

Article type: A-Regular research paper

# Effect of Annealing on Physicochemical, Optoelectronic and Gas Sensing Properties of Polyaniline Thin Films

Jayesh R. Pawar, Munjaji E. Dudhmal, Rajesh A. Joshi

Thin films and Nanotechnology Laboratory,

Department of Physics,

Toshniwal Arts, Commerce and Science College, Sengaon Dist. Hingoli 431542 MS

\*Corresponding Author: [urajoshi@gmail.com](mailto:urajoshi@gmail.com)

RECEIVED: 17 february 2025 / RECEIVED IN FINAL FORM: 30 may 2025 / ACCEPTED: 03 june 2025

**Abstract** : The present article describes about synthesis of polyaniline thin films by soft chemical solution polymerization method at room temperature over glass substrate and effect of air annealing at 100, 200 and 300°C on the physicochemical and optoelectronic properties intending to characterize as gas sensing materials. The as deposited and annealed thin films characterized for compositional, elemental, surface morphology, optical properties and electrical properties along with ammonia gas sensing applications. Slight shift in peaks positions from 1167, 1372, 1506 and 1593 cm<sup>-1</sup> and broadening of peak with increase in intensity recorded on Fourier transform infra-red spectra confirm annealing induced elemental variations, while Raman spectrum represents chemical bond shifting upon annealing polyaniline thin films which can be inferred as compositional modifications upon annealing. Fatty granular appearing surface morphology obtained in atomic force microscopy found to be coalesces into smaller granular shapes on post deposition treatments which can also be confirmed from the scanning electron microscopy images. Optical absorbance shows shift in absorbance peaks corresponding for excitation of polaron band which observed to be red shifted may be correlated to polygonization process i.e. absorbance of energy at the surface and utilizing in materials modifications. The ammonia gas sensing characteristics have represented the increase in gas response upto 85% for the sample annealed at 200°C The response and recovery time is observed to be lower than the as deposited and 300°C annealed samples, this can be correlated to the fact of structural saturations at moderate annealing.

**Keywords** : SEMICONDUCTORS, NANOMATERIALS, THIN FILMS, POLYMER, POLARON, COMPOSITIONAL MODIFICATIONS, SENSOR etc

Cite this article: Joshi et al OAJ Materials and Devices, vol.9, 0305 (2025) - DOI: 10.23647/ca.md20250305

## Introduction

Conducting polymers are a new class of sensing materials, which can be prepared by simple oxidative polymerization method over extended surface of the substrate. These polymeric materials also provide suitable structure for immobilization of ligands, enzymes and antibodies. Therefore, their use in the development of novel chemical

and biological sensors has received considerable attention [1-3]. Conducting polymer such as polyaniline commonly rely on charge conduction through network of hydrocarbon and nitrogen chain, this conductivity can be modified by two ways either by doping with suitable elements or by providing the post deposition treatment like annealing [4-6]. Although doping plays very vital role in material development with varying conductivity but if the annealing treatment is provided it could result in achieving the good stiochiometry along with

surface up-gradation. Since the present article deals with study of gas sensing applications, it majorly deals with surface and composition of materials hence considering these facts we have tried to achieve good stoichiometry thin films along with modifications of surface by providing the post deposition annealing treatment to solution polymerization synthesized thin films [5-6]. Now days, the pollution level have been regularly checked by different techniques however restricting and monitoring of gases like ammonia still need to pay more attentions. Most of ammonia in our atmosphere is emitted direct or indirect by human activity, like combustion from motor vehicles and chemical industries etc along with other natural sources [7-9]. These high concentrations of ammonia in the surrounding form threat to human health. The lower limit of human ammonia perception by smell is tabulated to be around 50 ppm [10]. However; even below this limit ammonia is irritating to the respiratory system, skin and eyes [11, 12]. The long term allowed concentration that people may work in is therefore set to be 20 ppm. Immediate and severe irritation of the nose and throat occurs at 500 ppm. Exposure to high ammonia concentrations, 1000 ppm or more, can cause pulmonary edema; accumulation of fluid in the lungs. It can take up to 24 h before the symptoms develop: difficulty with breathing and tightness in the chest. Short term exposure to such high ammonia concentrations can lead to fatal or severe long term respiratory system and lung disorders [13].

Henceforth, there is urgent need of ammonia gas sensor working at ambient temperature. There-fore the present article deals with synthesis of polyaniline thin films by solution polymerization method at room temperature on glass substrate at optimized preparative parameters and study of post deposition annealing treatment at 100, 200 and 300oC respectively over the physicochemical and optoelectronic properties [14]. These as deposited and annealed thin films have been studied for structural, compositional, surface and optical properties.

## Experimental Details

### Solution Polymerizations

Polymerization of aniline with ammonium peroxodisulphate as an oxidant agent has been reported. The both components are dissolved into 1 M hydrochloric acid and added dropwise to each other as the polymerization process is exothermic in nature. The polymer precipitate as small particles and the reaction product is dispersed in bath. The polymerization process occurs in few steps. In first stage the reaction of permigraniline salt oxidation state is formed. In the second stage the permigraniline is reduced to the emeraldine salt as aniline get oxidized to the radical cation. In the third stage the radical cation couple with emeraldine salt. The degree of polymerization (DP) is the aspect which determines the form of polyaniline. The DP is the number of repeat unit in an average polymer chain at time t in polymerization reaction [15].

$$DP = \frac{\text{Total molecular weight of polymer}}{\text{molecular weight of repeating unit}}$$

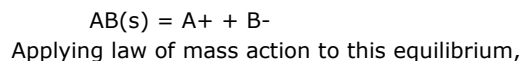
In polymerization to achieve high degree of polymerization (Xn) a high fractional monomer conversion is required.

$$X_n = M_n / M_0 \quad X_n = 1/(1 - \rho)$$

High monomer conversion would leads to forming expected polymer formation when the monomer conversion = 99 % then the DP becomes Xn = 100 %.

### Solubility product

When a sparingly soluble salt AB is placed in water, a saturated solution containing A+ and B- ions in contact with the undissolved solid AB is obtained and equilibrium is established between the solid phase and the ions in the solutions as.



$$K = \frac{C_{A^+} C_{B^-}}{C_{AB(s)}}$$

Where, CA+, CB- and CAB are the concentrations of A+, B- , and AB in the solution, respectively.

The concentration of a pure solid phase is a constant number,

$$\text{i.e. } CAB(s) = \text{a constant} = K'$$

$$K = \frac{C_{A^+} C_{B^-}}{K'}$$

or  $KK' = CA+CB-$  As K and K' are constants, the product KK' is also constant, say Ks, therefore equation (6) becomes,

$$Ks = CA+CB-$$

The constant Ks is called the solubility product (SP) and the expression (CA+CB-) is called as the ionic product (IP). When the solution is saturated, the ionic product (IP) is equal to the solubility product (SP). It follows that when the IP exceeds the SP i.e. IP/SP>1, the solution is supersaturated and precipitation occurs and ions combine on the substrate and in the solution to form nuclei. When the IP is less than SP, the solution will be unsaturated. The temperature, solvent and particle size are three main factors, which affect the SP [16-18].

### Precipitate formation in the solution

The formation of a solid phase from a solution involves two steps one is the nucleation growth and other is particle growth. The size of the particles of a solid phase is dependent upon the relative rates at which these two competing processes take place. It also depends on deposition temperature, rate of mixing reagents, concentration of reagents and the solubility of the precipitate during precipitation. All of these can be related to the relative supersaturation of the system. A state of supersaturation may be achieved by lowering the temperature of an unsaturated solution and formation of the solute in the solutions at a fixed temperature.

For any precipitate, there is some minimum number of ions or

molecules required to produce a stable second phase in contact with a solution called a nucleus. The rate at which nuclei formed in a solution is dependent on the degree of supersaturation. In highly supersaturated solution, the rate of nucleation increases exponentially.

$$\text{Rate of nucleation} = K_0(Q-S)^X$$

Where,  $K_0$  and  $X$  are constants and  $X > 1$ ,  $Q$  is the excess concentration above saturation and  $S$  is the concentration at saturation.

The second step is the growth of particles already present in the solution. This begins when nuclei or other seed particles are present. In case of ionic solid, the process involves deposition of cations and anions on appropriate sites. The rate of growth is directly proportional to the supersaturation.

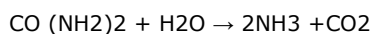
$$\text{Rate of growth} = K_0' A(Q-S)$$

Where ' $A$ ' is the surface area of exposed solid and  $K_0'$  is a constant that is characteristic of the particular precipitate. If the super saturation is maintained at a low level throughout the precipitation, the relatively few nuclei formed will grow to give a small number of large particles. With high super saturation, many more nuclei are formed initially and nucleation may occur throughout the entire precipitation process. As a result, there are many more centers upon which the growth process can take place, none of the particles can become very large and colloidal suspension is formed.

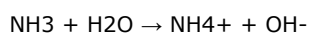
The colloidal suspension consists of finely divided solid particles in a liquid phase with diameters of 0.01 to 0.1  $\mu\text{m}$ . Under some circumstances, colloidal particles can come together and adhere to one another and the resulting solid is called a colloidal precipitate and the process by which it is formed is termed as coagulation or agglomeration. Colloidal particles when agglomerated have quite different properties from a crystalline solid since the particles are arranged irregularly.

*Controlled precipitation in the solution*

The degree of super saturation can be reduced by the slow, drop wise addition of the reagent and by the use of dilute solutions of both the ions to be precipitated and the reagent. In precipitation, from homogeneous solution, the precipitating agent is chemically generated in the solution. Local reagent excess does not occur because the precipitating agent appears slowly and homogeneously throughout the entire solution; the relative super saturation is thus kept low. The necessity for careful control of the pH has long been recognized. This is accomplished by making use of the hydrolysis of urea, which decomposes into ammonia and carbon dioxide as follows:



Ammonia hydrolysis in water provides  $\text{OH}^-$  ions according to the following equation.



Thus urea is often used for the homogeneous generation of hydroxide ion. Urea possesses negligible basic properties soluble in water and its hydrolysis rate can be easily

controlled. It hydrolyses rapidly at 363-373K and hydrolysis can be quickly terminated at a desired pH by cooling the reaction mixture to room temperature. The use of a hydrolytic reagent alone does not result in the formation of a compact precipitate. The physical character of the precipitate will be very much affected by the presence of certain anions. The main function of 'suitable anion' is the formation of a basic salt, which seems responsible for the production of a compact precipitate. The pH of the initial solution must be appropriately adjusted.

Moreover, by varying the rate of the chemical reaction producing the precipitant in homogenous solution, it is possible to alter further the physical appearance of the precipitate, the slower the reaction, the larger are the crystals formed. Homogeneous precipitation of crystalline precipitates also results in marked increase in crystal size as well as improvement in the purity. Thin film of polyaniline prepared by solution polymerization method using HCl as dopant, ammonium per-oxi-disulphate (APS) as an oxidant and aniline as monomer. Commercial glass slides supplied by Bluestar Company, Mumbai (India) were used as substrates for the deposition. Aniline was distilled under high pressure prior to use, the other chemicals were used as they received. Solution polymerization process proceeded as follow, 0.2 ml aniline was added in 1 ml concentrated HCl solution with constant stirring at room temperature then 0.25 ml APS was prepared in an aqueous media, before mixing, these reactants were pre cooled in an ice bath container. Thereafter 20 ml APS was added slowly to the aniline solution with constant stirring at room temperature. Cleaned glass substrates were immersed in the reaction bath using substrate holder after 40 minutes substrates removed from the reaction bath which then washed with distilled water to remove the granules attached with the surface of the substrate, dried and preserved in dark desiccators [15-16]. Solution polymerization technique is one among thin film deposition techniques which gives large area deposition with homogeneous morphology. These characteristic of thin film are especially useful in case of gas sensing applications because the exposure of large area to the gas leads to provide high sensitivity. These as deposited polyaniline thin films have been provided with the post deposition annealing treatment at 100, 200 and 300°C at ambient temperature. Image of Polyaniline thin films formations i.e. induction to obtaining of thin films can be seen in Fig. 1.



**Figure 1. Changes in color observed while induction and deposition of Polyaniline thin films.**

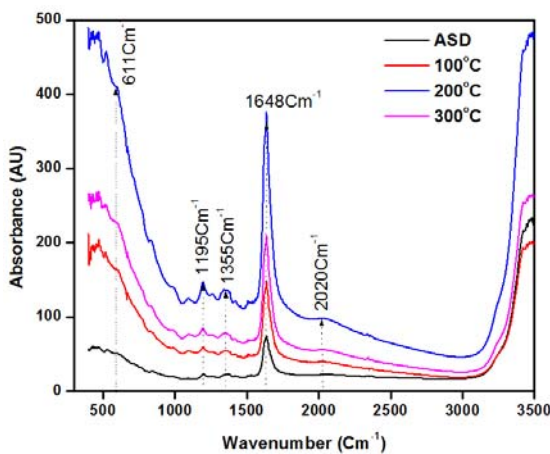
These as deposited and annealed thin films have been characterized for physicochemical and optoelectronic properties using Fourier transform infrared (FTIR) spectroscopy, Raman spectrum analysis along with scanning electron microscopy (SEM) imaging. The surface topography observed from the atomic force microscopy (AFM) shows surface up-gradations,

while UV-Vis absorbance spectroscopy used for gas sensing measurements.

## Results and Discussions

### Fourier transform infrared spectroscopy (FTIR)

Fig. 2 represents the FTIR spectrum of as deposited and annealed polyaniline thin films which shows asymmetric and symmetric stretching modes of hydro carbon and nitrogen based aniline bands which generally observed at 1648 and 1355 $\text{cm}^{-1}$  respectively [17-18]. This spectrum represents the bands at 611, 1195 $\text{cm}^{-1}$  corresponding for vibrations due to circular ring roll and stretching of quinoid and benzenoid rings of aniline monomers. Quinoid being backbone of the structure so, band at 1648 $\text{cm}^{-1}$  generated by quinoid bond stretching observed. Peak at 1195 $\text{cm}^{-1}$  corresponding to C-N bond stretching along with peak at 1355 $\text{cm}^{-1}$  is associated with C-N stretching vibration in quinoid-benzenoid-quinoid structured ring. The bands around 1195 $\text{cm}^{-1}$  attributed to B-(NH<sup>+</sup>)-Q structure which is formed during the protonation process. The significant lowering of the frequencies can be related to the hydrogen bonds formed between the oxygen of the nitro group and the hydrogen of the amine group [19-21]. The band at 611 $\text{cm}^{-1}$  can be attributed to in plane and out-of-plane C-H bending modes, respectively [22]. In addition to the above peaks, the spectrum of the polyaniline exhibits peaks at 3563 $\text{cm}^{-1}$  that could be attributed to NH<sub>2</sub> stretching mode and band located at 1648 $\text{cm}^{-1}$  related to NH<sub>2</sub> bending vibration. While on annealing these thin films at 100, 200 and 300 $^{\circ}\text{C}$ , the spectrum corresponding to C-H stretching, benzenoid and quinoid ring stretching out of planes observed to be increased, which it can be inferred as structural, compositional updations and dangling of charges across the elemental bonding.

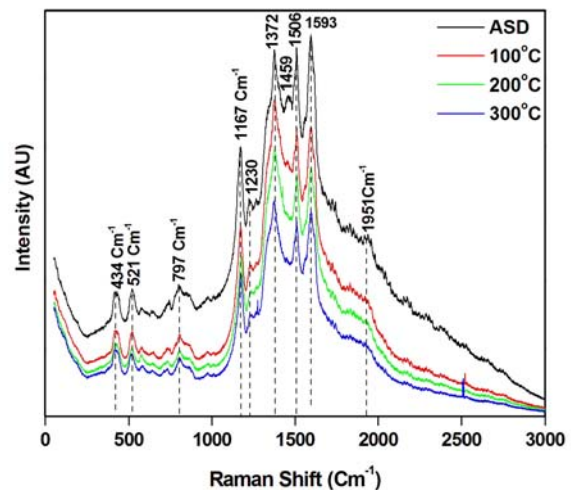


**Figure 2: FTIR spectrum of as deposited and annealed Polyaniline thin films.**

### Raman spectroscopy

Fig. 3 shows Raman spectroscopy analysis of as deposited and annealed polyaniline thin films. The band at 1372 and 1506 $\text{cm}^{-1}$  can be attributed to in-plane deformation of C-C bond in quinoid ring, [23-24]. This spectrum represents bands at 1506 and 1593 $\text{cm}^{-1}$  due to C,N- and C- N- stretching in quinoid and benzenoid rings, respectively. Band

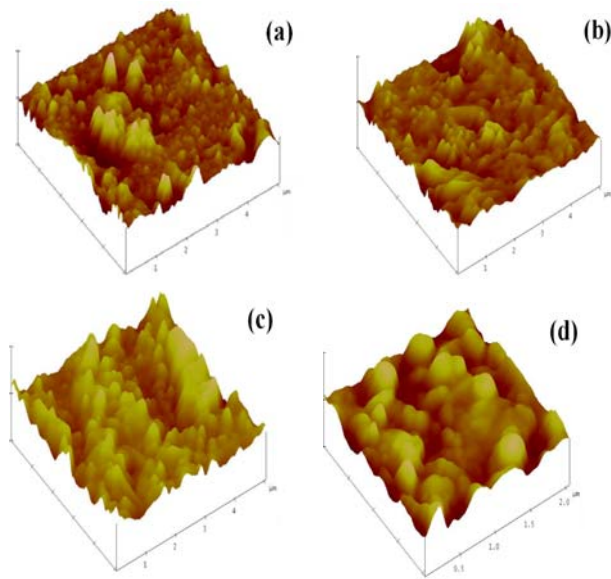
at 1167 $\text{cm}^{-1}$  may be assigned to in plane deformation of the C-C bond of the benzenoid ring of the polyaniline [25-27]. The bands at 1932 and 1593 $\text{cm}^{-1}$  correspond to C-N<sup>+</sup> stretching and C-C stretching of the quinoid ring respectively. Band at 1459 $\text{cm}^{-1}$  may be assigned to the formation of bipolarons [28]. The Raman shift at 1230 $\text{cm}^{-1}$  can be corresponding to C-N stretching in polaronic units [29-31], while peak observed in lower region at 434, 521 and 797 $\text{cm}^{-1}$  region are characteristic of polyaniline charge delocalization on backbone chain. These characteristics peak of polyaniline thin films are observed to be slightly modified upon annealing like peaks in the lower regions are observed to be restructured and coalesces which can be correlated to structural modifications upon annealing. Peaks corresponding to film annealed at 200 $^{\circ}\text{C}$  are observed to be increased in intensity with rising of new peaks across 1382, 1514 and 1603 $\text{cm}^{-1}$  related to charge dislocation and delocalization. On the other hand peaks observed for film annealed at 300 $^{\circ}\text{C}$  represents disappearance of significant peaks corresponding to benzenoid and quinoid which can be inferred as conversion of polymeric polyaniline into powdery materials upon higher heating.



**Figure 3: Raman spectrum of as deposited and annealed Polyaniline thin films.**

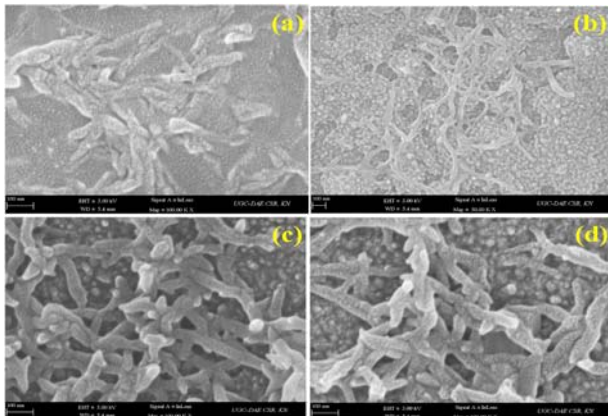
### AFM Analysis

The annealing treatment provided to the thin film would be first received by surface and transferred to the material hence primary effect is expected on the surface morphology, observed by atomic force microscopy (AFM) technique as shown in Fig. 4(a), (b), (c), and (d) representing as deposited, 100, 200 and 300 $^{\circ}\text{C}$ , respectively. AFM image of as deposited thin film shows uneven, irregular shape, size grains distributed over the substrate while on annealing grain growth can be observed. For 200 $^{\circ}\text{C}$ , annealed thin films this change can be well measured as an appearance of fatty grains with clear distinction of grain boundaries from each other, the AFM images of annealed samples shows clear evidence of enhancement in surface morphology and roughness along with compactness of the film surface [32]. From these observations, it is evident that annealing could improve crystallinity and quality of the thin films, while for films annealed at higher temperature i.e. 300 $^{\circ}\text{C}$  have represented conversion to powdery materials with no distinction between the grains.



**Figure 4 (a), (b), (c) (d): Surface morphology observed from atomic force microscopy (AFM) images of as deposited, 100°C, 200°C and 300°C annealed polyaniline thin films respectively.**

*SEM Analysis*

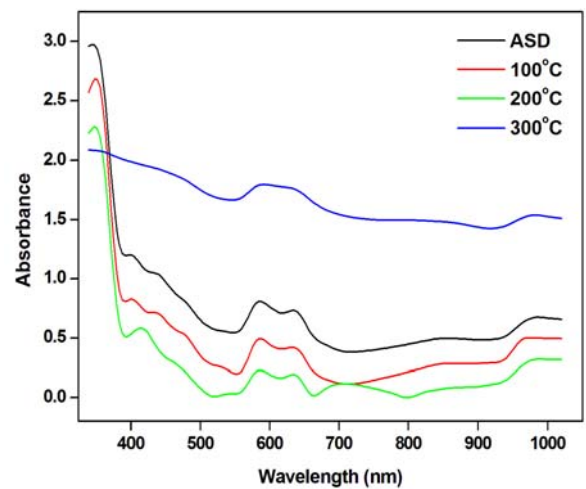


**Figure 5 (a), (b), (c) (d): Surface topology observed from scanning electron microscopy (SEM) images of as deposited, 100°C, 200°C and 300°C annealed polyaniline thin films respectively.**

The surface morphology of polyaniline thin films as deposited and annealed at 100, 200 and 300°C have been shown in Fig. 5(a), (b), (c), and (d) respectively, which represents extended rod like structures while on annealing it get shifted to compact nature. Annealed polyaniline becomes compact, the rod like interlinked structures at the as deposited being formed only on the layer surfaces. Melting of material grains under the action of external energy absorption and re-solidifications in the form of modified pattern, use of annealing treatment for material modifications is one of the efficient methods of properties alteration, since it enables controlled compositional,

interface and surface modifications. In the process of annealing, an external energy is provided to the thin film materials, which may be gained primarily by the surface grains and utilized in two ways such as increasing the surface energy and vibrational energy of the grain or atoms present in the material [33]. Hence on increasing the annealing temperature it may increase the vibrational energy of the crystallites, there by the phonon vibrations will increase means interaction of charges and lattice vibrations will also increase. These ionic displacements may correspond for increase in crystallite size and even it may also create vacancies and defects in the material which may results in material modifications [33-34].

*UV-visible spectroscopy*

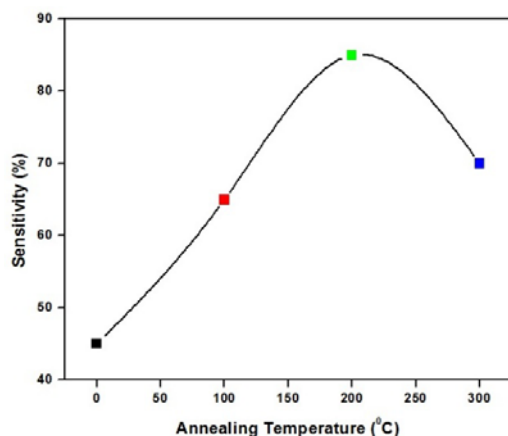


**Figure 6: Optical absorbance spectrum of the as deposited and annealed polyaniline thin films.**

The synthesized polymers were subjected to the physico-chemical characterization by using UV-vis spectroscopy as shown in Fig. 6, first absorption band of p-p\* bond has appeared at 380-424 nm, which can be assigned to the p-p\* transition of the benzenoid ring, it is related to coagulations between two consecutive hydrocarbon rings in polymer chain. The second absorption band located at 558-663 nm can be attributed to quinoid ring transition [35]. These bands are highly depending on the oxidation state of the polyaniline thin films. A characteristic band sloped between 420-538nm representing polaron-p\* transition appeared indicating conducting polyaniline emeraldine salt formations on HCl adding during the solution polymerization process [36]. The room temperature synthesis of polyaniline thin films the aniline in monomer chain get restricted for delocalization which can results in decrease in presence of alternating electron for transitions and thereby the conductivity may be lower while upon annealing the restructuring may provide an opportunity for increasing concentrations charge delocalization and charge transfer from of benzenoid to quonoid and vice versa rings this effects predominate over the electronic charge localizations effects and lead to increase in conductivity. This seems understandable since conductivity is dependent on the orientation of the phenyl rings as well as on the electron density of the ring. Tin films annealed at 100, 200 and 300°C have shown red shift in the absorbance band of the polyaniline tin films corresponding to as deposited materials. The

absorbance graph for thin film annealed at 300°C have resulted in uneven absorbance and peaks shifting which may correspond for structural destructions and uneven band transition in polyaniline thin films.

#### Ammonia gas sensing characteristics



**Figure 7: Ammonia gas sensitivity response of the polyaniline thin films prepared by solution polymerization method at room temperature.**

The optical absorption of the as deposited and annealed thin films measured in the 300-1100 nm wavelength region. It is observed that the change in absorbance of the polyaniline thin films starts from as deposited till 200°C, while it decreases after attending 200°C. The graph of sensitivity verses annealing temperature when drawn it clearly represented decrease in sensitivity after 200°C as per Fig. 7. This gas sensing phenomenon can be related to surface based chemisorptions phenomenon in which when polyaniline interacts with ammonia gas it undergoes the dedoping by deprotonation, as ammonia is an electron donor, hence when it interacts with the conducting form of polyaniline it will extract a proton from the (-NH-) site of polyaniline to form ammonium ion, this will lead to reduce the hole density in the emeraldine salt and converting it to the base form [37-38]. The change in film color was observed. Before applying the ammonia gas, the film color was green but after exposure to the gas it turned to blue this shows that on exposure to such a gas the charge transformation takes place in the film. The process of gas sensing is reversible when the gas supply cut down the ammonia ion will decompose to ammonia gas proton will be released in the film regaining its initial state. The gas sensitivity is observed to be higher for 200°C annealed polyaniline thin films, this can be correlated to saturated structural stoichiometry and charge transfer phenomenon though polaron interactions, while on increasing the annealing temperature the gas sensitivity is observed to be decreased, this can be related to surface and compositional

#### REFERENCES

1. B.K. Kim, Y.H. Kim, K. Won, H. Chang, Y. Choi, K.Kong, B.W. Rhyu, J.J.Kim and J.O. Lee, Electrical properties of polyaniline nanofibre synthesized with biocatalyst, *Nanotechnology* 16 (2005) 1177. <https://doi.org/10.1088/0957-4484/16/8/033>.

modifications upon annealing, the compact topology and partial conversion into power like nature of thin films.

#### Conclusion

From the present study it can be inferred that the polyaniline thin films can be grown by soft chemical route i.e. solution polymerization at room temperature over the glass substrate and optoelectronic and physicochemical properties of such chemically grown polyaniline thin films can be tailored by post deposition annealing treatment. The maximum acceptable temperature for the polyaniline thin films is found to be 200°C above which the composition of material starts disturbing and thereby may result in lowering of the output. Sensing being surface and composition dependant phenomenon hence high temperature annealing might destruct the surface morphology and compositional balancing too, thereby the sensing affected. The FTIR represented broadening of peak and intensity for the sample annealed at 200°C but above that the peaks get flattened and vanished, the same as been observed in the Raman spectra too, significant peaks at 1459  $\text{cm}^{-1}$  assigned to the formation of bipolarons and 1230  $\text{cm}^{-1}$  corresponding to C-N stretching in polaronic units get shifted towards higher wavelength related to compositional modifications upon annealing. Surface topology as observed from the AFM shows grain growth and coalescations after providing the external annealing treatment, same has been confirmed from the SEM imaging of the samples, this can be correlated to polygonization process where energy is absorbed at the surface and used for diminishing the grain boundries and thereby the charge delocalization may occur and conductivity can be reduced. These annealed thin films when characterized for ammonia gas sensing applications, it is observed that the thin films annealed at 200°C results in higher sensitivity which may be because of grain growth, correlated to saturated structural stoichiometry and charge transfer phenomenon though polaron interactions, hence for polyaniline thin films as sensor applications, 200°C annealing can be best suited.

#### Acknowledgement

One of the authors RAJ is thankful to Swami Ramanand Teerth Marathwada University, Nanded Maharashtra for financial grants through University minor research project APDS/Uni. MRP-VIII/Sci. & Tech. Physics/2023-24/1472 dated 25-08-2023. Authors are also thankful to scientific consortium UGC DAE CSR Indore, UGC DAE CSR Kolkata and UGC DAE CSR Kalpakkam for providing the thin films characterization facility.

2. C.P. Davi, LFMD Galdino, P. Borelli, J.O. Oliveira, M. Ferreira, Natural rubber latex LBL films: characterization and growth of fibroblasts. *J. of Appl. Pol. Sci.* 125 (2012) 2137-2147. <https://doi.org/10.1002/app.36309>
3. D.M. Xu, M.Y. Guan, Q.H. Xu, Y. Guo Multilayer films of layered double hydroxide polyaniline and their ammonia sensing behavior. *J Hazard Mat* 262 (2013) 64-70. <https://doi.org/10.1016/j.jhazmat.2013.08.034>
4. X.H. Xu, G.L. Ren, J. Cheng, Q. Liu, D.G. Li, Q. Chen Self-assembly of polyaniline-grafted chitosan/glucose oxidase nanolayered films for electrochemical biosensor applications. *J Mat Sci* 41 (2006) 4974-4977. <https://doi.org/10.1007/s10853-006-0118-4>
5. J. Wen, S. Wang, J. Feng, J. Ma, H. Zhang, P. Wu, G. Li, Z. Wu, F. Meng, L. Li and Y. Tian Recent progress in polyaniline-based chemiresistive flexible gas sensors: design, nanostructures, and composite materials *J. Mater. Chem. A*, 2024, 12, 6190-6210. <https://doi.org/10.1039/D3TA07687C>
6. R. Pal, S.L. Goyal, I. Rawal, S.K. Gupta Augmentation of room temperature gas sensing properties of PANI thin films by 100 keV Ar<sup>+</sup> ion irradiation *Appl Sur Sci* 657 (2024) 159739. <https://doi.org/10.1016/j.apsusc.2024.159739>.
7. N.C. De Souza, M. Ferreira, K. Wohnrath, J.R. Silva, O.N. Oliveira J.A. Giacometti, Morphological characterization of Langmuir-Blodgett films from polyaniline and a ruthenium complex (Rupy): influence of the relative concentration of Rupy *Nanotechnology* 18 (2007) 75713. <https://doi.org/10.1088/0957-4484/18/7/075713>.
8. S. Stafstrom, J.L. Bredas, A.J. Epstein, H.S. Woo, D.B. Tanner, W.S. Haung and A.G. MacDiarmid, polaron lattice in highly conducting polyaniline: Theoretical and optical studies *Phys. Rev. Lett.* 59 (1987) 1464. <https://doi.org/10.1103/PhysRevLett.59.1464>.
9. S.M. Conwell, C.B. Duke, A. Paton and S. Jaydev, Molecular conformation of polyaniline oligomers: Optical absorption and photoemission of three-phenyl molecules *J. Chem. Phys.* 88 (1988) 3331. <https://doi.org/10.1063/1.453927>.
10. J.B. Yadav, R.B. Patil, R.K. Puri, Vijaya Puri, Optical properties of the chopped and non-chopped vacuum evaporated polyaniline thin film *J. Non-Cryst. Solid* 353 (2007) 4691. <https://doi.org/10.1016/j.jnoncrysol.2007.06.060>.
11. H. Qiu, H. Li, K. Fang, J. Li, W. Mao, S. Luo. Micromorphology and conductivity of the vacuum-deposited polyaniline films *Synth. Met.* 148 (2005) 71. <https://doi.org/10.1016/j.synthmet.2004.08.025>.
12. M. Magnuson, J. H. Guo, S. M. Butorin, A. Aguli, C. Sathe, J. Nordgren and A. P. Monkam, The electronic structure of polyaniline and doped phases studied by soft x-ray absorption and emission spectroscopies *J. Chem. Phys.* 111 (1999) 4756. <https://doi.org/10.1063/1.479238>.
13. A. Kobayashi, H. Ishikawa, K. Amano, M. Satoh and E. Hasegawa, Electrical conductivity of annealed polyaniline *J. Appl. Phys.* 74 (1993) 296. <https://doi.org/10.1063/1.354106>.
14. S. Chaudhari and P.P. Patil Inhibition of nickel coated mild steel corrosion by electrosynthesized polyaniline coatings. *Electrochim Acta* 56 (2011) 3049-3059. <https://doi.org/10.1016/j.electacta.2010.12.096>.
15. G Decher, Fuzzy nanoassemblies: toward layered polymeric multicomposites. *Science* 277 (1997) 1232-1237. <https://doi.org/10.1126/science.277.5330.123>.
16. F. Fenniche, Y. Khane, A. Henni, D. Aouf, D.E. Djafri, Synthesis and characterization of PANI nanofibers high-performance thin films via electrochemical methods *Res. Chem* 4 (2022) 100596. <https://doi.org/10.1016/j.rechem.2022.100596>.
17. J. Luo, Y. Chen, Q. Ma, R.R. Liu, X. Liu Layer-by-layer assembled ionic-liquid functionalized graphene-polyaniline nanocomposite with enhanced electrochemical sensing properties. *J Mat Chem C* 2 (2014) 4818-4827. <https://doi.org/10.1039/C4TC00126E>.
18. D Li, Y Jiang, Z Wu, X,Chen Y Li Self-assembly of polyaniline ultrathin films based on doping-induced deposition effect and applications for chemical sensors. *Sensors Actuators B* 66 (2000) 125-127. [https://doi.org/10.1016/S0925-4005\(00\)00315-4](https://doi.org/10.1016/S0925-4005(00)00315-4).
19. G.B.V.S Lakshmi, A. Dhillon, A.M. Siddiqui, M. Zulfueqar, D. K. Avasthi, RF-plasma polymerization and characterization of polyaniline. *Eur. Polym. J.* 45 (2009) 2873-2877. <https://doi.org/10.1016/j.eurpolymj.2009.06.027>.
20. G.J. Cruz, J. Morales, M.M. Castillo-Ortega, R. Olayo, Synthesis of polyaniline films by plasma polymerization. *Synth. Met.* 88 (1997) 213-218. [https://doi.org/10.1016/S0379-6779\(97\)03853-8](https://doi.org/10.1016/S0379-6779(97)03853-8).
21. S. Ameen, M.S. Akhtar, M. Song, H.S. Shin, Metal Oxide Nanomaterials, Conducting Polymers and Their Nanocomposites for Solar Energy. In *Solar Cells-Research and Application Perspectives*; Intech: Rijeka, Croatia, 2013. <https://doi.org/10.5772/51432>.
22. S. Chaudhari, S.R. Sainkar, P.P. Patil, Anticorrosive properties of electro synthesized poly(o-anisidine) coatings on copper from aqueous salicylate medium. *J. Phys. D Appl. Phys.*, 40 (2007) 520-533. <https://doi.org/10.1088/0022-3727/40/2/028>.
23. N.E. Agbor, M.C. Petty, A.P. Monkman Polyaniline thin films for gas sensing *Sens Actuators B: Chemical* 28 (1995) 173-179 [https://doi.org/10.1016/0925-4005\(95\)01725-9](https://doi.org/10.1016/0925-4005(95)01725-9).
24. A.L. Kukla, Y.M. Shirshov, S.A. Piletsky Ammonia sensors based on sensitive polyaniline films *Sensors and Actuators B: Chemical* 37 (1996) 135-140 [https://doi.org/10.1016/S0925-4005\(97\)80128-1](https://doi.org/10.1016/S0925-4005(97)80128-1).
25. I Lupuleza, KP Matabol, LN Dlamini, TA Makhetha. Development of an In<sub>2</sub>S<sub>3</sub>/metal organic framework heterostructure coupled with an ionic liquid as a potential composite for environmental remediation, *Materials Research Bulletin* 185 (2025) 113271. <https://doi.org/10.1016/j.materresbull.2024.113271>.
26. S.M. Shaikh, J.Y. Lim and O.S. Joo Electrochemical supercapacitors of electrodeposited PANI/H-RuO<sub>2</sub> hybrid nanostructure. *Curr Appl Phys* 13 (2013) 758-761. <https://doi.org/10.1016/j.cap.2012.11.019>.
27. B.N. Grgur, V. Ristic and B.Z. Jugovic. Polyaniline as possible anode materials for the lead acid batteries. *J Power Sources* 180 (2008) 635-640. <https://doi.org/10.1016/j.jpowsour.2008.02.022>.
28. R.J. Mortimer, A.L. Dyer and J.R. Reynolds. Electrochromic organic and polymeric materials for display applications. *Displays* 27 (2006) 2-18. <https://doi.org/10.1016/j.displa.2005.03.003>.
29. G. Yu, J. Gao, J.C. Hummelen, Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions. *Science* 270 (1995) 1789-1791. <https://doi.org/10.1126/science.270.5243.1789>.
30. S.C.K. Misra, P. Mathur, B.K. Srivastava Vacuum deposited nanocrystalline polyaniline thin film sensors for detection of carbon monoxide, *Sen Act A* 114 (2004) 30-35. <https://doi.org/10.1016/j.sna.2004.02.026>.

31. A.Baba, R.C. Advincula and W. Knoll. In situ investigations on the electrochemical polymerization and properties of polyaniline thin films by surface plasmon optical techniques. *J Phys Chem B* 106 (2002) 1581-1587. <https://doi.org/10.1021/jp011837z>.
32. C.W. Wang, Z. Wang, M.K. Li. Well-aligned polyaniline nano-fibril array membrane and its field emission property *Chem Phys Lett* 341 (2001) 431-434. [https://doi.org/10.1016/S0009-2614\(01\)00509-7](https://doi.org/10.1016/S0009-2614(01)00509-7).
33. X. Zhang, W.J. Goux and S.K. Manohar. Synthesis of polyaniline nanofibers by nanofiber seeding. *J Am Chem Soc* 126 (2004) 4502-4503. <https://doi.org/10.1021/ja031867a>.
34. T. Borode, D. Wang, A. Prasad, Polyaniline-based sensor for real-time plant growth monitoring, *Sensors and Actuators A* 355 (2023) 114319. <https://doi.org/10.1016/j.sna.2023.114319>.
35. A. Groza, C.S. Ciobanu, C.L. Popa, S.L. Iconaru, L. Chapon, C. Luculescu, M. Ganciu, D. Predoi, Structural properties and antifungal activity against *Candida albicans* biofilm of different composite layers based on Ag/Zn doped hydroxyapatite-polydimethylsiloxanes. *Polymers* 8 (2016) 131. <https://doi.org/10.3390/polym8040131>.
36. X. Wang, G. Grundmeier, Morphology and Patterning Processes of Thin Organosilicon and Perfluorinated Bi-Layer Plasma Polymer Films. *Plasma Process. Polym.* 3 (2006) 39-47. <https://doi.org/10.1002/ppap.200500063>
37. T.C. Tsai, D. Staack, Low-Temperature Polymer Deposition in Ambient Air Using a Floating-electrode Dielectric Barrier Discharge Jet. *Plasma Process. Polym.* 8 (2011) 523-534. <https://doi.org/10.1002/ppap.201000171>.
38. X. Du, Y. Xu, L. Xiong, Y. Bai, J. Zhu, S. Mao, Polyaniline with high crystallinity degree: Synthesis, structure, and electrochemical properties. *J. Appl. Polym. Sci.* 131 (2014) 40827. <https://doi.org/10.1002/app.40827>.

**Important:** Articles are published under the responsibility of authors, in particular concerning the respect of copyrights. Readers are aware that the contents of published articles may involve hazardous experiments if reproduced; the reproduction of experimental procedures described in articles is under the responsibility of readers and their own analysis of potential danger.

### Reprint freely distributable – Open access article

**Materials and Devices is an Open Access journal** which publishes original, and **peer-reviewed** papers accessible only via internet, freely for all. Your published article can be freely downloaded, and self archiving of your paper is allowed and encouraged!

We apply « **the principles of transparency and best practice in scholarly publishing** » as defined by the Committee on Publication Ethics (COPE), the Directory of Open Access Journals (DOAJ), and the Open Access Scholarly Publishers Organization (OASPA). The journal has thus been worked out in such a way as complying with the requirements issued by OASPA and DOAJ in order to apply to these organizations soon.

**Copyright** on any article in Materials and Devices is retained by the author(s) under the Creative Commons (Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0)), which is favourable to authors.



**Aims and Scope of the journal** : the topics covered by the journal are wide, Materials and Devices aims at publishing papers on all aspects related to materials (including experimental techniques and methods), and devices in a wide sense provided they integrate specific materials. Works in relation with sustainable development are welcome. The journal publishes several types of papers : A: regular papers, L : short papers, R : review papers, T : technical papers, Ur : Unexpected and « negative » results, Conf: conference papers.

(see details in the site of the journal: <http://materialsanddevices.co-ac.com>)

We want to maintain Materials and Devices Open Access and free of charge thanks to volunteerism, the journal is managed by scientists for science! You are welcome if you desire to join the team!

**Advertising in our pages helps us!** Companies selling scientific equipments and technologies are particularly relevant for ads in several places to inform about their products (in article pages as below, journal site, published volumes pages, ...). Corporate sponsorship is also welcome!

**Feel free to contact us! [contact@co-ac.com](mailto:contact@co-ac.com)**