Chemical synthesis and compositional analysis of mixed [Mo(S$_{1-x}$Se$_x$)$_2$] semiconductor thin films

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The synthesis of binary MoS$_2$, MoSe$_2$ and mixed [Mo(S$_{1-x}$Se$_x$)$_2$] thin films onto a glass substrates using arrested precipitation technique (APT) is presented in this investigation. Growth kinetics and mechanism of film formation were studied for these films and are explained in brief. The stoichiometry of the film is confirmed by analyzing films using Extractive spectrophotometric (ESP), atomic absorption spectroscopic (AAS) and electron difftraction X-ray microanalysis (EDAX) techniques. The semiconductor solution containing Mo(VI) and Se(IV) is extracted with N-*n*-octylaniline in xylene and determined by ESP, AAS and EDAX techniques. Further these films are characterized for its semiconducting behavior to test the suitability of molybdenum chalcogenides as a photoelectrode to convert radiant energy into electricity. It is found that stoichiometry of the film formed by our recently developed arrested precipitation technique (APT) has strong influence on photoconduction in molybdenum chalcogenide photoelectrodes. © *2004 Kluwer Academic Publishers*

1. Introduction
Semiconducting molybdenum chalcogenide thin films have never before considered for solar energy applications although molybdenum is more abundant than most commercially interesting metals. Transition metal dichalcogenide MX$_2$ (M = Mo, W and X = S, Se, Te) are semiconductors that can act as efficient photovoltaic materials. Promising results have been obtained in the realization of photoelectrical or solid state device or solar cells using molybdenum, tungsten chalcogenides single crystals [1–5]. For economic reasons synthesis of MX$_2$ in thin film form would be interesting. Recent applications include intercalation compound [6] and long life photoelectrochemical (PEC) solar cells [7, 8]. Molybdenum dichalcogenides appear to be very promising semiconductor materials for various applications such as solar cells, photovoltaic cells, rechargeable batteries and solid lubricants. These applications arise from the optical, electrochemical and mechanical properties of these compounds [8–13]. They exhibit a layer type structure in which monolayer of molybdenum is sandwitched between monolayer of sulphur or selenium which are held together by relatively weak Van der waals forces. These materials have bandgaps in the range 1.86 to 1.42 eV, well matches with the solar spectrum. Despite all these promising characteristics, the wide use of molybdenum chalcogenides in optoelectronic devices is held back due to difficulty

in preparing thin films of these compounds with the desired properties. Particularly for (electro) catalytic applications, most projected use of these compounds require thin films with the basal plane parallel to the substrate, while most deposition methods result in films with the basal plane perpendicular to a greater or lesser extent to the substrate. Recently arrested precipitation technique (APT) has been widely used to deposit chalcogenide semiconductor thin films [14–16].

The techniques presently used for the synthesis of molybdenum chalcogenide semiconductors are, CVD, MOCVD spin coating, electro-deposition, spray pyrolysis, sputtering crystal growth and chemical bath deposition [13]. All these deposition techniques require specific deposition conditions and instrumentation. Among the chemical deposition techniques, arrested precipitation technique (APT) is relatively simple, inexpensive presently used by us for the deposition of V-VI, II-VI, II-V-VI & VI^B–VI^A molybdenum group chalcogenide thin films [14, 15]. The pure MoS$_2$, MoSe$_2$ and mixed [Mo(S$_{1-x}$Se$_x$)$_2$] thin films have been deposited onto a amorphous glass substrates from aqueous alkaline medium. The growth mechanism of film formation, chemical compositional analysis and optical studies of as deposited pure and mixed molybdenum sulphoselenide thin films are presented in this paper.

In the present investigation we have proposed for the first time, chemical compositional analysis of

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semiconducting metal chalcogenide thin films by spectrophotometric and AAS methods. Very few extraction and separation methods for molybdenum(VI) and selenium (IV) are available in the literature [17–20]. A novel extractant N-n-octylaniline has been used as an extractant for the extractive separation of Mo(VI) and Se(IV) from semiconducting materials. The method is rapid, sensitive, accurate and provides separation of selenium, tellurium, molybdenum, lead, antimony, copper, cadmium, zinc from the mixed semiconducting material. The result obtained by Extractive spectrophotometric (ESP) method shows close agreement with the results obtained by AAS and EDAX analysis.

2. Experimental details
2.1. Thin film synthesis
The MoS$_2$, MoSe$_2$ and [Mo(S$_{1-x}$Se$_x$)$_2$] composite thin films were obtained on good quality amorphous glass substrates under the same experimental conditions for all the samples by arrested precipitation technique. The equimolar solutions of AR grade molybdenum triethanolamine complex (Mo-TEA), thioacetamide and sodium selenosulphite were used as a basic ingredient. The total volume of reaction mixture was made 100 ml. The stoichiometric proportions of the above ingredients were finalized at the initial stages of deposition to obtain MoS$_2$, MoSe$_2$ and [(Mo(S$_{1-x}$Se$_x$)$_2$] ($x = 0$ to 1) thin films. All the chemicals were prepared in doubly distilled water. Chemomechanically and ultrasonically cleaned amorphous glass substrates were used as a support material for the chalcogenide thin films. The optimum conditions were finalized at the initial stages of deposition namely, speed of substrate rotation 50 rpm, temperature 65 $\pm$ 0.5°C, concentrations equimolar (0.25 M) except variations in amount of S^{2-} and Se^{2-} in case of mixed composites, pH = 9.5 $\pm$ 0.2. After a deposition period of 1^1/$_2$ hrs the samples were taken out, washed with distilled water & dried in constant temperature oven at 110°C for 3 h. The thickness of the thin film samples was determined by weight difference density method using electronic balance [Mettler Toledo GmbH CH-8606 Greifensee). Summery of the bath composition, temperature, time, thickness of the films is given in Table I.

TABLE I Optimum conditions and thickness of the molybdenum chalcogenide thin thin films

Films	Conditions of preparation		
	Bath composition	Temp°C	Duration (h)	Thickness (nm)
MoS$_2$	10.0 ml Mo-TEA + 20 ml Thioacetamide	65 $\pm$ 0.2	1^1/$_2$	40
MoSe$_2$	10.0 ml Mo-TEA + 20 ml Na$_2$SeSO$_3$	65 $\pm$ 0.2	1^1/$_2$	20
[Mo(S$_{1-x}$Se$_x$)]	10.0 ml Mo-TEA + 20 ml Thioacetamide 1 − x+ Na$_2$SeSo$_3$ x ($x = 0$ to 1)	65 $\pm$ 0.2	1^1/$_2$	20–40

2.2. Chemical compositional analysis technique
The chalcogenide semiconducting films of molybdenum were dissolved in a suitable solvent for the chemical compositional analysis. Presently we have used the solvent extraction and separation technique for analysis. The analysis of semiconducting solution containing Mo(VI) and Se(IV) were done using UV-visible spectrophotometer in the wavelength region 290 to 1300 nm and atomic absorption spectrophotometer. In order to determine Mo(VI) and Se(IV) by spectrophotometric method, standardization of Mo(VI) and Se(IV) were carried out using Oxime and Mathe's method respectively (21–25).

2.3. Characterisation technique
The optical absorption spectra for all the samples were recorded using UV-Visible spectrophotometer in the wavelength region 290 to 1300 nm (systronics digital spectrophotometer model 106 with 1 cm quart cells). The X-ray diffraction pattern for the samples were recorded on X-ray machine (Hitachi 1053) using CuK$_\alpha$ (1.54056 Å) radiation.
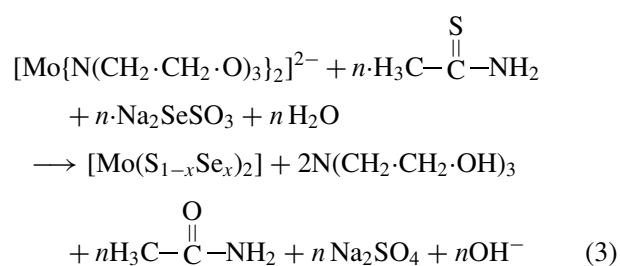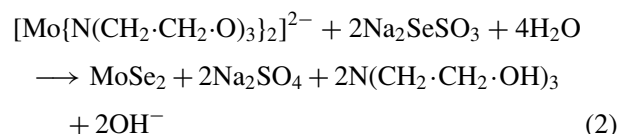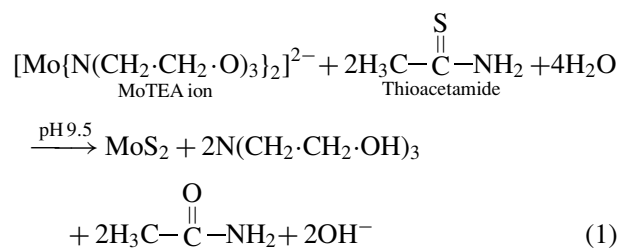
3. Results and discussion
In this paper combinatorial approach has been exploited for the synthesis of molybdenum sulphoselenide [Mo(S$_{1-x}$Se$_x$)$_2$] mixed/alloyed thin films onto a amorphous glass substrate using arrested precipitation technique (APT). We have presented a quantitative survey of the deposition process, mechanism of film formation, chemical compositional analysis and semiconducting properties of molybdenum sulphoselenide thin films.

3.1. The process of thin film deposition
Mo(VI) salts along with few ml of sodium dithionite have been used to generate Mo(IV) ions. These salts readily dissolve in water to form aqua ion [Mo(H$_2$O)$_6^{4+}$]. The aqua ions of molybdenum then arrested by the complexing molecules of triethanolamine [N(CH$_2$-CH$_2$-OH)$_3$] thereby forming stable [Mo{N·(CH$_2$·CH$_2$·O)$_3$}$_2$]$^{2-}$ charged complex. Thus in the present case Mo(IV) ions are well arrested using triethanolamine complexing agent to slow down the easy release of Mo(IV) ions in a reaction bath. In an aqueous alkaline medium Mo-TEA ionic complex slowly releases Mo^{4+} ions.
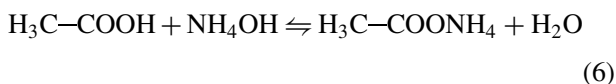
Thioacetamide and sodium selenosulphite are the sources of S^{2-} and Se^{2-} ions in an aqueous alkaline bath. These ionic species Mo^{4+}, S^{2-} and Se^{2-} condense ion-by-ion basis on to a rotating glass substrate surface where already formed nucleation centers act as a catalytic surfaces promoting the adherence of molybdochalcogen molecules. It is observed that, good quality highly reflecting strongly adhesive and uniform thin films of molybdenum sulfide (MoS$_2$), molybdenum selenide (MoSe$_2$) and mixed /alloyed molybdenum sulphoselenide [Mo(S$_{1-x}$Se$_x$)$_2$] get deposited on to a glass substrates. The thicknesses of the as deposited thin films are varied from 20 nm to 40 nm. Thickness

and quality of the films depend on optimum preparative parameters such as, temperature $65 \pm 0.2°C$, pH 9.5 ± 0.2, concentration equimolar 0. 25 M, and speed of substrate rotation 50 rpm. The reaction mechanism and kinetics of the film formation in aqueous alkaline medium is presented as follows

$$[Mo\{N(CH_2 \cdot CH_2 \cdot O)_3\}_2]^{2-} + 2H_3C\overset{\overset{\displaystyle S}{\|}}{C}-NH_2 + 4H_2O$$
$$\underset{\text{MoTEA ion}}{} \qquad \underset{\text{Thioacetamide}}{}$$

$$\xrightarrow{\text{pH 9.5}} MoS_2 + 2N(CH_2 \cdot CH_2 \cdot OH)_3$$

$$+ 2H_3C\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + 2OH^- \qquad (1)$$

$$[Mo\{N(CH_2 \cdot CH_2 \cdot O)_3\}_2]^{2-} + 2Na_2SeSO_3 + 4H_2O$$

$$\longrightarrow MoSe_2 + 2Na_2SO_4 + 2N(CH_2 \cdot CH_2 \cdot OH)_3$$

$$+ 2OH^- \qquad (2)$$

$$[Mo\{N(CH_2 \cdot CH_2 \cdot O)_3\}_2]^{2-} + n \cdot H_3C\overset{\overset{\displaystyle S}{\|}}{C}-NH_2$$

$$+ n \cdot Na_2SeSO_3 + n H_2O$$

$$\longrightarrow [Mo(S_{1-x}Se_x)_2] + 2N(CH_2 \cdot CH_2 \cdot OH)_3$$

$$+ nH_3C\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + n Na_2SO_4 + nOH^- \qquad (3)$$

In an aqueous alkaline medium TEA remains as it is in the reaction bath at deposition temperature, while thioacetamide on dissociation get converted to acetamide [H_3C-CO-NH_2]. Acetamide is unstable in

place as follows [20].

$$H_3C\overset{\overset{\displaystyle S}{\|}}{\underset{\text{Thioacetamide}}{C}}-NH_2 + OH^- \longrightarrow H_3C\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + SH^-$$

$$\qquad (4)$$

$$H_3C\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + 2H_2O \longrightarrow H_3C-COOH + NH_4OH$$

$$\qquad (5)$$

$$H_3C-COOH + NH_4OH \leftrightharpoons H_3C-COONH_4 + H_2O$$
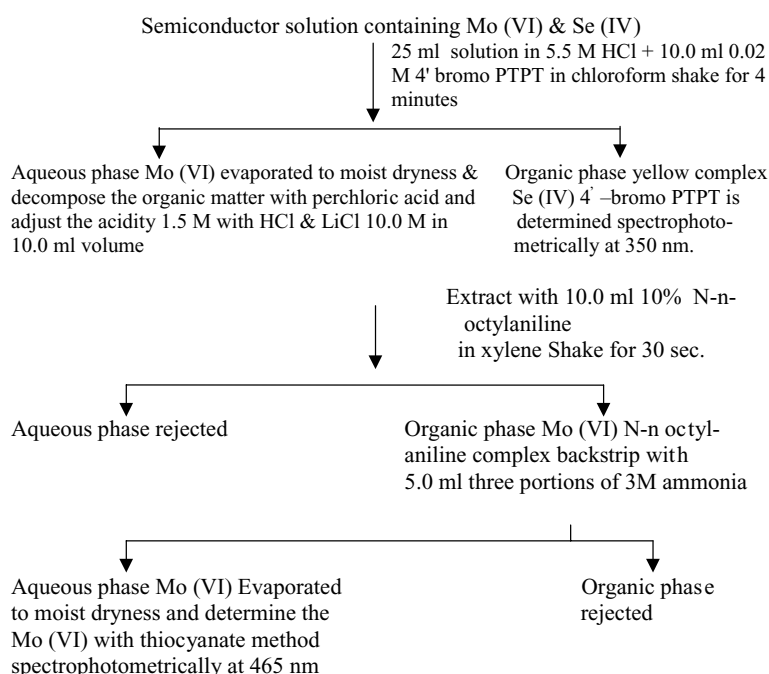
$$\qquad (6)$$
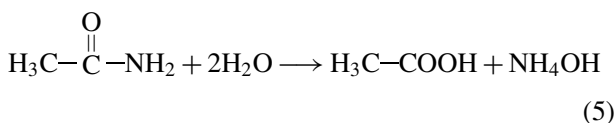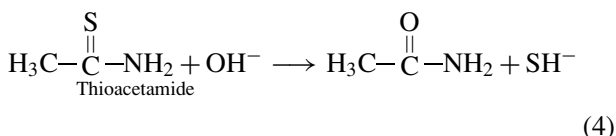
Formation and dissociation of CH_3COOH and NH_4OH buffer the reacting solution and maintain the pH in prescribed range. The preparative parameters have strong influence on quality of the films therefore at initial stages preparative parameters are optimized (Table I). It is seen from the visual observation and reaction mechanism of film formation that, the arrested precipitation technique (APT) can be used as a low cost selective method for the deposition of metal chalcogenide binary as well as mixed composite thin films.

3.2. Compositional analysis

As deposited films are analyzed by Extractive spectrophotometric (ESP), atomic absorption spectroscopic (AAS) and EDAX techniques for checking the stoichiometry of the films. The separation and analysis scheme for molybdenum sulphoselenide thin films by Extractive spectrophotometric technique is shown as follows.

Flow Sheet

Semiconductor solution containing Mo (VI) & Se (IV)

25 ml solution in 5.5 M HCl + 10.0 ml 0.02 M 4' bromo PTPT in chloroform shake for 4 minutes

Aqueous phase Mo (VI) evaporated to moist dryness & decompose the organic matter with perchloric acid and adjust the acidity 1.5 M with HCl & LiCl 10.0 M in 10.0 ml volume

Organic phase yellow complex Se (IV) 4' –bromo PTPT is determined spectrophotometrically at 350 nm.

Extract with 10.0 ml 10% N-n-octylaniline in xylene Shake for 30 sec.

Aqueous phase rejected

Organic phase Mo (VI) N-n octylaniline complex backstrip with 5.0 ml three portions of 3M ammonia

Aqueous phase Mo (VI) Evaporated to moist dryness and determine the Mo (VI) with thiocyanate method spectrophotometrically at 465 nm

Organic phase rejected

an alkaline medium (pH 9.5) and at deposition temperature (65°C). It dissociates to form acetic acid and ammonium hydroxide where in reversible reaction takes

The extracted content of Mo(VI) and Se(IV) from the semiconductor film and bath are summarized in Table II. From the Tables II and III it is found that

TABLE II Spectrophotometric analysis of molybdenum sulphoselenide [Mo(S$_{1-x}$Se$_x$)$_2$] thin films

Sample no.	Film composition	Spectrophotmetric analysis							
		Mo(VI) initially taken ppm	Se(IV) initially taken ppm	Mo(VI) obs. in bath ppm(B)	Mo(VI) obs. in film ppm(F)	Total Mo(VI) B + F ppm	Se(IV) obs. in bath ppm(B)	Se(IV) obs. in film ppm(F)	Total Se(IV) B + F ppm
1	[MoS$_2$]	2399.00	0.00	2240.50	156.30	2396.80	0.00	0.00	0.00
2	[Mo(S$_{0.8}$Se$_{0.2}$)$_2$]	2399.00	76.25	2237.00	159.00	2396.00	64.50	10.00	74.50
3	[Mo(S$_{0.7}$Se$_{0.3}$)$_2$]	2399.00	125.50	2239.00	157.00	2396.00	109.00	14.50	123.50
4	[Mo(S$_{0.5}$Se$_{0.5}$)$_2$]	2399.00	340.00	2238.50	158.00	2396.50	308.00	30.00	338.00
5	[Mo(S$_{0.3}$Se$_{0.7}$)$_2$]	2399.00	562.00	2237.00	152.00	2389.00	515.00	44.00	559.00
6	[Mo(S$_{0.9}$Se$_{0.1}$)$_2$]	2399.00	1038.00	2238.00	155.00	2393.00	967.50	58.00	1025.50
7	[MoSe$_2$]	2399.00	1200.00	2237.00	157.00	2394.50	1134.00	61.00	1195.00

TABLE III Mean average percentage error by spectrophotometric analysis

Metal	Average % error
Mo(VI)[a]	0.1867
Se(IV)[b]	1.1510

[a]Average of seven reading.

[b]Average of six reading.

the results obtained by extractive spectrophotometry and atomic absorption spectroscopy (AAS) analysis of molybdenum sulphoselenide are in good agreement with the theoretical concentration of Mo(VI) and Se(IV) initially taken for the deposition of mixed composites of the molybdenum chalcogenides. We have also confirmed the molybdenum and selenium content of the films by atomic absorption spectroscopy (AAS)
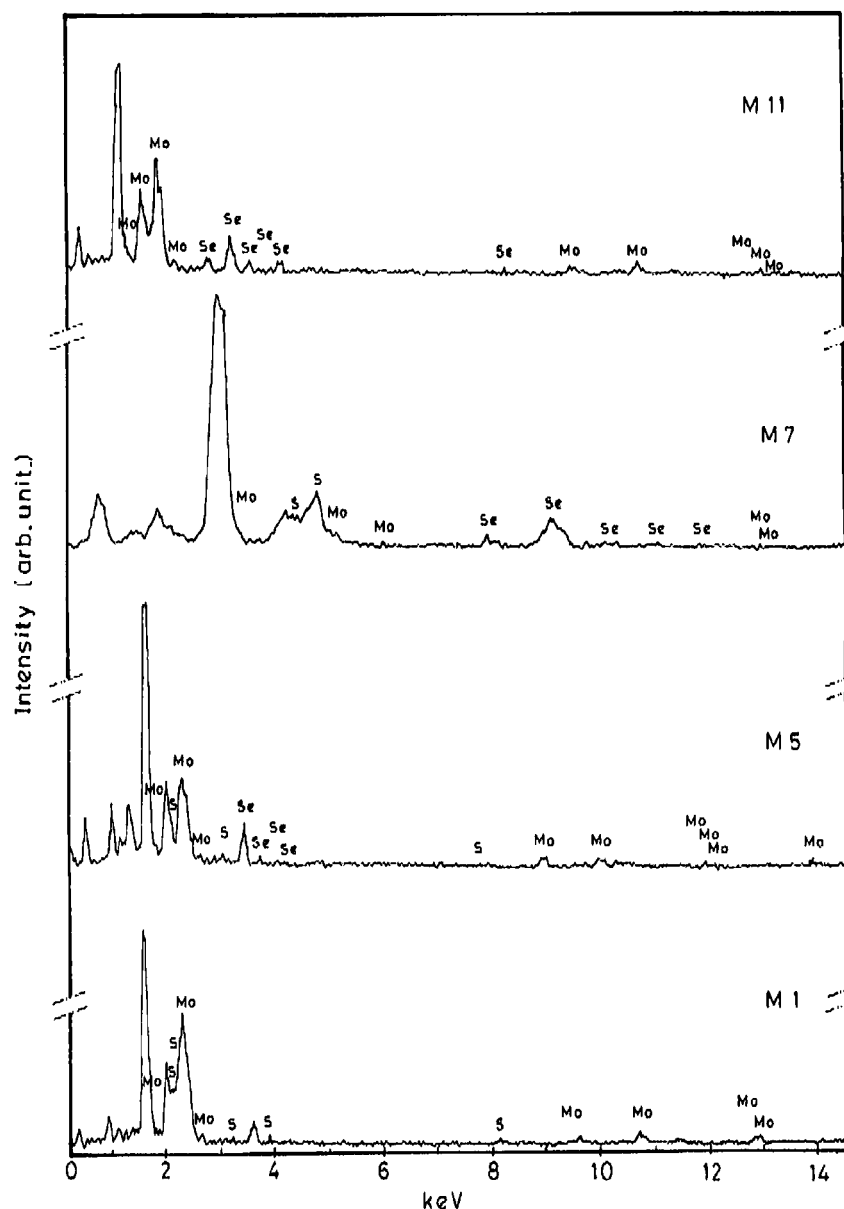

Figure 1 EDAX profile four typical samples of Molybdenum Sulphoselenide M$_1$-MoS$_2$, M$_7$-[Mo(S$_{0.6}$Se$_{0.4}$)$_2$], M$_9$-[Mo(S$_{0.4}$Se$_{0.6}$)$_2$] and M$_{11}$-MoSe$_2$.

TABLE IV Mean relative standard deviation for the seven typical samples of molybdenum chalcogenide thin films

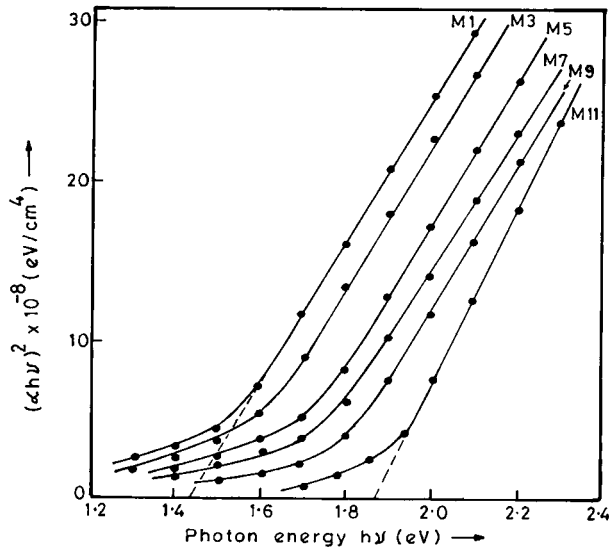| Metal	Relative standard deviation (RSD)	
	Spectrophotometry	AAS
Mo(VI)[a]	0.0198	0.0189
Se(IV)[b]	0.179	0.0190

[a]Average of seven reading.
[b]Average of six reading.

Figure 2 Variation of $(\alpha h\nu)^2$ versus photon energy (hν) for six typical samples.

and are well matched with the results of spectrophotometric analysis. Relative standard deviation tabulated in Table IV. Fig. 1 shows EDAX profile of MoS_2, $MoSe_2$ and $[Mo(S_{1-x}Se_x)_2]$ it is observed that mixed combinatorial films of molybdenum sulphoselenide are formed. The atomic weight percentage listed in Table V reveals that the mixed composition contains excess of Mo atoms which replaces S^{2-}/Se^{2-} atoms. This might be due to concentration of antisite defect [26]. When the VI^A/VI^B ratio close to 1.5 improved in crystallite size is observed. This might be due to better orientation of crystals in the films on addition of selenium.

The optical absorption spectra for pure MoS_2, $MoSe_2$ and mixed $[Mo(S_{1-x}Se_x)_2]$ thin films was recorded in the wavelength region 290 to 1300 nm. Variation of $(\alpha h\nu)^2$ vs photon energy (hν) shown in Fig. 2. The linear nature of the plot reveals that the forbidden gap for MoS_2 is 1.86 eV and for $MoSe_2$ is 1.42 eV. However in case of mixed $[Mo(S_{1-x}Se_x)_2]$ thin films of particular configuration $[Mo(S_{0.5}Se_{0.5})_2]$ forbidden gap is 1.65 eV. This clearly indicate that the forbidden gap decreases with increase in Se^{-2} concentration in the film and the forbidden gap 1.65 eV lies approximately at the midpoint of the forbidden gap of pure MoS_2 and $MoSe_2$. The band gap values for MoS_2 and $MoSe_2$ are found to be somewhat higher than the values reported for single crystal [26–27]. Since the slightly higher Eg in our case may be due to difference in co-ordination of Mo(IV) with S^{2-} and Se^{2-} as well as microcrystalline nature of the films. However, variation of absorption

MoS_2

$[Mo(S_{0.6}Se_{0.4})_2]$

$[Mo(S_{0.4}Se_{0.6})_2]$

$MoSe_2$

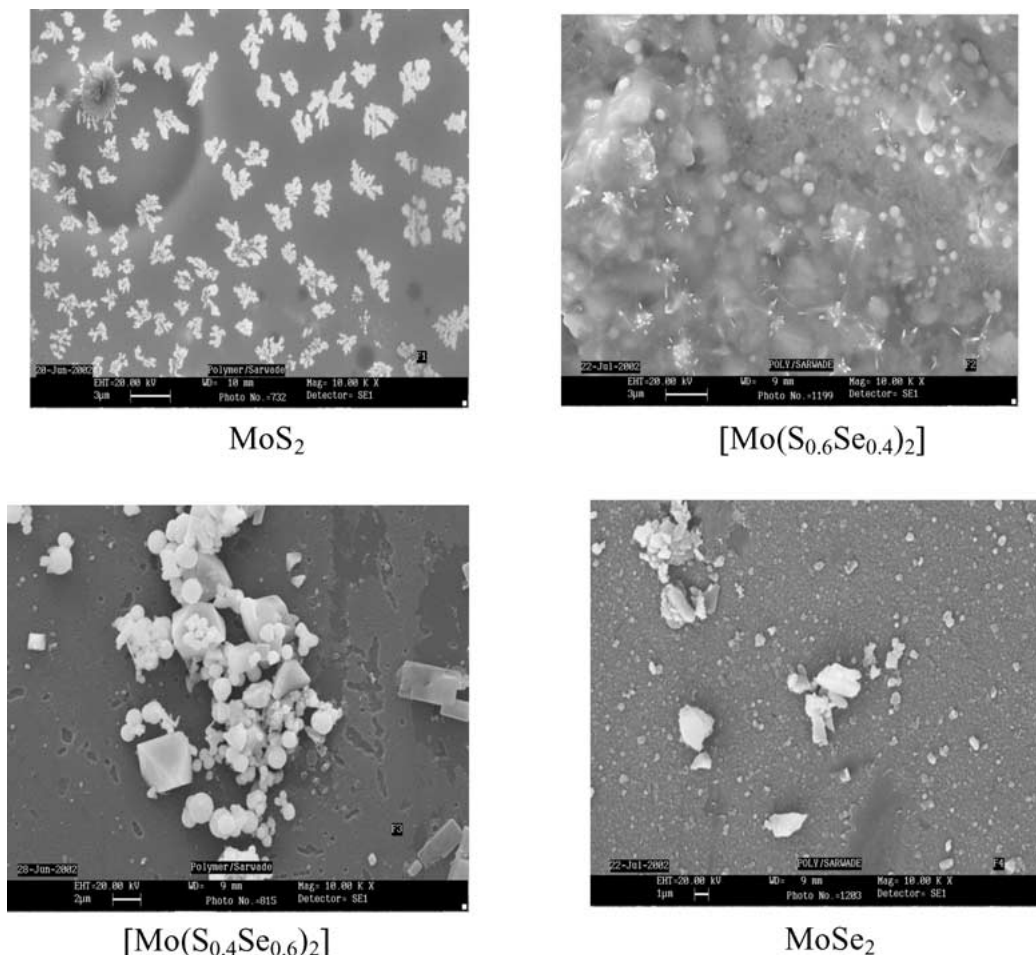*Figure 3* SEM photograph of four typical samples.

TABLE V EDAX analysis of molybdenum sulphoselenide [$Mo(S_{1-x}Se_x)_2$] thin films

| Sample | Elements | Atomic percentage | |
		Observed	Expected
MoS_2	Mo	40.56 ± 1.0	33.33 ± 1.0
	S	59.44 ± 2.0	66.66 ± 2.0
	Se	0.00	0.00
[$Mo(S_{0.6}Se_{0.4})_2$]	Mo	39.11 ± 1.0	33.33 ± 1.0
	S	32.33 ± 1.2	39.96 ± 2.2
	Se	28.56 ± 0.8	39.96 ± 2.2
[$Mo(S_{0.4}Se_{0.6})_2$]	Mo	39.78 ± 1.0	33.33 ± 1.0
	S	22.18 ± 0.8	26.71 ± 0.8
	Se	30.04 ± 1.2	39.96 ± 2.2
$MoSe_2$	Mo	38.82 ± 1.0	33.33 ± 1.0
	S	0.00	0.00
	Se	61.18 ± 1.0	66.66 ± 2.0

coefficient (α) with photon energy (hν) is linear. This reveals that the forbidden gap does not depend on the crystallanity of molybdenum chalcogenide thin films.

The micrographs of the above samples shown in Fig. 3 indicate that crystallites are not symmetrical in shape and morphology of the surface is improved with increase in selenium content of the films. When the VI^A/VI^B ratio close to 1.5 improved in crystallites is observed.

4. Conclusion
The arrested precipitation technique (APT) is found to be suitable for deposition of mixed chalcogenide thin films of transition and non-transition metals. The quality of the film formed on substrate materials largely depends on concentration of metal and chalcogen ions, pH, temperature, complexing agent and rate of agitation of reaction mixture. X-ray diffraction study shows microcrystalline nature of the molybdenum chalcogenide thin films. The UV-visible spectra and electrical studies shows that the molybdenum chalcogenide thin films are of direct band gap material with n-type conduction. The chemical compositional analysis of semiconducting molybdenum chalcogenide materials using ESP, AAS and EDAX techniques shows perfect stoichiometry of the films with the chemical formulae MoS_2, $MoSe_2$ and [$Mo(S_{1-x}Se_x)_2$]. The proposed analysis methods also permit quantitative extraction of very low concentration of selenium and molybdenum within a short period of equilibrium time.

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