(salisopropylamine)₂ and Co(salisopropylamine)₂ - Zn(salisopropylamine)₂ would be

constructed. The interphase relationships of a system are conveniently described with the help of phase diagrams. These are helpful in investigating the conditions in which various phases will constitute the systems of the type under consideration are of great importance in the study of metallic alloys and extended for the investigation of precursors. These precursors facilitate the coatings of mixed oxides which catalyze the reactions one way or the other. Precursors are an important source to make thin films and coatings in CVD. With help of these phase diagrams, the lowest melting point composition for preparing mixed metal oxide thin films through thermal CVD techniques, can be determined. To coat the oxides by thermal CVD, a detailed analysis of volatile precursors are required. The CVD of thin films of substitution oxides, such as $A_{1-x}B_xO_3$ [6-8], usually involves two precursors: One each for A and B. Greater homogeneity in film composition, uniformity and an easy coating by CVD are achieved with a single source precursors. These thin film oxides can be used for catalysis, solar cells and sensor applications [9-11].

Experimental

Synthesis of bis(N-isopropylsalicylaldimine)M(II) where M = (Co, Ni and Zn) :

1 mole of $(CH_3COO)_2M \cdot xH_2O$ (where M = Co, Ni and Zn) was dissolved in $10cm^3$ of water to which a solution of 2 mole of salicylaldehyde in $10cm^3$ of absolute ethanol and 6 mole of isopropylamine was added drop-wise under constant stirring in a 1:2:3 mole ratio. This reaction mixture was continuously monitoring the formation of a complex. The precipitate was digested at $60^\circ C$ over a water bath for 5 hours and was filtered, washed with ethanol and dried under vacuum.

Preparation of metal complexes for the phase diagram construction:

Binary phase system of the prepared volatile schiff base metal complexes, $Co_xNi_{1-x}(\text{salisopropylamine})_2$ (I), $Ni_xZn_{1-x}(\text{salisopropylamine})_2$ (II) and $Co_xZn_{1-x}(\text{salisopropylamine})_2$ (III) mixtures of two components were studied, covering the entire range of compositions. The mixtures of I (for brevity here after it is referred to as $Co_xNi_{1-x}(\text{salisopropylamine})_2$) and II (for brevity here after it is referred to as $Ni_xZn_{1-x}(\text{salisopropylamine})_2$); II and III (for brevity here after it is referred to as $Co_xZn_{1-x}(\text{salisopropylamine})_2$); I and III of various compositions between 0 and 1 mole fractions of components were prepared by weighing the appropriate amount and finely ground for half an hour each using mortar and pestle. This homogenized components were filled in the capillary tube to find its melting temperatures of different composition mixtures by using a calibrated digital melting point apparatus MP-D measured up to $\pm 0.5^\circ C$. From the melting point of each composition of the binary system the phase diagrams were studied for the following compounds I, II and III.

Deposition of thin film for bimetallic and tri-metallic oxide

There is an increasing trend in the chemical vapor deposition (CVD) of thin films of nickel, cobalt and Zinc on metallic, non-metallic and ceramic substrates owing to their special characteristics such as high oxidation, corrosion resistance, luster, low electrical resistivity and selective absorption. After studying the phase diagrams of binary and ternary system, the eutectic composition of I - II; II - III; I - III and I - II - III were taken, ground for half an hour and placed in the quartz boat. The silica substrates were cleaned and washed with acetone. They were subjected to ultra-sonication for 15 minutes and dried. The substrate surface was monitored for the absence of stains and any impurities. These high quality silica substrates were kept in the same quartz boat. Now the quartz boat was kept in the digitally controlled hot wall horizontal TCVD in which alumina serves as a chamber. The silica substrate was annealed at $500^\circ C$ for 2 hrs. Evaporation temperature of the eutectic mixtures was chosen according to TG/DTA data. Then the furnace was turned off and cooled down to room temperature. The obtained thin films were investigated for further analyses. Adhesion of the films obtained was estimated with the scotch tape test.

Results and Discussion

Characterization of the Complexes and the Eutectic Mixtures

Fourier Transform Infrared Spectroscopy analysis (FT-IR)

The FT-IR spectrum of bis(N-isopropylsalicylaldimine)cobalt(II), bis(N-isopropylsalicylaldimine)nickel(II) and bis(N-isopropylsalicylaldimine)zinc(II) is reproduced in the figure1. These studies reveal that various stretching frequencies and prominent functional groups are present in complexes. N-H stretching vibration was observed at 3450cm^{-1} , 3005cm^{-1} and 3389cm^{-1} . Aromatic symmetric and asymmetric frequencies [12-13] were observed at 1219cm^{-1} and 1534cm^{-1} respectively. CH_2 bending vibration observed at 1464cm^{-1} . Peaks at 465cm^{-1} corresponds to 1, 2, 4 substituted CH out of plane bending and Co-O stretching vibrations. M-O peaks [14-17] observed at 675cm^{-1} , 662cm^{-1} and 653cm^{-1} for bis(N-isopropylsalicylaldimine)cobalt(II), bis(N-isopropylsalicylaldimine)nickel(II) and bis(N-isopropylsalicylaldimine)zinc(II) respectively. The other stretching frequencies are tabulated in table 1.

Table 1

Wave number (cm^{-1})			
Peak Assignments	Bis(N-isopropylsalicylaldimine)cobalt(II)	Bis(N-isopropylsalicylaldimine)nickel(II)	Bis(N-isopropylsalicylaldimine)zinc(II)
N-H Stretching	3450	3005	3389
$\nu(\text{CH}_3)$	2957	2968	2916
$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{O})$	1534	1527	1531
$\delta(\text{CH}_2)$	1464	1440	1458
$\nu_s(\text{C}=\text{C})$ Aromatic stretching	1300	1292	1332
$\nu(\text{M}-\text{O})$	1219	1192	1186
$\pi(\text{C}-\text{H})$	935	851	848
Ring $\nu(\text{M}-\text{O})$	675	662	653

Electronic Spectra of the prepared complexes

The electronic spectra of Cobalt (II) complex showed a band in the region $24,937\text{Cm}^{-1}$ is assigned to $n \rightarrow \pi^*$ transitions. Nickel (II) showed a band at $25,188\text{Cm}^{-1}$ assigning to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ transition. Zinc (II) show a broad absorption exhibiting in the range 25510cm^{-1} and which may be due to the $n \rightarrow \pi^*$ interligand transitions. The charge-transfer transitions also occur at high energies (UV), that it is practically not observed in the spectrum. The visible transition has complex envelopes because a number of transitions to doublet-excited states occur in the same region and these acquire some intensity by means of spin-orbit coupling.

Characterization of Electron Ionization Mass Spectroscopy (EI-MS)

The EI-MS of bis(N-isopropylsalicylaldimine)cobalt(II), bis(N-isopropylsalicylaldimine)nickel(II) and bis(N-isopropylsalicylaldimine)zinc(II) is shown in the (fig.3) The cluster peak at $m/z = 384$ of cobalt is identified as the molecular ion peak $(\text{ML}_2 \dots \text{L})^+$, the m/z value exactly matches with the theoretical value of $m/z = 384$. Same way the molecular ion peak is observed at $m/z = 384$; $m/z = 390$ for nickel and zinc respectively. The molecular ion peak can be assigned for the binuclear arrangement in such a way

that with the parent molecule. The peak at $m/z=222$; $m/z=219$ and $m/z=236$ corresponds to the species $(ML.....M)^{+}$ including metal and $m/z = 164$; $m/z = 160$ and $m/z = 164$ closely corresponds to the theoretical value for the fragment L^{+} without the metal atom for bis(N-isopropylsalicylaldimine)cobalt(II), bis(N-isopropylsalicylaldimine)nickel(II) and bis(N-isopropylsalicylaldimine)zinc(II) complexes respectively.

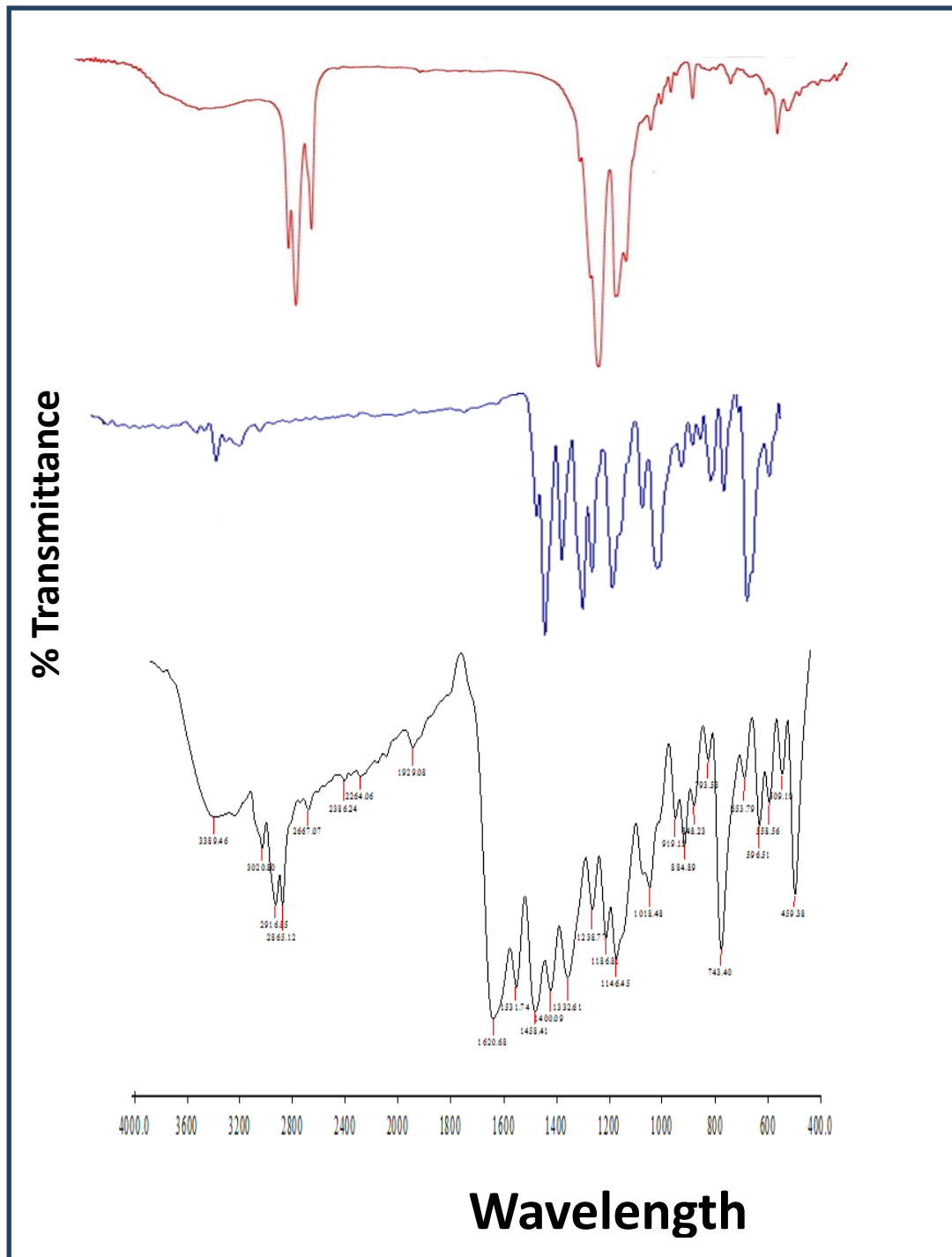


Figure 1. FT-IR Spectroscopy of (a) $Co(salisopropylamine)_2$ (b) $Ni(salisopropylamine)_2$ (c) $Zn(salisopropylamine)_2$

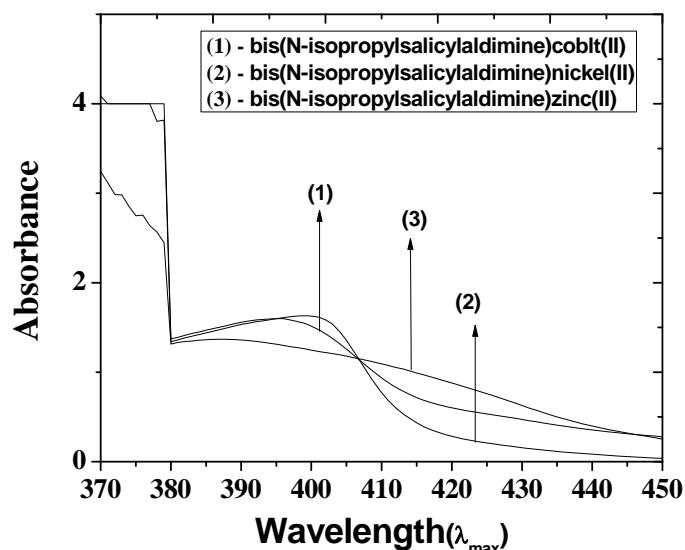


Figure 2. Uv-Visible Spectroscopy of (a) $\text{Co}(\text{salisopropylamine})_2$ (b) $\text{Ni}(\text{salisopropylamine})_2$ (c) $\text{Zn}(\text{salisopropylamine})_2$

TG/DTA Analysis

Volatility is thermodynamically defined as the partial pressure of the vapor existing in equilibrium with the gas and condensed phase and the volatility of a precursor gives an indication of its evaporation rate in an actual CVD process [18]. Volatility and decomposition of the precursor is the crucial part of the CVD process, and a good understanding of it is necessary to screen for potential and ideal precursor to obtain desired coatings. The thermogram of the complexes were recorded using commercial horizontal Pyris Diamond TG/DTA-Perkin Elmer instrument with the heating rate of $10\text{ }^\circ\text{C min}^{-1}$ and $200\text{ cm}^3\text{ min}^{-1}$ (200 Scm) of high pure Nitrogen was used as the gas. The melting point, sublimation, decomposition and weight loss were revealed from the TG/DTA studies. The TG/DTA results of $\text{Co}(\text{salisopropylamine})_2$, $\text{Ni}(\text{salisopropylamine})_2$ and $\text{Zn}(\text{salisopropylamine})_2$ is shown in the figure 4 and figure 5. The weight loss starts at $212\text{ }^\circ\text{C}$, $224\text{ }^\circ\text{C}$ and $239\text{ }^\circ\text{C}$ for $\text{Co}(\text{salisopropylamine})_2$, $\text{Ni}(\text{salisopropylamine})_2$ and $\text{Zn}(\text{salisopropylamine})_2$ respectively. A mass loss of about 99% was observed till $250\text{ }^\circ\text{C}$ and decomposition continued resulting in total pyrolysis. This indicated that the above prepared Schiff base complexes are good precursors for CVD. These complexes left no residue and showed that these complexes and eutectic metal complexes can act as a single source precursor for bimetallic oxide thin film deposition.

Phase Rule Studies of Binary System

In this method, a well-mixed sample containing known amounts of solid is heated slowly. A wide capillary tube, similar to those used for determining melting points in the lab is used. The temperature, at which the first minute drops of liquid appear, that is the eutectic for a given system and that at which the last trace solid just disappears is the melting point. The binary system of I, II and III systems were studied here. Melting temperature of $\text{Co}(\text{salisopropylamine})_2$ is $218\text{ }^\circ\text{C}$. $\text{Ni}(\text{salisopropylamine})_2$ shows its melting temperature is $198\text{ }^\circ\text{C}$ and melting temperature of $\text{Zn}(\text{salisopropylamine})_2$ is $225\text{ }^\circ\text{C}$. The points A and B represent the melting points of pure components. The binary phase diagram show the eutectic point with 30:70 mole fractions of I (Fig.6), 60:40 mole fraction of II (Fig.7) and 50:50 mole fraction of III (Fig.8). Generally the melting point is lowered by the addition of another substance. Therefore addition of component B to component A will lower the freezing point of the system along the curve AC. The curve AC is known as the freezing point curve of the component A and represents the composition of the

solution in equilibrium with the solid component A, at different temperatures. Hence two phases that is solid A and its solution with B are present and so the system becomes univariant. Similarly the curve BC is known as the freezing point of component B and shows the effect of adding component A to component B. The temperature of freezing point of the system is lowered along the curve BC. The two phases present along BC are solid and its solution with A. Hence the system is univariant along BC. The two curves AC and BC meet at the point C where the temperature and composition at which two solid components A and B can exist in equilibrium with that solid solution. The three phases, viz, solid A, solid B and solid solution AB exist in equilibrium at C, hence it is non-variant. In the liquid phase, the molecular complex may remain either in dissociation or in the molecular form. This simple eutectic system shows that there is dissociation occurs in the molten state. The observed eutectic point of these binary phase equilibria indicating that 3:7 mole ratio of $\text{Co}(\text{salisopropylamine})_2$ - $\text{Ni}(\text{salisopropylamine})_2$, 3:2 mole ratio of $\text{Ni}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ and 1:1 mole ratio of $\text{Co}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ addition compound is capable of existing in solid form in equilibrium with a liquid of the same composition.

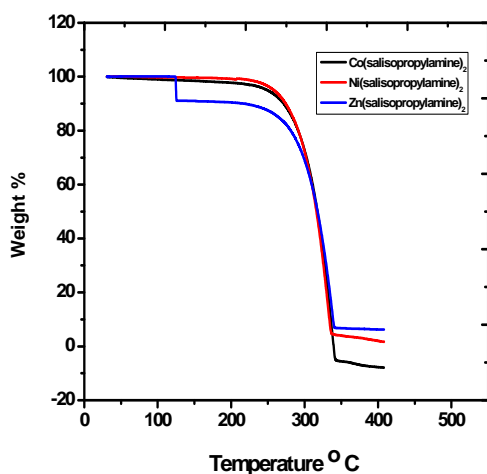


Figure.4 Thermogravimetry Analysis of $\text{Co}(\text{salisopropylamine})_2$, $\text{Ni}(\text{salisopropylamine})_2$ and $\text{Zn}(\text{salisopropylamine})_2$

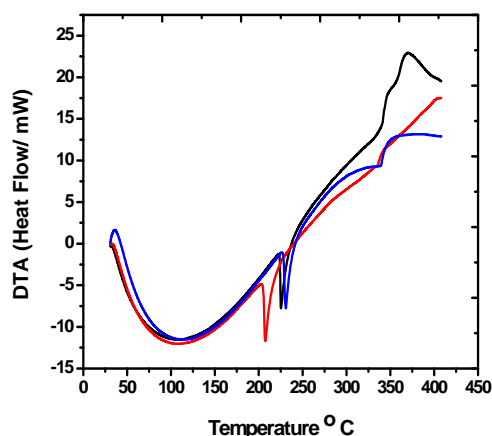


Figure.5 Differential Thermogravimetry Analysis of $\text{Co}(\text{salisopropylamine})_2$, $\text{Ni}(\text{salisopropylamine})_2$ and $\text{Zn}(\text{salisopropylamine})_2$

Consider the phase changes which occur on cooling. If a liquid mixture of composition x is cooled at constant temperature will fall without any change in the composition until the point y on the curve AC is reached. At this point the component A will begin to separate out. Now the system becomes univariant as it consists of two phases. The temperature will now fall with a change in the composition of liquid mixture along AC. As the cooling continues, component A keeps on separating out while the solution becomes richer and richer in B. When the eutectic temperature is reached, the second solid phase, B begins to crystallize out. The system becomes invariant at C. The two solids A and B will separate out together in fixed ratio on further cooling, so that the composition of the solution remains constant as shown by point C. The temperature also remains constant. The eutectic temperature was found to be 192°C, 194 °C and 212 °C for I, II and III binary system respectively. When the solution phase has completely disappeared as solid phase, the system consists of a solid A and B that is below the solidus DD' two solid phases A and B can coexist. If a liquid solution of composition represented by a point x' is cooled, its temperature will fall without any change in the composition along x'y'. At y' solid B begins to crystallize out and the system becomes univariant. Further cooling will shift the equilibrium along y'C,

when component A goes on separating out and the solution becomes richer and richer in component A. When the eutectic temperature is reached component A begins to crystallize out. Further cooling will not change the temperature as well as three phases are present at C. When the solution phase solidifies only then the temperature falls below solidus DD', within which two solid phases component A and component B co-exist.

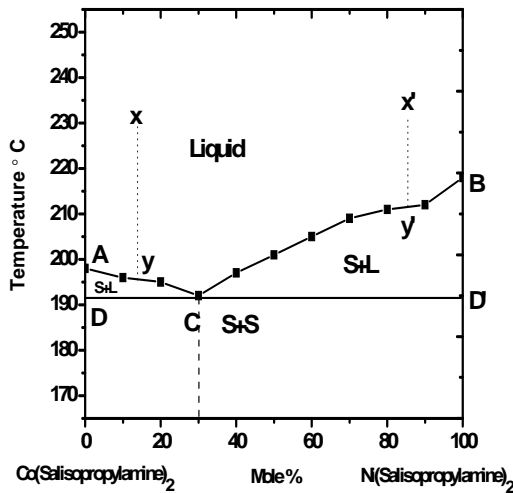


Figure 6. Binary phase diagram of Co(salisopropylamine)₂-Ni(salisopropylamine)₂

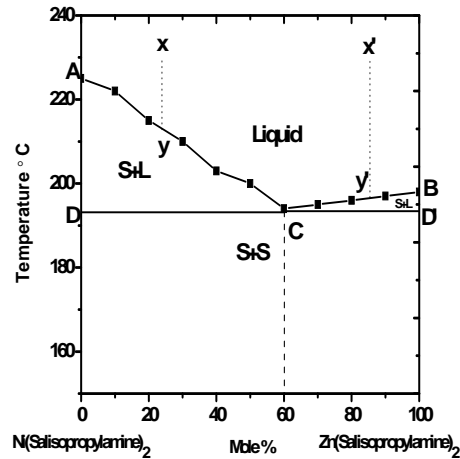


Figure 7. Binary phase diagram of Ni(salisopropylamine)₂-Zn(salisopropylamine)₂

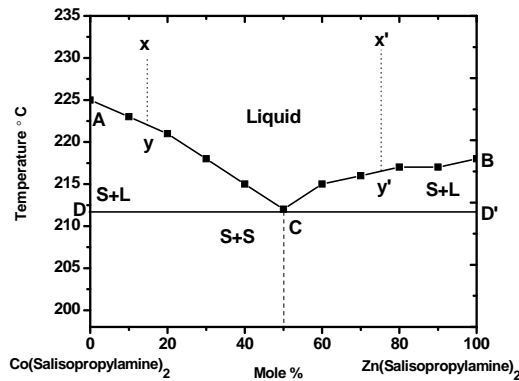


Figure 8. Binary phase diagram of Co(salisopropylamine)₂ - Zn(salisopropylamine)₂

Characterizations of Coating of Thin Films Obtained By Thermal CVD

In the thermal CVD equipment, the suitable precursors were loaded and heated. The precursors volatilize and touch the hot silica substrates. The compounds undergo decomposition over the silica surface leading to the coating of the oxides. These coated films were administered for SEM/EDAX analyses.

SEM/EDAX Analysis

SEM and EDAX are used to study the morphology, surface structure and composition of the deposited films. The surface morphology of the film is determined by the rate of precursor transport,

decomposition reaction, surface diffusion and lattice incorporation during the deposition process. It revealed a progressive grain growth with increasing temperature. The SEM micrographs (Fig 9, 10 and 11) on the silica substrate show the uniformity of the film indicating no defect formation. These annealed composite films of $\text{Co}(\text{salisopropylamine})_2$ - $\text{Ni}(\text{salisopropylamine})_2$ (3:7 mole ratio); $\text{Ni}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ (3:2 mole ratio) and 1:1 mole ratio of $\text{Co}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ are studied under different magnification and shows the films are densely packed with agglomerated globular particles.

Energy Dispersive X-ray analysis, carried out for bimetallic composite thin film on Si(100) substrate indicated peaks corresponding to Co, Ni and oxygen (fig.9); Ni, Zn and oxygen (fig.10); Co, Zn and oxygen (fig. 11). No sizeable carbon contamination could be detected, which shows the purity of the film deposited by the TCVD process. In EDAX analysis of deposited thin films, zinc peak has high intense peak than nickel and cobalt in $\text{Ni}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ and $\text{Co}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ system. Cobalt and Nickel peaks are suppressed by Zinc indicating that deposition rate of zinc is higher than cobalt and nickel. In EDAX of $\text{Ni}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ and $\text{Co}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ binary system weight % of zinc is 39.6 and 39.4 respectively. $\text{Co}(\text{salisopropylamine})_2$ - $\text{Ni}(\text{salisopropylamine})_2$, The weight % of cobalt is 47.06 which is higher than nickel. From these EDAX analysis, we can conclude that the rate of deposition of metal oxide over silica thin film is $\text{ZnO} > \text{Co}_2\text{O}_3 > \text{NiO}$.

Conclusion

Chemical vapor deposition is a developing technology in the last few decades. There is an increased interest in coatings for catalysis, sensors, microelectronics and energy applications. To emerge a new technique to make CVD process is more easy, the developments of single-source precursors are essential. In spite of the above requirements, the present work has been designed to synthesize single source precursors. The metallorganic complexes $\text{Co}(\text{salisopropylamine})_2$, $\text{Ni}(\text{salisopropylamine})_2$ and $\text{Zn}(\text{salisopropylamine})_2$ were synthesized and qualitatively and quantitatively analyzed for the presence of the metals and then the complexes were characterized by FT-IR, UV-VISIBLE, EI-MS and TG/DTA analyses. The melting point analyses were performed by using digital MP-D melting point apparatus to check the purity of the compounds. The melting point of the pure compounds were found to be $\text{Co}(\text{salisopropylamine})_2$ is 218 °C, $\text{Ni}(\text{salisopropylamine})_2$ is 198 °C and $\text{Zn}(\text{salisopropylamine})_2$ is 225 °C. The FT-IR studies were used to confirm the presence of groups $-\text{C}=\text{O}$, $\text{C}-\text{CH}_3$, $\text{M}-\text{O}$, etc., in the complexes with respective to stretching frequencies. The d-d Transitions and transitions and the molar absorptivity coefficients of the complexes were calculated from the UV-Visible spectrometer. TG-DTA analyses were done to study the volatility, melting point, sublimation and evaporation pattern of the complexes. The prepared $\text{Co}(\text{salisopropylamine})_2$, $\text{Ni}(\text{salisopropylamine})_2$ and $\text{Zn}(\text{salisopropylamine})_2$ has completely evaporated leaving no residue. Hence we are concluding that the prepared complexes are volatile. From the TG/DTA analysis, the melting points were found to be 218°C, 198 °C, and 225°C for the $\text{Co}(\text{salisopropylamine})_2$, $\text{Ni}(\text{salisopropylamine})_2$ and $\text{Zn}(\text{salisopropylamine})_2$ respectively. The melting temperatures are compared well with value observed from MP-D melting apparatus. The phase diagrams were constructed for $\text{Co}(\text{salisopropylamine})_2$ - $\text{Ni}(\text{salisopropylamine})_2$, $\text{Ni}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ and $\text{Co}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$. The lower melting composition can be used as good precursors for getting metal oxide thin films through CVD method. The eutectic temperature was found to be 192°C, 194 °C and 212 °C for $\text{Co}(\text{salisopropylamine})_2$ - $\text{Ni}(\text{salisopropylamine})_2$, $\text{Ni}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ and $\text{Co}(\text{salisopropylamine})_2$ - $\text{Zn}(\text{salisopropylamine})_2$ binary systems respectively. The above results give a new direction for preparation of single source precursors. We have succeeded the coating of binary metal oxide thin films such as Co_2O_3 - NiO ; NiO - ZnO and Co_2O_3 - ZnO by Thermal Chemical Vapour Deposition (TCVD) technique and the formation of bimetallic oxide was proved by SEM/EDAX analyses.

References

- [1] P.A. Premkumar, A. Dasgupta, P. Kuppusami, P. Parameswaran, C. Malliga, K.S. Nagaraja, V.S. Raghunathan, *Chemical Vapour Deposition*, 2004, 12, 39.
- [2] T. Maruyama, T. Tago, *Journal of Material Science*, 1993, 28, 5345.
- [3] J.Crofton, P.G. McMillan, J.R. Williams, M.J. Bozack, *Journal of applied physics*, 1995, 77, 1317.
- [4] M.W. Cole, C. Hubbard, C.G. Fountzoulas, D. Demaree, A. Natarajan, R.a. Miller, *Electrochemical and Solid-State Letters*, 1999, 2, 97.
- [5] L. Brissonneau, C. Vahlas, *Annales de Chimie Science des Materiaux*, 2000, 25, 81.
- [6] V. Raghavan, *Journal of Phase Equilibria and Diffusion*, 2012, 33, 55.
- [7] A.L. Johnson, N. Hollingsworth, G. Koclock-Kohn, *Inorganic Chemistry*, 2008, 47, 2040.
- [8] A.P.Millanov, R.A. Fisher, A. Devi, *Inorganic Chemistry*, 2008, 47, 11406.
- [9] Q.Wen, N.Yu, D.R. Clarke, *Journal of Applied Physics*, 1996, 80, 3587.
- [10] M.G. Zhao, *Journal of Chemical Physics*, 1998, 109, 8003.
- [11] R.J.VanWijk, J.I. Dijkhuis, H.W. Wijn, *Journal of Physics: Condensed Matter*, 1991, 3, 3099.
- [12] A.H. Kianfar, M. Paliz, M. Roushani, M. Shamsipur, *SpectrochimicaActa*, 2011, 82, 44.
- [13] A.Z. El-Sonbati, A.A. El-Bindary, *Polish Journal of Chemistry*, 2000, 74, 621.
- [14] L. F. Audriet, *Inorganic Syntheses*, Vol.III, MCGraw-Hill, Newyork, 1950.
- [15] D.A. Thornton, *Coordination Chemistry Reviews*, 1990, 104, 173.
- [16] F.A. Cotton, J. Lewis, R.G. Willkinson, *Modern Coordination Chemistry*, Interscience, New York, 1986.
- [17] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Willey Interscience, 1986.
- [18] G.A. Battiston, R. Gerbasi, *Chemical Vapour Deposition*, 2001, 7, 225.