Chapter-V

$Cd_{1-x}Ni_xSe$ THIN FILMS:
STRUCTURAL, MICROSCOPIC AND OPTOELECTRONIC STUDIES
5.1 Introduction

The area of solid state chemistry generally deals with experimental investigations and theoretical interpretation of the various physical properties of matter in solid condensed phase. In the 21st century, the properties at the interfaces have become important due to increased industrial applications and tremendous development in electronics and computer technology. Of course, the pre-requisite for such studies is the knowledge of structure, bonding and characterization of the electrode-electrolyte interaction.

The characterization of semiconductor thin film is the prime step in the development of devices. The properties of the thin film material can be studied by using various characterization techniques like thickness measurements; X-ray diffraction, scanning electron microscopy, atomic absorption spectroscopy, optical absorption measurement, electrical resistivity, thermo-electrical studies etc. Thus, characterization is an essential part of all the investigations dealing with thin film materials.

The important aspect of characterization includes structure identification, analysis of defects, compositional homogeneity, microscopic studies, chemical composition, optical band gap, electrical resistivity, etc. X-ray diffraction is suitable tool for understanding the crystal structure of any unknown material, whether the sample is single crystal or polycrystal.\textsuperscript{1-3} The optical and structural parameters like crystallinity, the crystal phase, the lattice constant, the average stress and strain, the grain size orientation, absorption, absorption co-efficient, etc. are strongly dependent on the deposition parameters.\textsuperscript{4-6} The study of optical properties of the thin film is very important, because the optical properties determine the efficiency of the devices particularly tandem solar cells. Moreover, the optical properties are closely related to the composition of the film and microstructural parameters which again depend on film thickness and substrate temperature besides other factors.\textsuperscript{7} Measurement of optical properties of semiconducting films allow us to obtain critical information about electronic band structure, optical transitions and relaxation mechanism. Knowledge of absorption co-efficient
in semiconductors is often of interest in the design and analysis of heterostructure layers as well as other opto-electronic devices utilizing these semiconductors.\textsuperscript{8-9} The film resistivity has been found to depend on various parameters such as thickness, deposition rate, substrate temperature, etc. Electrical properties are sensitive to stoichiometric deviations and hence a range of useful conductivity is obtained.\textsuperscript{10-12} It is therefore pertinent to review the essential features of the different characterization techniques suitable for thin films obtained during this work.\textsuperscript{13}

This chapter deals with the structural, microscopic, optical and electrical properties of the Cd$_{1-x}$Ni$_x$Se thin film material.

5.2 Characterization Techniques

5.2.1 X-ray Diffraction (XRD)

In 1912 scientist V Laue noted that incident X-rays are diffracted when the wavelength of incident X-rays is equal to the interatomic distance in crystals. X-rays were believed to have wavelengths of the order of 10^{-8} cm and that crystals were consisted of periodic arrays of atoms having similar dimensions. Therefore, the crystals could serve as grating for the diffraction of X-rays. X-ray diffraction has provided a wealth of important information to science and industry. X-ray diffraction also provides a convenient and practical means for the qualitative identification of crystalline compound.\textsuperscript{14-15}

When a beam of X-ray incident on a plane at an angle ‘θ’ will be reflected making the same angle with the plane. The reflection is caused by the interaction of the electromagnetic radiation with the electron of the atoms at the lattice points. In order that the reflection is sufficiently intense, reflection from successive planes separated by the distance‘d’ should be superimposed. This would require the path difference of the parallel beams from the source to the detector via the respective reflecting planes to be equal to an integral multiple of the wavelength of the radiation. The path difference due to two successive parallel planes having interplanar distance‘d’ is 2dsinθ. Hence, Bragg’s law of diffraction is given as
\[ n\lambda = 2d\sin\theta \]  

where \( n \) is a positive integer, \( \lambda \) is the wavelength of the X-rays used. By measuring the diffraction angle ‘\( \theta \)’, it is possible to determine the corresponding interplanar distance ‘\( d \)’.\(^{16,17}\) In diffractometer, a moving X-ray detector records the 2\( \theta \) angles at which the beam is diffracted giving a characteristic diffraction pattern. This diffraction pattern acts as “fingerprint” of the material. This method is used for structure determination, determination of orientation, particle size, stress/strain measurements, etc.\(^{18}\)

1) Determination of Crystal Structure

The identification of the sample from powder diffraction pattern is based upon the position of the lines and their relative intensities. The diffraction angle 2\( \theta \) is determined by the spacing between a particular set of planes; with the aid of the Bragg equation and the distance ‘\( d \)’ is calculated by known wavelength of source and the measured angle. XRD provides the data which is used for the determination of crystal structure. The various types of crystal structures such as cubic, hexagonal, tetragonal, monoclinic etc. are easily interpreted.

2) Phase Identification

Every crystalline compound has its own characteristic diffraction pattern which may be used for its identification. Diffraction patterns of a pure crystalline material are given in the standard Powder Diffraction File (known as the JCPDS File or, formerly as the ASTM File). Substances are indexed by any one of the two methods. The Hanawalt index method uses the eight most intense lines and the Fink index method uses the first eight lines of longest d-spacing in the powder pattern. The mixture of substances may be identified provided; the patterns of the component phases are available for comparison.

The amount of a particular crystalline phase in a mixture may be determined by quantitative X-ray powder diffraction. An internal standard method can also be used to identify the phases. A line in the powder pattern of the phase of interest is selected and its intensity is compared with that of internal standard line. The proportion of phase present can be determined by
interpolation from a previously constructed calibration graph of intensity against composition.\(^{19}\)

3) **Determination of accurate unit cell parameters**

The positions (d-spacing) of the lines in a powder pattern are governed by the values of the unit cell parameters \((a, b, c, \alpha, \beta, \gamma)\). The shape and size of the unit cell is determined from the unit cell parameters. Unit cell parameters are normally determined by single crystal method. But accurate cell parameters may be obtained from powder pattern, provided Miller indices (hkl) and their positions have been measured accurately. There are several computer programs available for determination of unit cell parameters. Accurate unit cell parameters are particularly useful for (a) enabling complex powder patterns to be indexed, (b) studying the effect of composition on cell parameters and (c) measuring thermal coefficients.

4) **Solid Solution**

There are two main ways in which powder diffraction may be used to study solid solution. In former way, simple fingerprint method in which qualitative phase analysis is carried out. The objective is to determine the crystalline phases that are present in a sample without necessarily measuring the patterns very accurately. The second way is to measure the powder pattern in order to obtain information about the composition of solid solution. Usually, the unit cell undergoes a small contraction or expansion as the composition varies across a solid solution series. Once a calibration graph of d-spacing or cell volume against composition has been drawn, the composition of solid solution may be obtained from measurement of their unit cell parameters or the d-spacing of certain lines in the powder X-ray pattern. According to Vegard’s law, unit cell parameters should change linearly with composition. In practice, Vegard’s law is often obeyed only approximately and accurate measurements can reveal departures from linearity. Deviations from Vegard’s law occur in metallic solution. In non-metallic solid solution, deviation from Vegard’s law is much less common.
5) Particle size measurement

X-ray powder diffraction is used to measure the average crystal size in a powdered sample, provided the average diameter is less than 2000 Å. The lines in a powder diffraction pattern are of finite breadth but if the particles are very small, the lines are broader than usual. The broadening increases with decreasing particle size. The crystallite size is calculated from full width at half maximum (FWHM). The average crystallite size is determined by Scherrer’s formula

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

Where, \( \beta \) is the broadening of diffraction line measured at FWHM in radians, \( D \) is the particle size, \( \lambda \) is the wavelength of X-ray used and \( K \) is the constant related to the shape of the crystallites. It varies from 0.9-1.3. It is best approximated to a value of 0.9, when little is known about crystallite size and shape. The FWHM becomes noticeable when \( D \) is near 1000 Å and becomes appreciable near 200 Å. If all the lines are broadened uniformly, the crystals are more or less equidimensional in all directions. Any plane or planes with smaller broadening denote an extension of the crystal in the direction normal to the plane.

6) Intensity Studies

Intensity of X-ray reflections is important for two main reasons. Firstly, quantitative measurement of intensity is necessary to determine unknown crystal structure. Secondly, qualitative or semiquantitative intensity data is needed in using the powder diffraction method to characterize materials and especially in using the powder diffraction file to identify unknowns. X-ray intensities of diffracted beam depend on several factors such as polarization factor, structure factor, multiplicity factor, Lorentz factor, absorption factor and temperature factor.
5.2.2 Scanning Electron Microscopy (SEM)

Electron microscopy is an extremely modern technique capable of providing structural information over a wide range of magnification. At one extreme, scanning electron microscopy (SEM) complements optical microscopy for studying the texture, topography and surface features of powders or solid pieces, because of the depth of focus of SEM instruments, the resulting photographs have a definite three-dimensional quality. At the other extreme, high resolution electron microscopy (HREM) is capable of giving information on atomic scale by direct lattice imaging. The resolution of ~ 2 Å has been achieved.

Electron microscopes are of either transmission or reflection design. For studying transmission, sample must be thinner than ~ 2000 Å. This is because electrons interact strongly with matter and are completely absorbed by thick particles. Thinning technique like ion bombardment is generally used, but ion bombardment may lead to structure modification of the solid. The scanning voltage of the order of 1 Mega volt is used. When thicker sample is used, the beam is more penetrating as well as the amount of background scatter is reduced and higher resolution may be obtained.

Sample thickness and sample preparation is not a problem in reflection instruments. The sample is coated with a thin layer of metal; especially if the sample is a poor electrical conductor, in order to prevent the build-up charge on the surface of the sample. The main reflection instrument is the SEM. It covers the magnification range between the lower resolution limit of optical spectroscopy (~ 1 μm ) and the upper practical working limit of transmission electron microscopy (~ 0.1μm).

In the scanning electron microscope, electrons from the electron gun are focused to small spot, (50 to 100 Å in diameter) on the surface of the sample. The electron beam is scanned systematically over the sample. The secondary electrons, emitted by the samples, are used to build up an image of the sample surface and which is displayed on a screen. A limitation with SEM instruments is the lower limit of resolution (~ 100 Å).
5.2.3 Optical Absorption Study

Optical measurements constitute the most important need for determining the band structure of semiconductor. Photon-induced electronic transitions can occur between different bands, which lead to the determination of the energy band gap, or within a single band such as the free-carrier absorption. Optical measurement can also be used to study lattice vibrations. The optical photon incident on any material may undergo transmission, reflection or absorption. The absorption of radiation in a material is considered to be due to inner shell electrons, valence band electrons, free carriers and electron bound to localized impurity centers or defects of some type. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorptivity at the wavelength corresponding to the gap energy. This feature in optical spectrum is known as the optical absorption edge. For these structures with band gap in the range of 0.3 -3.0 eV, the optical absorption edge can be easily measured by conventional optical spectroscopy. Measurement of the entire interband absorption spectrum by direct transmission requires films with thickness of 10-100 nm.

Near the absorption edge, the absorption coefficient can be expressed as

\[ \alpha \approx (h\nu - E_g)^r \]

5.3

Where, \( h\nu \) is the photon energy, \( E_g \) is the band gap and \( r \) is a constant. In the one-electron approximation \( r \) equals \( \frac{1}{2} \) and \( \frac{3}{2} \) for allowed direct transitions and forbidden direct transitions respectively. The constant \( r \) equals 2 for indirect transitions, where phonons are involved. In addition, \( r \) equals \( \frac{1}{2} \) for allowed indirect transitions to exciton states, where an exciton is a bound electron-hole pair with energy in the band gap and moves through the crystal lattice as a unit.

Near the absorption edge, where the values of \( (h\nu - E_g) \) become comparable with the binding energy of an exciton, the coulomb interaction between the free hole and electron must be taken into account. For \( h\nu \leq E_g \) the absorption merges continuously into the absorption caused by the higher
excited states of the exciton. When $h\nu \gg E_g$, higher energy bands participate in the transition process and complicated band structure is reflected in the absorption coefficient.\textsuperscript{23-24}

By plotting the graph of $(ah\nu)^{1/r}$ versus $h\nu$ for various values of $r$, it is possible to determine the nature of transition involved and the intercepts of the straight line portion of the respective plot corresponding to zero absorption on energy axis give values of energy gaps. The values of $r$ for above transitions may be confirmed by evaluating slope of ln $(ah\nu)$ versus ln $(h\nu-E_g)$ plot. This is 0.5 and 3.0 for direct transition and indirect transition respectively.

5.2.4 Electrical Transport Properties

a) Electrical Conductivity

The nature of chemical bonding plays a vital role in determining the type of the conductivity. The parameters of main interest in this study are the conductivity, conductivity type ($n$ or $p$), mobility and carrier concentration. Thus, electrical transport properties play an important role in determining all these parameters related to thin films.

When the temperature is not very low, the semiconductor will conduct electricity due to movement of the electrons in the conduction band and that of the holes in the valence band. The drift velocity per unit field is called mobility ($\mu$). The electrical conductivity for semiconductors lies in between $10^{-5}$ to $10^{13}$ $(\Omega\text{cm})^{-1}$.

The contact method is most widely used for the measurement of the electrical conductivity. The method includes two probes and four probes. The two probe method is simple, easy to use and useful for high resistive thin film. In this method, constant ‘dc’ voltage ‘$V$’ is applied between two fixed positions on surface of the thin film. The current passing through a sample of known dimensions (length ‘$l$’ and cross sectional area ‘$A$’) is measured with an appropriate current meter. For a sample of uniform thickness, the conductivity is given by

$$\sigma = (d/A) (I/V)$$

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109
\[ A = t \cdot b \] \quad \text{---5.5}

Where, \( t \) is thickness and \( b \) is width of film.

In case of semiconductors, carrier density increases exponentially with temperature. The electrical conductivity increases with increasing temperature. The thermal activation energy \( E_a \) is calculated by using relation

\[ \sigma = \sigma_o \exp \left( -\frac{E_a}{kT} \right) \] \quad \text{---5.6}

Where, \( \sigma \) is the conductivity of the sample at temperature \( T \). \( \sigma_o \) is a parameter that depends on sample characteristic such as thickness, structure etc., \( E_a \) is the thermal activation energy of electrical conduction and \( k \) is Boltzmann constant. The slope of \( \log \sigma \) versus \((1000/T)\) is proportional to the thermal activation energy.

**b) Thermoelectrical Power**

When a temperature gradient is maintained across a semiconductor in addition to an applied electric field the total current density is, \(^{24}\)

\[ J = \sigma \left( \frac{1}{T} \frac{dE_F}{dx} - P \frac{dT}{dx} \right) \] \quad \text{---5.7}

Where, \( \sigma \) is the conductivity, \( E_F \) the Fermi energy and \( P \) the differential thermoelectric power. The thermoelectric power is negative for n-type semiconductor and positive for p-type semiconductor, a fact often used to determine the conduction type of a semiconductor. The thermoelectric power can also be used to determine the position of the Fermi level relative to band edges. The thermally generated voltage is directly proportional to temperature difference created across the semiconductor. The carrier density can be determined from thermo-emf measurements. From the polarity of potentiometer terminal connected at cold end (negative or positive) of the sample, one can easily determine the sign of the predominant charge carriers and hence the type of semiconductor (\( n \) or \( p \)-type). \(^{25}\)

**5.3 Experimental Procedure**

**5.3.1 Preparation of Cd\(_{1-x}\)Ni\(_x\)Se thin film**

Cd\(_{1-x}\)Ni\(_x\)Se thin films were deposited on non-conducting glass substrates by a chemical bath deposition. It is based on slow release of Cd\(^{2+}\), Ni\(^{2+}\) ions from complexed state and decomposition of selenosulphate in
aqueous ammoniacal solution. A solution containing Cd$^{2+}$, Ni$^{2+}$, tartaric acid, ammonia, sodium hydroxide, hydrazine hydrate and sodium selenosulphate was kept initially at 278 K. Properly cleaned substrates were mounted on substrate holder and rotated in reaction mixture at a speed of 50±2 rpm. The temperature of the bath was allowed to increase slowly to 298 K. The detailed procedure has been given in chapter III.

5.3.2 XRD Studies

The X-ray diffraction pattern of the films were recorded by using Philips-PW-1710, (Holland) X-ray diffractrometer, in 2θ range from 10°-100° using Cu Kα₁ line. (λ = 1.54056 Å). The crystal structure, grain size and lattice parameters were determined from X-ray diffraction pattern. The spectra for pure CdSe [JCPDF Card No.08-0459] and pure NiSe [JCPDF Card No.75-0610] were used for identification purpose.

5.3.3 SEM Studies

Scanning electron microscopy (SEM) photographs were obtained using a 250 MK-III, Stereoscan, Cambridge (UK). These photographs were used to investigate surface morphology of the thin film and also for determining the grain size parameter.

5.3.4 Optical Studies

The absorption spectra of thin film samples were measured at room temperature as function of wavelength without considering losses due to reflection and scattering. A Hitachi-330 (Japan) UV-VIS-NIR Double beam spectrophotometer was used for this purpose. A substrate absorption correction was made by placing an identical uncoated glass substrate in reference beam. The absorption spectra were recorded from 400-1200 nm wavelength range in steps of 2 nm each. The absorption spectra were used to calculate energy band gap, type of optical transition involved and absorption coefficient, etc.
5.3.5 Electrical Transport Properties

a) Electrical Conductivity

The dark ‘dc’ electrical conductivity of the films was measured in the 300-525 K temperature range. A two-point probe press contact method was adopted for this purpose. A regulated power supply (Aplab make) was employed to pass the current through samples. The current flowing through the circuit was measured by sensitive nanometer. A calibrated chromel-alumel thermocouple (24 gague size) was used to sense the working temperature.

b) Thermoelectric Power

The thermoelectric power measurements were carried out on thin film samples between 300-550 K ranges of temperature. To sense the working temperature, a calibrated chromel-alumel thermocouple (24-gauge size) was used. The thermo-voltage was measured with a Hewlett-Packard, 6 ½-digit multimeter.

5.4 Results and Discussion

5.4.1 X-ray Diffraction Analysis

The crystallographic data of Cd\(_{1-x}\)Ni\(_x\)Se thin films were obtained by using Philips PW-1710 X-ray diffractometer with CuK\(_{α1}\) line (\(λ = 1.54056 \text{ Å}\)) in the 2\(θ\) range from 10\(^0\) - 100\(^0\). The X-ray diffraction (XRD) spectra of annealed Cd\(_{1-x}\)Ni\(_x\)Se thin films deposited on glass substrate are shown in Fig.5.1.

The presence of large number of peaks indicates that the films are polycrystalline in nature. The analysis of spectrum indicated that the ternary films are having hexagonal structure in the whole range of compositions studied. The analysis of XRD patterns in terms of hkl planes, interplanar distances, cell size, and lattice parameters have been carried out by considering hexagonal structure and data is given in Table 5.1.

In the present investigation, CdSe exhibited hexagonal phase and were indexed according to hexagonal structure. NiSe also shows hexagonal structure. The diffused background is due to amorphous glass substrate and also to some amorphous phase present in CdSe, NiSe and Cd\(_{1-x}\)Ni\(_x\)Se thin
films. For CdSe (100) (102) (110) (103) (112) (203) planes of a hexagonal phase are observed. The highest intense reflection at $d = 3.712$ Å can be normally indexed as hexagonal (100). For NiSe, (100) (102) (110) (103) (112) (203) planes of a hexagonal phase are observed. It appears that $\text{Cd}_{1-x}\text{Ni}_x\text{Se}$ exists only in hexagonal form. The most intense reflections observed for $\text{Cd}_{1-x}\text{Ni}_x\text{Se}$ thin films was originating from (100) and (102) planes. The addition of Ni in CdSe has shown to shift (100) and (102) planes to lower $d'$ value (i.e. higher $\theta$ values). The variation were observed to be smooth from 3.712 to 3.224 Å at the extremes (i.e. $x=0.1$ to $x=0.9$). This clearly indicates the formation of whole range of solid solution. The shift in peak position with the composition shows incorporation of Ni in CdSe up to $x \leq 0.5$ forms alloy in the form of solid solution. A small decrease in lattice parameters with gradual addition of Ni in CdSe is observed. The ionic radius of Ni$^{2+}$ ions is known to be less than the Cd$^{2+}$ ion; addition of Ni in CdSe gradually compresses the cell uniformly. The lattice parameter is observed to decrease gradually with the increase in composition parameters (i.e. Ni concentration).

The variation in lattice parameters has also been examined for all thin films. It is found that as composition parameter ($x$) increases, the lattice parameter changes smoothly from 5.3456 (for $x = 0.1$) to 5.2251 Å (for $x = 0.9$) and 3.5394 (for $x = 0.1$) to 3.3452 Å (for $x = 0.9$). The variation obeys Vegard’s law for solid solution. The average crystallite size was determined by using Scherrer’s formula (equation 5.2)

The average crystallite size was calculated by resolving the highest intensity peak. The average crystallite size for all the thin films falls in the range of 273-397 Å. The average crystallite size is listed in Table 5.1.
Fig. 5.1 XRD patterns of chemically deposited Cd$_{1-x}$Ni$_x$Se thin films for nickel content (a) $x = 0.1$ (b) $x = 0.3$ (c) $x = 0.5$ (d) $x = 0.7$ (e) $x = 0.8$ (f) $x = 1.0$
5.4.2 Scanning Electron Microscopy

Scanning electron microscopy is a convenient technique to study the microstructure of thin films. Samples with various nickel compositions in the host cadmium selenide were examined under scanning electron microscope. The polycrystalline nature of all the films was supported by SEM photographs. The SEM micrographs of annealed Cd\(_{1-x}\)Ni\(_x\)Se thin films are shown in Fig. 5.2 at 10,000X magnification.

In Cd\(_{1-x}\)Ni\(_x\)Se thin films, most of the grains are incorporated to each other and no pores are visible. The Cd\(_{1-x}\)Ni\(_x\)Se thin films are homogenous, without cracks or pinholes and well cover the glass substrate. From the figures of surface morphology we can clearly observe the well-defined, spherical and compact grains. Smooth background may correspond to some amorphous phase of NiSe as well as CdSe. The presence of fine background is an indication of one step growth by multiple nucleations. When the nickel is incorporated in CdSe lattice, the grain size increases and number of grains decreases. Micrographs show polycrystalline texture composed of small, single type of microcrystals.

A SEM micrograph of NiSe shows a globular structure of single type of densely closed small spherical microcrystals. The average grain size was obtained by using Contrell’s method.\(^{26}\) The method relates the number of intercepts of grain boundary per unit length ‘\(P_L\)’ and is given by

\[
P_L = \frac{n}{2\pi r} M
\]

Where, \(n\) is the total number of intercepts, \(r\) is the radius of curvature, \(M\) is the magnification used. Using PL the grain size ‘\(L\)’ was determined by using the following relation

\[
L = \sqrt{\frac{1}{P_L}}
\]

The grain size increases continuously from 286 Å to 400 Å as the composition parameter (x) increases. The observed grain size is listed in Table 5.1.
Fig. 5.2 SEM micrographs of chemically deposited Cd$_{1-x}$Ni$_x$Se thin films for nickel content (a) x = 0.1 (b) x = 0.3 (c) x = 0.5 (d) x = 0.7 (e) x = 0.9 (f) x = 1.0
5.4.3 Optical Studies

The optical absorption spectra for various Cd$_{1-x}$Ni$_x$Se thin films onto glass substrate were studied at room temperature in the wavelength range of 400-1200 nm without considering losses due to reflection and transmission. The optical absorption spectra of representative films are shown in Fig. 5.3. The analysis of spectrum was done by using the value of absorption at every step of 2 nm. The spectra were used to evaluate the absorption coefficient ($\alpha$), nature of transition involved and optical band gap ($E_g$). The study shows the presence of absorption edge of exponential shape, which is a characteristic of II-VI compound. It is due to homogeneity of the films and normal band structure. The spectra shows two regions, one for higher wavelength with practically lower absorption and other for lower wavelength in which absorption increases steeply. Due to incorporation of Ni in CdSe, the absorption decreases at higher wavelength. As the ‘x’ parameter increases, absorption shows a decreasing trend with the wavelength and the fundamental edge is shifted towards longer wavelengths. The values of absorption coefficient ‘$\alpha$’ at various wavelengths has been calculated and found to be dependent on both radiation energy ($h\nu$) and composition for all the samples. The data were systematically studied in the vicinity of the absorption edge on the basis of three-dimensional model. The interpretation of the results can be easily drawn with the help of formula derived for three-dimensional crystal. The simplest form of equations obeyed near and above absorption edge is:

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where, $\alpha$ is the absorption coefficient (cm$^{-1}$), $h\nu$ the photon energy (eV). A and n are constants. A is complex parameter, which depends on temperature, photon energy, phonon energies etc. The n values are 0.5, 1.5, 2 and 3 for allowed direct, forbidden direct, allowed indirect and forbidden indirect transition respectively. $E_g$ is the direct band gap energy. A plot of ($\alpha h\nu$)$^2$ vs. $h\nu$ should be a straight line whose intercept to the x-axis gives the optical band gap. The graphs of ($\alpha h\nu$)$^2$ vs. $h\nu$ for ‘as deposited’ samples are shown in Fig. 5.4.
The band gap of CdSe and NiSe were found to be 1.72 eV and 1.25 eV respectively. It is observed that the optical band gap decreases for ternary films as the composition parameter ‘x’ is increased. The variation of band gap with nickel content is found to be non-linear. The values of band gap of different compositions are listed in Table 5.2. The non-linear variation of band gap is found to be due to local non-stoichiometry, quantum size effect and large density of dislocations. The variation of band gap with composition parameter (x) is shown in Fig. 5.5. The plots of \((\alpha h\nu)^2\) vs. \(h\nu\) are linear in high energy region indicating direct band to band type transition. The mode of optical transitions in these materials has been determined. The equation can be represented as:

\[
\ln (\alpha h\nu) = \ln A + 0.5 \ln (h\nu - E_g) \quad \text{-------------------------5.11}
\]

For direct allowed type of transition the plot of \(\ln (\alpha h\nu)\) versus \(\ln (h\nu - E_g)\) should give a straight line with slope equal to 0.5 (power factor).

![Absorption spectra of chemically deposited Cd\(_{1-x}\)Ni\(_x\)Se thin films for nickel content; x = 0.0, 0.1, 0.3, 0.5, 0.7, 1.0](image_url)

**Fig. 5.3** Absorption spectra of chemically deposited Cd\(_{1-x}\)Ni\(_x\)Se thin films for nickel content; x = 0.0, 0.1, 0.3, 0.5, 0.7, 1.0
Fig. 5.4 Determination of band gap for chemically deposited Cd$_{1-x}$Ni$_x$Se thin films for nickel content (a) x = 0.0 (b) x = 0.1 (c) x = 0.3 (d) x = 0.5 (e) x = 0.7 (f) x = 1.0
5.4.4 Electrical Transport Properties

The electrical transport properties play important role in deciding the quality as well as applications of the semiconductor devices. These properties are strongly influenced by their structural characteristics, purity, nature and concentration of the impurities.\textsuperscript{30-32} At low temperatures, the thermal energy is just sufficient to allow migration of carriers into vacancies already present in the materials. At higher temperature the thermal energy is sufficient to create vacancies, which are responsible for movement of charge carriers.\textsuperscript{15}

a) Electrical Conductivity

The dark ‘dc’ electrical conductivity of all samples was measured by using two probe method in temperature range of 300-525K for heating and cooling cycles. The electrical conductivity variation with temperature during heating and cooling cycles was found to be different and this shows that the ‘as-deposited’ film undergoes irreversible changes due to annealing out of non-equilibrium defects during first heating. The specific conductance of CdSe and NiSe at room temperature were found to be of the order of $10^{-12}$-$10^{-14}(\Omega \text{ cm})^{-1}$ respectively. The specific conductance decreases for ternary films.

**Fig. 5.5** Variation of band gap with composition parameter (x) for Cd$_{1-x}$Ni$_x$Se thin films.
with composition parameter ‘x’. The values of specific conductance of different composition at 300K and 525K are listed in Table 5.3. The conductivity of the samples increases with increase in temperature, showing semiconducting behavior of the films.

The plots of log $\sigma$ vs.1000/T are shown in Fig.5.6 for the films. There are two distinct linear regions, indicating the presence of two-conduction mechanisms, the low temperature intrinsic and high temperature extrinsic. In the low temperature range (300-375 K) the curve is characterized by small slope. In the higher temperature range, the curve is characterized by large slope. A general increase in the electrical conductivity may be due to decrease in the band gap of the films and increase in grain size with increase in the composition parameter ‘x’. The grain size increases as internuclear space decreases and reduces the height of grain boundary potential resulting in increase in the carrier concentration as well as the mobility and hence electrical conductivity ($\sigma$). The activation energy is calculated using equation 5.6. The activation energies obtained from the slope of straight lines of log $\sigma$ vs.1000/T plots are included in Table 5.3. The values were found to be between .088 eV and 0.877 eV.

b) Thermoelectric Power

In order to have clear understanding of the mechanism, attempts were also made to measure the carrier mobility ($\mu$) and carrier concentration (n) as function of the working temperature and the composition.

Thermoelectric power measurement of all the films exhibits similar behavior of increasing thermoelectric power with increasing temperature. The increase in thermoelectric power with temperature suggests the degenerate nature of the films. In thermoelectric power measurements, the open circuits thermovoltage generated by samples, when a temperature gradient is applied across 2-cm length of samples was measured. From the sign of terminal connected to cold end of the sample, one can decide the sign of the predominant charge carrier.\textsuperscript{25} In our study, the positive terminal was connected to cold end therefore all the films show p- type conductivity.
Fig. 5.6 Plot of log $\sigma$ versus 1000/T for chemically deposited Cd$_{1-x}$Ni$_x$Se thin films for nickel content (a) $x = 0.1, 0.3, 0.5, 0.7$ (b) $x = 1.0$
Fig. 5.7 The temperature dependence of thermoelectric power for chemically deposited \( \text{Cd}_1-x\text{Ni}_x\text{Se} \) thin film for nickel content \( x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9 \) and 1.0

The temperature dependence of thermoelectric power \( (P) \) is shown in Fig. 5.7. It is seen that the thermoelectric power is increased as composition parameter \( (x) \) increased from 0 to 1. The TEP dependence is almost linear at low temperature region, where as it deviates at high temperature. The temperature dependence of thermoelectric power is given by:\textsuperscript{33}

\[
P = (-K/e) \left[ A + \ln \left\{ \frac{2 (2\pi m K T)^{3/2}}{\hbar^3} \right\} \right] \tag{5.12}
\]

where, \( A \) is a thermoelectric factor which depends on the various scattering mechanisms and other terms have their usual significance. Equation 5.12 can
be solved and rearranged for the value of \( n \) and the temperature dependence of
the carrier concentration becomes .

\[
\log n = \frac{3}{2} \log T - 0.005 P + 15.7198
\]

The carrier densities have been calculated at different temperature and the
relation;

\[
\mu = \sigma/\text{n}e
\]

was used to determine the carrier mobility. The plot of carrier density against
the temperature is shown in Fig.5.8 for representative samples. As the
compositional parameter (x) increases, the carrier concentration and mobility
increase. However, the carrier concentration as well as mobility increases as
the temperature increases. The dependence of carrier mobility on temperature
suggests the possibility of scattering mechanism associated with the intergrain
barrier potential as proposed by Petriz. According to Petriz, the temperature
dependent grain boundary mobility is related to grain boundary potential as;

\[
\mu = \mu_0 \exp (-\Phi_B/ KT)
\]

Where, \( \Phi_B \) is the height of the potential barrier of the grain boundary in eV, \( \mu_0 \)
is the pre-exponential factor, which on assumption that the current over the
barrier flows by thermionic emission, depends on the grain size D and
effective mass of electron as;

\[
\mu_0 = \frac{eD}{(2mKT)^{1/2}}
\]

The \( \Phi_B \) is determined by a plot of \( \log \mu T^{1/2} \) against 1000/T. The slope of this
variation is \( \Phi_B \). Fig. 5.9 shows such variations for few representative samples.
It is seen that, \( \Phi_B \) varied from 0.329 eV to 0.260 eV for the change of x= 0 to
1. The values of \( \Phi_B \) obtained are listed in Table 5.3.
Fig. 5.8 The temperature dependence of carrier density for chemically deposited $\text{Cd}_{1-x}\text{Ni}_x\text{Se}$ thin films for nickel content
(a) $x = 0.0, 0.1, 0.3$ (b) $x = 0.5, 0.7, 0.9, 1.0$
Fig. 5.9 Plot of log $\mu T^{1/2}$ versus 1000/T for chemically deposited Cd$_{1-x}$Ni$_x$Se thin films for nickel content; x = 0.1, 0.3, 0.5, 0.7, 1.0
Table 5.1 Crystallographic data of Cd\textsubscript{1-x}Ni\textsubscript{x} Se thin films

<table>
<thead>
<tr>
<th>Composition</th>
<th>Observed ‘d’ values (Å)</th>
<th>Std. ‘d’ values(Å)</th>
<th>Grain Size(Å)</th>
<th>Cell Parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>3.712 2.502 2.119 1.937 1.802 1.429</td>
<td>3.720 2.554 2.151 1.980 1.834 1.456</td>
<td>100 110 103 112 203</td>
<td>273 244</td>
</tr>
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<td>Cd\textsubscript{0.9}Ni\textsubscript{0.1}Se</td>
<td>3.664 2.502 2.119 1.937 1.802 1.429</td>
<td>3.169 2.039 1.830 1.549 1.509 1.183</td>
<td>289 286 a=3.5394 c=5.3456</td>
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</tr>
<tr>
<td>Cd\textsubscript{0.8}Ni\textsubscript{0.2}Se</td>
<td>3.610 2.450 2.087 1.894 1.769 1.401</td>
<td>3.169 2.039 1.830 1.549 1.509 1.183</td>
<td>306 309 a=3.5172 c=5.3284</td>
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</tr>
<tr>
<td>Cd\textsubscript{0.7}Ni\textsubscript{0.3}Se</td>
<td>3.555 2.398 2.055 1.851 1.737 1.374</td>
<td>3.169 2.039 1.830 1.549 1.509 1.183</td>
<td>318 322 a=3.4794 c=5.3063</td>
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</tr>
<tr>
<td>Cd\textsubscript{0.6}Ni\textsubscript{0.4}Se</td>
<td>3.499 2.346 2.023 1.808 1.705 1.346</td>
<td>3.169 2.039 1.830 1.549 1.509 1.183</td>
<td>328 334 a=3.4558 c=5.2858</td>
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<td>c</td>
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<td>Peak 2</td>
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<td>2.151</td>
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<td>1.549</td>
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Table 5.2 Optical parameters of Cd$_{1-x}$Ni$_x$Se thin film

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Composition</th>
<th>Band Gap(eV)</th>
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<tbody>
<tr>
<td>01</td>
<td>CdSe</td>
<td>1.72</td>
</tr>
<tr>
<td>02</td>
<td>Cd$<em>{0.9}$Ni$</em>{0.1}$Se</td>
<td>1.68</td>
</tr>
<tr>
<td>03</td>
<td>Cd$<em>{0.8}$Ni$</em>{0.2}$Se</td>
<td>1.65</td>
</tr>
<tr>
<td>04</td>
<td>Cd$<em>{0.7}$Ni$</em>{0.3}$Se</td>
<td>1.61</td>
</tr>
<tr>
<td>05</td>
<td>Cd$<em>{0.6}$Ni$</em>{0.4}$Se</td>
<td>1.54</td>
</tr>
<tr>
<td>06</td>
<td>Cd$<em>{0.5}$Ni$</em>{0.5}$Se</td>
<td>1.50</td>
</tr>
<tr>
<td>07</td>
<td>Cd$<em>{0.4}$Ni$</em>{0.6}$Se</td>
<td>1.45</td>
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<tr>
<td>08</td>
<td>Cd$<em>{0.3}$Ni$</em>{0.7}$Se</td>
<td>1.42</td>
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<tr>
<td>09</td>
<td>Cd$<em>{0.2}$Ni$</em>{0.8}$Se</td>
<td>1.36</td>
</tr>
<tr>
<td>10</td>
<td>Cd$<em>{0.1}$Ni$</em>{0.9}$Se</td>
<td>1.30</td>
</tr>
<tr>
<td>11</td>
<td>NiSe</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 5.3 Electrical parameters of Cd$_{1-x}$Ni$_x$Se thin film

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Composition</th>
<th>Specific Conductance (Ω cm)$^{-1}$</th>
<th>Activation energy (eV)</th>
<th>$\Phi_B$ (eV)</th>
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<tr>
<td></td>
<td></td>
<td>At 300 K</td>
<td>At 525 K</td>
<td>HT</td>
</tr>
<tr>
<td>01</td>
<td>CdSe</td>
<td>9.96 x 10$^{-12}$</td>
<td>6.89 x 10$^{-8}$</td>
<td>0.877</td>
</tr>
<tr>
<td>02</td>
<td>Cd$<em>{0.9}$Ni$</em>{0.1}$Se</td>
<td>9.62 x 10$^{-12}$</td>
<td>6.55 x 10$^{-8}$</td>
<td>0.845</td>
</tr>
<tr>
<td>03</td>
<td>Cd$<em>{0.8}$Ni$</em>{0.2}$Se</td>
<td>4.46 x 10$^{-12}$</td>
<td>5.02 x 10$^{-8}$</td>
<td>0.825</td>
</tr>
<tr>
<td>04</td>
<td>Cd$<em>{0.7}$Ni$</em>{0.3}$Se</td>
<td>1.03 x 10$^{-12}$</td>
<td>4.42 x 10$^{-8}$</td>
<td>0.812</td>
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<tr>
<td>05</td>
<td>Cd$<em>{0.6}$Ni$</em>{0.4}$Se</td>
<td>9.77 x 10$^{-11}$</td>
<td>3.07 x 10$^{-8}$</td>
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<td>06</td>
<td>Cd$<em>{0.5}$Ni$</em>{0.5}$Se</td>
<td>1.82 x 10$^{-11}$</td>
<td>2.95 x 10$^{-8}$</td>
<td>0.755</td>
</tr>
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<td>07</td>
<td>Cd$<em>{0.4}$Ni$</em>{0.6}$Se</td>
<td>1.36 x 10$^{-11}$</td>
<td>2.71 x 10$^{-8}$</td>
<td>0.720</td>
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<td>08</td>
<td>Cd$<em>{0.3}$Ni$</em>{0.7}$Se</td>
<td>1.11 x 10$^{-11}$</td>
<td>2.39 x 10$^{-8}$</td>
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<td>09</td>
<td>Cd$<em>{0.2}$Ni$</em>{0.8}$Se</td>
<td>1.01 x 10$^{-11}$</td>
<td>1.16 x 10$^{-8}$</td>
<td>0.642</td>
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<td>10</td>
<td>Cd$<em>{0.1}$Ni$</em>{0.9}$Se</td>
<td>1.82 x 10$^{-8}$</td>
<td>0.70 x 10$^{-5}$</td>
<td>0.593</td>
</tr>
<tr>
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<td>NiSe</td>
<td>2.72 x 10$^{-4}$</td>
<td>4.20 x 10$^{-3}$</td>
<td>0.088</td>
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5.5 Conclusions

A ternary Cd$_{1-x}$Ni$_x$Se thin films can be deposited easily by adopting chemical bath deposition method using tartarate bath containing Cd$^{2+}$, Ni$^{2+}$, Se$^{2-}$ ions, with an alkaline aqueous medium at 298 K. Factor involved in the formation of solid solution are pointed out.

Crystallographic studies revealed that the NiSe and Cd$_{1-x}$Ni$_x$Se exhibit hexagonal structure. As the composition parameter ($x$) increases, the ‘d’ value and lattice parameter decrease and particle size increases smoothly. The grain size calculated by using scanning electron micrograph agrees with the particle size determined by X-ray diffraction.

The films are highly absorptive and show direct type of transition. As the compositional parameter increases, the absorption edge shifts towards longer wavelength. The band gap decreases from 1.72 eV to 1.25 eV as the compositional parameter is increased.

The specific conductance of Cd$_{1-x}$Ni$_x$Se thin films at room temperature were found to be of the order of $10^{-12}$-$10^{-8}$ ($\Omega$ cm)$^{-1}$. There are two distinct linear regions, indicating the presence of two-conduction mechanism, the low temperature intrinsic and high temperature extrinsic. Electrical conductivity increases while activation energy decreases as x parameter is increased. The activation energy of electrical conductivity was found to be in between 0.088 to 0.877 eV. All the samples were found to be p-type in nature. The carrier density, carrier mobility increases with compositional parameter, but grain barrier height decreases.
References


