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Design and Development of Automated Liquid Flow Deposition method for thin film formation

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ABSTRACT

An automated thin film formation technique is developed using the microcontroller PIC16F877 for NiO film formation at low temperatures for different molarities. Then the formed films were annealed at 310^{o}C to get better crystalline structure. The Structural and optical properties were studied for the grown thin films with the developed instrument. The band gap of the formed thin films is in the range of 3.73 eV to 3.35 eV. The optical studies revealed that the transmittance of the grown film is upto 80 % and decreases with increase of molarity of the solution. The design scheme of the developed instrument is also discussed.

Keywords: Liquid Flow Deposition, PIC16F877, Thin films, NiO, Structural properties, optical properties.

INTRODUCTION

Transparent conduction oxide (TCO) thin films have excellent range of applications and getting more attention now a days. NiO is a p-type TCO material[1] having several potential applications such as electrodes for battery, solar thermal absorbers, photoelectron catalysts[2], gas sensors [3] etc. Due to its high electro chromic efficiency, large dynamic range, good cyclic reversibility, and low material cost, it has greater importance in the filed of material research. Thin films of NiO can be prepared by various methods such as sputtering[4], electron beam evaporation [5] and by some chemical methods such as solgel [6], spray pyrolysis [7], chemical bath deposition[8]. In recent years thin film deposition using chemical methods are widely used due to their simplicity. Further, films can be formed even in room temperature also. In this work we automate one of the chemical method named liquid flow deposition[9] to form NiO thin films using the microcontroller PIC16F877. The description of the designed instrument is discussed. Structural, surface morphlogical and optical studies of the grown film with this instrument is discussed.

MATERIALS AND METHODS

2.1 Instrument Design

An automated PIC16F877 microcontroller based liquid flow deposition system is developed to form NiO thin films. The block diagram of the developed instrument is shown in the Figure(1).

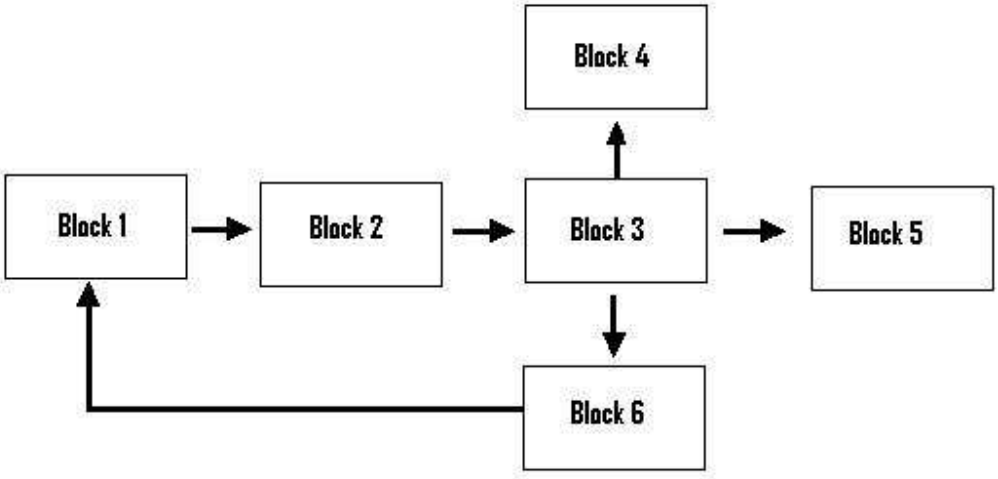

Figure 1 Block Diagram of Automated Liquid Flow Depostion Technique

In Block 1 the precursor buffer is placed. The precursor buffer contains the medium that is going to flow on the substrate which is kept at the substrate compartment in block 3 by means of a peristaltic pump in block 2. The peristaltic pump uses a silicon/PTFE tubing as the pressure chamber[10] which avoids the contamination of the precursor with the pump. Usually peristaltic pump offers a constant flow rate of the precursor solution over the substrate [11]. The substrate compartment in block 3 is designed with the dimensions of 6 cm x 9 cm in area and the height is about 1 cm . The compartment is heated to desired temperature by means of a heater coil and the temperature is monitored by a temperature sensor. The temperature sensor LM35DT(in block 4) is interfaced with microcontroller to monitor and maintain the substrate compartment at a desired temperature by entering the temperature input through keypad. An LCD is placed in block 5 to display the temperature of the substrate compartment. In block 6, a reverse pump is placed to feedback the precursor solution from the substrate compartment outlet to the precursor buffer in block1

2.2 Hardware design

2.2.1 Microcontroller:

A 40 pin Microchip's PIC16F877 microcontroller is selected to automate the instrument because of its salient features and simplicity in programming. It is an Accumulator based Machine which has 8k x 14 Flash Based Instruction Memory,368 x 8 Static based data memory,35 Instructions, 3 addressing modes (direct, indirect and relative),10 bit analog to digital converters and 33 I/O ports.

2.2.2 Temperature Sensor:

Low cost LM35DT (From National Semiconductors) is used as a temperature sensor to monitor the temperature of the substrate compartment. It has a sensing range of -55^{o} C to $+150^{o}$ C and it

is calibrated directly to Celsius (Centigrade) measurement. The LM35DT's low output impedance, linear output and precise inherent calibration make interfacing to read out or control the circuitry very easily[13].

2.2.3 Display and Input Unit:

A 2 x 16 alphanumeric Liquid Crystal Display(LCD) is interfaced with the microcontroller to display the temperature of the substrate compartment as well as to show the input temperature by the keyboard. The advantage of LCD is, it consumes less power and are compatible with low power electronic circuits and can be powered for long duration[10].

A 4 x 4 keypad is interfaced with the microcontroller to give temperature input for the substrate compartment.

2.3 Hardware Interfacing:

The interfacing circuit of the temperature sensor, display unit and keypad with the microcontroller is shown in the Figure 2.

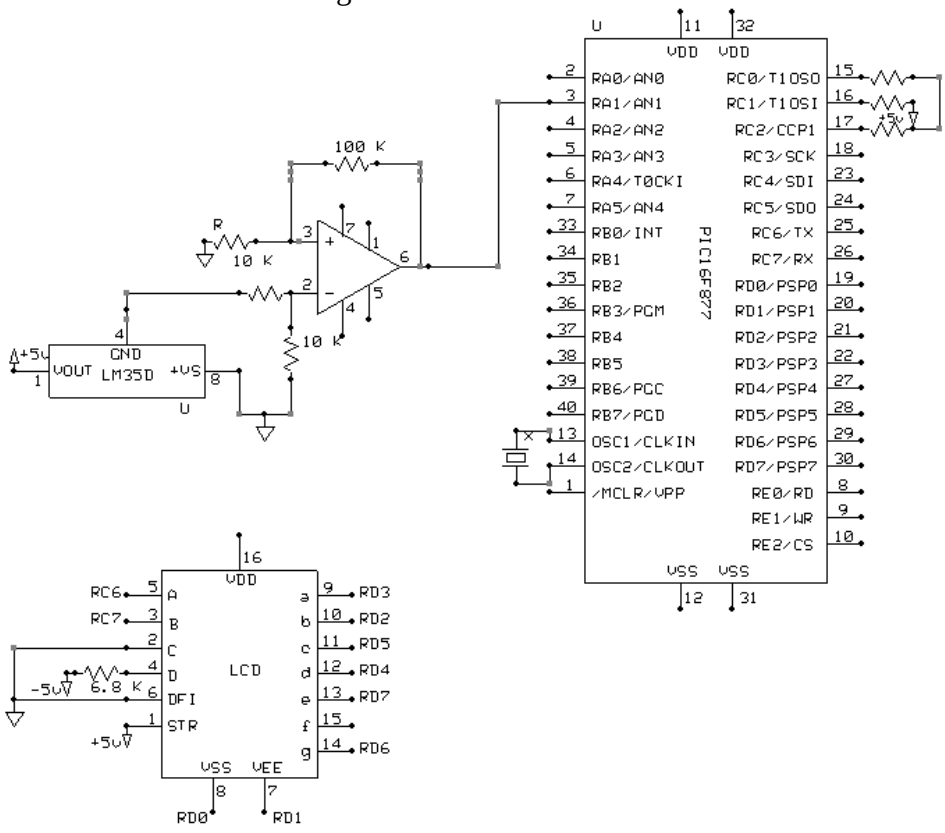

Figure 2 Hardware interfacing Circuit

The PIC16F877 microcontroller uses separate memory for program and data. A reset switch is provided so that the program can be executed from 0000 after the power is switched on. A two row alphanumeric LCD is interfaced to port D as shown in the figure to display the temperature of the substrate compartment. The output of the temperature sensor is connected to the inverting input of the operational amplifier (signal conditioning) which amplifies the weak signal. The

714 part is a monolithic instrumentation operational amplifier which has low noise, low drift and high gain properties. The output of the instrumentation amplifier is given to one of the pin of the PORT A. The PIC16F877 microcontroller reads data from ADC for processing.

3. Experimental Detail for NiO film preparation

To form NiO thin films under liquid flow deposition, the precursor solutions were prepared for different molarities 0.1, 0.2 and 0.3 with the chemicals $Ni(NO_3)_2$ $.6H_2O$ as a source of Nickel and aqueous ammonia. The preparation and formation mechanism of NiO is described elsewhere [13]. The precipitation of $Ni(OH_2)$ is removed by adding additional aqueous ammonia. The pH of the solution is maintained between 11 to 12. The flow rate of the precursor is maintained at 1.5 ml/min and the resident time [11] of the precursor solution on the substrate is also maintained.

The temperature of the substrate compartment was maintained at 80^o C. The deposited films then annealed in air about 1 hour at a temperature of 310^o C in order to get pure NiO thin films.

The structural and optical properties of the deposited films were studied.

RESULTS AND DISCUSSION

4.1 Structural properties

X-ray diffraction patterns of the annealed NiO films at 310^oC were recorded by varying diffraction angle (2θ) from 20^o to 80^o, with the step width of 0.02^o. **Figure 3** shows the XRD patterns of the samples.

The film with 0.1M concentration was found to be amorphous. However the films with 0.2 and 0.3M concentrations show well defined peaks having orientations in the (1 1 1), (2 0 0) and (2 2 0) planes. This reveals that the films are polycrystalline in nature with a cubic structure. There was preferential growth along (1 1 1) and (2 0 0) planes as the solution molarity increases. This may be due to increase in the grain growth associated with largest thickness or increase in the degree of crystallinity as the molarity increases.

The crystallite size D and strain in the samples have been calculated by the relation:

$$\beta = \frac{k\lambda}{D\ Cos\theta} - \varepsilon_s \tan\theta \qquad (1)$$

where constant k is equal to unity, β is FWHM in radians,

D is the crystallite size and ε_s is the strain present in the sample.

The dislocation density (δ) of the film was calculated by the relation [13]:

$$\delta = \frac{n}{D^2} \qquad (2)$$

where n is a factor equal to unity.

The number of crystallites 'N' has been estimated using the relation:

$$N = \frac{t}{D^3} \text{ / unit area} \qquad (3)$$

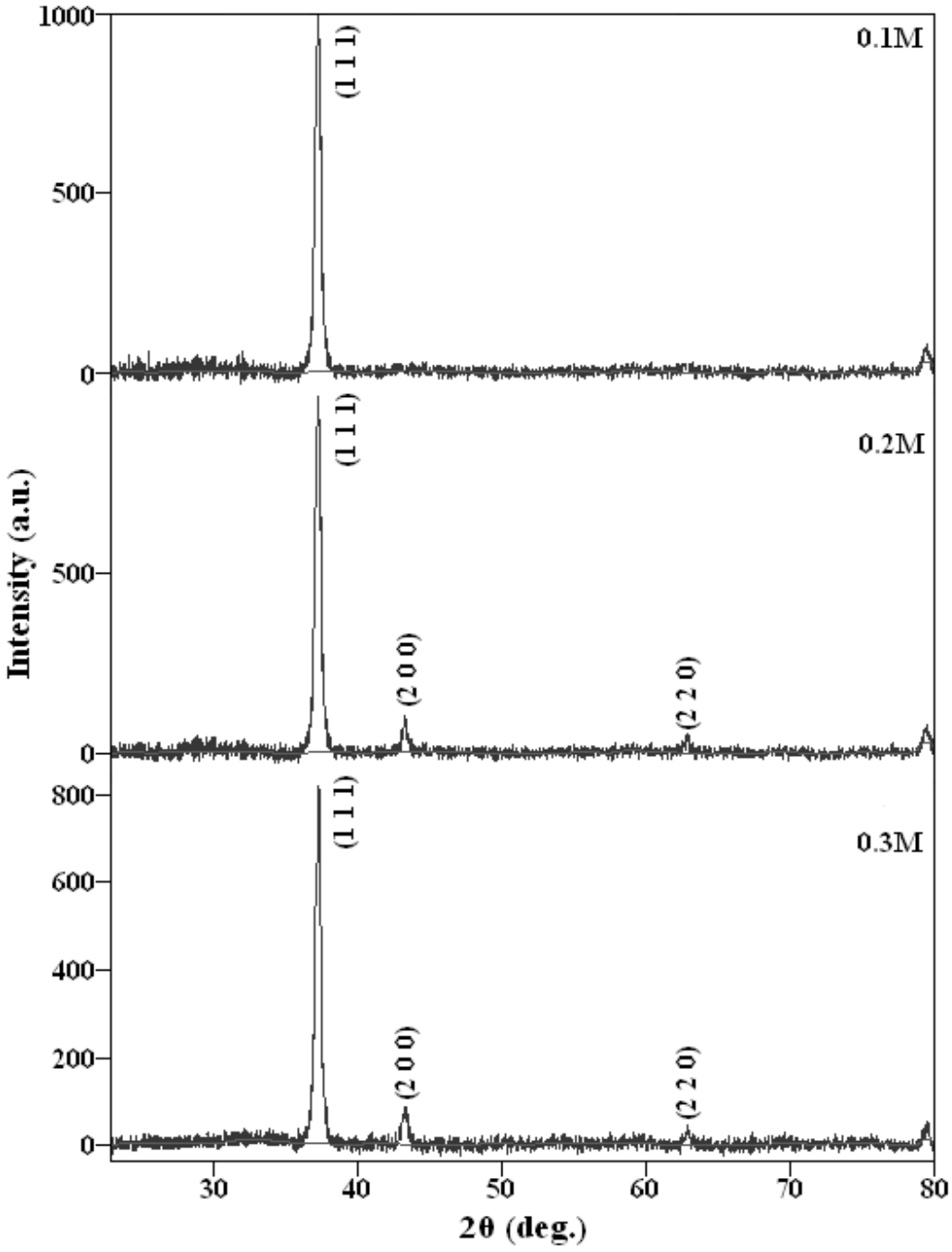

Figure 3 XRD patterns for the as-deposited samples

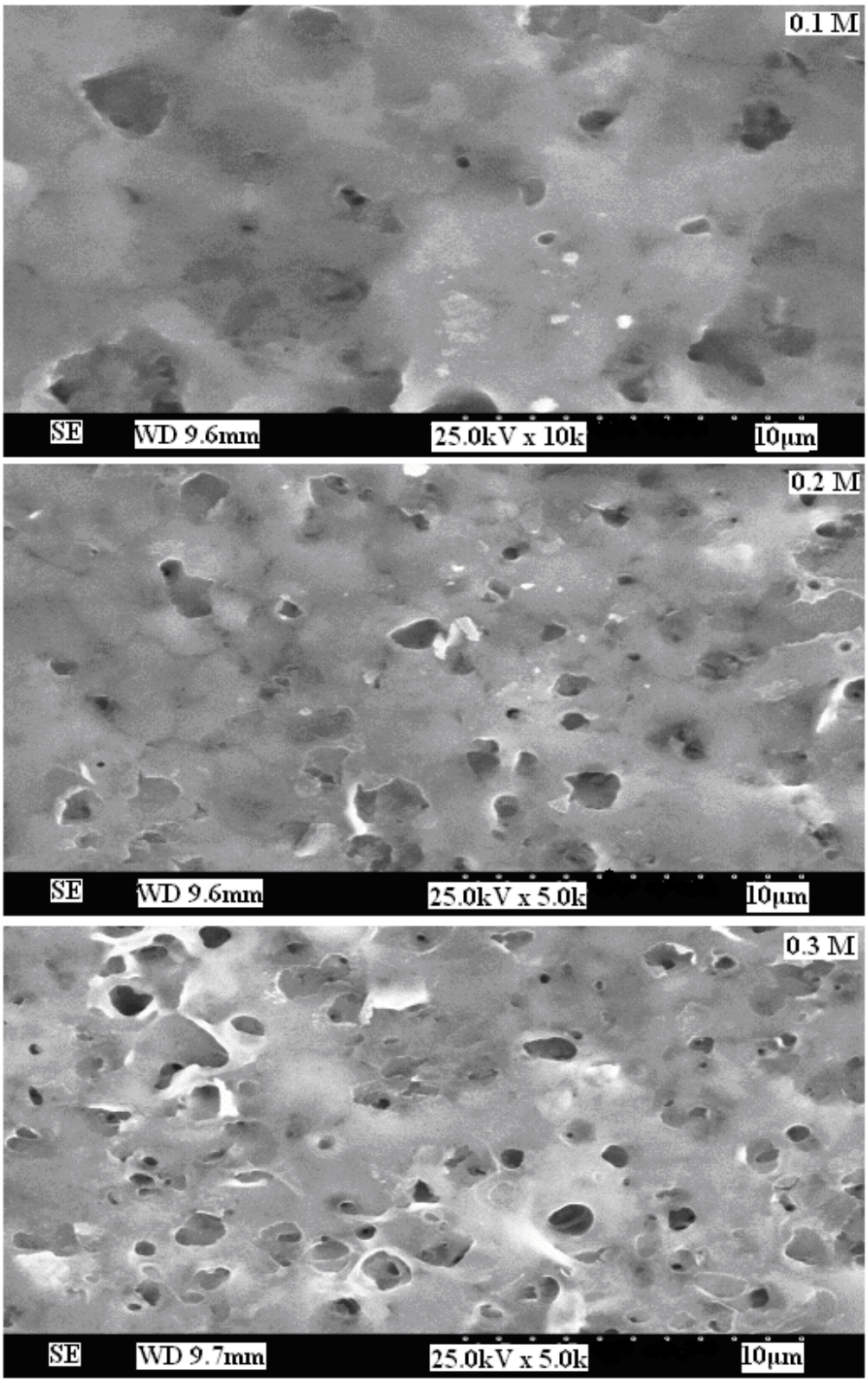

Figure 4 SEM micrographs of the NiO films

4.2 Surface morphological studies

Figure 4 shows the SEM micrographs of the NiO films with different molarities at 310^{o}C.

The SEM pictures show that the films are uniform, well adherent and completely devoid of pinholes and cracks. Film with 0.1M of solution concentration has smooth surface and no grains were perceptible. With 0.2M of solution, the surface starts to modify and smaller granular particles found uniformly distributed randomly over the surface. When the solution concentration is increased to 0.3 M, the surface becomes probably filled with the clusters of the larger grains.

4.3 Optical absorption

Measurements of spectral transmittance and reflectance of the samples showed that the films are transparent with transmittance upto 80 % as shown in **Figure 5**.

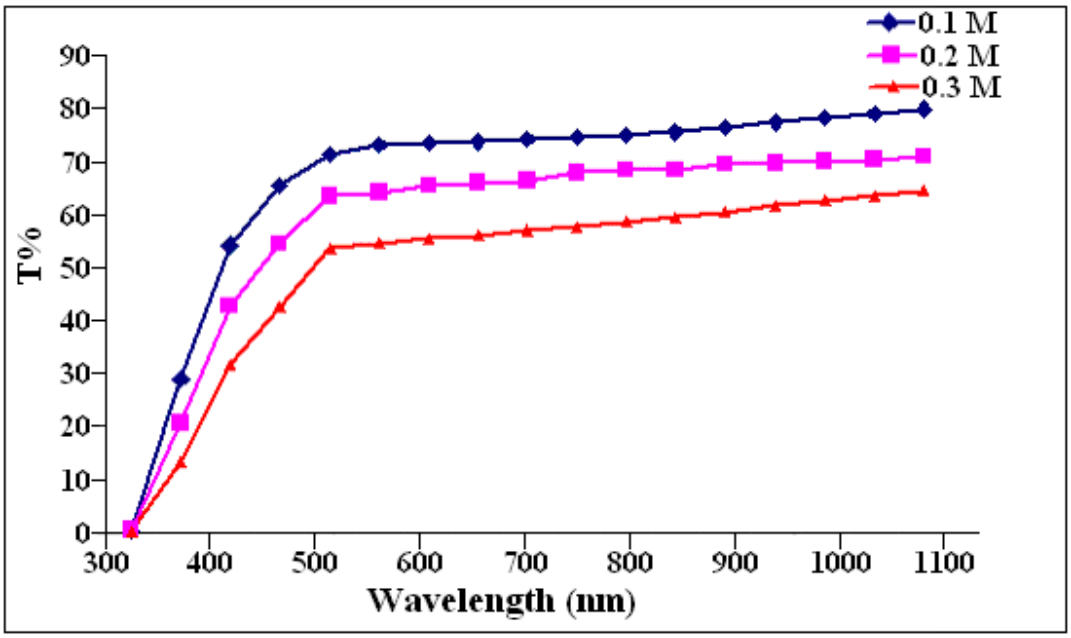

Figure 5 Transmittance and Reflectance of NiO films

The transmittance decreases with increase in the molarity of the solution. The absorption coefficient α was obtained using the relation:

$$\alpha(\lambda) = \frac{10^4}{t} \log_{10} \left[\frac{(1 - R(\lambda))^2}{T(\lambda)} \right] \qquad (4)$$

where R(λ) and T(λ) are the reflectance and transmittance at the specified

wavelength λ. It is observed from the optical absorbance versus wavelength graph shown in **Figure 6**, that absorbance decreases with increase in wavelength.

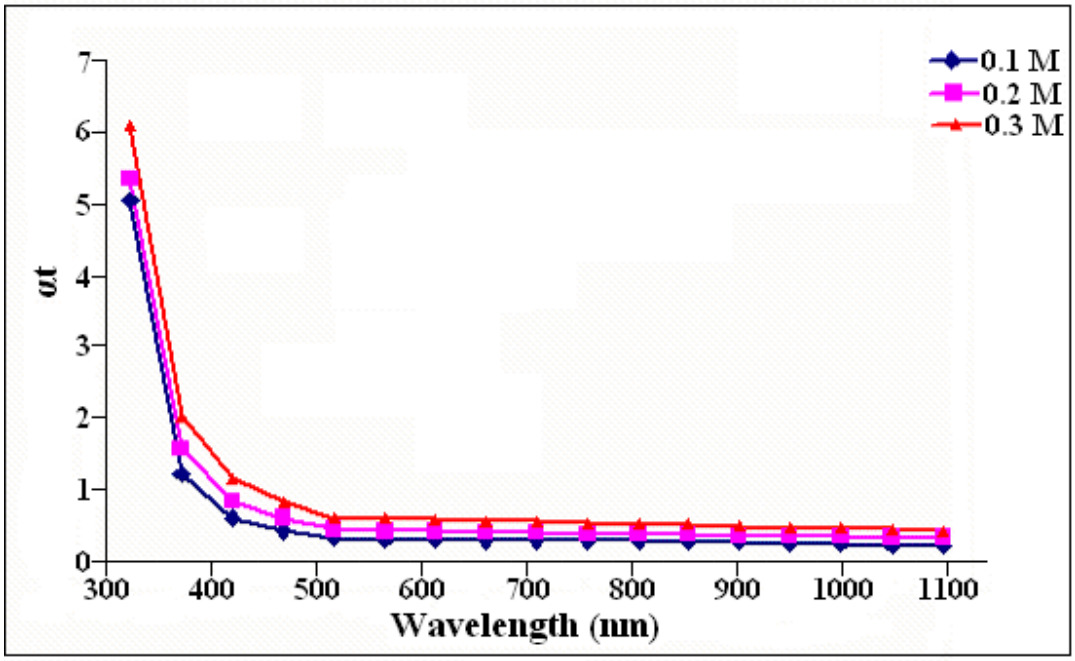

Figure 6 Absorbance versus Wavelength of NiO films

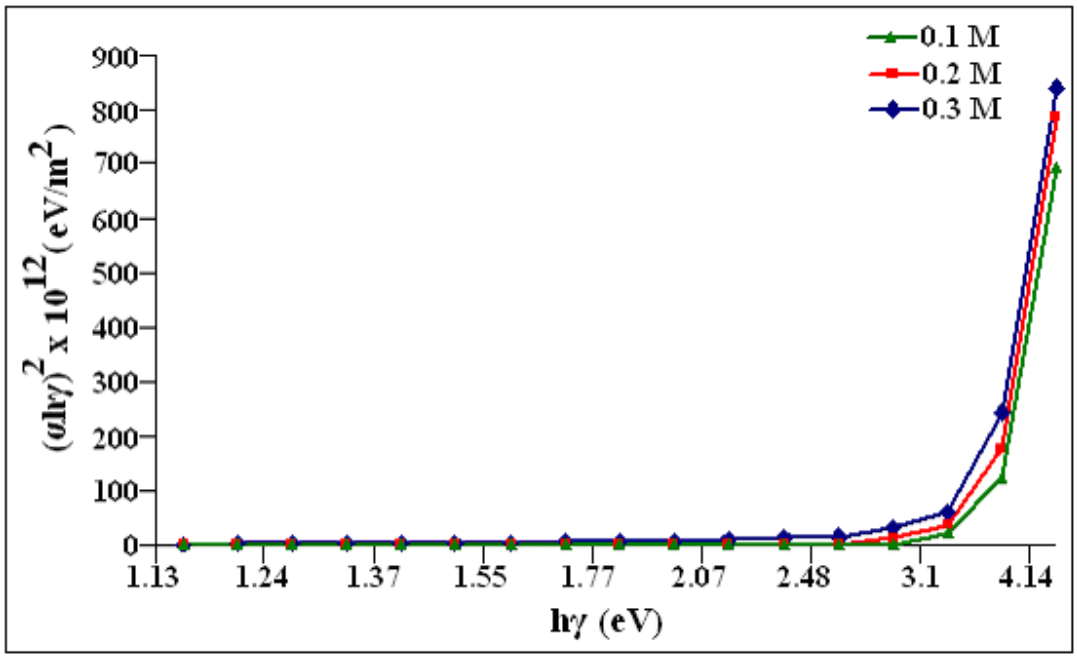

Figure 7 variation of $(\alpha h\gamma)^2$ versus $h\gamma$

The absorption coefficient is found to be in the order of 10^4 cm^{-1}. The optical absorption coefficient is related with the energy band gap by the equation (5):

$$\alpha = A\,(h\gamma - E_g)^n \qquad (5)$$

where A is a constant, hγ is the incident photon energy, and
n = 1/2 or 3/2 for direct allowed and direct forbidden transitions, and n = 2 or 3 for indirect allowed and indirect forbidden transitions.

The plot of variation of $(\alpha h\gamma)^2$ versus hγ shown in **Figure 7**, is a straight line indicating the presence of direct transition.

The indirect band gap energy is obtained by extrapolating the linear portion of $(\alpha h\gamma)^2$ versus hγ to energy axis at α = 0. The indirect band gap energy for the NiO film varies from 3.73 eV to 3.35 eV as the solution concentration varies from 0.1M to 0.3M. The extrapolation of the linear part of $(\alpha h\gamma)^{1/2}$ versus hγ gives the value of direct energy gap which is equal to 3.69 eV. The values of direct and indirect transition agree with the reported values of band gap [14, 15, 16].

CONCLUSION

One of the simple methods for thin film formation at low temperatures, the liquid flow deposition technique is automated using the microcontroller PIC16F877. A temperature sensor unit using LM35DT is interfaced with the microcontroller to monitor the temperature. NiO thin films were deposited for 0.1M, 0.2M and 0.3 M using the developed instrument at 80^{o}C and structural, optical studies were studied. The band gap of the films varies from 3.73 eV to 3.35 eV as the solution concentration varies from 0.1M to 0.3M. Optical studies shows that the transmittance of the grown films is upto 80% and it decreases with increase in the molarity of the solution.

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