Properties of Vacuum Evaporated Vapour Chopped Polyaniline Thin Film: Effect of Synthesis Method

J B Yadav¹, SV Jhadav², R K Puri¹* and Vijaya Puri²
¹Vacuum Techniques & Thin Film Lab., USIC, Shivaji University, Kolhapur-416004 (M. S.) India.
²Department of Physics, Shivaji University, Kolhapur-416004 (M. S.) India
Email - rkp_usic@unishivaji.ac.in
vrp_phy@unishivaji.ac.in

Abstract The paper reports optical properties and adhesion of polyaniline thin film prepared by vacuum evaporated polyaniline powder synthesized in acidic and nonacidic medium respectively. The effect of vapour chopping on its optical and adhesion properties is also studied. Maximum transmittance 85% and 90% was obtained for polyaniline thin film deposited from polyaniline powder synthesized from nonacidic and acidic medium respectively. Due to non-acidic medium, the film showed absorption peak at 420 nm, whereas due to acidic medium it shifts below 350 nm. Refractive index of PANI from nonacidic medium is higher than the refractive index from acidic medium. After vapour chopping the refractive index decreases and transmittance increases. Adhesion of the film measured by direct pull of method was higher due to acidic medium ~68 Kgf/cm². After chopping adhesion of the film increases. Polyaniline thin film deposited from acidic polyaniline powder are more stable and gives lower refractive index with higher adhesion. Vapour chopping also improves the properties of these thin films.

1. Introduction
Polyaniline is an electro active polymer having outstanding physical, chemical and electrical properties. Major advantage is that it can be prepared as conductor, semi conductor or insulator and interconverted in to each other by treating with acid or base. Because of the interconverting nature, environmental stability and low cost of synthesis make it applicable in the integrated optics for the development of active and passive optical devices.

This paper reports the effect of synthesis method and vapour chopping on the optical and mechanical properties of polyaniline thin film deposited by vacuum evaporation. To date there are only few reports on polyaniline thin film by vacuum evaporation. The polyaniline powder was synthesized in acidic and nonacidic medium. This synthesized PANI powder was used for deposition of thin film. The effect of vapour chopping on the optical and mechanical properties was also studied. The effect of vapour chopping on vacuum evaporated oxide thin films has been studied in our laboratory previously [1-2].

2. Experimental
Polyaniline powder was prepared by oxidation polymerization of aniline monomer in acidic and nonacidic medium. Double distilled aniline (0.2 M) was dissolved in 300 ml of (1M) HCl solution maintained at 0 to 5 °C. A calculated amount of ammonium per oxidisulphate (APS) (0.5 M) was
dissolved in pre-cooled 200 ml of (1M) HCl. Ammonium peroxidisulphate solution was added drop wise in aniline solution over a period of one hour with constant stirring. The reaction was carried out for 6 hours which resulted in dark green PANI salt as precipitate. The precipitate was collected and washed by (1M) HCl until the filtrate obtained was colorless and again washed by acetone and methanol followed with distilled water. The precipitate was collected on a filter paper and dried at 80°C. The precipitate of PANI salt was de-protonised by ammonia solution. The product was filtered and washed with distilled water, acetone and methanol and dried under vacuum at 80°C.

The resultant PANI base powder was evaporated by resistive heating using tantalum boat at 10^-4 Torr. The chopper was a V-shaped cut out of metallic vane (angle 155°C) fixed to a motor inside the vacuum chamber placed in the path between the substrate and boat [3] this V-shaped cut provides passage for vapour. Chopper provides growth flux interruption at constant rate. The speed of the rotation of the chopper was ~5-6 rot/sec.

Thickness of the film of ~150 nm was measured by Tolansky interferometric method [4]. The optical transmittance in the wavelength range 350 - 850 nm of the PANI films were measured by spectrophotometer (U-2800, HITACHI, JAPAN). The refractive index was measured by Abele’s method [5].

3. Result and Discussion

The confirmation of the as deposited and vapour chopped PANI thin film from FTIR was done in previous work [6-7]. The optical transmission spectra of nonacidic and acidic PANI thin films in wavelength range 350-850 nm is shown in the figure 1. From this figure, it is seen that maximum transmittance 80% and 85% was obtained for polyaniline thin film deposited from synthesized nonacidic and acidic medium powder. The film prepared from nonacidic medium powder showed absorption peak at 420 nm indicating that PANI in thin film form is not completely deprotonized in emeraldine base form [8], whereas for these films from acidic medium powders absorption peak shifts below 350 nm. PANI thin film deposited from both acidic and nonacidic powder showed large transmittance 85% and 95% respectively after vapour chopping.

![Figure 1: Transmittance data of polyaniline film prepared from A) acidic powder B) nonacidic powder.](image)

The refractive index of polyaniline thin film deposited from nonacidic and acidic powder at experimental wavelength 590nm is shown in table 1. From the table it is seen that, the refractive index of polyaniline thin film deposited from nonacidic powder is higher than the refractive index of film from acidic powder. After vapour chopping refractive index of both the films increased. The refractive index of the film depends on the wavelength difference between experimental wavelength and maximum absorption wavelength [9]. As the wavelength difference increases refractive index decreases. The wavelength difference in film prepared from nonacidic powder is lower due to which
an increase in refractive index of the film is obtained.
Vapour chopping increases the surface smoothness and reduces voids due to that the surface scattering reduces and transmittance increases which increases refractive index also.

| Deposition technique | Refractive Index |      |
|---------------------|-----------------|------|
|                     | Non-acidic      | Acidic |
| As-Deposited        | 1.843           | 1.822 |
| Vapour chopped      | 1.808           | 1.715 |

The adhesion is a significant factor for determining the reliability of thin film. It also gives the information about the interaction between the film-substrate interfaces. The adhesion of the film prepared from acidic and nonacidic powder is shown in table 2. From this table it is seen that, adhesion of the film prepared from acidic powder is greater for both as deposited and vapour chopped thin film. The vapour chopping process changes the morphology of the film, due to growth flux interruption the wetting characteristic is modified and smaller crystallite size is obtained (SEM data). This produces films with lesser defects so that long range order is decreased, which causes increase in adhesion of vapour chopped thin film.

| Deposition technique | Adhesion X 10^4 N/m^2 |      |
|---------------------|-----------------------|------|
|                     | Non-acidic            | Acidic |
| As-Deposited        | 192±4                 | 631±5 |
| Vapour chopped      | 223±3                 | 913±4 |

4. Conclusion
Preparation method of polyaniline powder affects the optical and mechanical properties vacuum evaporated PANI thin film. Polyaniline synthesized in acidic medium has lower refractive index, higher adhesion and is more stable than the film deposited by nonacidic powder. Vapour chopping improves the optical and mechanical properties. The PANI thin film deposited from PANI powder synthesized in acidic medium shows superior properties suited for optical coating especially for passive optical waveguiding element. Vapour chopping makes it still better.

Acknowledgements:
The author J. B. Yadav is thankful to Shivaji University, Kolhapur for the award of Departmental Research Fellowship (DRF). Vijaya Puri gratefully acknowledges the UGC award of Research Scientist ‘B’ and UGC-DRS-SAP-II

Reference:
[1] Puri R K and Puri Vijaya 2003 Jpn. J. Appl. Phys. 42 6892.
[2] Patil P V, Puri R K and Vijaya Puri 1997 Mat. Chem. Phys. 49 156.
[3] K.Vijaya, Puri R K and Karekar R N 1980 Thin solid films 70 105.
[4] Yadav J B, Patil R B, Puri R K and Puri Vijaya 2007 Mat. Sci. Eng. B 139 69.
[5] Abeles F 1958 J. Phys. Radium 19 327.
[6] Yadav J B, Puri R K and Puri Vijaya 2007 Applied Surface Science In Press.
[7] Yadav J B, Puri R K and Puri Vijaya 2007 Journal of Non-Crystalline Solid In Press.
[8] Inoue M, Navarro R E and Inoue M B 1989 Synth. Metal 30 199.
[9] Hougham G, Tesoro G, Vichbeck A, Chapple J D, and Sokol C 1994 Micromolucule 27 5964.