Cd1-xNixSeTHIN FILMS: GROWTH MECHANISM, KINETIC STUDIES AND COMPOSITIONAL ANALYSIS

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Abstract

There has been an increasing interest during the last few decades in the synthesis of binary and ternary semiconducting chalcogenide thin films, because of the widespread applications in various fields of science and technology leading to a drastic cut in the cost of production of semiconductor devices.[1-6] The growth of thin films is a thermodynamically non-equilibrium process, meaning that the same system may exhibit drastically different growth behavior under different deposition conditions (e.g., layer-by-layer growth at low deposition rates, the formation of three-dimensional islands at high deposition rates, etc.)[7-8] In the thin film formation, the properties are strongly dependent on preparatory technique used.[9] Among the various deposition techniques, the chemical bath deposition is a low temperature soft method for the growth of thin films. This article deals with the theoretical background of chemical bath deposition method. The reaction mechanism, growth kinetics, thickness measurement, physical properties and compositional analysis are elaborated.

Keywords : *Measurement****,*** *Deposition****,*** *Effect****,*** *Experiment****,*** *Preparatory*

There has been an increasing interest during the last few decades in the synthesis of binary and ternary semiconducting chalcogenide thin films, because of the widespread applications in various fields of science and technology leading to a drastic cut in the cost of production of semiconductor devices.[1-6] The growth of thin films is a thermodynamically non-equilibrium process, meaning that the same system may exhibit drastically different growth behavior under different deposition conditions (e.g., layer-by-layer growth at low deposition rates, the formation of three-dimensional islands at high deposition rates, etc.)[7-8] In the thin film formation, the properties are strongly dependent on preparatory technique used.[9] Among the various deposition techniques, the chemical bath deposition is a low temperature soft method for the growth of thin films. This article deals with the theoretical background of chemical bath deposition method. The reaction mechanism, growth kinetics, thickness measurement, physical properties and compositional analysis are elaborated.

1. Theoretical Background of Chemical Bath Deposition

The chemical bath deposition (CBD) method uses a controlled chemical reaction to effect the deposition of a thin film by precipitation. In a typical experiment, substrates are immersed in an alkaline solution containing the chalcogenide source, the metal ion and added base. A chelating agent is also added to control the release of the metal ion. The process relies on the slow decomposition of chalcogen source into Se-2 ions in an alkaline solution in which the free metal ion is buffered at a low concentration. The free metal ion concentration is controlled by the formation of complex species. A large number of physico-chemical factors such as solubility product, supersaturation, type of precipitation, etc., control the growth of the deposit under a specified set of reaction conditions.

1.1.1 Concept of Solubility and Ionic Product

The solubility product of the compound plays a vital role in the deposition of the thin film. Various properties such as stoichiometry, homogeneity and adhesiveness are mainly dependent upon the solubility. When a sparingly soluble salt ‘AB’ is added to water, a saturated solution containing A+ and B- ions in contact with undissolved solid ‘AB’ is obtained and equilibrium is established between the solid phase and in the solution as;

AB(s) ↔ A+ (sol) + B(sol) --1.1

Applying law of mass action, we get

K = (aA+ x aB-)/ (aAB) --------------------------------------1.2

Where, aA+, aB- and aAB are activities of A+ , B and undissociated AB in the solution, respectively. The mean-activity coefficient of ions are considered to be unity due to low concentrations, therefore,

K = (CA+ x CB-)/ (CAB) --------------------------------------1.3

However, the concentration of pure solid is constant and taken as K’. Therefore, the above equation can be written as;

K.K’ = CA+ x CB- ---1.4

Since, both K and K’ are constant, the product of K.K’ is also a constant, called solubility product (SP) and is represented as;

Ksp = CA+ x CB- ---1.5

The product CA+ x CB- is called as ionic product (IP). When the ionic product is equal to the solubility product then the solution becomes saturated (IP=SP).When the ionic product exceeds the solubility product, the solution become supersaturated (IP/SP = S>1, where S = degree of supersaturation). At this condition, ions in the solution combine on the surface of the substrates, to form deposition. There are three main factors namely temperature, solvent and particle size, which affect the solubility product.[10-12] The solubility product can be measured using different methods like conductivity, polarography, cation exchange, colorimetry, ion exchange, etc.[13-14] The solubility product data for CdSe and NiSe compounds are 10^{-33} and 2×10^{-26}, respectively at 300 K temperature in water.

1.1.2 Supersaturation and Relative Supersaturation

A key factor in chemical bath deposition method is the supersaturation with respect to an individual solution phase.[15] The solubility depends upon particle size. A supersaturated solution is one that contains a greater concentration of solute than corresponding to the equilibrium solubility at the temperature under consideration. It is, therefore, an unstable state, which may be brought to a state of stable equilibrium by addition of crystal of solute (seeding) or some other substances or by mechanical means such as shaking and stirring. Supersaturation is given by;

Supersaturation = Q-S-----------------------------------1.6

Where, Q is the molar concentration of product formed momentarily in the solution at any instant and S is the molar equilibrium concentration in a saturated solution of the same solute. According to Von Weimarn,[16] relative supersaturation plays an important role in the determining particle size of a precipitate. The relative supersaturation 'Rs' is defined by;

Rs = (Q-S)/S --1.7

Where, (Q-S) denotes the supersaturation at the moment precipitation commences. The formation of precipitate and particle size depends upon temperature, rate of mixing of reagents, concentration and solubility product of the precipitate.

1.1.3 Formation of Precipitate in the Solution

Solution The process of precipitation involves two steps i) Nucleation and ii) Growth of particle

The minimum number of ions or molecules required to produce a stable second phase in contact with a solution is called a nucleus. The rate at which nuclei form in a solution depends on the degree of supersaturation. The rate of nucleation increases exponentially in highly supersaturated solution i.e

Rate of nucleation = K (Q-S)x ----------------------------------1.8

Where, Q is the concentration of solute in solution and K and x are the constants and x > 1.

2) Growth of particle

The second step is the growth of the particles already present in solution. In the case of ionic solids, the process involves the combination of cation and anion on appropriate sites.[17]

$(AB)_n + A+ + B- \leftrightarrow (AB)_{n+1}$ -----------------------------------1.9

$(AB)_{n+1} + A+ + B- \leftrightarrow (AB)_{n+2}$ --------------------------------1.10

Where, n is the number of A+ and B- required for forming stable phase $(AB)_n$. The rate of growth is directly proportional to the supersaturation.

Rate of growth = K x a (Q-S) ---------------------------------1.11

Where, 'a' is the surface area of exposed solid and K is a constant, which is the characteristic of particular precipitate. If the supersaturation is maintained at low level throughout the process, the precipitation occurs, instead of film formation. Due to this, a large number of nucleation centers are formed, upon which growth can occur. As a result, none of the particle grows very large and a colloidal suspension consisting of finely divided solid particle is formed. Under the same circumstances, colloidal particles come together and adhere to one another. The resulting solid is called coagulation. Colloidal particles when coagulated have different properties from a crystalline solid, since the particles are arranged irregularly.

1.1.4 Mechanism of Film Formation

Chemical bath deposition method is a very attractive method for producing thin films by large area deposition at low cost. The method requires the presence of chalcogen ions and complexed metal ions. Complexation provides small metal cation concentration to produce the controlled homogenous precipitation of the thin films on the solid substrate.[18]

Thin film formation by chemical bath deposition proceeds through various reaction steps at the substrate surface. First step is the nucleationtaking place on the substrate surface. An impurity already deposited on the substrate or adsorbed cation or anion or impurities on substrate surface in contact with reaction mixture can act as nucleation centers. Once the layer of material is formed, further growth takes place by adsorbing more and more ions from the solution giving a uniform and continuous film. The film growth take place either by an ion-by-ion condensation or by adsorption of colloidal particles on substrate surface.[19] However, concentration of ions decreases as deposition proceeds & therefore, growth rate is found to decrease.

1.2 Kinetic Studies and Growth Mechanism of $Cd1_{-x}Ni_xSe$ Thin Films

The rate of deposition of thin films is mainly dependent upon supersaturation (S), temperature of the bath, pH and composition parameter. The formation of film on the substrate surface from the solution phase is a two step process.[20] Formation of nucleation centers in the solution and on the substrate is the first step, while growth of particle is the second step. The formation of film takes place when the ionic product of metal ion and chalcogen ion exceeds the solubility product. When this condition is maintained the solution becomes supersaturated. The ions combine to form the MX nuclei on the substrate. Once MX is formed, it acts as a catalyst for the further deposition of fresh portions of the MX preferentially. In pseudobinary cadmium chalcogenide thin films CdX acts as seeding nuclei.[21-23.]

The overall growth process occurs by either ion-by-ion or cluster-by-cluster process. The ion-by-ion growth results in the thin, uniform and adherent films.[24] The cluster-by-cluster growth results in the thick, powdery and diffusely reflecting films.

For the deposition of $Cd_{1-x}Ni_xSe$ thin films by chemical bath deposition reaction mixture can be prepared by mixing cadmium sulphate octahydrate, nickel sulphate, tartaric acid, ammonia, sodium hydroxide, hydrazine hydrate and sodium selenosulphate. It is noted that a clear solution is formed at 278 K, and no film or precipitate is observed even when the solution is kept for long time. This is due to the fact that metal ions are in the stable complxed state $[M\ (A)_n]$. Low temperature lowers kinetic energy of the ions and avoids precipitation. The release of metal ions by the complexing species is a thermally activated process.[25] As the temperature increases slowly to the room temperature, it results in dissociation of metal complex and favors the formation of an alloy in the form of thin film. Hydrazine hydrate acts as complementary complexant, which improves compactness and adherence of the films. The kinetic of growth of the films can be understood from the following reaction.

$M^{+2} + nA^{-2} \leftrightarrow [M\ (A)\ n]^{-2(n-1)}\ (M^{+2} = Cd^{+2}/Ni^{+2})$-------------------------1.12

$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe$ --1.13

$HSe^- + OH^- \rightarrow H_2O + Se^{-2}$ ---1.14

$(1-x)\ [Cd\ (A)_n]^{-2(n-1)} + x\ [Ni\ (A)_n]^{-2(n-1)} + Se^{-2} \rightarrow Cd_{1-x}Ni_xSe + nA^{-2}$------1.15

In chemical bath deposition method, the ionic product exceeds the solubility product and precipitation take place by recombination of ions on the substrate surface via nucleation followed by growth process. The solubility product of NiSe is greater than that of CdSe [Ksp (CdSe) =10-33 and Ksp (NiSe) = 2×10^{-26}]. In case of pseudo-binary chalcogenide films obtained from alkaline medium, $Cd(OH)_2$ is known to act as seeding nucleus.[26] As the temperature increases free Cd^{2+} ions are created which combine with Se^{2-} ion preferentially on the substrate than Ni^{2+} ions producing orange layer of CdSe. This layer act as a catalyst for further growth of the film.[27-28] The formed layer grows further by adsorbing more and more Cd^{2+}, Ni^{2+} and Se2- ions to form ternary $Cd_{1-x}Ni_xSe$ films.

Lower the supersaturation, slower is the formation of MSe material. At higher pH, the concentration of Cd^{+2} ions decreases so that the ionic product of ions become less than solubility product of CdSe, as a result the formation CdSe is not possible .The nucleation is not observed within the first 30 minutes and hence the process requires an induction period for the nucleation on substrate. This suggests the ion-by-ion growth mechanism instead of cluster-by-cluster. The present investigation indicates that homogenous $Cd_{1-x}Ni_xSe$ films have been deposited at 240 min. The thickness was measured every 30 min and plotted against time as shown in Fig. 1.1. From the figure, the thickness varies linearly with time, but above 240 min. the concentration of the reactive species decreases and results indecrease in thickness. All the films were homogenous well adherent to the substrate. Fig 1.2 shows growth kinetics for the formation of a typical Cd0.5Ni0.5Se films. It has been observed that the growth rate in the early stages of the film deposition varies linearly with deposition temperature and then decreases after typical temperature. At higher temperature, the rate of release of M^{+2} and Se^{-2} ions is faster, so precipitation occurs instead of film formation. 50±2 rpm rotation speed was selected to deposit $Cd_{1-x}Ni_xSe$ thin films. At higher speed, very thin film was deposited. At lower speed, thick non-adherent films were obtained. The optimum conditions in the deposition process for yielding good quality deposits are 298K as deposition temperature and 240 min as deposition time.

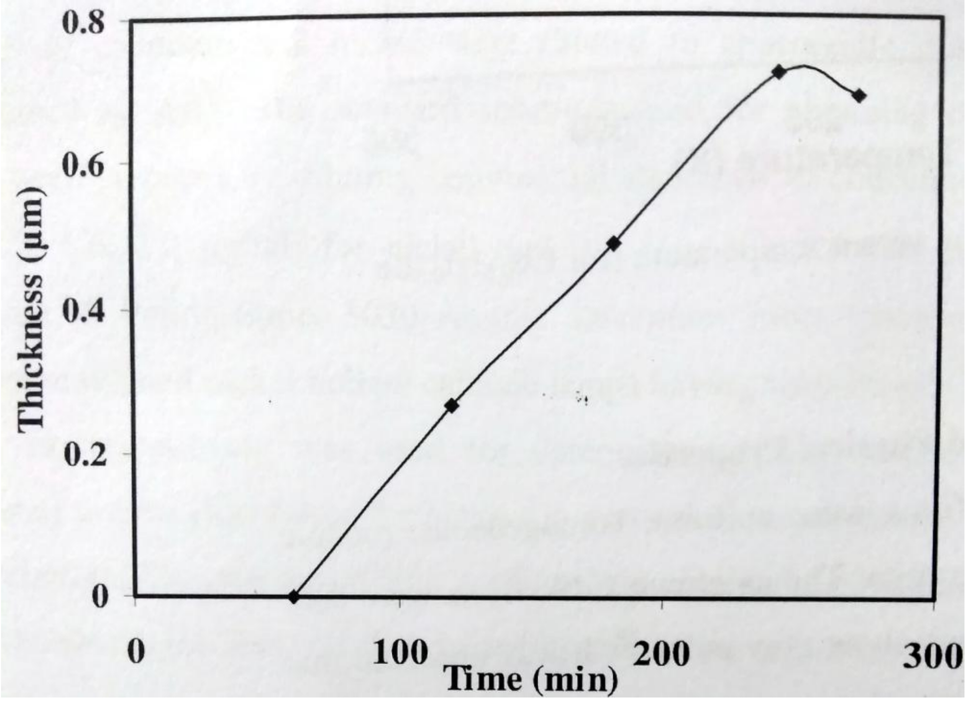


Fig. 1.1 : A plot of thickness versus time (for $Cd_{0.5}Ni_{0.5}Se$ thin film)

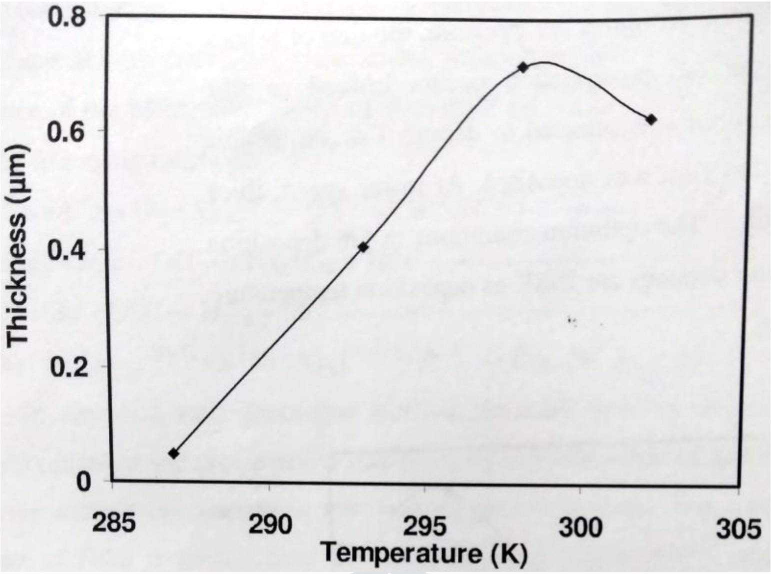


Fig. 1.2 : A plot of thickness versus temperature (for $Cd_{0.5}Ni_{0.5}Se$ thin film)

1.3 Thickness Measurement and Physical Properties

All the deposited films were uniform, homogeneous, pinhole free and well adherent to the substrate. The as grown CdSe films were dark orange red in color and NiSe films show grey color [29]. It was observed that the color of the films were changed from an orange red to grey as the composition parameter (x) was varied from 0 to 1. The change in color is observed due to substitution of Cd^{2+} ions by Ni^{2+} ions in the lattice of CdSe. The terminal thickness of the films has been measured by weight difference density consideration method. The variation of terminal thickness with composition parameter (x) is shown in the Fig.1.3. It was found that the terminal thickness varies almost linearly with the composition parameter (x). This is attributed to the difference in rates of deposition with respect to the formation of NiSe and CdSe thin films. The deposition of CdSe is found to be faster than that of NiSe material.

1.4 Compositional Analysis

Atomic absorption spectroscopy has proved itself the most powerful instrumental techniques for the quantitative determination of metallic elements. The composition of cadmium and nickel in the sample was determined by atomic absorption studies. The weighed film was dissolved in small quantity of AR grade concentrated HNO_3 to yield the products as shown in the following reactions:

$$CdSe + 2\,HNO_3 \rightarrow Cd(NO_3)_2 + Se + H_2O \text{ ----------------1.16}$$

$$NiSe + 2\,HNO_3 \rightarrow Ni(NO_3)_2 + Se + H_2O \text{ ----------------1.17}$$

Below pH 7, the selenium is precipitated as free element,[30] while watersoluble cadmium nitrate and nickel nitrate remain in the solution. The precipitate was filtered through a gooch crucible and subjected to selenium estimation using a standard gravimetric method. The filtrate containing nitrates of cadmium and nickel were diluted to appropriate dilution and determined by AAS. The standard solutions used for obtaining calibration curve were prepared by diluting commercial standards to concentration 0.4, 0.8, 1.2, 1.6, 2.0 µg/mL for nickel and 0.4, 0.8, 1.2, 1.6, 2.0 µg/mL for cadmium. A Perkin-Elmer 3030 Atomic absorption spectrophotometer was with cadmium and nickel hollow cathode lamps having wavelength 228.8 and 232.0 nm respectively was used for determination. The instrument was calibrated to zero absorbance for blank aqueous solution containing no nickel and cadmium. The average of three readings was obtained for better accuracy. The selenium in the film was determined by employing a standard gravimetric method.

The ratio of [Cd]/[Ni] ion concentration in the films were matchable with that taken in the bath. This indicates that the stoichiometry is maintained in the whole range of composition studied. The results obtained from the analysis are reported in the Table 1.1.

Composition Parameter(x)

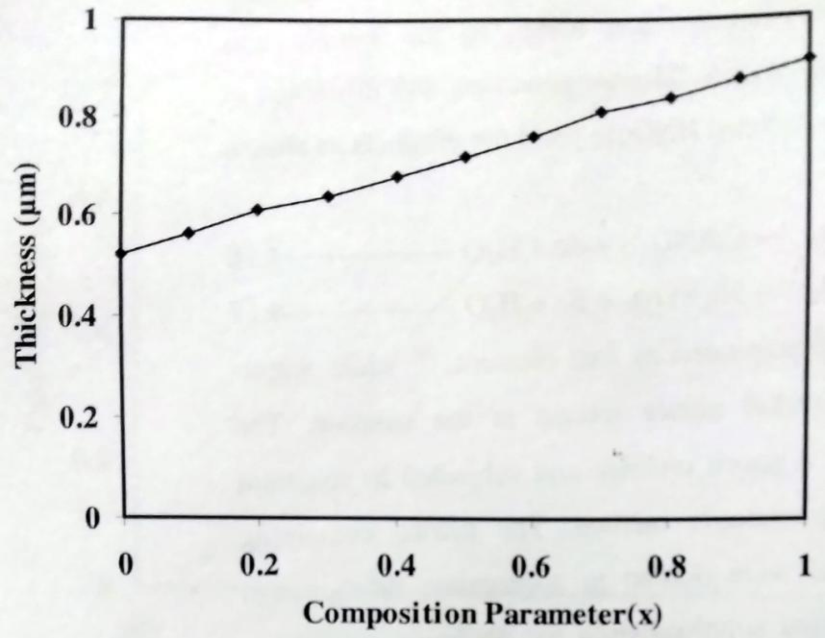
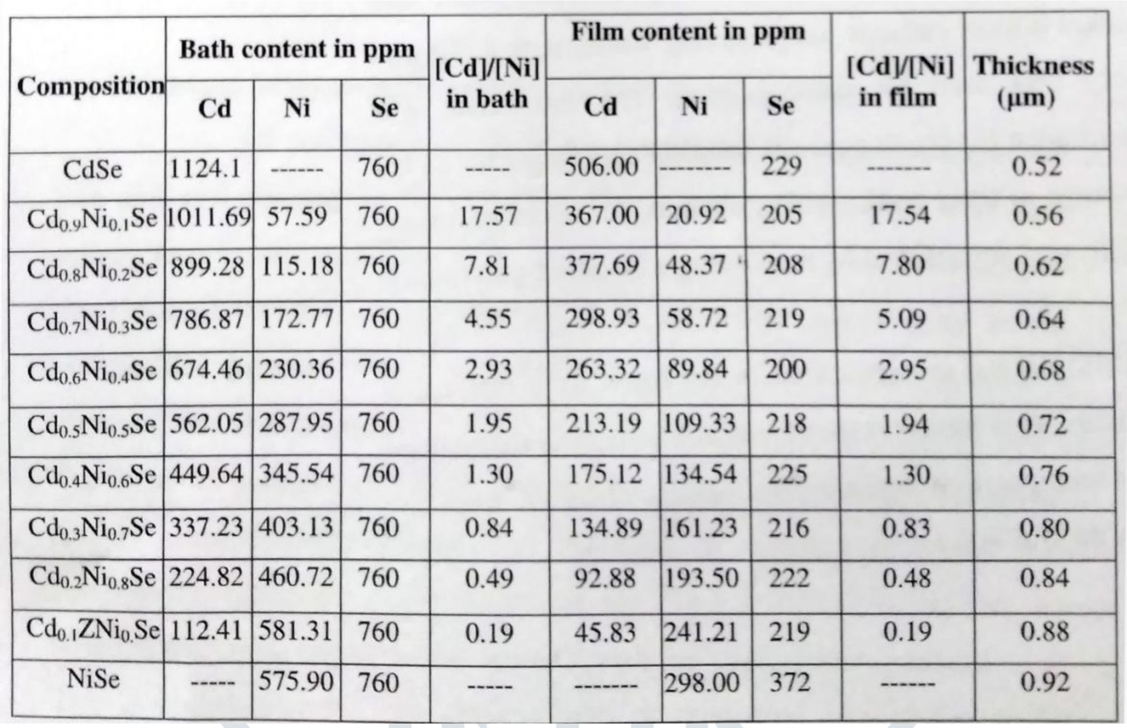


Fig. : A plot of thickness with composition parameter(x)

Table : Compositional analysis of $Cd_{1-x}Ni_{x}Se$ thin films.



Composition	Bath content in ppm			[Cd]/[Ni] in bath	Film content in ppm			[Cd]/[Ni] in film	Thickness (μm)
	Cd	Ni	Se		Cd	Ni	Se		
CdSe	1124.1	------	760	-----	506.00	--------	229	-------	0.52
Cd$_{0.9}$Ni$_{0.1}$Se	1011.69	57.59	760	17.57	367.00	20.92	205	17.54	0.56
Cd$_{0.8}$Ni$_{0.2}$Se	899.28	115.18	760	7.81	377.69	48.37	208	7.80	0.62
Cd$_{0.7}$Ni$_{0.3}$Se	786.87	172.77	760	4.55	298.93	58.72	219	5.09	0.64
Cd$_{0.6}$Ni$_{0.4}$Se	674.46	230.36	760	2.93	263.32	89.84	200	2.95	0.68
Cd$_{0.5}$Ni$_{0.5}$Se	562.05	287.95	760	1.95	213.19	109.33	218	1.94	0.72
Cd$_{0.4}$Ni$_{0.6}$Se	449.64	345.54	760	1.30	175.12	134.54	225	1.30	0.76
Cd$_{0.3}$Ni$_{0.7}$Se	337.23	403.13	760	0.84	134.89	161.23	216	0.83	0.80
Cd$_{0.2}$Ni$_{0.8}$Se	224.82	460.72	760	0.49	92.88	193.50	222	0.48	0.84
Cd$_{0.1}$ZNi$_{0.}$Se	112.41	581.31	760	0.19	45.83	241.21	219	0.19	0.88
NiSe	-----	575.90	760	-----	-------	298.00	372	------	0.92

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