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Phase Diagram Studies and Thin Film Coatings of bi and tri-metallic oxides using Tris β-Diketonates of Aluminium (III), Chromium (III) and Iron (III) as a Single source precursor

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Abstract: $Al(acac)_3$, $Cr(acac)_3$ and $Fe(acac)_3$ (acac = acetylacetonate) were prepared and found to be volatile by thermal analysis that can be used for the metal oxide deposition on silica substrate by Thermal Chemical Vapour Deposition (TCVD). The aim is to deposit eutectic bimetallic and tri-metallic oxides by TCVD method. Different mole ratios of the above mentioned metal complexes were found to reduce the melting points from which binary and ternary phase diagrams of $Al(acac)_3$-Cr(acac), $Cr(acac)_3$-$Fe(acac)_3$, $Al(acac)_3$-$Fe(acac)_3$ and $Al(acac)_3$-$Cr(acac)_3$-Fe $(acac)_3$ were constructed and their eutectic temperatures were determined. The eutectic temperature was obtained at 1: 1 ratio for its binary systems. From the binary phase diagram, ternary phase diagram was constructed. The parent complexes and eutectic complexes were characterized by FT-IR, UV-VIS, XRD, TG/DTA and SEM/EDAX analyses. These binary and ternary eutectics were used for the deposition of the metal oxide thin films over silica by TCVD method. Al_2O_3 coating over silica catalyses the coating of Cr_2O_3 or Fe_2O_3. Bimetallic and tri-metallic oxide thin films can be employed as catalyst for the formation of carbon nanotubes (CNT) by CVD and catalysts.
Key Words: Metal acetylacetonates, Binary and Ternary systems, Thermal analysis, Phase diagrams, Thermal Chemical Vapour Deposition (TCVD).

Introduction

An understanding of phase diagram is fundamental and essential in the study of material science. The metal complex eutectic systems have not been studied extensively in the potential area of investigation in coordination chemistry. However, low melting temperature of transformation and detection of compound formation are the special features, which have prompted a number of research groups to undertake some physiochemical aspects of organic eutectics and molecular complexes. 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. Aluminium alloys for elevated temperature applications have become a subject of considerable interest especially in automotive and aerospace industry due to their good strength to weight ratio. Multilayer thin film of iron-chromium has been subject of intensive study because of the anti ferromagnetic interlayer coupling and the large magneto resistance which has been found for such structures[1-3]. Different bimetallic oxide compositions can be achieved by using the required precursors in the vapour medium. Another option is to get the precursor with a strict set ratio of metals. This is possible for β-diketonates of metals which form solid solutions [4]. Coatings are important from both applied and fundamental points of view. They are used in advanced nuclear reactor applications due to their corrosion resistance combined with good mechanical properties. Thin films of Cr_2O_3-doped alumina have applications as sensors damage caused by ion irradiation [5], as pressure sensors [6], and acoustic phonons [7] and for strengthening metal- carbon interfaces. In order to get a film with the desired composition, morphology and purity, the precursor must undergo controlled thermal decomposition at substrate temperatures. Hence the investigations on phase diagram studies of gaseous precursors are important in CVD work. We are interested in the construction of phase diagram, the aluminium acetyl acetonate [Al(acac)$_3$], chromium acetyl acetonate [Cr(acac)$_3$] and iron acetyl acetonate [Fe(acac)$_3$] as these are volatile complexes phase diagrams of binary and ternary systems of β- diketonate complexes of Al (III), Cr (III), and Fe (III) which possess volatility can be used for metal oxide coating by thermal chemical vapour deposition (TCVD). The aim of this work is to investigate mixed metal precursors from the metallo-organic complexes using the phase rule. The complexes of Al, Cr and Fe with homoleptic ligand [acetylacetone (acac)] would be useful as a single source precursor for bimetallic and tri-metallic oxide thin film [8-11] coating. The CVD of thin films of substitution oxides, such as $A_{1-x}B_xO_3$, usually involves two precursors: One each for A and B. Greater homogeneity in film composition, uniformity and a 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. To coat the oxides by thermal CVD, a detailed analysis of volatile precursors are required. In this paper, the results pertaining to the studies concerning its phase diagram, spectral behaviour, thermal properties, thermal chemical vapour deposition and powder X-ray structural properties of Al(acac)$_3$-Cr(acac)$_3$, Fe(acac)$_3$-Cr(acac)$_3$, Al(acac)$_3$-Fe(acac)$_3$ (1:1 ratio), Al(acac)$_3$-Cr(acac)$_3$- Fe(acac)$_3$ (1:1:1 ratio) and the parent complexes are reported.

Experimental

1. Preparation of metal complexes for the phase diagram construction

The β-diketonate complexes of aluminium acetyl acetonate [Al(acac)$_3$], chromium acetyl acetonate [Cr(acac)$_3$] and iron acetyl acetonate [Fe(acac)$_3$] complexes were prepared according to the literature [12-17]. Before constructing the ternary phase system of the binary phase diagrams has to be studied. In this method, binary phase system metal complexes, Al_xCr_{1-x}(acac)$_3$, Cr_xFe_{1-x}(acac)$_3$ and Al_xFe_{1-x}(acac)$_3$ mixtures of two components were studied, covering the entire range of compositions. 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. The homogenized components were filled in the capillary tube to find its melting temperature. Melting points of different mixtures were determined by using a calibrated digital melting point apparatus MP-D measured up to ± 0.5°C. From the melting point of each composition of the binary system the phase diagrams were studied for the following compounds Al_xCr_{1-x}(acac)$_3$, Cr_xFe_{1-x}(acac)$_3$ and Al_xFe_{1-x}(acac)$_3$. By knowing the eutectic point of the above systems ternary phase diagram was constructed from the Gibb's triangle on which the pure components are representing by each corner.

2. Deposition of thin film for bimetallic and tri-metallic oxide

Thin films are extensively used in many industrial applications and can be prepared as resistors, insulators, conductors and semiconductors. Chemical vapor deposition is a widely used method for thin deposition and high quality films well defined composition and structural uniformity. The final objective of the present work is to deposit the eutectic composition of bimetallic and tri-metallic oxide thin films by thermal chemical vapour deposition. After studying the phase diagrams of binary and ternary system, the eutectic composition (1:1 mole ratio) of Al(acac)$_3$-Cr(acac)$_3$; Fe(acac)$_3$- Cr(acac)$_3$; Al(acac)$_3$- Fe(acac)$_3$ and Al(acac)$_3$-Cr(acac)$_3$-Fe(acac)$_3$ were taken, ground for half an hour and placed in the quartz boat. The silica substrates were degreased 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 °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.

3. Characterisation of the eutectic complexes and coating of thin film

The infrared spectral studies were carried out for the parent and the eutectic 1:1 ratio of Al_xCr_{1-x}(acac)$_3$, Cr_xFe_{1-x}(acac)$_3$ and Al_xFe_{1-x}(acac)$_3$. The spectra were recorded by Perkin Elmer FT-IR spectrometer using KBr medium in the region 4000-400 cm^{-1}. The electronic absorption spectra of the above complexes were recorded on Elico spectrophotometer using ethanol as a solvent. The purpose of non-isothermal TG was to identify the complexes that could function as precursors for CVD and to indentify the mass loss steps. The analysis was carried out by Pyris Diamond TG/DTA. Here alumina serves as the reference and ultra high pure nitrogen gas as carrier gas at the flow rate of 100 mL/min and heating rate of the substrate being 10 °C/min. at one atmosphere pressure for all the measurements. The eutectic metal oxide coated films were characterised by X-ray diffraction (XRD) using Philps X'pert wide angle X-ray diffractometer, operating in step scan mode with Cu Kα radiation (1.54060 A°). The diffraction patterns were collected in the range of 3 to 75° of 2θ values. The morphology of the thin films was investigated by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray analysis (EDAX).

Results and Discussion

Characterization of the Complexes and the Eutectic Mixtures

1. Fourier Transform Infrared Spectroscopy analysis (FT-IR)

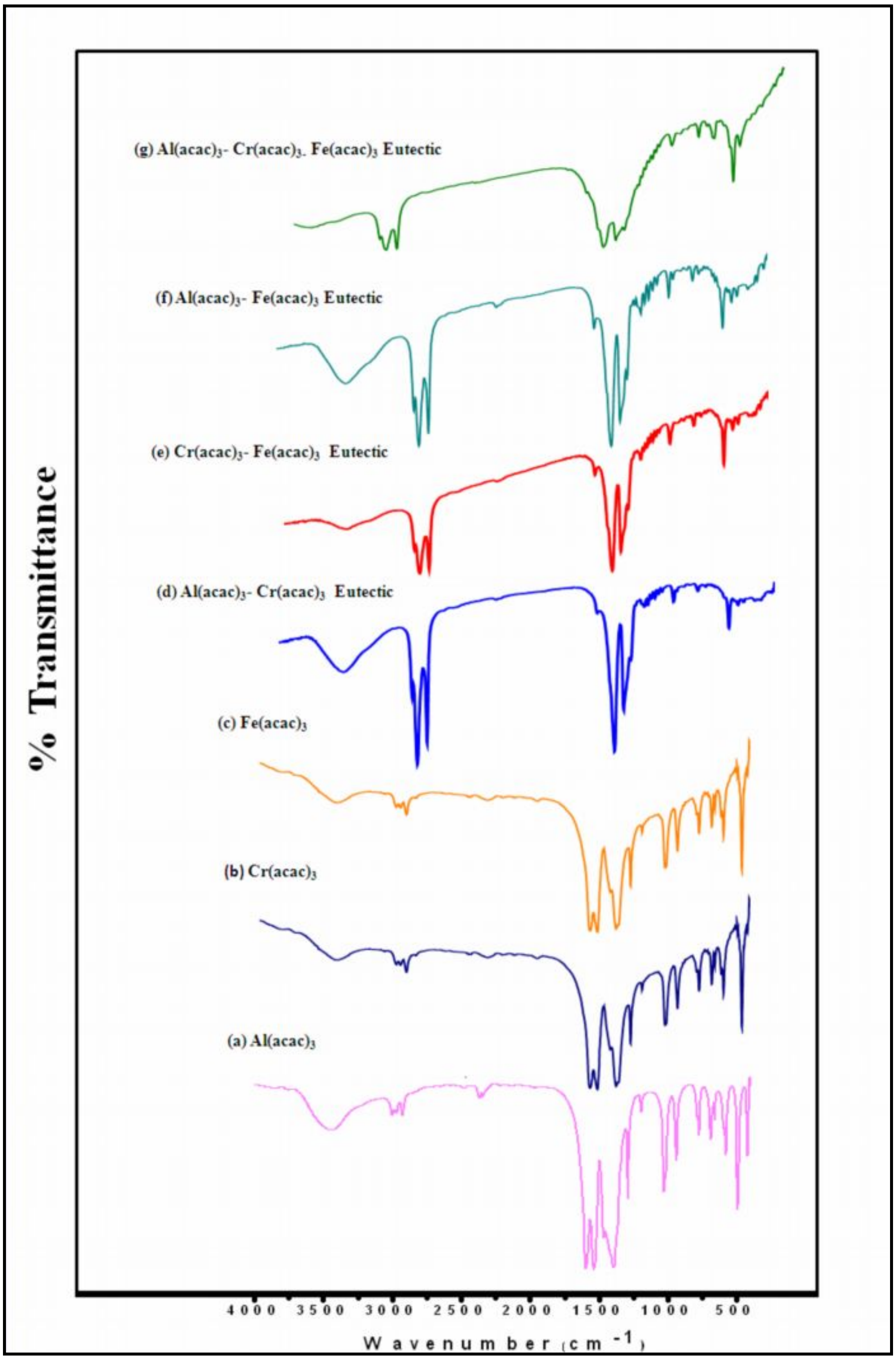


Figure 1. FT-IR analysis of $Al(acac)_3$, $Cr(acac)_3$, $Fe(acac)_3$, binary and ternary eutectic mixtures

IR spectra of the complexes (a) to (g) exhibited several signals in the IR region (4000-400 cm^{-1}) indicating the presence of the organic functional groups. The percentage transmission versus wavelength (cm^{-1}) of aluminium, chromium and iron β-diketonate complexes, binary eutectic mixture, and ternary eutectic mixture are shown in the fig 1. The functional group frequencies are summarized in the table1. Each spectrum exhibits similar characteristics carbonyl stretching frequencies near 1675 cm^{-1} region. The peak at 2900 cm^{-1} corresponds to υ (C-H). Infrared spectra provide valuable information regarding the quasi-aromatic behavior of the six membered chelate rings. A strong absorption band was absorbed between 1562 cm^{-1} and 1550 cm^{-1}. These bands correspond to the carbonyl group which is weakened by resonance between C-O-M and C=O…M. The second band near 1520 cm^{-1} which was attributed to the C=C bond [18]. The IR bands at ν_1=3440 cm^{-1} in fig (1a), 3448 cm^{-1} fig (1b) and 3433 cm^{-1} fig (1c) revealed the formation of tri-hydrate of $Al(acac)_3$, $Cr(acac)_3$, and $Fe(acac)_3$ complexes which was further confirmed by bands at 936 and 1035 cm^{-1}. The 936 cm^{-1} peak was noticeably stronger than the 1035 cm^{-1} peak in the anhydrous compounds and monohydrates but was weaker than the 1035 cm^{-1} peak in the di- and tri-hydrates. The single band at 773 cm^{-1} also confirmed the tri-hydrate nature of the complex. The water was probably hydrogen bonded to the oxygen atoms in the chelate ring. Davis and Frckler[19] reached a similar conclusion in their studies of interactions of transition metal acetylacetonates with water, chloroform and methanol. The bond located at 420 cm^{-1} conform the formation of M-O bond [20-23].

Table 1. (a) $Al(acac)_3$ (b) $Cr(acac)_3$ (c) $Fe(acac)_3$ (d) Eutectic mixture of $Al(acac)_3$- $Cr(acac)_3$(e) Eutectic mixture of $Cr(acac)_3$- $Fe(acac)_3$ (f) Eutectic mixture of $Al(acac)_3$- $Fe(acac)_3$ (g) Eutectic mixture of $Al(acac)_3$-$Cr(acac)_3$-$Fe(acac)_3$

….. Peak Assignments	Wave number (cm^{-1})						
	Parent Complexes			Eutectic mixtures			
	$Al(acac)_3$	$Cr(acac)_3$	$Fe(acac)_3$	$Al(acac)_3$-$Cr(acac)_3$	$Cr(acac)_3$-$Fe(acac)_3$	$Al(acac)_3$-$Fe(acac)_3$	$Al(acac)_3$-$Cr(acac)_3$-$Fe(acac)_3$
υ (CH_3)	2924	2922	2920	2920	2915	2918	2921
υ (C=C) + υ (C=O)	1594	1574	1578	1525	1531	1529	1534
υ(C-CH_3)+υ (C=C)	1277	1269	1272	1275	1273	1265	1259
π(C-H)	768	760	764	740	735	737	746
Ring υ(M-O)	570	587	583	535	540	548	534

Table 2. TG/DTA analysis of (a) $Al(acac)_3$ (b) $Cr(acac)_3$ (c) $Fe(acac)_3$ (d) Eutectic mixture of $Al(acac)_3$-$Cr(acac)_3$(e) Eutectic mixture of $Cr(acac)_3$- $Fe(acac)_3$ (f) Eutectic mixture of $Al(acac)_3$- $Fe(acac)_3$ (h) Eutectic mixture of $Al(acac)_3$-$Cr(acac)_3$-$Fe(acac)_3$

S.no	Complexes / Binary and ternary system	Weight (mg)		Final		Nature/ end residue
		Initial	Final	Residue %	T ° C	
1.	$Al(acac)_3$	2.547	0.027	1.1	395.9	Volatile
2.	$Cr(acac)_3$	0.4622	0.0163	3.4	442.5	Volatile
3.	$Fe(acac)_3$	1.110	0.013	0.4	266.6	Volatile
4.	$Al(acac)_3$-$Cr(acac)_3$ (1:1 ratio)	2.522	0.054	2.1	406.5	Volatile
5.	$Cr(acac)_3$-$Fe(acac)_3$ (1:1 ratio)	0.8621	0.0071	0.5	335.4	Volatile
6.	$Al(acac)_3$-$Fe(acac)_3$ (1:1 ratio)	1.205	0.076	6.3	544.1	Volatile
7.	$Al(acac)_3$-$Cr(acac)_3$-$Fe(acac)_3$ (1:1:1 ratio)	0.8221	0.0063	0.8	473.8	Volatile

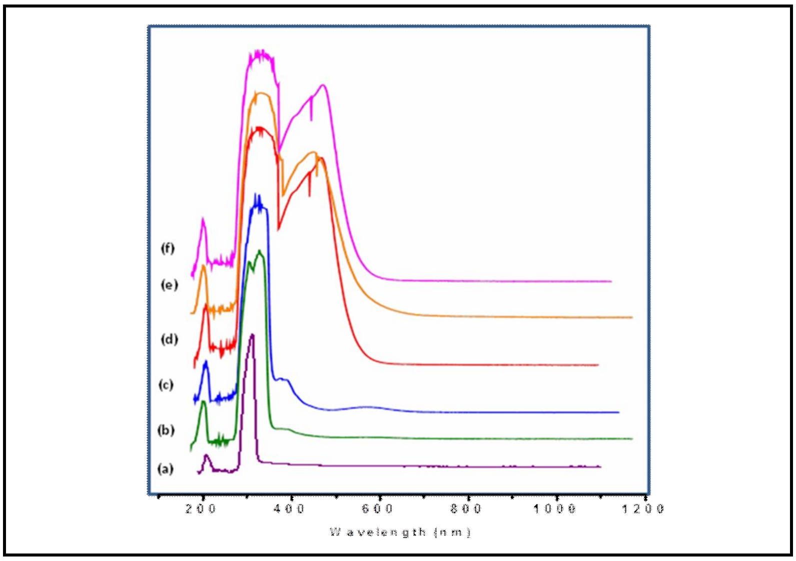


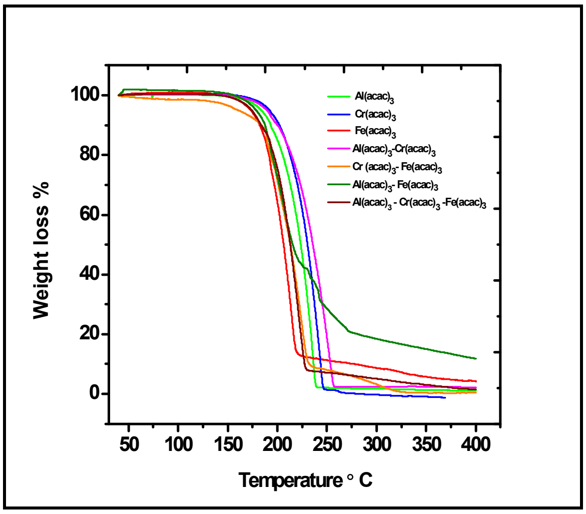
Figure. 2. (a) Al(acac)$_3$ (b) Cr(acac)$_3$ (c) Fe(acac)$_3$ (d) Al(acac)$_3$- Cr(acac)$_3$ eutectic mixture (e) Cr(acac)$_3$-Fe(acac)$_3$ eutectic mixture (f) Al(acac)$_3$- Fe(acac)$_3$ eutectic mixture in ethanol

2. UV-Visible Spectroscopy

Electronic spectra of β-diketonates of Al^{3+}, Cr^{3+} and Fe^{3+} complexes in ethanol as solvent were recorded. The bands observed at 288 nm, 366 nm and 270 nm[24] corresponds to Al(acac)$_3$, Cr(acac)$_3$ and Fe(acac)$_3$ respectively. The 1:1 ratio eutectic complexes bands have the two λ max values, for example the 1:1 ratio of Al(acac)$_3$-Cr(acac)$_3$ shows the peaks at both 288 nm and 366 nm. The intensive absorption bands are observed in the wavelength range of 250-700 nm [25, 26].

3. Thermal 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 [27] .



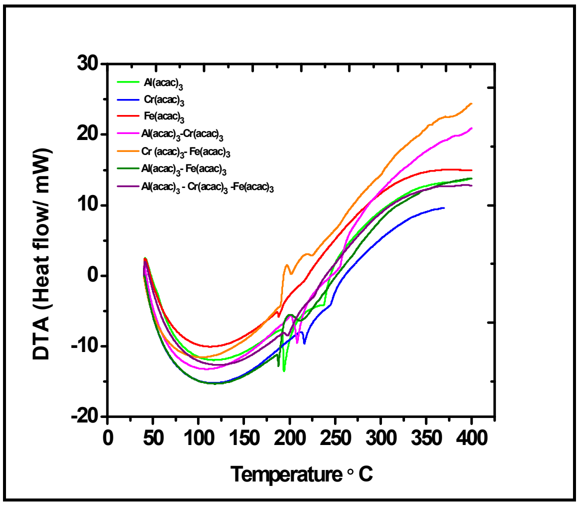


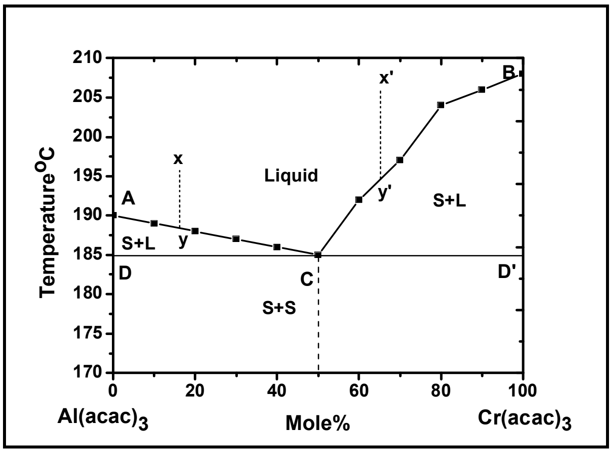
Figure.3 Thermogravimetry Analysis of Al(acac)$_3$, Cr(acac)$_3$, Fe(acac)$_3$ and Eutectic mixtures

Figure.4. Differential Thermogravimetry Analysis of Al(acac)$_3$, Cr(acac)$_3$,Fe(acac)$_3$ and Eutectic mixtures

The TG/DTA analysis was performed at a heating rate of 10 °/min. in flowing nitrogen at one atmosphere pressure.The TG/DTA results of Al(acac)$_3$ (I), Cr(acac)$_3$ (II)[28] and Fe(acac)$_3$ (III) are shown in the fig.3 and 4. The thermograms of I exhibits two endothermic events at 195°C and 247 °C, II at 210 °C and 260 °C and III at 184 °C and 231 °C . The TG curve does not show any change till 200 °C for I, 225 °C for II and 210°C for III. A mass loss of about 99% was observed till 250 °C and decomposition continued resulting in total pyrolysis. This indicated that aluminium, chromium and iron acetyl acetonates are good precursors for

CVD. Non-isothermal TG/DTA of eutectic mixture of $Al(acac)_3$- $Cr(acac)_3$ (IV) showed a single weight loss step at 186 °C which correspond to sublimation shift to a higher temperature monotonically as a function of chromium complex concentration. The melting point temperature of the metal substituted complexes decreased as the concentration of the III increases, and lies between the melting temperature of pure $Al(acac)_3$ and $Cr(acac)_3$. Similarly, single weight loss step observed at 170 °C for the eutectic mixture of $Cr(acac)_3$- $Fe(acac)_3$ (V) and 175 °C for the eutectic mixture of $Al(acac)_3$- $Fe(acac)_3$ (VI) which correspond to sublimation shift to a lower temperature as a function of the concentration of iron and aluminum complexes. The melting point temperature of the metal substituted complexes decreases as the concentration of the III and II increased, and lies between the melting temperatures of pure complexes. From the TG/DTA analyses, the parent complexes [$Al(acac)_3$, $Cr(acac)_3$ and $Fe(acac)_3$] and binary eutectic 1:1 metal complex of ratio [$Al(acac)_3$- $Cr(acac)_3$; $Cr(acac)_3$- $Fe(acac)_3$; and $Al(acac)_3$- $Fe(acac)_3$] left no residue and showed that these complexes and eutectic metal complexes can act as a single source precursors for bimetallic and tri-metallic oxide thin film deposition. Reaction occurring between the precursors may lead to a small amount of residue. Each component hinders the volatility of other in this composition. The thermogram of $Al(acac)_3$ - $Fe(acac)_3$ and $Cr(acac)_3$ - $Fe(acac)_3$ did not show a smooth single step decomposition as in the case of $Al(acac)_3$ - $Cr(acac)_3$. This was reflected in the poor deposition of Fe_2O_3 and Cr_2O_3 over silica from its mixture which was confirmed by SEM/EDAX analysis.

4. Phase Rule Studies of Binary System



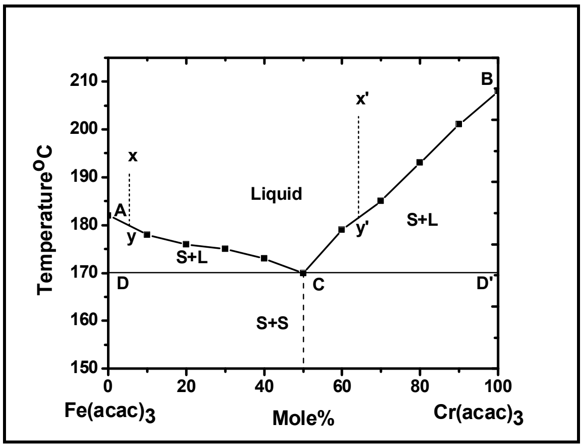


Figure.5 Binary phase diagram of $Al_xCr_{1-x}(acac)_3$ Figure. 6. Binary phase diagram of $Cr_xFe_{1-x}(acac)_3$

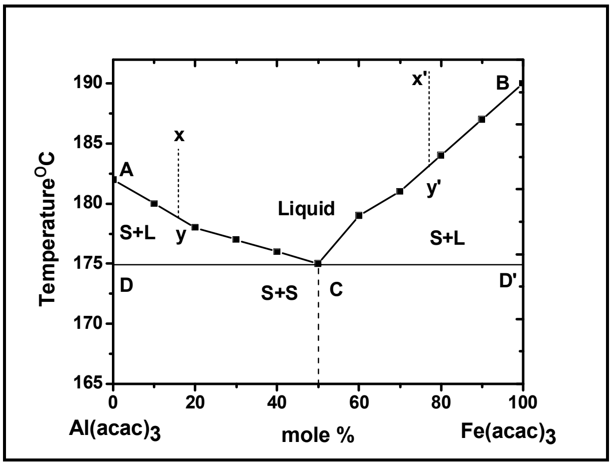


Figure.7 Binary phase diagram of $Al_xFe_{1-x}(acac)_3$

The binary phase equilibria of $Al(acac)_3$ - $Cr(acac)_3$ (IV) ; $Cr(acac)_3$ - $Fe(acac)_3$ (V) ; $Al(acac)_3$-$Fe(acac)_3$ (VI) is plotted in the form of temperature ad composition is shown in the figure 5, 6 and 7 respectively. The points A and B represent the melting points of pure components IV (Fig.5); V (Fig.6) ; VI (Fig.7) respectively. The binary phase diagram show the eutectic point with 0.5 mole fraction of IV (Fig.5), V (Fig.6) and VI (Fig.7). The melting point of IV, V and VI are 185 °C, 170 °C and 175 °C respectively. 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[29]. 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 1:1 addition compound is capable of existing in solid form in equilibrium with a liquid of the same composition.

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. 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 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 crystallise 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.

5. Phase Rule Studies of Ternary System

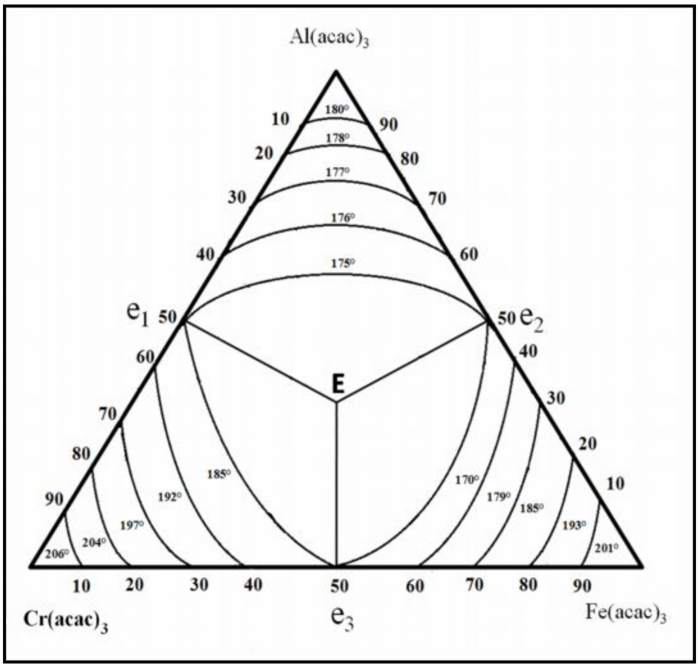


Figure.8. Ternary phase diagram of $Al(acac)_3$-$Cr(acac)_3$-$Fe(acac)_3$

The equilibrium diagram for the ternary system $Al(acac)_3$-$Cr(acac)_3$-$Fe(acac)_3$ is given in Fig (8). The melting points of the three components are represented by points on each apex. Every apex represents a monovarient system. The points e_1 (185° C), e_2 (175°C), and e_3 (170 °C) are the eutectic points for the components $Al(acac)_3$ -$Cr(acac)_3$; $Cr(acac)_3$- $Fe(acac)_3$; $Al(acac)_3$ - $Fe(acac)_3$ respectively. On adding $Al(acac)_3$

to the eutectic mixture of $Cr(acac)_3$ and $Fe(acac)_3$ at e_3 the temperature at which the two solid phases $Cr(acac)_3$ and $Fe(acac)_3$ co-exist in equilibrium with the liquid which is lowered along e_1E. Similarly on adding $Fe(acac)_3$ to the eutectic mixture of $Al(acac)_3$ and $Cr(acac)_3$ at e_1 the temperature at which $Al(acac)_3$ and $Cr(acac)_3$ are in equilibrium with the liquid phase is lowered along e_1E. Similarly on adding $Fe(acac)_3$ to the eutectic mixture of $Al(acac)_3$ and $Cr(acac)_3$ at e_1 the temperature at which $Al(acac)_3$and $Cr(acac)_3$ are in equilibrium with the liquid phase is lowered along e_1E. Similarly e_2E gives the equilibrium between $Al(acac)_3$ and $Fe(acac)_3$ and ternary solutions. At E, known as ternary eutectic point of all the three solid phases, viz, $Al(acac)_3$, $Cr(acac)_3$, $Fe(acac)_3$ are in equilibrium. Any system represented by a point in the upper of the space diagram is entirely liquid[30]. Below the freezing point or liquidus surfaces (e_1E, e_2E, e_3E) the pure solids and ternary liquids exist together. Below the eutectic point and corresponding solidus surface, the whole system of the three components will exist as solid.

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, XRD analyses.

6. SEM/EDAX Analysis

SEM and EDAX investigated 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. The surface morphology of the film revealed a progressive grain growth with increasing temperature. The SEM micrographs (Fig 9, 10 11and 12) shows the uniformity of the film indicating no defect formation. These annealed composite films are studied under different magnification and shows the films are densely packed with agglomerated globular particles. The XRD and SEM examination of these films coated over Si (100) exhibits the same phase.

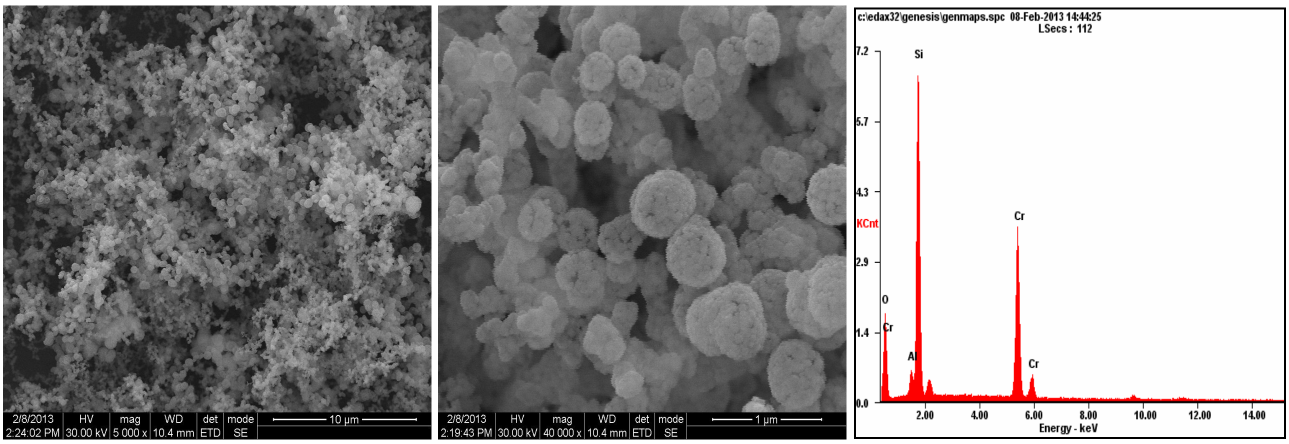


Figure 9. Formation of Al_2O_3 and Cr_2O_3 bimetallic thin film on silica substrate and their respective EDAX analysis

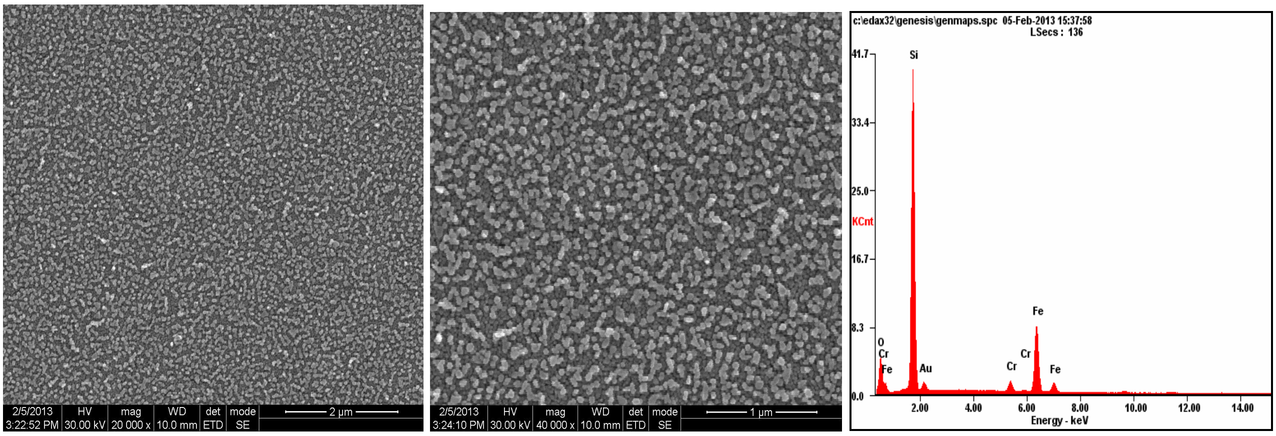


Figure 10. Formation of Cr_2O_3 and Fe_2O_3 bimetallic thin film on silica substrate and their respective EDAX analysis

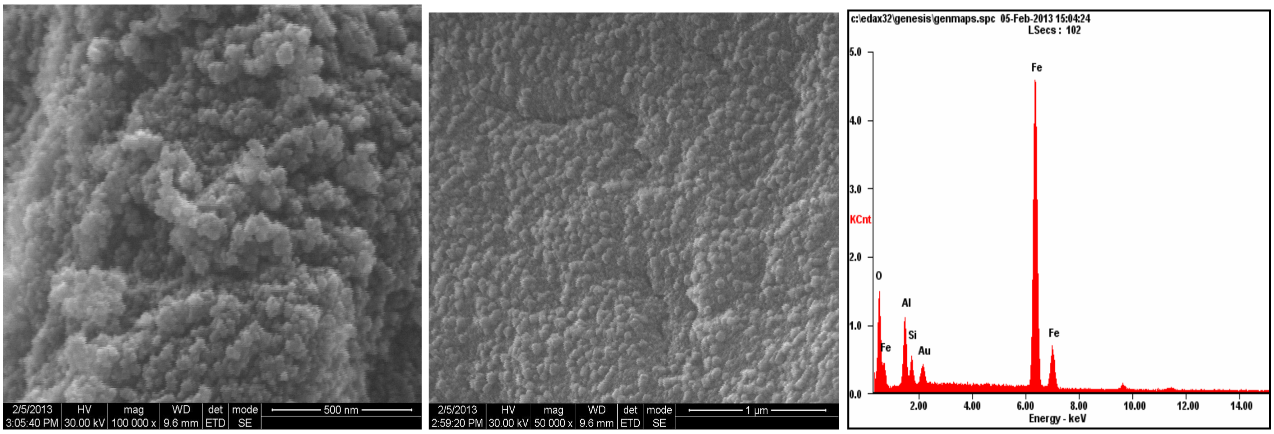


Figure 11. Formation of Al_2O_3 and Fe_2O_3 bimetallic thin film on silica substrate and their respective EDAX analysis

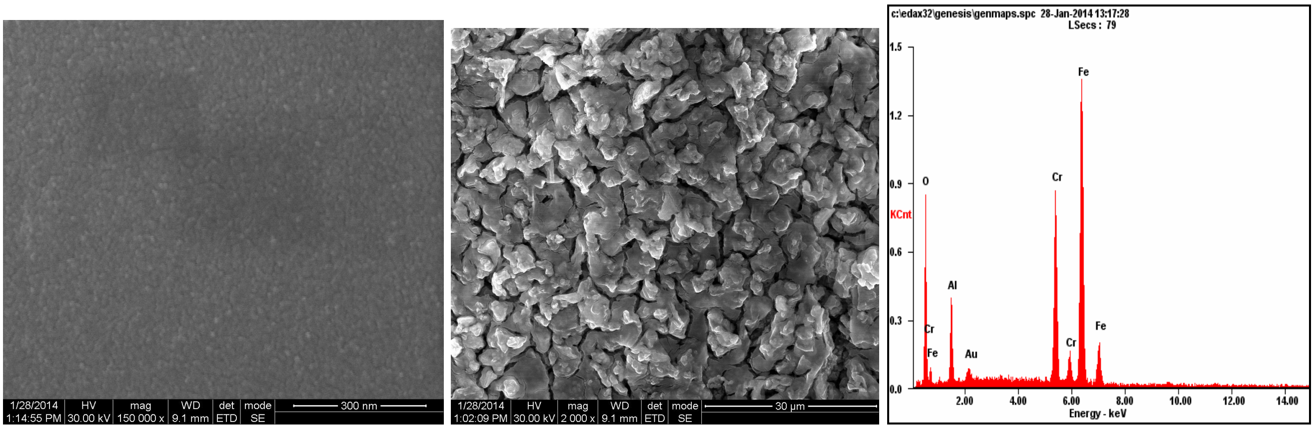


Figure 12. Formation of Al_2O_3, Cr_2O_3 and Fe_2O_3 tri-metallic thin film on silica substrate and their respective EDAX analysis

Energy Dispersive X-ray analysis, carried out for Al_2O_3 and Cr_2O_3 bimetallic composite thin film on Si(100) substrate indicated peaks corresponding to Al, Cr and oxygen (fig.9); Cr, Fe and oxygen (fig.10); Al , Fe 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 Al-Cr and Al-Fe, deposited thin films, aluminium peaks are suppressed by chromium and iron respectively in fig (9) and (11). The elemental composition of annealed tri-metallic film was found to have Al, 11.45Wt. %, Cr, 11.33 Wt. % Fe, 42.66 Wt. %. In EDAX of $Al(acac)_3$-$Cr(acac)_3$ the chromium was found to be higher by a few per cent than the aluminium content in their oxide coatings. It can be concluded that deposition rate for the chromium component is higher than that of the aluminium component. The EDAX gave significant results. The coating of Cr_2O_3 and Fe_2O_3 over silica could not occur satisfactorily. But the combination of Al_2O_3 with Cr_2O_3 or Fe_2O_3 could be coated very successfully. This is due to that Al_2O_3 coating enhances or catalyses the coating of Cr_2O_3 or Fe_2O_3. Al_2O_3 acts as thermal barrier and removes the mismatch between the silica surface and Cr_2O_3 and Al_2O_3. Further Al_2O_3 coating over silica surface helps in seeding and diffusion of Cr_2O_3 or Fe_2O_3. In biphasic or tri-phasic matrix, Al_2O_3 plays a significant role in enhancing the Cr_2O_3 or Fe_2O_3 coating over silica surface, when Al_2O_3 coating occurs on the surface, it catalyses the coating of Cr_2O_3 or Al_2O_3.

7. Powder X-Ray Diffraction Analysis (XRD)

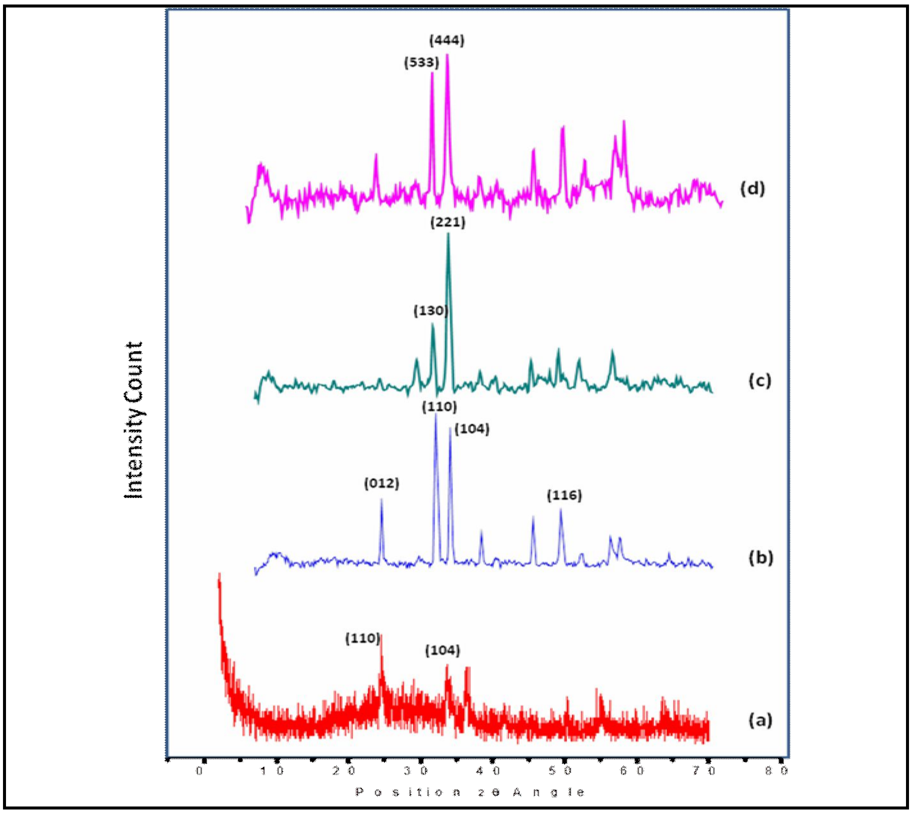


Figure 13. XRD analysis of (a) $Al(acac)_3$- $Cr(acac)_3$ oxides (b) $Cr(acac)_3$- $Fe(acac)_3$ oxides (c) $Al(acac)_3$-$Fe(acac)_3$ oxides (d) $Al(acac)_3$-$Cr(acac)_3$-$Fe(acac)_3$ oxides

The XRD analysis was recorded for the eutectic e_1, e_2 and e_3 for bimetallic eutectic phases and for ternary eutectic phases. The XRD patterns of the coated metallic composite oxides Fig (10), revealed the crystalline film structure as indicated by the strong reflections. The XRD patterns obtained for coated $Al(acac)_3$-$Cr(acac)_3$ [Fig. 13(a)] eutectic metal oxide four strong peaks corresponding to (104), (110), (012) and(116) planes (JCPDS no.87-0711) reveals that the structure of the eutectic bimetal oxide compound is rhombohedral[31-33]. Similarly for eutectic metal oxides of $Cr(acac)_3$- $Fe(acac)_3$ [Fig. 13(b)] , (104), (110), (012), (113), (116), (214), and (300) planes are observed (JCPDS no. 35-1112)[34] and shows that the eutectic bimetal oxide is rhombohedral in nature. For the eutectic bimetal oxide of $Al(acac)_3$- $Fe(acac)_3$ [Fig. 13(c)], (311), (220), (422), (511) and (440) planes are observed (JCPDS no. 82-1584) which reveals the cubic nature [33] of the compound. For the coating with ternary metal oxide Al-Cr-Fe system [Fig. 13(d)] shows (533) and (444) planes are cubic structure (JCPDS no.03-0873).

Conclusion

Precursors are important source to make thin films and coating in CVD. The objective of this work is to investigate mixed metal precursors from the metallo-organic complexes using the phase rule. The oxides of aluminium, chromium and iron may be coated as thin films from the individual volatile precursors. The metal oxide thin film can be used for catalysis. Thermal analysis of volatile precursors contain two or three components like $Al(acac)_3$, $Cr(acac)_3$ and $Fe(acac)_3$ have been carried out to find out the lower melting temperature which is at the eutectic composition. This will be useful as a single source precursor to deposit two and three metallic oxide thin film which is useful in solar cells, catalytic activity and sensor applications. Al_2O_3 enhances the coating of Cr_2O_3 or Fe_2O_3, which removes the mismatches between the substrate and the Cr_2O_3 or Fe_2O_3. It catalyses or enhances the diffusion mechanism during the deposition.

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