Chapter 4

Ag, Au and Ag-Au core shell nanoparticles in polymers by chemical route for humidity sensing

4.1 Introduction

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The chapter is on two topics briefly i) synthesis for the silver nanoparticles of various sizes by electrochemical route. These were dispersing into polyaniline matrix while polymerizing aniline at low temperature (0-5 °C). The humidity sensing is carried out by optical route; ii) in situ chemical synthesis of Ag, Au, Ag-Au core-shell nanoparticles grown in polyvinyl pyroloidone (PVP) matrix. The samples are tested for humidity sensing measuring their response in terms of electrical resistance.

In the first section, the synthesis of Ag nanoparticles by electrochemical technique in the presence of a surfactants Tetra Octyl Ammonium Bromide (TOAB) and Cetyl Trimethyl Ammonium Bromide (CTAB) is presented. CTAB acts as rod inducing micelle and an electrolyte in the solution for the growth of Ag nanoparticles. The Branch like Ag structures are characterized by using Uv-Vis absorption, SEM, XRD and TEM. The size of the nanostructures is about 3-5 μm in length and about 100-500 nm in diameter. The Ag nanoparticles are dispersed in aniline while polymerizing to get metal-polymer nanocomposite and then used for humidity sensing by optical method. The effect of particle size on humidity sensing is optimized; the maximum sensitivity is obtained for lowest size (15 nm) of nanoparticles. The sensor response is fully reversible having around 1 % of standard deviation. Response time of the sensor is 30 s with a slow recovery of 90 s.

In the second section the synthesis and humidity sensing study of Ag/Au nanoparticles grown in situ in PVP matrix by chemical route is presented. The samples are characterized by using Uv-Vis absorption, XRD and FESEM. The humidity sensing study is carried out by electrical resistance measurements by using half bridge method. In Ag/Au-PVP nanoparticles, it is found that the Ag-PVP samples showed higher sensitivity. The tailor ability of the sensors, governed by film thickness as a parameter guiding the humidity range is demonstrated.
4.1 Introduction

Nano-scale transition metal clusters are of current interest in the field of catalysis, nano electronics and materials science. By implementing various synthetic techniques such as physical vapor deposition, solvo-thermal, laser ablation, etc.; It is possible to obtain different chemical properties of the nanoparticles due to the change in capping agent, processing conditions and shape of the nanoparticles [1].

The choice of the synthesis procedure depends on the particular application. In order to make gas sensors out of nanoparticles; nanoparticles well adhered to the inert substrates in the form of film are preferred. For using nanoparticles in biological applications metal nanoparticles (Ag/Au) with size small (< 10 nm) in the biocompatible solvent such as water are needed; which can be achieved by chemical route [2]. The nanoparticles to be employed in electronic applications are preferred to be patterned in an array on a semiconductor substrate such as Si, which can be carried out by physical vapor deposition technique followed by photolithography if required. Therefore, to take maximum advantage of nano materials, various synthetic methods are needed in which significant control can be exercised over the size and shape of the nanostructures.

Study on metal nanoparticles is of significant importance from point of view of the optical properties. The metals such as Ag/Au/Cu have been synthesized by mainly using chemical routes. Optical properties of metal nanoparticles are studied by various groups [3]. The fantastic variation in change in colour of metal colloidal solution is demonstrated with the change in size of the nanoparticles. However the control over the shape of nanoparticles is yet a challenge. In the present study CTAB is implemented as a co-surfactant for the rod shaped structure formation of nanostructures by using electrochemical route. Colloidal metal preparation
methods offer the possibility of developing synthetic protocols for the
preparation of nanoparticles of metals and bimetals with control of particle
size distribution. Still, particle morphology remains an important challenge
in the preparative metal colloids [3]. In addition to metal, the bimetallic
nanoparticles are synthesized as the addition of another metal may further
enhance the properties possessed by the metal nanoparticles [4]. The
formation of a bimetallic bond leads to large changes in the band structure
of the metal [4]. A major goal in the previous studies on bimetallic
nanostructures was to identify phenomena that accompany the formation
of heteronuclear metal-metal bonds and study the dependence of
properties of these bonds on the interacting metals and on the geometrical
structure of the surface [4].

Various studies have been implemented by groups such as R. M.
Dikson, M. El. Sayed for the synthesis of metal colloids and their shape
variations. The surfactants such as TOAB and CTAB are used by them for
the synthesis of Ag/Au nanorod structures [3]. Rodlike and triangular
nanomaterials of Ag and Au were achieved in this study. The use of various
polymers such as Polyamidoamine dendrimer (PAMAM) which are useful in
medical applications have been used by R.M.Dikson [2]. Au nanoparticles
are trapped inside the dendrimer during the synthesis and that acquire the
shape and size of the polymer.

In the recent years humidity sensors have been widely used for
measurement and control in an industrial or household environment in
process control, storage, electrical applications, etc. The humidity sensors
in low humidity measurements are required; the applications are in food
production industries for example, milk powder industry and in other
industries such as in paper making [5, 6]. It is important to produce the
humidity sensor that will show high sensitivity in the low humidity range
(0-20 %RH). The humidity below 1 %RH can be measured by using sensing
elements of spinel compounds. The spinel compounds belong to a large
group of oxides with a general composite of \( \text{AB}_2\text{O}_4 \). A can be a divalent
metal element, especially in group II, group IIB, and VIIIB. B generally represents a trivalent metal, for example iron, chromium, and aluminum. The structure of this group is tetrahedron (diamond) always with high density of defects. These materials have ionic sensing properties probably due to their low operating temperatures. When the pore size is very small (100-300 nm), the lower humidity detection limit can be down to 1 %RH.

The sensor materials used are either polymeric or ceramic [7-13]. The polymeric type sensors are superior in performance because of their stability towards a variety of chemical species and fast response to the changes in humidity [9-13]. The principle of humidity measurement with the polymeric sensors is the change in electrical conductance due to water chemi / physi sorption and/or capillary condensation in the pores of the active sensor material [7, 13]. The change in conductance of the films was measured with respect to the relative humidity. The relative humidity i.e. %RH- is defined as the ratio of actual vapor pressure of water to the saturated vapor pressure at the same temperature multiplied by hundred. In the present study, the optical transmitted light through an optical multimode waveguide is used for studying the material for humidity sensing. The material is used as an active clad over an optical fiber or in the form of a film on a planar glass. Ag dispersed in polymers is used as a sensing material in the study.

As of today, polymers have occupied a major pivotal place in the field of material science and sensors as they represent an attractive class of materials; they offer many advantages over other classical sensor materials employed in the fabrication of sensors [13, 14]. Polyaniline and polyaniline doped by various acids and further doped by metallic nanoparticles appear to be very popular humidity sensing material. It was reported that the electrical conductivity of polyaniline (PANI) and its derivatives strongly depend on the red-ox state, doping level and moisture content in the film [15]. This property provides a possibility of using this polymer as a humidity sensing material. The optical properties of Ag PANI nano
composites studied for humidity sensing was reported by Madhavi et. al. [16-20]. The humidity sensing properties of the m-Nitro Aniline (mNA) doped Au nanoparticles in Poly Vinyl Alcohol (PVA) matrix by electrical measurements was reported [20]. The humidity sensing behavior of the films by mere addition of Ag, Au nanocomposites in PVA and PANI matrix or in any biological matrix showed improved properties [16-20]. In case of metal-polymer composites this was attributed to the structural properties of these polymers. PVA is having the property of trapping and releasing water molecules which is useful for sensing humidity and hence is responsible for the conduction mechanism [16]. In case of PANI, at high humidity, the polymer adsorbs water molecules and the polymer chains get hydrated resulting in the swelling of the polymer chains, followed by uncurling of the compact coil to form straight chains. The chains are aligned with respect to each other making the geometry favorable for the enhanced mobility of the dopant ion or the charge transfer across the polymer chains enhancing their conductivity [9, 10].

The humidity sensors are having material dependent properties and have showed different sensitivity regions in the response curve for the film. Both the polymers i.e. PANI and PVA, when doped by metallic nanoparticles like Co (Co dispersed in polymer insitu), exhibited almost linear response to the widest range of relative humidity. In case of Ag or Au, where metal nanoparticles were synthesized by chemical route and then mixed with PANI, show humidity response of the first order exponential decay with decreasing humidity from 94-4 %RH. The maximum resistance observed in that film was 60-75 MΩ. Therefore it can be inferred that the variation in the matrix and the synthesis procedure imply change in the humidity response of the films.

PVP is a non-conducting polymer similar to that of a PVA. Ag-PVA, Ag-PVP and Au-PVP nano composites were prepared by using chemical route [21, 22] in order to reduce the resistance of the sensor films. In situ growth of Ag or Au into the polymer matrix can increase the conductivity of the
resistive type polymeric sensor in dry atmosphere and hence make the measurement of low humidity possible. In these references stable colloidal silver has been prepared by reduction of silver nitrate with 254 nm UV light in the presence of poly (N-vinylpyrrolidone), Au nanoparticles were prepared by the chemical reduction of HAuCl₄ for studying nonlinear optical response of the film. The present study focuses on the possible humidity sensing application of the synthesized materials.

In the study below, in section I, the synthesis and characterization of Ag nanoparticles by electrochemical route is presented. The preparation of metal-polymer nanocomposite in Polyanilene (PANI) and further their humidity sensing by optical transmission is included. In section II, synthesis and characterization of Ag/Au nanoparticles and core shell of these in Poly Vinyl Pyrrolidone (PVP) matrix is carried out. The samples are characterized for humidity sensing by electrical measurements.

The main goal of the study is to explore the possibility of using (Ag, Au) in PANI and PVP matrix as a humidity sensor material.

Section I

4.2 Synthesis of Ag nanoparticles by electrochemical route

4.2.1 Experimental

The electrochemical synthesis method for Ag nanoparticles used in the present study is a modified version of the one originally used by Reetz and Helbig [25] for the synthesis of Pd nanoparticles. The method is suitable for the synthesis of metal nanoparticles.

A two electrode electrochemical cell is devised in which the sacrificial anode is in the form of bulk metal sheet to be transformed into
corresponding metal ions (metal nanoparticles). Platinum in the form of a foil, served as a cathode. The distance between the two electrodes is maintained to about 1.0 cm. An electrolyte, containing a mixture of 40 ml of Acetonitrile and 10 ml of Tetrahydrofuran (THF) (ratio 4:1), along with 0.275 gm of capping agent viz. Tetra Octyl Ammonium Bromide (TOAB) is used. The rod inducing micelle i.e. Cetyl Trimethyl Ammonium Bromide (CTAB) is used in the proportion of 0.02M. The solvents used are freshly distilled. The experimental set-up is shown in Figure 4.1a). Electrolysis is carried out at room temperature, under nitrogen atmosphere for few hours in constant current mode. The experimental procedure is as follows. Initially the solvents i.e. acetonitrile and THF were taken in the electrochemical (E/C) cell and nitrogen bubbling was started with continuous stirring of the solution for about two hours. After about two hours, the capping agent i.e. TOAB was added to the E/C cell which dissolves immediately in the mixture of solvents. The electrolyte was continuously stirred using magnetic stirrer during the electrolysis period to disperse the nanoparticles uniformly in the acetonitrile. Thus, in the overall process the bulk metal is oxidized at the anode, the metal cations migrate to the cathode, and reduction takes place with formation of metal in the zero oxidation state. Agglomeration with formation of undesired metal powders is prevented by the presence of the ammonium stabilizers as described in scheme 1.

Scheme 1. Electrochemical Synthesis of Stabilized Metal Nanoparticles

\[
\begin{align*}
\text{Anode:} & \quad \text{Met}^{\text{n+}} & \rightarrow & \quad \text{Met}^{\text{n+}} + n\text{e}^- \\
\text{Cathode:} & \quad \text{Met}^{\text{n+}} + n\text{e}^- + \quad \text{Stabilizer} & \rightarrow & \quad \text{Met}_{\text{cell}}/\text{Stabilizer} \\
\text{Sum:} & \quad \text{Met}_{\text{bulk}} + \quad \text{Stabilizer} & \rightarrow & \quad \text{Met}_{\text{cell}}/\text{Stabilizer}
\end{align*}
\]
Figure 4.1 a) Electrochemical cell to synthesize metal nanoparticles b) Formation of electrochemically grown TOAB capped metal nanoparticles.
On application of current, the anode dissolves forming metal ions. Higher current density is responsible for faster dissolution of the anode. The mechanism of capping can be explained as follows. The surface of metal clusters is negatively charged. TOAB in solution dissociates to give R₄N⁺ and Br⁻ ions. These R₄N⁺ ions electro-statically bind to negatively charged metal surface thereby preventing further agglomeration. Figure 4.1b) shows the formation of electrochemically produced TOAB capped metal nanoparticles and non-covalent bonding with the metal clusters. The nanoparticles were separated by centrifugation and washed at least three times with acetonitrile. They were immediately dried at room temperature. The nanoparticles can be stored at room temperature in the form of a powder and can be re-dispersed in organic solvents like acetonitrile for further characterization.

The different parameters related to the electrochemical synthesis and the size of metal nanoparticles are as follows:

### 4.2.2.1 The Role of Current Density

The critical size of the nanoparticles is given by [25]

\[
a_{\text{crit}} = \frac{2MT}{tF\eta N}
\]

where \( M \) = molecular weight, \( T \) = surface tension, \( F \) = Faraday constant, \( \eta \) = overpotential, \( N \) = density of the clusters and \( t \) = valency. Accordingly, \( a_{\text{crit}} \) is inversely dependent on the over potential \( \eta \) which is directly related to the current density. The equation explains the relation between the particles size as a function of charge flow. Clearly showing that higher the current density narrower is the size distribution and at lower charge flow large is the particles size for both Ag and Au nanoparticles [25].

In the present study we have varied the current density between 5 mA to 30 mA and the particle size is varied between 15 nm to 30 nm.
4.2.2.2 Solvent Effects

It was reported that polarity of solvent plays a vital role in the growth process of nanoparticles [25]. Higher polarity enhancing the probability of further growth. A reduced electrostatic interaction between the metal colloid and the surfactants in a polar surrounding would be the possible explanation. In a less polar solvent the stabilizing shell (TOAB and CTAB in this case) would more effectively shield the particle against further growth, exact mechanism of growth is not clear as of today [25].

4.2.2.3 Effect of Electrode Distance

It was reported that inter electrode distance has a distinct influence on particle size. It was found that when the distance between anode and cathode was small then the particle size was larger and increases speed of electrolysis. Higher distance produces monodispersed particles. This behavior could be probably due to the transport rates and electrophoretic mobilities [25], which are proportional to the fields and current between the electrodes [25].

4.2.2.4 Formation of metal polymer nanocomposites

All the chemicals and monomers used were of Analytical Reagents (AR) grade and used as received. The solutions were prepared using double distilled water. The polymerization was initiated by drop wise addition of the oxidizing agent, (NH₄)₂S₂O₈ (dissolved in minimum amount of water) in an acidified solution of monomer containing 50 wt% of silver nanoparticles under constant stirring at 0–5 °C. Para toluene sulphonic acid (p-TSA) was used as a dopant, during the in-situ polymerization. The monomer to oxidizing agent ratio was kept as 1:1. After complete addition of the
oxidizing agent, the reaction mixture was capped by stopper and kept under stirring for 24 hours. The greenish black precipitate of the polymer was isolated by filtration and conditioned by washing and drying in an oven at 60°C for 12 hours. The solution before drying in the oven was further used for experimentation.

4.2.2.5 Ag-Polyaniline Sensor

To fabricate Ag-Polyaniline-based humidity sensor, plastic optical fiber (POF) of length 30 cm was used. At the central portion of optical fiber, insulating cover was removed and then carefully the clad of the fiber was removed by heat treatment. This bare portion of the fiber was dip coated with Ag-Polyaniline nanocomposite to get humidity sensitive clad. The coated fiber was further bent to a 'U' shape with a bent radius of 10 mm taking into considerations the penetration depth as reported by Gupta et. al. [26] and Khijwania et. al.[27]. The plastic optical fiber has a polymethylmethacrylate (PMMA) core of approximately 980 μm thickness, with 20 μm thick cladding made of fluoride containing carbon polymer. The refractive indices of the core and cladding are 1.492 and 1.417 respectively. The total diameter of the plastic optical fiber is 2.2 mm with PVC protecting sheath. The fiber ends were wet polished with 600-grain sandpaper for predetermined time to maximize the optical power coupling to the plastic optical fiber. The ends of the plastic optical fiber were connected to a transmitter and receiver. Siemens PFC (plastic fiber components) emitters and detectors were used, which are low cost components. SFH450 emitter diode having a peak emission wavelength of 950 nm and a phototransistor SFH350 (responsivity of 0.3 μA/μW) was used as a transmitter and detector, respectively. The advantage of the Siemens PFC's is the housing aperture into which a plastic optical fiber was introduced without having to remove the cladding, with an additional
benefit of directly centering the fiber onto the transmitter and the detector. A +5V power supply was used to power the transmitter and the detector. The experimental setup is as shown in Figure 4.2.

![Figure 4.2 Experimental setup for measurement of relative humidity](image)

A dome of 6 liter capacity was used for RH measurement; values of RH were adjusted by proper inlet of wet/dry air at room temperature (25–30 °C). The transmitted output light intensity was measured with respect to relative humidity for various values of clad length and particle size of Ag in polyaniline. First the length of cladding was optimized and then the particle size dependence was studied. The change in the %RH was measured directly, using a precalibrated hygrometer (Vaisala Humidity & Temperature Indicator HMI 31). The output voltage of the receiver (detector) as a result of change in humidity was measured using a Rishcom digital multimeter (Agilent DMM U1241A). The material characterization was done by X-Ray Diffraction (XRD), Uv–Visible spectroscopy (UV), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).
4.3 Structural characterization of pure Ag nanoparticles as well as polymerized (PANI) samples

X-Ray diffraction was performed with a Philips X-Ray diffractometer (Cu Kα as radiating wavelength). Uv-Vis spectra of the nanocomposites in acetonitrile were recorded by using Perkin Elmer spectrophotometer in the range of 200–800 nm. FTIR spectra of the samples were recorded on a Perkin Elmer-Spectrum 2000 spectrophotometer operated between 400 and 4000 cm⁻¹ in a KBr medium. The powder morphology of the composites in the form of film was investigated with an analytical Scanning Electron Microscope JEOL JSM 6360 A.

4.3.1 TEM

TEM of one of the representative samples of pure Ag nanoparticles (Figure 4.3) show that the size of the spherical nanoparticles to be less than 10 nm.

Figure 4.3 TEM images of the samples

This data was taken in the initial stages only to confirm that the nanoparticles are formed. A one to one comparison between the size obtained from TEM and XRD was not possible due to lack of TEM facility.

Size of Ag nanoparticles in other samples was calculated from XRD by using Scherer formula. The particles were dispersed in polymer (PANI) to
study humidity sensing further. The presence of pure Ag nanoparticles was confirmed by using XRD.

4.3.2 XRD of Ag pure and Ag-Polyaniline nanocomposite

XRD of Ag pure and dispersed in PANI is presented. The Ag pure sample shows peaks which confirms that the samples are polycrystalline in nature. The XRD spectra confirms that the structure is FCC with \( a = 4.0862 \) Å (PCPDF card no 04-0783) (Figure 4.8a)). Generally polyaniline is amorphous in nature and hence there are no sharp peaks found for Polyaniline. Literature study shows that polyaniline is having peaks at 11°, 19°, 26° and 56°. Figure 4.8b) shows the XRD spectra of Ag-Polyaniline nanocomposite with variable sizes of silver nanoparticles where intense peaks are having 2θ values of 26° and 56° correspond to the peaks for polyaniline [28]. Especially the sharp peak at 26° (in our case) reveals the crystalline nature of the composite resulted due to the sequential growth of polyaniline chain on the silver nanoparticles. Intense sharp peaks of silver sulphide are seen at 2θ values 35° and 37.2° with corresponding planes (0 2 2) and (1 0 3). Peaks corresponding to 2θ values 38.2° and 44.2° reveal the crystalline nature of silver in planes (1 1 1) and (2 0 0) respectively. 2θ values of 53.9° give the corresponding peak of AgCl in (2 0 1) plane. The particle size of silver nanoparticles is calculated from XRD with the help of Scherer formula. Figure 4.4 shows the variation of particle size of silver nanoparticles where the peak intensity is shifting as per the particle sizes. As particle size increases, XRD peak height increases for the same material [31]. The sizes shown in the inset are calculated by considering the most intense peak with an error of about ±5 nm.
4.3.3 Uv-Vis absorption

The Uv-Vis absorption of the pure Ag nanoparticles and nanorods are presented as shown in Figure 4.5. It shows two absorption peaks corresponding to the transverse and longitudinal plasmon resonance. The Uv-Vis absorption spectrum of Ag nanoparticles is presented in Figure 4.5a). A sharp peak at 413 nm is obtained corresponding to the Ag bulk nanoparticles. This was the case when only TOAB surfactant was used. With the addition of CTAB as a co surfactant then the shape of the nanoparticles changed to rod like. The shape change can be estimated from the Uv-Vis, where in addition to the Surface Plasmon Resonance (SPR) at 420 nm (absorption peak corresponding to bulk Ag) there is one more peak appearing at 681 nm. The peak at around 420 nm is due to
transverse surface plasmon and higher wavelength is attributed the longitudinal oscillations in the surface plasmon [30]. Figure 4.6 shows Uv-Vis absorption spectra of Ag-Polyaniline nanocomposite for different silver particle sizes. The absorption peaks around 400-420 nm are originating from the surface plasmon resonance absorption of nanosized silver particles. Uv-Visible spectra show that the prominent peak of silver is shifting from 420 to 400 nm with decrease in particle size. Particle size reduction is supported by shift in absorption peak from red to blue region of wavelength [31]. Thus for bigger particle size of silver (30 nm), the absorption peak is found at 420 nm and for smaller particle size (15 nm) that is shifting towards 400 nm.
4.3.4 SEM

The SEM of pure Ag nanorods prepared by using surfactants TOAB and CTAB in an appropriate proportion is presented in Figure 4.7. From the SEM, (Figure 4.7), it can be concluded that the structures are formed in a branchlike fashion with a diameter of about 500 nm and length is about 10-15 μm. More experimental optimization is required in order to make isolated uniform rod structures. The optimization of parameters such as the ratio of TOAB to CTAB, the proportion of current and the time of current flowing through the anode needs to be optimized further. The SEM studies with the increasing particle size of Ag nanoparticles in Ag-PANI nanocomposites for the humidity sensing study are presented (Figure 4.8). The dispersion state of particles affects the performance of the sensor. Here the Ag nanoparticles are dispersed while polymerization of aniline. Hence more or less they are dispersed in the same way. From Figure 4.8 it is clear that the clad is more porous for small particle size. Hence smaller particle size of Ag nanoparticles offers more sites for interaction of water molecules offering maximum sensitivity. For higher particle size the
numbers of voids are reducing which results in lower sensitivity for humidity.

![SEM images of rod shaped silver nanoparticles](image)

Figure 4.7 SEM of rod shaped silver nanoparticles

### 4.4 Humidity sensing study

Optical fiber-based Ag-Polyaniline humidity sensor works on the principle of the evanescent wave adsorption. As the electromagnetic wave in the form of incident light guided propagates through the sensing region, the optical power in evanescent tail of the propagating mode is absorbed with the change in the environmental parameter i.e. humidity. This results in a modulated output from the fiber, which is used as the criterion for detecting and determining the relative humidity in the surrounding environment. As there is a difference between refractive indices of core and cladding, the light traveling through the fiber is divided into two parts. A
Figure 4.8 Scanning Electron Micrograph (SEM) of Ag-Polyaniline nanocomposites for different Ag particle sizes (nm): a) 15 b) 18 c) 21 d) 24 and e) 30.

small portion of the optical power in the guided modes extends to the cladding region and interacts with the clad and larger portion of the optical power is available in the sensing region as the surface evanescent waves. This light is interacting with the mediating reagent in the coated film, which gives an outward shift in the peak intensity of the light travelling through the fiber. This phenomenon of sensing is also supported by bending of the fiber. The response of the optical fiber towards humidity is checked for bare i.e. PMMA based fiber. As PMMA itself is a good sensing material for humidity, the correction for the same is done. The optical fiber has a core refractive index of 1.492 which is greater than the refractive index (1.413) of the coated film used. The core and clad refractive index
difference results in more leaky radiation field. For higher humidity the confinement of light in the fiber is more as the refractive index decreases with increase in the humidity and vice versa. The change in output with respect to change in input is known as sensitivity which increases with increase in humidity. To study the Ag-Polyaniline-based humidity sensor in detail, several experiments for clad-length variation of optical fiber and particle size variation of Ag in polymeric nanocomposite were done. Figure 4.9 shows the effect of variation of Ag-Polyaniline deposited clad of an optical fiber on humidity response. The length of deposited clad was varied from 2-8 mm. From Figure 4.9 it is clear that the clad with 6 mm length shows maximum sensitivity towards humidity. There is gradual increase in the sensitivity with increase in the clad length up to 6 mm. This is because the increase in the clad length causes availability of larger interacting area for adsorption of hydroxyl ions which causes increase in the sensitivity. Adsorption of water changes the transmission properties of nanocomposite films, which leads to a change in the effective refractive index. As the evanescent tail has only a small fraction of power, a longer portion of fiber is needed to be coated to have an effective interaction of light with the nanocomposite and hence a detectable change at the output. Bending the fiber transfers power from the guided modes to the leaky modes, providing more power to interact with the nanocomposite in the sensing region. This results in high sensitivity with a relatively small interaction length [26, 27]. Hence 6 mm of clad length was considered as an ‘optimal length’ which gives maximum confinement to the transmitting beam. Though the clad-length variation study shows 10 mm optimized clad length for Co-Polyaniline nanocomposites reported by Vijayan et al. [31], 6 mm is optimized for the Ag-Polyaniline nanocomposite. This variation in clad length is because the different material properties of the nanoparticles used as a cladding material. Because of the Co nanoparticles, more attenuation takes place in the transmitted light. Hence the active surface area available for sensing mechanism increases resulting in the large clad
length of 10 mm for maximum sensitivity. The larger surface area Ag nanoparticles require smaller active area for higher sensitivity applications. Hence the 6 mm of clad length is optimized for Ag-Polyaniline nanocomposite. Thus beyond the clad length of 6 mm, the sensitivity of this typical Ag-Polyaniline sensor decreases because of the decrease in confined light through the fiber. This might be happening due to the absorption of transmitted light by cladding material in addition to the obvious losses offered by the fiber which decreases the intensity relatively the sensitivity. This optimized clad length was used for further experimentation for particle size variation (15–30 nm) of Ag nanoparticles in Polyaniline composite. Figure 4.10 shows the response of particle size variation of Ag nanoparticles in Ag-Polyaniline nanocomposite for relative humidity sensor with better sensitivity. As the relative humidity increases, the sensitivity increases. The adsorption of water molecules on the film surfaces with large surface area and capillary pores increases the sensitivity. The water molecules adsorbed on the grain surface as well as in the pores (grain boundaries). The Ag- Polyaniline films are having nanosized grains and pores which play vital role in humidity sensing. The nanoscale grain size leads to many boundaries and nanopores, leading to more active sites available for condensed water to react [32]. The higher surface area provides more sites for water adsorption [33]. From the graph it is clear that as the particle size of Ag nanoparticles decreases, the sensitivity of the sensor increases. Particle
Figure 4.9 Humidity response of Ag-Polyaniline nanocomposite for 2–8 mm clad lengths.

size of 15 nm shows a maximum sensitivity (28.78 mV/%RH) for 6 mm clad length with almost linear fit of the plot. It is obvious that the increasing particle size, decreases the sites for adsorption of water molecules which reduces the sensitivity. This behavior is also supported by the SEM (Figure 4.8). The dispersion state of particles affects the performance of the sensor. Here the Ag nanoparticles are dispersed while polymerization of aniline. Hence more or less they are dispersed in the same fashion. From Figure 4.8 it is clear that the clad is more porous for small particle size. Hence smaller particle size of Ag nanoparticles offers more sites for interaction of water molecules offering maximum sensitivity. For higher particle size the numbers of voids are reducing which results in lower sensitivity for humidity. Due to the pores light penetrates deeper inside the clad elongating evanescent field of guide into clad. During this process some part of the light reflects back to the guide from clad-guide interface or scatters from the pores of the clad and overlaps with Evanescent Field (EF) of guide at the clad-guide interface. This maintains
the coupling between the guide and clad. The smallest Ag particle size of 15 nm gives higher

![Graph showing humidity response for variable Ag particle sizes](image1)

**Figure 4.10** Humidity response of Ag-Polyaniline nanocomposite for variable Ag particle sizes (15–30 nm) in polymeric composite for fixed clad length of 6 mm.

![Graph showing sensitivity towards humidity](image2)

**Figure 4.11** Humidity response for variable particle sizes of Ag in Polyaniline nanocomposite at 5 %RH.

sensitivity towards humidity. This statement is supported by Figure 4.11 which shows the response of variable particle sizes of Ag nanoparticles in polyaniline composite for sensing humidity at fixed humidity of 5 %RH. Also concentration of the Ag particles plays a vital role in enhancing the sensitivity of the sensor [34]. For smaller particle size, surface to volume
ratio increases. Hence the number of particles in the same area increase. As conducting particle density increases, effectively sensitivity of the sensor also increases. Small particle size of Ag in Polyaniline provides large number of sites for conduction mechanism. Due to its small size it appears to be having good mobility and hence has enhanced sensitivity. The smaller particle size gives larger specific surface area [35].

The water molecules first physically adsorb on the surface of the film and then penetrate inside the film. After penetrating deep inside the film, chemisorption takes place. The dissociation of water molecule can be considered as surface reaction leading to the formation of surface oxides. This effectively changes the boundary conditions at cladding-guide interface increasing the beam confinement in the guide. Therefore, the output intensity through the cladded guide increases. The nanoparticles study states that for particular size of the nanoparticles, critical quantum confinement takes place. Because of this the properties of the material changes a lot. Hence for smaller Ag particle size (<15 nm) may the quantum confinement take place which may either increase or decrease the sensitivity of the sensor. Interaction of water molecules with the film surface causes the sensing of humidity. The sensitivity curves of Ag-Polyaniline nanocomposite show almost two regions of sensitivity, which may be due to surface adsorption of water vapor; being away from the actual guide will have lesser effect producing less sensitivity in lower humidity region. The diffusion of the vapors deep in the pores and adsorption on the pore wall exhibiting higher sensitivity in higher humidity region. In the present case the physisorbed and chemisorbed water molecules add to refractive index (RI) enhancing the effective clad index. The increase in clad index enhances evanescent field (EF) and hence losses in the clad. The initial RI of the clad are less than guide RI as required for optical waveguides. These are higher than air RI therefore they offer higher transmission loss and leaky field in the clad. The leaky field increases with
increase of clad RI and may be quite high as the clad RI goes beyond the guide RI leading to quite high radiation loss.

![Hysterisis Curve](image)

**Figure 4.12** Hysteresis curve of Ag-Polyaniline nanocomposite having 15nm Ag particle size.

Addition of Ag nanoparticles plays great role in sensing humidity. When the film of Ag-Polyaniline was exposed to low humidity, sensitivity of the sensor is found to be low. This is because under dry conditions the polymer chains tend to curl up into a compact, coil form restricting the mobility of the Ag particles. On the other hand, at higher humidity, polymer adsorbs water molecules and gets hydrated uncurling of the compact coil takes place and they form straight chains that are aligned with respect to one another. Physisorption or chemisorption will change two parameters effectively viz. electrical conductivity and refractive index of the material. In this case the refractive index of the material of the clad changes with the relative humidity. The charge transfer or proton ion formation gives an increase in conductivity while the presence of water molecules in the film contributes towards the change in refractive index. The measurement of either parameter will give response to ambient in which the material is present [34]. The maximum difference in the two outputs (increasing and decreasing cycle) at the same RH level is defined as hysteresis which is observed to be nearly 1 % for all the particle sizes.
Figure 4.12 shows the hysteresis graph of the particle size of 15 nm. Slow desorption of the water from the pores of the capillary results in the hysteresis at lower humidity. The hysteresis and nonlinearity in the response is attributed to the capillary condensation which occurs at higher humidity, and forms a meniscus over the capillaries of the film. The sensor shows quick response of 30 s (10–95 % RH), recovery time of 90 s (95–10 % RH). In this case the response is quite fast and recovery is slow.

4.5 Ag, Au nanoparticles in PVP matrix by chemical route for humidity sensing

4.5.1 Experimental

This section deals with the method of material synthesis by chemical route. The experimental set up of home made humidity sensor is discussed.

4.5.1.1 Material synthesis

All chemicals used were of AR grade. Gold and Silver Chloride solution (0.01 M) of 10 mL (to maintain the final concentration of Au (0), Ag (0) about 2 wt% of PVP) was added to a viscous solution of 1 gm of PVP and was dissolved in 25 mL water. The molecular weight of PVP is 10,000. The reaction mixture was stirred at room temperature. A separate solution of a diluted hydrazine hydrate was prepared in water. 2 μL of it was added by a micro syringe in the above reaction mixture. Ag/Au-PVP nanocomposite is characterized by X-Ray Diffraction, Uv-Visible spectroscopy, Scanning Electron Microscopy (JEOL JSPM 5200). The films of these are characterized for humidity sensing further.
4.5.1.2 The sensor arrangement and humidity sensing study

A simple experimental set-up is fabricated in order to investigate the humidity sensing properties of the film as shown in Figure 4.13 a). It consists of a closed glass chamber (volume- 6 liters), with a neck for inserting a sample under test and a probe of standard vaisala humidity meter (humidity range-0 to 100 %RH with an accuracy of 1-5 %RH for different humidity ranges). The chamber was kept on an aluminium plate and was sealed from outside by modeling clay to make the system airtight. The substrates used are ceramic rods having built-in electrodes. The PVP and Ag or Au composite nanostructures were drop coated (2 µlit of each drop) on the substrates as shown in Figure 4.13 b).

Special care is taken to get a uniform film on the ceramic cylindrical substrates. The resistors were dried at room temperature and then they were kept inside the jar where humidity is controlled by passing hot water vapors (Figure 4.13 a)). After achieving the maximum humidity the vapor supply was stopped and phosphorus pentoxide (P₂O₅) was inserted inside the jar for dehumidification. The resistance of the films was measured with decreasing humidity by using the formula

\[ R_s = R_{ref} \times (\frac{V}{V_{ref}}) - 1) \]

Where,
- \( R_s \) = Resistance of the sensor
- \( R_{ref} \) = Reference Resistance
- \( V \) = Applied Voltage
- \( V_{ref} \) = Voltage drop across the reference resistance.
The resistance of the sample was measured as a function of relative humidity by using the half bridge method. The circuit diagram is as shown in Figure 4.13c). In half bridge method a constant DC supply of 5 V is applied across the film and reference resistance. The voltage drop across the reference resistance was measured. The film resistance is calculated using equation 4.2. The sensitivity of the film was defined as the \((\Delta R / \Delta \%RH) \ \Omega/\%RH\).

4.5.1.3 **Determination of water sorption in the sensors**

The humidity sorption capacity of each film is measured by finding out the weight change of the film at room temperature RH and in the presence of highest humidity i.e. 90 \%RH. (Weighing balance mode number AX 26, Delta range settler Toledo and accuracy-0.002 mgm).
4.5.2 Results

This section presents the results obtained out of the above mentioned synthesis procedure. Humidity sensing results are presented further. The samples are studied by using Uv-Vis for optical characterizations, XRD for finding out the phases of the samples. SEM of the samples is taken to study the variation in surface morphology with increasing thickness. Finally the humidity sensing study is presented.

4.5.2.1 Uv-Vis absorption

The Uv-Vis absorption spectra are presented as in Figure 4.14 a) for Au-PVP and b) Ag-PVP nanocomposites. The absorption peak in both the graphs at 220 nm is corresponding to polymer PVP [21, 22]. The absorption peaks of 528 nm and 408 nm are present corresponding to absorption of Au and Ag nanoparticles respectively due to surface plasmon resonance. The Uv-Vis absorption data reveals that two distinct absorption peaks are present in the nanocomposites. This confirms that there is no mixed phase or alloy like coreshell material present in the system and the nanocomposite consists of metal nanoparticles and polymer PVP working as a matrix, individually.
4.5.2.2 XRD study

XRD of Au/PVP is as shown in Figure 4.15 a), the peaks corresponding to 38.4°, 44.6° and approximately at 64° correspond to Gold(111), Gold(200), Gold(220) corresponding to the face centered cubic (fcc) structure of Gold. The XRD pattern of Ag/PVP nanocomposite film is shown in Figure 4.15 b). The XRD pattern revealed that silver nanoparticles were in the form of face-centred cubic (fcc) crystal in PVP matrix film, as indicated by the diffraction peaks with 2θ values of 38.3°, 42.5°, 63.5° corresponding to the (111), (200) and (220) crystal faces of the fcc crystalline silver. The characteristic peaks of PVP are found to be in the lower diffraction angle range. The broad peaks between 17°-24° (Figure 4.15) are attributed to the amorphous nature of pure PVP [21, 22].
Figure 4.15 XRD spectra of a) Au-PVP b) Ag-PVP nanocomposite

4.5.2.3 Humidity sensing study

In this section first the choice of the sensor design and sensor study is discussed.

4.5.2.4 Choice of sensor design

Most of the gas sensors are fabricated either to form a parallel capacitor with the sensing ceramic sandwiched between two electrode plates [34] or in the form of a resistor. The capacitive type of sensor exhibits a high sensitivity to humidity change in the higher RH level because of higher dielectric constant of water (~81). However, it has a long response time since the water molecules must diffuse through the electrodes to reach the sensing layer. Usually, a very thin evaporated metallic film of tens of nanometers is used for electrodes in order to improve the response characteristic. Unfortunately, the thinnest screen printed films are about few μm thick, i.e. about 1000 times thicker than an evaporated film. As a consequence long response times are expected from thick-film sensors with a parallel capacitor configuration. The other configuration has an interdigitated electrode printed below the sensing layer [36-38]. This type
of sensor has a shorter response time since water molecules can directly reach the sensing ceramic surface, but the sensitivity is low, especially at low humidity values. In the present study cylindrical ceramic rods with built-in electrodes are used as substrates and sensing material is coated between these electrodes for electrical measurements. The size of the resistor is as shown in Figure 4.13 b).

From Figure 4.16 a) it is observed that for the first layer thick film Au/Ag-PVP nanocomposite that the samples are sensitive to humidity. The sensitivity range of the samples is 90-42 %RH for Au-PVP sample and 90-58 %RH for Ag-PVP sample. The resistance of the film goes on decreasing at high humidity. The sensitivity for one layer thick films of Au-PVP nanocomposites for the range of 90-60 %RH is 1.35E7/%RH and in the range of 50-60 %RH the sensitivity 4.515E9/%RH. In the same region for 90-58 %RH however the sensitivity of Ag-PVP nanocomposite is 10E7/%RH, Figure 4.16 b).

![Graph showing sensitivity vs humidity range](image)

Figure 4.16 a) Au-PVP sample layer1 and Ag-PVP sample layer1 b) Sensitivity (%RH) Vs Humidity range covered.

The sensitivity of Ag-PVP nanocomposite is higher than that of Au-PVP nanocomposite. It is attributed to the smaller size of Ag-PVP and higher mobility of Ag than Au. From the sensitivity values it is observed that the
films are highly sensitive to humidity and the sensitivity goes on increasing with decreasing humidity. The increase in conductivity of the film at high humidity range is due to humidity absorption. The humidity absorption phenomenon is attributed to the surface pores on the films. These pores will provide more adsorption sites for humidity.

In order to study the thickness effect in the film towards humidity sensing, two to six layer thick films of Au-PVP and Ag-PVP nanocomposites were prepared. It was observed that with the increasing thickness the film resistance decreases under identical humidity conditions as shown in Figure 4.17 a) and b). This is because the increasing thickness induces more number of Ag/Au nanoparticles in the film and the intergrain distance decreases. Maximum range of humidity (3-90 %RH) is covered for six layers thick films of both the samples as shown in Figure 4.17 a) and b).

![Figure 4.17 Humidity response curve for 1-6 layer films of a) Au-PVP b) Ag-PVP](image)

The high sensitivity of the films is expected in general because of the presence of metal nanoparticles in the film. The nanostructures are known to have more surface area providing more number of adsorption sites for the humidity. The nanoscale grain size leads to much more grain boundaries and nanopores, leading to more active sites available for
condensed water to react [36-38]. The water vapor is adsorbed on the grain surface and in the pores. For one to four layers the films show large increase in resistance with decrease in humidity up to 30 %RH. With further increase in the thickness, more number of sites are available for the humidity sorption. The porosity of the film is increased with the increase in thickness because the pore column height and may be the number of pores increase with the increasing thickness. Increase in porosity of the film is confirmed by measuring the weight change in the film before and after exposure to the humidity as shown in the Figure 4.18.

![Figure 4.18 Water absorption capacity of a) Au-PVP sample b) Ag-PVP sample](image)

The measurements were taken at room temperature and at higher humidity i.e. about 30% and 90% humidity. It is observed that with the increase in thickness the amount of moisture sorption in the film goes on increasing. The increase in porosity of the films was confirmed further by taking Scanning Electron Microscopy (SEM) of the samples as shown in Figure 4.19 and 4.20. The size of gold nanoparticles embedded in PVP is about 1 μm. Au particles are seen distinctly on the film due to their higher size and density. Ag nano particles are found to be embedded fully in the PVP matrix. It can be observed that in case of Au-PVP samples, structures
are not dispersed in PVP matrix as observed in SEM and show lower resistance in the electrical measurements as compared to Ag-PVP film. At higher thickness the Ag-PVP structures are agglomerated but the structures are properly dispersed. Spongy structures of Ag-PVP samples are observed for one layer thickness as shown in SEM.

The films of Ag-PVP samples at higher thickness are showing self aligned layer like formation with spongy nature and voids are created in the film. These voids and sponge like structures provide more number of pores and adsorption sites for humidity. Sensitivity curves for six layer thick films of Au-PVP and Ag-PVP plotted as shown in Figure 4.21 a). The range covered by Au-PVP sample is more than that of Ag-PVP sample Figure 4.21 b). However the sensitivity of Ag-PVP sample is higher than that of Au-PVP
samples. This is attributed to small size of Ag nanoparticles than that of Au particles. The Ag nanoparticles size less than 50 nm.

Therefore more number of Ag nanoparticles is present on the surface of Ag-PVP films than that of Au-PVP film samples for their same layer thickness. These particles provide more number of sites for humidity absorption. Thus, water adsorbing capacity of the film is increased at higher thickness.
Therefore the film shows conducting behavior (Low resistance) till very low (3 %RH) humidity for six layer thick film. The sensitivity of the films is especially noticeable in 3-10 %RH range as shown in Figure 4.21 b). PVP is a bad conductor. The conduction is governed by the amount of Ag or Au nanoparticles and also the inter grain distance. As

![Figure 4.21 Sensitivity of a) Au-PVP nanocomposite and Ag-PVP nanocomposite at 6 layer thickness b) bar chart of sensitivity](image)

a result, the variation in the distance among Ag or Au nanoparticles and their number in the film go on increasing with the thickness. Thus the water sorption capacity of the film is also increased. Due to swelling of the surface facing water vapor and contraction of the surface near to the substrate for 5th and 6th layer the resistance of the films is comparatively low at lower humidity as shown in Figure 4.17 a) and b). The resistance of these samples changes slightly with the decreasing %RH and senses up to considerably low humidity. The sensitivity of the Ag nanoparticles is more than that of Au-PVP particles (Figure 4.21b)). This is because the atomic number of gold is 79 while that of silver is 47, thus at the ionic level the mass carried by the Ag nanoparticles is smaller than that of Au particles of the same size. Therefore the mobility of Ag nanoparticles is more than Au nanoparticles in the same matrix.
The repeatability of the results is checked for six layer thick films as shown in Figure 4.22 a) and b). Three films of the both the samples are tested. It can be seen that the films show excellent repeatability.

![Repeatability curve of Au-PVP and Ag-PVP film](image)

**Figure 4.22** Repeatability curve of a) Au-PVP b) of Ag-PVP film

The protonic conduction for humidity sensing is explained in general on the basis of Grotthuss mechanism. The low resistance or the change in sensing behavior in five and six layer thick films in the presence of low humidity (below 20 %RH) can be justified on the basis of the composition of the nanocomposites. In humidity sensor the two constituents (Ag or Au and PVP organic-inorganic composite) of the nanocomposite are responsible for sensing the humidity. The concentration of water molecules surrounding the polymer affects the film resistance. PVP is having high affinity towards water. It adsorbs water molecules at higher humidity decreasing the resistance of the film. Due to the adsorption of water molecules swelling occurs [36]. At low humidity, some water molecules from PVP are removed; which increases the film resistance. Except the first monolayer the water molecules are not very tightly or loosely bound to the film. Hence even at low humidity range the actual percentage of water molecules inside the film may be considerable to keep the resistance low. This is a reversible process carried out between dry and wet states [35]. The sensitivity contribution at one layer thickness is mainly due to surface adsorption layers. At this thickness the surface layer is the dominating
parameter for humidity sorption. With the increasing thickness the pores and the pore walls in the film start developing hence the sensitivity is attributed to adsorption at the pores capillary. With the increasing thickness the pores and the pore walls in the film start developing hence the sensitivity is attributed to adsorption at the pores capillary.

Figure 4.23 The adsorption phenomena of water molecules on film a) At lower humidity (surface adsorption) b) At intermediate humidity (adsorption on capillary walls) c) At higher humidity (full capillary condensation)

In our study the sensitivity curves were divided into three regions, -1. The sharp drop at lower humidity region. 2. Curved region between the extreme high resistance and extreme high humidity (low resistance) 3. Flat region at higher humidity value. The sharp increase in resistance at lower humidity in every film is attributed to the available surface sites as shown in Figure 4.23 a). The sensitivity is highest for this region as shown in Table 4.1. With desorption of humidity from the surface sites the resistance of the film increases rapidly. It is observed that the films are having same order of sensitivity in this particular region for all thickness as shown in Table 4.1, indicating that the surface contribution is
unchanged with the increase in thickness. In the second region the sensitivity is attributed to two phenomena. First is the adsorption at the pore walls; second is the capillary condensation in the pores of the films as shown in Figure 4.23 b). With the increase in the thickness width of this sensitivity region goes on increasing 13 %RH and 18 %RH at one layer thickness to 43 %RH and 35 %RH in 4 layer thick films of Au-PVP and Ag-PVP. However when the wide range of sensitivity is covered the sensitivity is found to decrease as shown in Table 4.1 and 4.2. At 5, 6 layer thick films the wider range of humidity is covered however the sensitivity is remaining low as compared to the first four layers. Therefore it can be inferred that, wider range of humidity is covered by these films at the cost of the lower sensitivity at higher thickness. In the third region when the highest humidity is present between 70-90 %RH, the sensitivity is dominated by the capillary condensation and the film shows conducting behavior. The sensitivity of all the films up to first four layers is of the same order at high humidity. Thus sensitivity is highest in first region of the films. Indicating that humidity sensing mechanism is due to surface sites. These surface sites are responsible for the measurement of low humidity at room temperature.

Thus in order to use these samples from a particular application point of view; a compromised balance between sensitivity of the film or a wide humidity range has to be achieved. Also, appropriate selectivity in the humidity range can be achieved by choosing appropriate thickness. In order to justify the proposed phenomena of surface adsorption, pore wall adsorption and the capillary condensation; sensitivity curve fitting was obtained for first, second and third order exponential decay.

a) one layer thick film- 1st order decay  
b) Two layer thick film- 2’nd order decay  
c) Three layer thick film-2’nd order decay  
d) Four layer thick film- 3rd order decay
e) Five layer thick film - 3rd order decay
f) Six layer thick film - 3rd order decay

Figure 4.24 Sensitivity curves for one to six layer thickness of Au-PVP nanocomposite

Figure 4.25 Sensitivity curves for one-six layer thickness of Ag-PVP nanocomposite
a) One layer thick film - 1st order decay
b) Two layer thick film - 2nd order decay
c) Three layer thick film - 2nd order decay
d) Four layer thick film - 3rd order decay
e) Five layer thick film 3rd order decay
f) Six layer thick film 3rd order decay

It is observed that the sensitivity curves are showing exponential decay of first and second order for initial three layers as shown in Figure 4.24 a)- c) and 4.25 a)- c); shows third order exponential decay for higher thickness (4-6 layers) as shown in Figure 4.24 d)- f) and 4.25 d)- f). The physical significance of the first order exponential decay in sensitivity is contributed by the surface sites. The second order exponential decay in the sensitivity curve signifies that desorption of humidity from the film depends on two phenomena namely: 1) the surface desorption and 2) from the pore columns present in the film. As the film thickness goes on increasing the sensitivity curve shows third order exponential decay. The third order exponential decay signifies that desorption depends on three parameters namely 1) desorption from surface 2) desorption from wall surface sites of the pores 3) desorption from the pore column inside the thick film or from capillary condensation. In one and two layers thick films the thickness is very low. Therefore desorption from pore walls surface sites is negligible. The increase in thickness of the film induces the pore walls and the pore size is increased. Hence the humidity desorption depends on the three parameters at higher thickness. From the above discussion, the proposed mechanism of the surface adsorption, pore wall adsorption and the capillary condensation are justified on the basis of exponential decay curves.
<table>
<thead>
<tr>
<th>Au-PVP Film</th>
<th>sharp fall region and its range</th>
<th>Sensitivity in the sharp fall region.*10 (^{\Omega}/%\text{RH})</th>
<th>Second/middle region and its range</th>
<th>Sensitivity in the second/middle region.*10^{\Omega}/%\text{RH}</th>
<th>third region and its range</th>
<th>Sensitivity in the third region(\text{High humidity region})*10^{\Omega}/%\text{RH}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>(43,50)</td>
<td>3595.3</td>
<td>(50,63)</td>
<td>736.72</td>
<td>(63,90)</td>
<td>10.97</td>
</tr>
<tr>
<td>Layer 2</td>
<td>(32,45)</td>
<td>3998.7</td>
<td>(45,66)</td>
<td>165.62</td>
<td>(66,90)</td>
<td>7.18</td>
</tr>
<tr>
<td>Layer 3</td>
<td>(28,34)</td>
<td>3827.0</td>
<td>(34,69)</td>
<td>40.49</td>
<td>(69,90)</td>
<td>9.99</td>
</tr>
<tr>
<td>Layer 4</td>
<td>(25,29)</td>
<td>6333.7</td>
<td>(29,72)</td>
<td>9.34</td>
<td>(72,90)</td>
<td>3.37</td>
</tr>
<tr>
<td>Layer 5</td>
<td>(8,13)</td>
<td>1778.3</td>
<td>(13,75)</td>
<td>2.03</td>
<td>(75,90)</td>
<td>1.58</td>
</tr>
<tr>
<td>Layer 6</td>
<td>(3,11)</td>
<td>1110.1</td>
<td>(11,77)</td>
<td>1.77</td>
<td>(77,90)</td>
<td>7.05</td>
</tr>
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</table>

Table 4.1 Au-PVP sensitivity over three regions
Table 4.2 Ag-PVP sensitivity over three regions

<table>
<thead>
<tr>
<th>Ag-PVP Film</th>
<th>First region and its range</th>
<th>Sensitivity in the first region*10^6 Ω/%RH</th>
<th>Second/middle region and its range</th>
<th>Sensitivity in the second/middle region*10^6 Ω/%RH</th>
<th>Third region and its range.</th>
<th>Sensitivity in the third region (High humidity region) *10^6 Ω/%RH</th>
</tr>
</thead>
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<td>Layer1</td>
<td>(62,55)</td>
<td>6347.7</td>
<td>No Second region for the first layer</td>
<td>(55,90)</td>
<td>2.26</td>
<td></td>
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<tr>
<td>Layer2</td>
<td>(44,50)</td>
<td>1935.0</td>
<td>(50,68)</td>
<td>35.81</td>
<td>(68,90)</td>
<td>12.88</td>
</tr>
<tr>
<td>Layer3</td>
<td>(37,46)</td>
<td>2210.3</td>
<td>(46,71)</td>
<td>30.19</td>
<td>(71,90)</td>
<td>0.80</td>
</tr>
<tr>
<td>Layer4</td>
<td>(30,41)</td>
<td>1586.2</td>
<td>(41,76)</td>
<td>27.57</td>
<td>(76,90)</td>
<td>15.86</td>
</tr>
<tr>
<td>Layer5</td>
<td>(12,36)</td>
<td>1355.2</td>
<td>(36,78)</td>
<td>3.25</td>
<td>(78,90)</td>
<td>0.95</td>
</tr>
<tr>
<td>Layer6</td>
<td>(3,13)</td>
<td>2787.0</td>
<td>(13,79)</td>
<td>2.94</td>
<td>(74,90)</td>
<td>3.93</td>
</tr>
</tbody>
</table>

Table 4.2 Ag-PVP sensitivity over three regions

4.6 Ag-Au core shell nanoparticles

Preliminary study of Ag core and Au shell nanoparticles grown in situ in PVP matrix is carried out. The sample is characterized by using FESEM, Uv-Vis absorption and XRD. Their humidity sensing study is carried out by using a method mentioned in the previous section and the results are presented below.
4.6.1 FESEM study

The formation of core shell is confirmed by using FESEM as shown in Figure 4.26. Formation of bright colored silver occurs at the centre and gold is a shell. The existence of core shell material is confirmed by EDAX. Still, further characterization is necessary for the confirmation of Ag core and Au shell nanoparticles. With the information at our disposal from FESEM it can be inferred that the core shell particles of approximately 500 nm diameter are formed which are quiet big as compared to Ag/Au nanoparticles in PVP matrix in earlier study.

<table>
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<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgL</td>
<td>33.69</td>
<td>48.12</td>
</tr>
<tr>
<td>AuL</td>
<td>66.31</td>
<td>51.88</td>
</tr>
<tr>
<td>Matrix</td>
<td>Correction</td>
<td>ZAF</td>
</tr>
</tbody>
</table>

Figure 4.26 a) Ag-Au core shell nanoparticles b) EDAX data of the sample.

4.6.2 Uv-Vis absorption of Core shell particles

Figure 4.27 Uv-Vis absorption spectra of Ag core Au shell in PVP matrix
As revealed in Figure 4.27, one observes the feature only due to gold even if amount of silver released in the chemical bath is same as that of gold. Broad gold SP resonance peak is observed. Calculations based on Mie theory as well as experimental investigations [38] indicate that core/shell Au/Ag nanoparticles show a single feature. In the present case, Ag shell does not reveal separate plasmon feature. In other words, Ag does not attain metallic behavior in this case. The optical absorption studies of Au/Ag core/shell nanostructure described by Bright et al. [39] indicate single absorption feature corresponding to either Ag or Au depending on the thickness of the over-layer.

4.6.3 XRD

The peak around 25° is attributed to the amorphous nature of pure PVP matrix [32], whereas there are two peaks at 38° and 43.4° corresponding to Ag/Au core shell structures. XRD confirms that the samples are crystalline in nature (Figure 4.28).

![Figure 4.28 XRD spectra of Ag-Au core shell particles in PVP](image)
Sensitivity curve for Au/Ag core shell-PVP and Ag/Au core shell PVP are for single layer drop coated films shown in Figure 4.29 a). It is observed that the films are sensing up to 42 %RH for Au core Ag shell-PVP samples and up to 45 %RH for Ag core Au shell-PVP samples. The resistance shows exponential decay. It shows two clear regions at relatively low humidity range and high sensitivity range. The sensitivity in the first region is of eleven orders of magnitude and in the second region it is about three orders of magnitude change. The log of resistance against humidity is plotted as shown in Figure 4.29 a). From this figure it can be observed that the films are sensitive to humidity and their sensitivity is plotted as shown in Figure 4.29 b).

4.6.4 Humidity sensing study

![Graphs showing sensitivity curves for one layer thick films of core-shell structures](image)

Figure 4.29 a) Sensitivity curves for one layer thick films of core-shell structures b) Sensitivities for one layer thick films.

The sensitivity at one layer is due to surface sites. Hot water vapors are adsorbed at these sites. The humidity range will increase if more number of sites are available for humidity adsorption. This can be done either by increasing the surface area of the film so that surface sites are available or by increasing the thickness so that more number of pores and pore walls are available for humidity sorption. The choice of increasing thickness is
considered in this study as this will keep the sensor size small. In order to see the effect of thickness; one to four layers thick films were prepared. It was observed that with the increasing thickness the film resistance decreases as shown in Figure 4.30. This is because the increasing thickness induces more number of Ag/Au core shell nanoparticles in the film causing decrease in intergrain distance.

The humidity sensing curves were obtained for these. As shown in Figure 4.30 a). The wide humidity range i.e. 3-90 %RH is covered for four-layer thickness. The graph is plotted for Log R Vs Humidity 4.30 b). That clearly shows the sensing behavior. The sensing behavior in general can be explained due to the presence of nanoparticles in the films.

Au-PVP and Ag-Au-PVP (core shell particle) results can not be really compared in the present study as in the Au-PVP samples the size of the Au particles is large (about 1 μm) and in Ag-Au core shell-PVP films the size is about 500 nm. The Ag-Au interactions might have also contributed in the humidity response. Still, a comparison between the optical and electrical measurements can be attempted. The optical fiber based sensors rely on the diminishing evanescent field by the waveguide. The sensitivity curve
shows more or less linear behavior. The optical fiber has a core refractive index of 1.492 which is greater than the refractive index (1.413) of the coated film used. The core and clad refractive index difference results in more leaky radiation field which maintains total internal reflection in the cladding. The adsorbed humidity coating increases the RI of the sensing material than the core of the optical fiber and due to that there is total internal reflection. This induces maximum output at higher humidity and goes on decreasing with the decrease in humidity. This curve can roughly be divided into two regions. I) Low sensitivity in low humidity region II) high sensitivity in high humidity region. In case of resistive type humidity sensor there is an exponential decay in the sensitivity curve which can be roughly divided into three regions I) sharp fall (low humidity region) II) flat region (high humidity) III) Intermediate region between high and low humidity regions. The films show high sensitivity at low humidity range.

The optical fiber based sensor can be used for applications where entire humidity range is to be covered. In case of electrical response though, as per the humidity range under consideration, the thickness of the film can be optimized. Therefore optimization of the humidity range can be achieved by properly selecting the thickness of the films. More study is to be carried out for lower size of core shell particles.

### 4.7 Conclusions

Ag-Au nanoparticles samples are prepared in PVP matrix in situ by chemical route. The Ag particles are having size of the order of 50 nm and Au nanoparticles are about 200-250 nm size. The Ag nanoparticles are fully embedded in PVP matrix as seen in SEM. The films of these samples show excellent humidity sensing properties Viz-1) high sensitivity over full range (Including 0-20 %RH) 2) Tailor ability of the thickness of the films to measure the humidity range from the application point of view. The Ag-PVP
nanocomposites are showing good response than Au-PVP due to higher mobility and lower size of Ag than Au nanoparticles. For the six layers thick films three humidity absorption phenomena are proposed. Depending on the humidity sensing curves and sensitivity measurements in three regions the proposed phenomena is well justified. PVP can be considered as the candidate for humidity sensing study. The optical fiber clad of Ag-Polyaniline nanocomposite shows good response towards humidity with a wide range of 5–95 %RH. Thus Ag-Polyaniline nanocomposite is a competent material for humidity sensing. Here a simple POF type optical humidity sensor with a cladding layer of nanocomposites has been studied successfully, which is based on the POF structure change from leaky to guided, affected by the adsorption of water molecules. The particle size effect of silver nanoparticles is studied in brief. The smaller particle size facilitates adsorption of more water molecules on the film surface. This sensor has a fast response of 30 s and recovery of 90 s.

References

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