

Low temperature processing of 1-aminoanthracene films for optoelectronic applications

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The development of low-cost electronics for flat-panel displays, sensor arrays and flexible circuitry depends heavily on high-throughput fabrication processes and a choice of materials with appropriate performance characteristics. The solution processing schemes with high performance has been developed, but these require high annealing temperatures, which are incompatible with flexible polymeric materials and substrates. Here we report the low temperature processing of highly crystalline thin layers of 1-aminoanthracene compound onto the glass substrate using hot wall technique. These films have been studied for their structural, optical and electrical properties. X-ray diffraction and atomic force microscopy investigations on these films indicate their crystalline nature. Analysis of the optical absorption measurements indicate that interband transition energies lies in the range of 3.86-3.98 eV. Photoluminescence measurements on these films show prominent green emission peak. Room temperature conductivity of these films suggests their semiconductor behaviour with activation energy in the range 0.48- 0.55 eV.

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1. Introduction

The ability to fabricate light-weight, eco-friendly, biodegradable and flexible optoelectronic devices with scalable processing has initiated numerous research activities in the scientific community. Organic conjugated materials have shown significant applications in electronic devices like light emitting devices, photovoltaic, chemiresistor gas sensors, field effect transistors and optical mass memories due to their unique optical, electrical and photoelectrical properties [1-3]. In order to produce highly efficient devices, there has been a growing spectacular research effort in organic electronics to improve the semiconducting, conducting and light emitting properties of organic materials. In this direction, organic compounds derived from anthracene have attracted a lot of attention due to their high architectural flexibility in structure, which facilitates the tailoring of their physical, optoelectronic and chemical parameters over a very broad range. The anthracene and its derivatives have been extensively studied by different researchers [4-10]. Thin films of anthracene based materials are widely used in in OLEDs, solar cells, sensors and organic thin film transistors (OTFTs) [11-14]. Among anthracene derivatives, aminoanthracene has attracted considerable interest because of their applications in optoelectronics devices [15 -17]. A number of potential molecular devices which can arise from these materials depend upon the fabrication of anthracene based materials as thin films. Accordingly, there is a continuing interest in depositing anthracene materials in this type of formulation, with research focused on the selection of suitable derivatives for providing ordered and reproducible films. We have already reported the growth of anthraquinones, phthalocyanine and a few anthracene based highly ordered

films [17-19]. The position of substituents in organic semiconductors can significantly affect and tailor its properties. Keeping these facts in consideration, we report the growth of 1-aminoanthracene films and their structural, optical and electrical characterization in this communication.

2. Experimental

1-aminoanthracene ($C_{14}H_{11}N$) material of $\geq 90\%$ purity has been procured from Fluka. It is olive green in colour having melting point 388 K and molecular Weight 193.24 a.m.u. The 1-aminoanthracene powder was taken in a single-evaporation zone known as hot wall set up which has been demonstrated for low temperature processing of thin films [20]. Two separate resistive windings of nicrome were used to heat the evaporation port and walls of the column. A radiant heater was used to heat the substrate in the temperature range 310 to 340 K. The temperatures of the different zones were controlled by PID temperature controllers using K-type thermocouple obtained from Omega Eng. (USA). The temperature of the source, wall and substrate were adjusted between 385-390 K, 405-415 K and 310-340 K. Chemically and ultrasonically cleaned glass slides were used as substrate material. The whole apparatus was fitted onto the base plate of the vacuum chamber of Hind High vacuum coating unit 12A4H. The chamber was then evacuated to pressure of order less than 10^{-3} Torr after mounting the substrate and making other desired adjustments. Before carrying out the deposition, the vacuum chamber was baked at 350 K for one hour. After attaining the desired experimental conditions, the source heater was switched on and the substrate holder was positioned on the top of the tube to make it a closed system. The temperature of the

substrate was monitored by a copper constantan thermocouple. The details and advantages of hot wall method for low temperature processing of thin films have been explained in details for the fabrication of complex chalcopyrite films [20].

After depositing films at particular substrate temperature the system was allowed to attain room temperature (298 K) and then samples were removed for further studies. The thickness of the films was measured using depth profiler (Dektak 3030 - XT). The chemical identification of these films has been carried out by IR spectroscopy taken in absorption mode in the 500-4000 cm^{-1} range using FTIR 8300 (Shimadzu, Japan) spectrophotometer. The XRD patterns of the films were recorded using Shimadzu XRD-7000 diffractometer using $\text{Cu K}\alpha$ (wavelength = 1.54 Å) and step size (2θ) = 0.02 per sec in the 2θ range 5-70 degrees. Atomic force microscope (Nanosurf. Switzerland) has been used in static force operating mode with cantilever (Cont A1-G) to describe morphology of surface layer. To study the optical properties, the transmittance and absorbance spectra of the samples were obtained in the photo energy range 1.12-4.13 eV by using UV-1601PC (Shimadzu, Japan) spectrophotometer. All structural and optical measurements were performed at room temperature (298 K). The electrical conductivity of the films were determined by Keithley electrometer 6517A using two probe technique in the temperature range 290 - 380 K under a pressure of 10^{-1} Torr. Silver contacts were used to connect thin copper wires to the films.

3. Results and discussion

3.1 Structural characterization of 1-aminoanthracene films

Fig. 1 shows the FTIR spectra of 1-aminoanthracene powder and corresponding hot wall grown film deposited on glass substrate kept at 340 K. The comparison of FTIR spectra of powder and corresponding film shows that the compound remains unaffected during vacuum deposition and annealing processes because of unchanged vibrational frequencies (cm^{-1}). However, the intensities of the absorption bands in case of film samples are found to be altered, in comparison with those observed in case of powdered sample. These modifications of the intensities of absorption peaks so obtained may be attributed to the different thickness and molecular packing of films and powder. The melting point of 1-aminoanthracene powder was 388 K whereas it was found to lie in the range of \approx 392 K for hot wall grown films. This increase in melting point of films may be due to increase in the purity of organic compound. Thus, sublimation under vacuum is a very efficient process in order to purify the compound. Therefore, we do not require any sort of purification process before the deposition of films. The low melting point of 1-aminoanthracene as compared with the 2-aminoanthracene [17] make the former more suitable for industrial applications. The thickness of 1-aminoanthracene films prepared at different substrate temperatures lies between 1.1-1.2 μm . X-ray diffraction patterns of powder and hot wall grown films of 1-aminoanthracene sample are shown in Fig. 2. XRD pattern of films show three high

intensity sharp and well resolved peaks with d-values 9.690, 9.321, 4.8049, 4.65 Å which confirms their crystalline behaviour. The films deposited at higher substrate temperature show comparatively intense diffraction peaks. Moreover, a decrease in full width measured at half maxima (FWHM) of diffraction peaks has been noticed, thus suggesting a higher degree of crystallinity. It is important to mention here that XRD pattern of powder sample shows low intensity diffraction peaks with d-values 9.27, 5.18, 5.01, 4.59, 3.94 and 3.55 Å as compare to their films. These observations reveal that the films are textured along three preferred orientations out of the orientations of the powder.

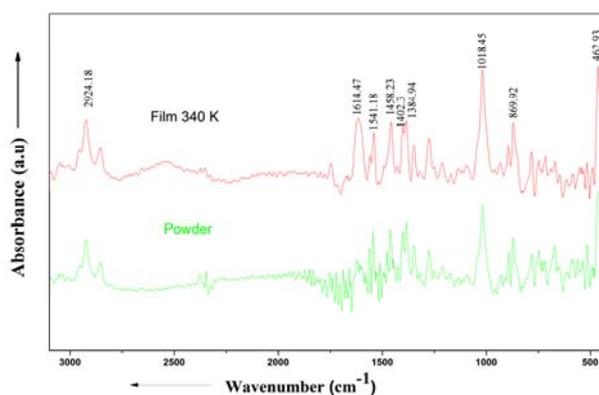


Fig. 1. FTIR spectra of 1-aminoanthracene powder and films deposited at substrate temperature of 340K.

The average particle size has been found using Debye-Scherrer formula

$$D = 0.9\lambda / \beta \cos \theta$$

where λ is the wavelength of X-rays, β is the full width at half maximum (FWHM) in radians and θ is Bragg's angle, and found to be in the range 30-100 nm for films deposited onto glass substrate kept in the range of 310-340 K. Thus, particle size is also increased with increase in substrate temperature. These results conclude that the substrate temperature plays a crucial role in controlling the crystallographic properties of films.

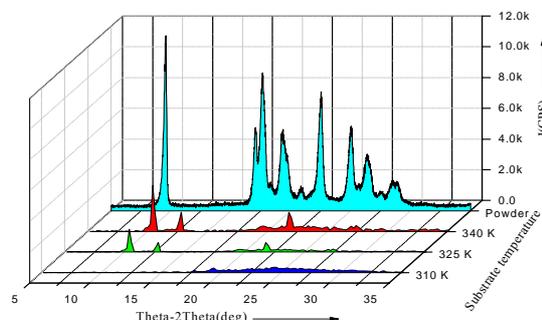


Fig. 2. XRD of 1-aminoanthracene powder and films deposited onto glass substrate kept at different substrate temperature.

The increase in crystallinity with increase in substrate temperature may be explained on the fact that ad-atom mobility in case of films deposited at lower substrate temperature is comparatively smaller than films deposited at elevated temperature. This enhanced ad-atom mobility increases the collision between the 1-aminoanthracene molecules before condensation gives rise to the formation of smaller number of stable nuclei. Subsequently these nuclei grow in large size grains and improve the crystallinity of films and decrease the lattice strain [20].

Scanning electron micrographs of 1-aminoanthracene films prepared on glass substrate kept at different temperature are shown in Fig. 3. It delineates the shapes and the distribution of the crystallites. It is observed that films show dense-packing and grains size appears to increase with increase in substrate temperature (Table 1). The surface morphologies of the 1-aminoanthracene films prepared at different substrate temperatures were studied using an atomic force microscope in the contact mode and the results are shown in Fig. 4. It suggests the crack free, continuous, dense and uniform deposits in selected line profiles. Moreover, 3D-images show the growth of pyramid shaped crystallites with typical peak-valley height lies in the range of 530 nm to 784 nm (Fig. 3b). The roughness of these films has also been calculated and found to be 113.92 nm, 138.09 nm and 146.54 nm for films deposited at substrate temperatures of 310 K, 325 K and 340 K respectively. Observations reveal that an increase in deposition temperature results in an increase in roughness of the film. This may be attributed to the growth of grains with preferred orientation dictated by the surface, grain boundary diffusivity, the ad-atoms mobility and induced thermal stresses [21-22]. The rough surfaces are thought to encourage reduction in reflection and trapping of photons within the film due to scattering at the surface [21,23]. Thus these hot wall-grown films appear to contain good morphology well suited for optoelectronic devices.

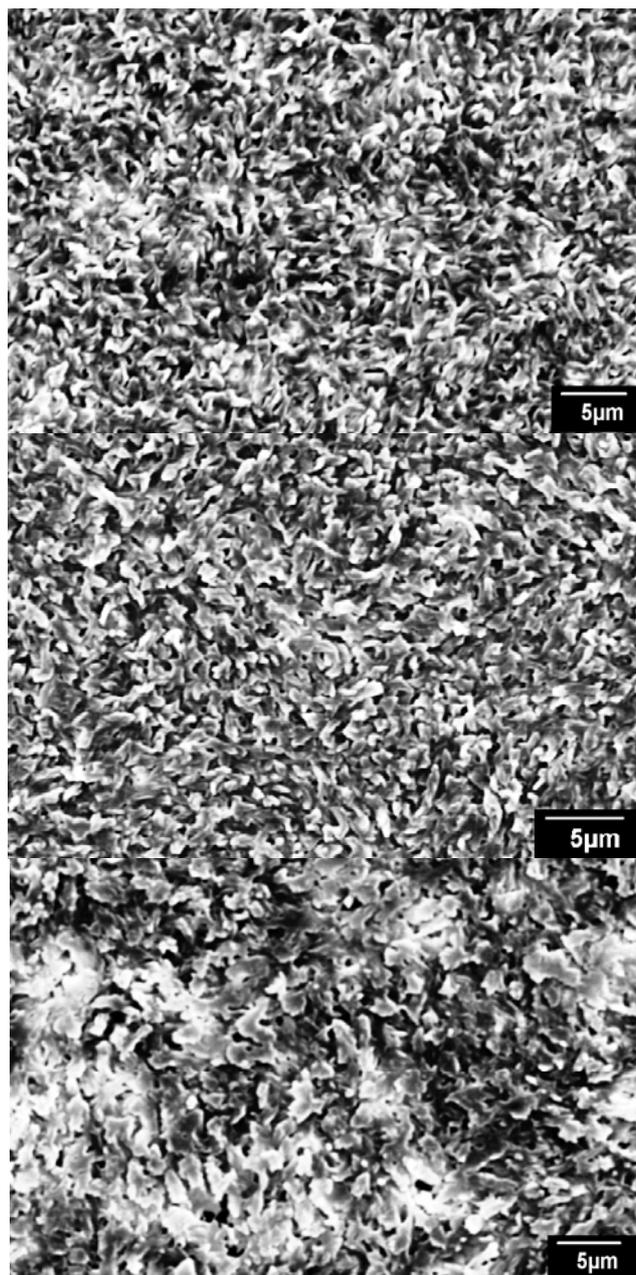


Fig. 3. SEM images of 1-aminoanthracene film deposited on glass kept at different temperature (a) 310K, (b) 325 K and (c) 340K.

Table 1

Compound	Substrate Temperature (K)	Band gap (eV)	Activation energy (eV)	Grain size SEM (μm)
1-aminoanthracene	310	3.86	0.55	1.29
	325	3.96	0.51	1.90
	340	3.98	0.48	3.32

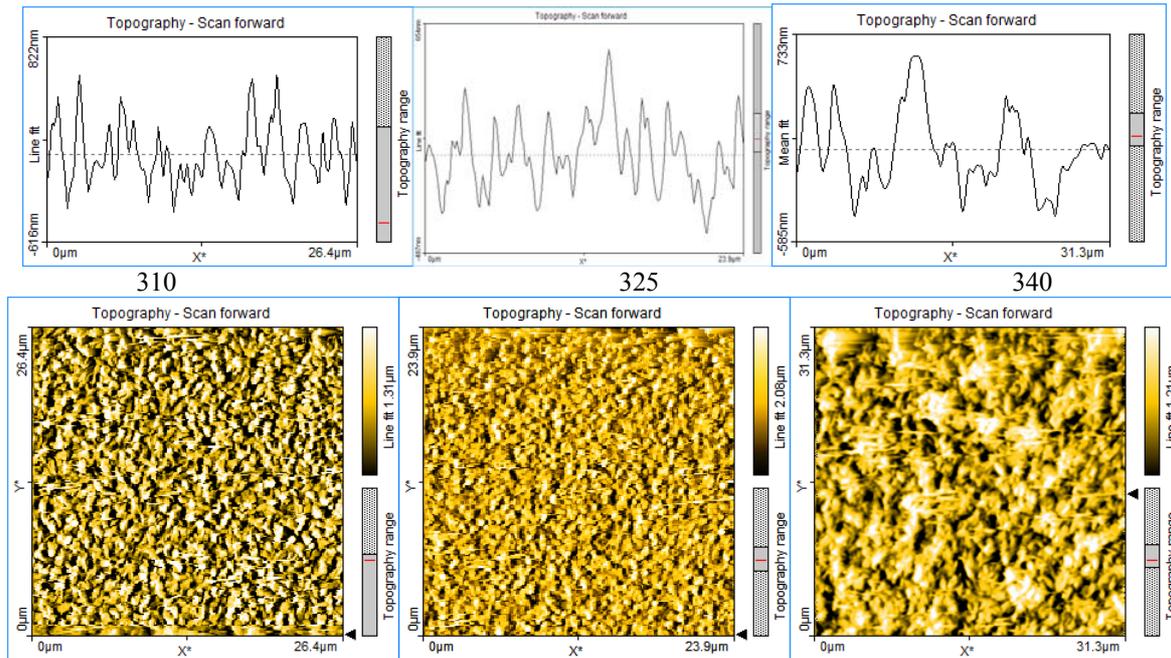


Fig. 4 2D-AFM of 1-aminoanthracene film deposited on glass kept at different temperature (a) 310K, (b) 325 K and (c) 340K.

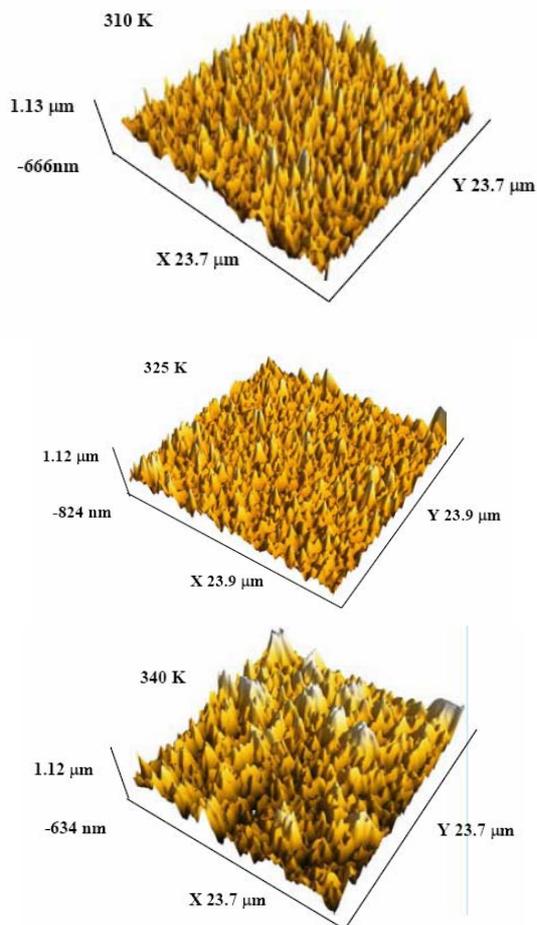


Fig. 4(b). 3D-AFM of 1-aminoanthracene film deposited on glass kept at different temperature (a) 310K, (b) 340 K and (c) 340K.

3.2 Optical properties

The optical absorption spectra of the films have been recorded in the wavelength range from 300 to 1100 nm and show fundamental absorption hump in the photon energy range $3.7 > h\nu > 4.2$ eV and were examined in terms of an allowed direct band transition. The linear nature of the plot near the absorption edge confirms that 1-aminoanthracene films show semi-conducting behavior with a direct band gap [24] as calculated using the equation of Bardeen et al. [25]

$$\alpha h\nu = B(h\nu - E_g)^{1/2}$$

where E_g is the optical band gap, B is a constant and ν is the frequency of the incident light. The extrapolation of the linear portion to $(\alpha h\nu)^2 = 0$ gives the value of optical band gap E_g , under direct allowed transition for the 1-aminoanthracene films (Fig. 5) and found to be lie in the range 3.86-3.98 eV (Table. 1). It is important to note here that the substituent position (amino) has significantly affected the optical properties [17]. Also increase in optical band gap may be attributed to the formation of more ordered structure at higher substrate temperature which gives a comparatively small contribution to the absorption, thus shifting the absorption edge to higher energy. These results are in agreement with the corresponding XRD, SEM and AFM data.

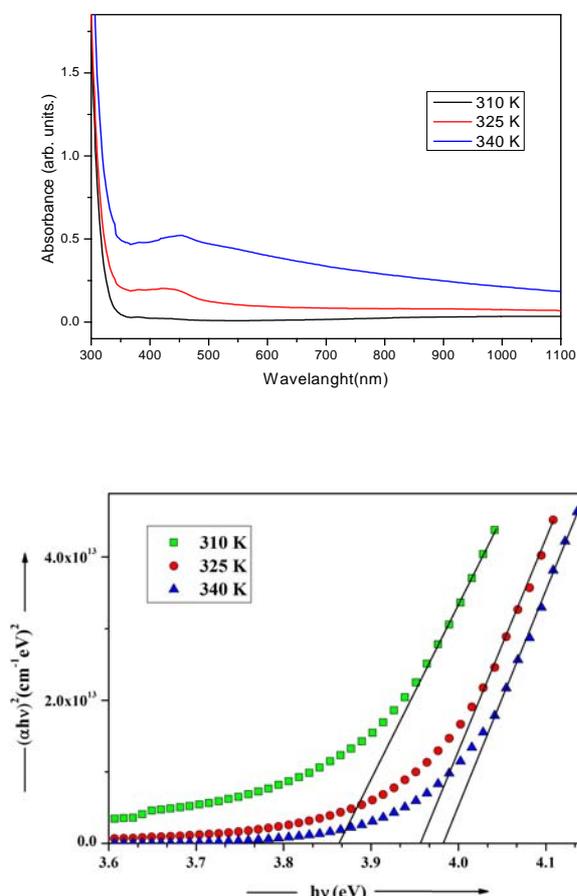


Fig. 5. Spectral variation of absorption coefficient under direct interband transition for 1-aminoanthracene films deposited at different substrate temperatures.

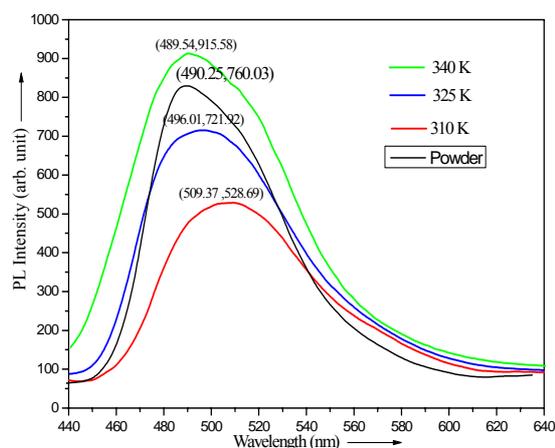


Fig. 6. PL for 1-aminoanthracene powder and films deposited at different substrate temperatures.

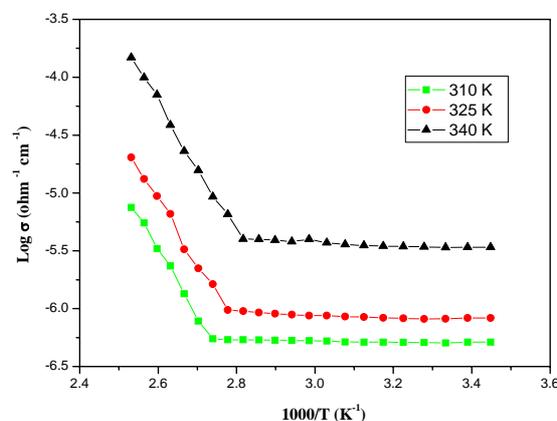


Fig. 7. Variation of log of conductivity with inverse absolute temperature for 1-aminoanthracene films deposited at different substrate temperatures.

Fig.6 illustrate the room temperature photoluminescence (PL) spectra of 1-aminoanthracene grown on different temperature substrates. All the samples are excited at fixed wave length 382 nm. A strong broad green emission centered at 490 nm for powder sample, and at 509 nm , 496 nm , 489 nm for films deposited at substrate temperature 310K, 325K and 340K respectively have been noticed. A shift of few nm in the emission peaks for film samples have been noticed as compare to powder sample. Moreover, the intensity of the green emissions found to increase with increase in substrate temperature. The enhancement in luminescence yield with increase in substrate temperature may be due to the surface modification such as more roughness, large grains and improved crystallinity. From these results it can be concluded that the substrate temperature and substituent position has a great influence on the type and concentration of defects. The emission is blue shifted for 1-aminoanthracene films as compared with 2- amino anthracene suggesting dominant role of substituent position [17].

3.3 Electrical properties

The electrical conductivity vs. temperature plots of the films deposited onto the glass substrate kept at different temperatures is shown in Fig. 7. It has been observed that electrical conductivity increase with an increase in the temperature, and the dependence of conductivity on temperature can be represented by the equation:

$$\sigma = \sigma_0 e^{(-\Delta E / 2kT)}$$

where ΔE is the activation energy, k is Boltzmann's constant and T is the absolute temperature. It has been also observed that the electrical conductivity increases with increase in substrate temperature. The increase in conductivity can be due to the fact that at higher substrate temperature, the charge carriers has to cross narrow inter-crystalline barriers as compare to films deposited at low temperatures due to their larger grains and more ordered structure. The results of electrical resistivity in the temperature range 290-380 K indicate similar variations

for all the films and suggest that they are essentially semiconductors. The inverse absolute temperature dependence of the log of conductivity for these films indicates two distinct temperature regions 290-350 K and 350-380 K (Fig.7). It suggests that the two different conduction mechanisms are operating at different temperatures, i.e. at low temperatures, the charge carrier tunnels slowly through the sample, as if in a band, and at high temperatures, they move from site to site by thermally-activated hopping [26]. Similar observations have also been observed for other anthracene compounds [4]. The activation energies for the low and high temperature ranges obtained from the slopes of the Arrhenius plots (Fig.7) are found to be in the range 0.011-0.003 eV in low temperature range and 0.48-0.55 eV in high temperature range respectively. The activation energy found to be decreased with the increase in substrate temperature. It is also important to note here that substituent position (amino) appears to affect the activation energy of the anthracene based materials [17].

4. Conclusions

Effects of substituent position on the properties of anthracene based organic semiconductor are presented. Highly crystalline and uniform films of 1-aminoanthracene have been prepared using hot wall technique which has importance for low temperature processing of thin films. The substrate temperature appears to be important parameter for molecular packing in solid state structure and influence the properties of the films. Films deposited at higher substrate temperatures show comparatively higher crystallinity, electrical conductivity and optical band gap. These films exhibit efficient green emission in the range 489-509 nm and emission peak intensity shows 73% increase with an increase in substrate temperature from 310 K to 340 K. These investigations suggest that 1-aminoanthracene films are suitable candidate for the optoelectronic applications.

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