Effect of silane/amine-based dopants on polymer-metal interaction of sub-surface silver nanoparticulate films

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ABSTRACT

The optical and morphological properties of the vacuum-evaporated silver (Ag) nanoparticulate films on softened polyvinyl alcohol (PVA) modified with the 3-mercaptopropyl trimethoxysilane (MPTMS) and 3-aminopropyl trimethoxysilane (APTMS) dopants are reported. The topography of the particulate films is characterized by the field-emission scanning electron microscopy. The optical spectra broadening, red-shift, and the increase in the intensity values of the plasmonic resonance peak with the nature of dopant have a strong dependence on the particle size, shape, and inter-particle separation. The conducted experimental optical studies are supported by Finite Difference Time-Domain (FDTD) simulation results. Quantitative analysis of the Fourier-Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy studies confirm the surface modification of Ag nanoparticulate films on doped PVA substrates. The amount of polymer-metal interaction caused by the strongly interacting silane groups of the dopants and their influence on the morphology and optical properties are discussed.
1 Introduction

The dispersion of nanomaterials in a polymer matrix is estimated to influence their optical, electrical and structural properties, which could be used for applications such as in the energy harvester [1], the transparent conductor [2], in the field of flexible organic electronics [3], and in the optoelectronic devices [4]. The polymer matrix supports to immobilize the dispersing nanoparticles, whereas the dispersed metal particles enhance the optical and electrical properties of the composite thin film. A uniform and a non-agglomerated thin film is an essential aspect for desired properties as well as for applications. Several studies have been carried out by employing different physical and chemical methods to enhance the performance in controlling the morphology of the particulate films. One of the feasible approaches to form such structures is through the vacuum evaporation of metals on a softened substrate [5]. It is well known that the Volmer-Weber growth formation results in a particulate structure when the metals are evaporated on to the substrates at suitable conditions. The degree of sub-surface formation or embedding of metal nanoparticles in a polymer is largely dependent on the physical and chemical nature of the substrate used. Rutherford’s backscattering spectroscopy (RBS) method showed that silver forms the sub-surface structure at a depth of 50 nm in polystyrene [6]. By controlling the fluidity, the tuned chemical nature of the polymer can enhance the polymer-metal interaction, and this could lead to an exciting organization of particulate films. So, the polymer-metal interaction can be tuned by selecting an inert polymer as a substrate [7], modifying the polymer characteristics by electron beam irradiation [6], and also by the blending of an inert-polymer-like polystyrene with an interacting polymer like poly (4-vinyl pyridine) [8]. The other way to tune the metal-polymer interaction and enhance the properties is by selecting a polymer with an interacting side molecular group [9].

Polyvinyl alcohol (PVA) is a water-soluble low-cost synthetic polymer that has got unique advantages such as good mechanical strength, excellent biocompatibility etc. Also, it has shown high flexibility, stretchability, and dopant-reliant optical and electrical characteristics [10–13]. Thus, these properties make it a suitable candidate for many applications such as wearable sensors [14], soft actuators [15], soft strain sensors [16] and such others are some of the prominent examples. It is well known that the functionalization of the substrate surface with the organosilanes plays a vital role in anchoring the metal particles. For instance, the presence of hydrophilic groups such as 3-mercaptopropyltrimethoxysilane (MPTMS with thiol group) and 3-aminopropyltrimethoxysilane (APTMS—with amine active group) promotes the anchoring of the metal particles [17–19]. Therefore, we can expect possible interesting interactions of the silver particle with amine and thiol active groups, thereby influencing the structural and optical properties. Hence, in this investigation, an attempt has been made to tune the polymer-metal interaction by doping PVA with MPTMS and APTMS, and thus tuning their morphology and optical properties of sub-surface silver particulate films. Furthermore, modelling of Ag sub-surface nanoparticulate-undoped and MPTMS-doped PVA substrates were carried out using FDTD simulation to realize the plasmonic resonance shift of metallic nanoparticle systems.

2 Experimental details

The PVA (molecular weight, \( M_w = 30,000–70,000 \)) and the dopants, both MPTMS and APTMS, are procured from Sigma-Aldrich Chemicals Pvt. Ltd. One gram of PVA is dissolved in 20 ml of double-distilled water and is taken in three separate vials to form a homogenous solution. 0.5 ml of APTMS, 0.5 ml of MPTMS, and 0.5 ml of each dopant are added to the individual vials containing the PVA solution and the solutions are thoroughly dissolved. Cleaned glass slides are coated with modified PVA substrates of about 10 \( \mu \)m thickness using HOLMARC dip-coating unit at a controlled rate. Silver depositions are carried out at a temperature much above the glass transition temperature of the corresponding polymer to obtain the sub-surface particulate films. The silver films were evaporated onto the modified PVA substrates held at 413 K in the high vacuum of \( 1.0 \times 10^{-5} \) Torr as shown in Fig. 1. At the time of deposition, a constant distance of 16 cm was maintained between the source and the substrate. The deposition rate and total thickness of the material deposited were measured using INFICON quartz crystal monitor. The deposition rate was maintained at 0.1 nm s\(^{-1}\) for all the films, and the films are
annealed for 30 min at 413 K in vacuum. Afterwards, the samples are allowed to cool to the room temperature in the same vacuum condition. The optical absorption studies were performed by using the SHIMADZU UV–Vis 1800 spectrophotometer at a resolution of 1 nm. To avoid the influence of substrate on the optical properties, same substrate i.e. PVA or doped PVA is used as a reference for the optical spectra of the corresponding films. The morphological analysis was performed using a Field Emission Scanning Electron Microscope (FESEM; Carl Zeiss; EVO-18). Raman spectra recorded using (Horiba XploRA ONE Raman microscope) the backscattered geometry, and laser having an excitation wavelength of 523 nm, were used. The Raman spectra were taken at a 100 × objective length with laser power of ~2 – 5 mW at the sample surface. FTIR studies were carried out using Shimadzu IRSpirit spectrophotometer.

3 Results and discussion

3.1 Optical investigation

It is well known that the optical properties like absorption maxima, peak position, peak sharpness, broadening, and intensity of the sub-surface particulate films depend on the features of material, particle size, particle shape, density of the particles, inter-particle separation, and dielectric medium surrounding the particle [20]. Figure 2a–c show the optical properties of silver films deposited on softened modified PVA substrates at a rate of 0.1 nm s⁻¹.

Generally, for the silver clusters in a polymer matrix, the surface plasmon resonance absorption occurs at a wavelength of ~ 430 nm [6, 7, 21]. In Fig. 2a, it is observed that the silver nanoparticles formed in the undoped PVA substrate show an absorption maximum at ~ 418 nm. The absorption maxima (λ_max) shows a bathochromic shift towards the higher wavelength region, for the films deposited on MPTMS-doped PVA substrates with λ_max at 547 nm, indicating a significant morphological change for the films deposited on the doped PVA substrates compared to the films on undoped PVA. Furthermore, for the 50 nm films, an interesting shift in the pattern is observed. In Fig. 2b, with the increment of thickness by 25 nm, i.e. for the silver films with 50 nm deposited at 413 K, there is a significant shift in λ_max from 421 to 561 nm. Interestingly, this shift is exhibited by the silver films deposited on the APTMS + MPTMS-doped PVA substrates, owing to an increase in agglomeration compared to its undoped counterpart for the same thickness. Therefore, its spectra show a broader distribution compared to Fig. 2a.

Fig. 1 Experimental procedure employed for obtaining sub-surface nanoparticulate films
A similar bathochromic shift is repeated for 75 nm film as shown in Fig. 2c. Besides, with the increasing silver film thickness, the APTMS + MPTMS-doped PVA substrates depict a lower value for absorption maxima of 541 nm compared to its 50 nm counterpart in Fig. 2b. Furthermore, the broad spectra in Fig. 2c speculates a higher probability for non-uniform silver nanoparticle formation on the APTMS + MPTMS-doped PVA substrates. The plasmon resonance properties of nanoparticles are strongly influenced by the substrates as they are often produced on the surfaces [22]. Furthermore, the intensity variation for the doped and the undoped sample is visible in the absorption spectra. Accordingly, the doping has witnessed that the enhancement in silver nanoparticles accounts for the enhanced formation of the silver nanoparticles as the intensity of absorption increases with the silver concentration [23, 24].

Figure 3 shows the absorption spectra for 25 nm films deposited at a rate of 0.4 nm s\(^{-1}\) on modified softened PVA substrates. In the thermal evaporation, the deposition rate and the kinetic energy of the evaporant atoms are related. As the deposition rate increases, the kinetic energy of the evaporant atoms also increases, which then favours the formation of highly agglomerated films due to enhanced mobility. Therefore, the bathochromic shift owing to increased agglomeration is noticed in Fig. 3. The spectrum is broader for silver on APTMS-modified substrate compared to MPTMS-modified substrate, indicating more surface coverage with agglomerated non-uniform structures. Further, as expected, the shift in peak position for both dopants in PVA is in between that of films on APTMS-modified PVA and MPTMS-modified PVA substrates. It elucidates that even a minor change in evaporation rate during the doping of APTMS or MPTMS to the PVA can result in a significant bathochromic shift of absorbance. However, we restricted our investigation with MPTMS-doped PVA because it showed maximum shift at lower evaporation rate. Furthermore, our future investigations are aimed at development of device applicative studies of APTMS, MPTMS, and their
combined effects, respectively. An analytical modelling has been carried out in the later section using Lumerical FDTD method to confess the aforementioned experimental yields.

Furthermore, significant adhesive properties for silver nanoparticles were exhibited by APTMS and MPTMS dopants, through the amine or silane or both groups on PVA polymer to metal bonds [23, 24]. This bond formation is due to the interactive sites offered by the dopants that also accounts for the variation in $\lambda_{\text{max}}$ owing to the higher agglomeration trend in APTMS-modified PVA substrate.

3.2 Morphological study

The SEM micrograph in Fig. 4a, b shows the silver nanoparticle distribution deposited on undoped and doped PVA substrates. The deposition rate and thickness are vital factors in determining the film morphology. For 25 nm films deposited on the MPTMS-doped PVA substrates, large, uniform, and agglomerated particles are observed in comparison to its undoped counterpart. This confirms the sharp peak of the absorption spectra ($\lambda_{\text{max}}$) at 547 nm as it corresponds to a high concentration of uniform size silver nanoparticles. These results are quantified by the histograms in Fig. 4c, d, where the average particle size is 40 nm and 80 nm, correspondingly. Furthermore, disproportionate particle size coupled with an increase in agglomeration is noticed in Fig. 5b for the 50 nm silver films deposited on APTMS + MPTMS-doped PVA substrates compared to the films deposited on the undoped PVA in Fig. 5a. The broad peak, as noticed in the absorption spectra, corresponds to the lack of uniformity in the particle size, reinforced by the SEM micrograph. Also, Fig. 5c, d reinforce these findings that average particle size tends to increase from 47 to 65 nm upon doping. Similarly, the SEM micrograph in Fig. 6b for the 75 nm silver films deposited on the APTMS + MPTMS-doped PVA substrates shows a highly

![SEM images](image-url)
agglomerated irregular structure with more surface coverage accounting for a broader absorption spectrum compared to Fig. 6a.

Figures 4, 5, and 6 demonstrate the increment in the particle density and structural changes (elongated spherical) through high surface coverage when the silver films are deposited on doped substrate. The Maxwell Garnett theory predicts the position of the maxima and the shift in the absorption maxima to a higher wavelength with the increase in particle density [25, 26] as supported by the earlier investigations [27]. Lance Kelly et al. have emphasized the influence of size and shape of the particles on the optical studies of the particulate films [20]. The shape of the particles tends to be elongated spherical when dopants are added to the PVA compared to the spherical nature exhibited with undoped PVA. The same can be observed in the Fig. 5b where silver nanoparticles with elongated spherical nature having negligible inter-particle separation in a highly agglomerated form. This ensures a high surface coverage of particles with dopant substrates (Fig. 6b).

As inter-particle separation is decreasing, quadrupole and higher resonances become important in addition to the contribution from inter-particle dipole interactions and aggregation for the observed modifications in the optical properties [28, 29].

The dopants provide a bonding site (amine and silane groups) for the silver particles, which in turn results in the increase in nucleation sites, smaller inter-particle separation, and higher particle density (Fig. 4b, 5b, and 6b), whereas increased agglomeration with larger inter-particle separation is observed for the films on undoped PVA due to the lack of bonding sites from the substrate. Thus, a narrow peak with less broadening in optical spectra for the particles in undoped PVA was observed, further confirmed by the SEM images (Fig. 4a, 5a, and 6a).

Fig. 5 SEM images of 50 nm silver films deposited on a PVA, b APTMS + MPTMS-doped PVA and their corresponding histogram analysis of silver on c PVA, d APTMS + MPTMS-doped PVA at 413 K.
3.3 Raman spectroscopy

The Raman spectra of silver films coated on undoped and doped PVA are shown in Fig. 7. Raman peaks and their associated corresponding vibration modes for the undoped PVA are listed in Table 1, which are in concordance with the reported values [30, 31]. From Fig. 7b, new peaks are clearly observed at 1507 cm\(^{-1}\) and 1591 cm\(^{-1}\) after the formation of sub-surface silver nanoparticles in PVA substrates. The absence of these peaks in undoped PVA substrate (Fig. 7a) evidences the emergence of silver nanoparticles in PVA substrate. Similarly, a peak with a small shift towards a higher wavenumber 1533 cm\(^{-1}\) and a shoulder peak at 1591 cm\(^{-1}\) are observed for silver nanoparticles in MPTMS-doped PVA substrate (Fig. 7c), which clearly indicates the initiation of merging of these peaks. Furthermore, a clear single peak is observed at 1591 cm\(^{-1}\) for sub-surface silver nanoparticles on the APTMS + MPTMS-doped PVA substrate. One possible reason for observing the clear two peaks in Fig. 7b may be due to the shifting of 1435 cm\(^{-1}\) (i.e. C–H bend and O–H bend vibration), and with the addition of the dopant (MPTMS), the peaks start merging (Fig. 7c). With the addition of both MPTMS and APTMS to PVA, complete merging is observed as shown in Fig. 7d. The observed peak shift started at 1507 cm\(^{-1}\) continued till 1533 cm\(^{-1}\) eventually leading to the merging of these both peaks at 1591 cm\(^{-1}\). This could be due to the binding of
silver nanoparticles resulting in the sub-surface modification and influencing the inter-particle distances within the undoped and doped PVA substrates. It is well known that metallic nanoparticles are good substrate materials for the Surface-Enhanced Raman Spectroscopy (SERS) [32, 33]. In addition, there is a significant enhancement in the peak intensity of undoped and doped PVA substrates in the presence of silver nanoparticles. These results indicate that the addition of dopants (-amino and silane) play a significant role in binding the silver nanoparticles to the substrate, which is further confirmed by morphological studies (Figures 4, 5, and 6).

3.4 FTIR–spectroscopy analysis

The Fourier-Transform Infrared Spectroscopy (FTIR) spectra of undoped and doped PVA substrates before and after silver deposition on modified substrates is shown in Fig. 8 and quantitatively summarized in Table 2. The peak corresponding to C–H group of PVA is observed around 2700–3000 cm\(^{-1}\) [34, 35] and remains identical for undoped and doped PVA films. The peak observed in the range of 3200 to 3600 cm\(^{-1}\) indicates the presence of O–H group and hydrogen bonds [34–38] tend to shift to higher wavelength with doped PVA substrate. This may be due to the structural changes occurring in the polymer substrate which may result in the formation of new bonds with the neighbouring atoms or clusters with doping confirmed by the FTIR and Raman analysis [39, 40].

3.5 FDTD simulations

The Lumerical FDTD [41] uses 2D, 3D Maxwell’s equation solvers directly where the corresponding electric and magnetic fields are discretized in both time and space on a spatial grid. Figure 9a. depicts the schematic representation of FDTD setup where the sub-surface silver NPs are embedded in the polymer matrix irradiated by the electromagnetic (EM) wave. A plane wave of wavelengths ranging from 300 to 1000 nm is set to propagate in Z-direction while its electric and magnetic fields are oscillating in X- and Y-axes in P-polarized state. Here, the entire structure has been discretized by default meshing mechanism and the Maxwell’s equations are solved on a discrete spatial and temporal grid and thereby the data are collected and interpolated. As mentioned above, we assumed a monolayer of Ag NPs embedded in polymer matrix (undoped and MPTMS-doped PVA) structure shown in Fig. 9b with the periodic (along X, Y- axes) and perfectly matched layer (PML) (along Z–axis) boundary conditions (BCs). To avoid discrepancies and unambiguity, we chose the system to be periodic allowing it to be an analytical model.

Comparing the experimental and simulated absorbance for the silver film thickness of 25 nm or average diameter of 40 nm (undoped PVA) and 80 nm (MPTMS-doped PVA) as illustrated in the Fig. 10a, we can see a clear bathochromic shift from 413 to 529 nm confessing the experimental yields. XZ planar view of the electric field (E) intensity distributions in Fig. 10b for the respective resonance wavelengths are also corroborating that. However, the additional peak at 457 nm in MPTMS-doped PVA signifies the possibility of multi-reflection resonance due to the narrow separation of the NPs arranged in a plane. In other words, the plane of these NPs tends to behave like a film with negligible gap existing among the particles.

3.6 Applications and scope

In general, optical studies are defined by spectroscopic characterizations; in absorption studies, the peak shift in spectra towards a lower or higher wavelength defines specific applicability. Thus, for the specific application, one can tailor the material

| Table 1 | Raman peaks and their corresponding vibration modes of undoped PVA |
| Wavenumber (cm\(^{-1}\)) | Vibration modes |
|----------------|------------------|
| 841            | Stretching of C–C |
| 922            | Stretching of C–C |
| 1094           | C–O stretching   |
| 1365           | C–H₂–O–H bend vibration |
| 1435           | C–H bend,–O–H bend vibration |

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morphology and characteristics by adding dopants to the substrate. In our studies, we have explained the tuned optical properties of the films on undoped and doped PVA substrates, specifically absorption spectra with respect to silver particle size, particle density in the films, and dopants. These films are potential candidates for the futuristic applications. Nowadays, the research is advancing towards the materials which are transparent and flexible in nature. The polymer substrate offers several advantages over the rigid substrates (ex. glass, silicon etc.) viz. less weight, soft, stretchable, flexible, and easy to integrate. Moreover, by tuning the chemical and physical nature of the polymer substrate by doping with the functional groups (such as amine, and silane groups etc.), it is possible to use them for different potential applications. The present work i.e. sub-surface silver particulate films would give a direction for tuning the morphology of the particles thereby tuning their electrical, optical properties to a significant extent (ex.

| Sample                          | Wavenumber (cm$^{-1}$) | Transmittance (%) |
|--------------------------------|------------------------|-------------------|
| PVA                            | 3296                   | 76.69             |
| PVA + MPTMS                    | 3366.84                | 81.64             |
| PVA + MPTMS + APTMS            | 3245.63                | 94.35             |
| PVA + Ag                       | 3309                   | 80.67             |
| PVA + MPTMS + Ag               | 3315                   | 79.12             |
| PVA + MPTMS + APTMS + Ag       | 3247                   | 95.21             |

**Table 2** Quantitative FTIR data of samples

**Fig. 8** FTIR spectra of undoped PVA and doped PVA substrates before and after silver deposition

**Fig. 9** a Schematic representation of the Lumerical FDTD modelling of Ag sub-surface particles embedded in polymer matrix. Here, E- Electric field, k-propagation vector. b Real simulation environment of a monolayer Ag NPs subsurfaced in MPTMS-doped PVA polymer matrix. R and T are the transmission monitors.
A shift in absorption maxima by \( \sim 140 \text{ nm} \) (Fig. 2) by the addition of small amount of MPTMS + APTMS to the PVA substrate. Since these metal nanoparticles are embedded at a certain depth inside the polymer substrate, the properties could remain stable without degradation over a period of few years. These films are flexible and depending on the polymer substrate they are stretchable too.

These films find applications in the field of flexible electronics [3, 46, 47], bio-compatible devices [48, 49], photovoltaics [50], OLEDs [51], solar cells [52–54], EMI shielding [55], food packaging [56], biomedical applications in imaging, cancer therapies and drug delivery [57], biosensors [58], piezoelectric energy harvester [59], solar energy generation [60], etc. The future scope of this work can be extended to the detailed study of APTMS, MPTMS and their combined effects, respectively, in tuning the electrical, optical properties of the sub-surface particulate films for the flexible electronics applications and testing their suitability for the potential futuristic device development.

### 4 Conclusion

A shift in the plasmon resonance peak towards longer wavelengths is observed in the case of the silver particulate films deposited on softened modified PVA substrates compared to films on undoped PVA showing a change in the morphology of the sub-surface nanoparticle formation. The plasmonic response of silver particulate films deposited on modified PVA indicates the formation of elongated spherical silver nanoparticles for MPTMS-doped PVA substrate, whereas for MPTMS + APTMS-doped substrate, it indicates non-uniform and irregular particles as confirmed by FESEM. The tabulated results of the Fourier-Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy studies quantitatively visualize the substrate modification by the addition of dopants. Further, the experimental optical results are attested by the FDTD simulation results. This study indicates a stronger role of polymer-metal interaction by surface modification with dopants, and dopants play an important role in tuning the optical and morphological properties of the particulate films deposited by thermal evaporation. We conclude that these nanostructures, as they are embedded at a certain depth below the polymer surface, are quite promising for flexible electronic applications.

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**Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

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