Ag nanoparticle decorated Sb₂O₃ thin film: synthesis, characterizations and application

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Abstract

The property modifications in a thin film when its surface undergoes a nanoparticle decoration process in addition to its surface nanostructuring are investigated this paper. In specific, it describes the property modifications of antimony trioxide and its annealed variant, when their surface is decorated with Ag nanoparticles. Along with the modifications brought to the thin films, the morphology variations or agglomeration effects happening to Ag nanoparticles through/after this decoration process is also discussed here. We observe a mutual tuning of morphology as well as properties of thin film and nanoparticles. A fractal like cluster formation of Ag nanoparticle on the surface of nanostructured Sb₂O₃ thin film was witnessed. Whereas on the surfaces of Sb₂O₃ (annealed) thin film and glass plate, clustering of Ag nanoparticle is found to be different. On annealed Sb₂O₃ thin film surface, instead of forming fractal clusters most of the Ag nanoparticles fill in the voids between the thorns like structure of the film. The surface modification highly influences the optical absorption as well as the hydrophilicity of antimony trioxide samples. Due to the introduction of Ag nanoparticle, the absorption of Sb₂O₃ thin film in the visible region increased. All the synthesized films have roughness coefficient > 1 and all are hydrophilic in nature. Nano structured Sb₂O₃ thin film is extremely hydrophilic and they become hydrophilic due to the introduction of Ag nanoparticle. The filling of Ag nanoparticles in the voids between the thorn structures might have prevented the water droplet penetration into these voids. Consequently, a partial wetting occurs on the film surface. High SERS efficiency factor (EF) and good reproducibility of Ag/Sb₂O₃/Glass make it a good candidate for SERS application.

1. Introduction

Incorporation of metal nanoparticles, such as Ag and Au onto the surface of semiconductor nanostructures like thin films, nanotubes, nanorods etc has shown improvement in their properties and performance [1–3]. These systems are usually known as nano-hybrids or nanocomposites and they have exhibited good photocatalytic activity [4], photodetection [5], antibacterial activity [6], photovoltaic efficiency [7, 8], Electrochromism [3], photoelectrochemical water splitting [2], SERS [9], gas sensing [10] etc. These enhanced performances are achieved by morphology modifications, large surface area as well as the surface plasmon effect brought in by the size, shape and the arrangement of metal nanoparticles introduced onto the surface of the nanostructures [8, 11, 12]. Depending on the method selected for the deposition of metal nanoparticle on these surfaces the size, shape and arrangement of the nanoparticle differ [13, 14]. There is always a chance of agglomeration of nanoparticles on the surfaces and it prevents the enhancement of the properties/performances of these nano-hybrids. This agglomeration depends on surface morphology of the nanostructure on which we are intend to introduce the metal nanoparticle which is termed as decoration in this paper [4, 6, 10].

Usually these nano-hybrid formations employ nanostructured metal oxide surfaces for nanoparticle decoration. Liu et al introduced Ag nanoparticle decorations to ZnO hexagonal nanoplate arrays for enhanced
SERS applications [15]. Wei and co-workers performed Polydopamine-assisted decoration of ZnO nanorods with Ag nanoparticles for its performance as a photoelectrochemical anode [13]. The synthesis process of the nanostructured metal oxide surface, prior to the incorporation of metal nanoparticle plays a crucial role on its performance, as their surface morphology highly influences the size, shape and spatial arrangement of the metal nanoparticle deposited onto it [6]. Nanostructured metal oxide can be prepared by different synthesis techniques such as wet chemical methods, physical vapour deposition, electrodeposition, sputtering etc [1, 10, 16, 17]. Antimony trioxide (Sb₂O₃) is a good UV absorber and flame retardant, which can be synthesized in a wide variety of morphologies [18–20]. As it is difficult to achieve Ag doping in Sb₂O₃ due to large contrast in ionic radius (Sb³⁺ = 0.76 Å, Ag⁺ = 1.26 Å) and charge difference it is better to perform surface modification in Sb₂O₃ using Ag nanoparticles than doping.

To the best of our knowledge Ag nanoparticle decoration effect on the properties of Sb₂O₃ thin film has not been published yet. This report of work presents the influence of Ag surface modification on the optical absorption as well as the hydrophilicity of antimony trioxide samples. We observe a fractal like cluster formation of Ag nanoparticle on the surface of nanostructured Sb₂O₃ thin film. Thus the Ag/Sb₂O₃ hybrid structure formed has hydrophilic nature and their contact angle varies with the surface modification of Sb₂O₃ thin film. We also studied the use of the prepared thin films for SERS application.

2. Methods

2.1. Synthesis of nanostructured Sb₂O₃ thin film

Nanostructured Sb₂O₃ thin film has been synthesized using the vacuum thermal evaporation technique, which is explained in our previous paper [21]. Sb₂O₃ powder purchased from Merck India Pvt. Ltd with a purity of 99.99% was used as the starting material. Microscopic glass slides of dimension 75 mm × 25 mm × 1.45 mm are used as the substrate.

2.2. Synthesis of Ag nanoparticles

Ag nanoparticles are green synthesized using Neem (Azadirachta indica) leaf extract. The process of Ag nanoparticle synthesis is well explained and given in supplementary data is available online at stacks.iop.org/NANOX/1/020005/mmedia. Thus synthesized Ag nanoparticles dispersed in water was used for decoration purpose.

2.3. Synthesis of Ag nanoparticles decorated nanostructured Sb₂O₃ thin film

Ag nanoparticles dispersed uniformly in water are drop cast on the surface of Sb₂O₃ thin films by slowly pouring 5 drops onto the 2 cm × 2 cm thin film surface with the help of a micro-pipette. It is then dried at room temperature to evaporate water from the film surface.

2.4. Experimental

The structural characterizations of the samples are carried out by x-ray diffraction (XRD) technique using Cu Kα radiation (λ = 0.154 06 nm) of Bruker AXS D8 Advance diffractometer and compared the results with JCPDS data files. The morphological characterizations of the samples are conducted by field-emission scanning electron microscopy (Carl Zeiss ΣIGMA HV FESEM instrument) and High resolution transmission electron microscopy (FEI TECNAI F20 G2 high resolution transmission electron microscope). The Energy dispersive spectrum (EDS) of the samples is obtained along with HRTEM analysis. UV–vis absorption spectra are recorded with PG instruments T90 + UV/VIS spectrometer. Static Contact angle measurements are performed with SEO Phoenix Contact angle analyzer using DI water. Atomic force microscopy (AFM) and Surface enhanced Raman scattering (SERS) studies are carried out using Confocal Raman microscope WITec Alpha 300 RA.

3. Results and discussion

3.1. Structure and surface morphology

3.1.1. XRD analysis

Our previous paper provides the complete characterization of bare Sb₂O₃ thin film. It exhibits a cubic structure having a lattice constant of 11.0515 Å (JCPDS file no.721334) [21]. Figure 1 shows the XRD pattern of Sb₂O₃ thin film and annealed Sb₂O₃ thin film decorated with Ag nanoparticle. No peak corresponding to metallic Ag is seen in the XRD patterns of the Ag decorated Sb₂O₃ thin film and annealed Sb₂O₃ thin film which suggests that the concentration of Ag is much below the detection limit of XRD instrument. But with introduction of Ag there occurred intensity variation of XRD peaks as well as shift in peak positions of the Sb₂O₃ and annealed Sb₂O₃ thin films. The main intense peak is (222) in the case of Sb₂O₃ thin film and annealed Sb₂O₃ thin film [21]. After Ag
decoration the main intense peak is (440). This change in intensity and peak position indicates a composition change giving the insight of Ag/Sb2O3 hybrid structure formation [22]. Sharp intense peaks indicate that all the samples are highly crystalline in nature. 

Crystal size of the samples has been calculated using the Scherrer formula [22]. From our previous paper, we can see that the average crystal size of Sb2O3 and its annealed counter-part (here sample annealed at 400 °C) is obtained as 21.6 nm and 31.3 nm respectively [21]. In the case of Ag nanoparticle decorated Sb2O3 and its annealed counter-part, the average crystal size is found to be 24 nm and 32 nm respectively. That is, the crystal size shows only a slight increase after Ag nanoparticle introduction. Hence, we can conclude that Ag nanoparticle decoration has no significant effect on the crystal size of Sb2O3 thin film and its annealed counter-part because of its small amount.

3.1.2. Field emission-SEM (FESEM) analysis

As explained in our previous paper, we could achieve a thorn like surface morphology for Sb2O3 thin film due to the inclined arrangement of substrate with respect to the source. These thorns like structures with surface cracks are randomly oriented on the film surface and in between these shapes a large number of voids are present. These results are clearly observable from the FESEM images that we presented in our previous paper [21]. Thorn heights vary between 200 nm to 400 nm.

FESEM analysis helped to understand the size, shape and arrangement of Ag nano particles introduced on to the surface of nanostructured Sb2O3 thin film. The FESEM images of Ag nano particles drop casted onto the surface of Sb2O3 thin film is shown in figure 2. We can clearly observe that on the surface of Sb2O3 thin film, Ag nanoparticles self-assembled to form fractal like micro-clusters (figure 2(C1 to C8)). Studies say that fractal clusters grow on the surface where there is some kind of defects present or (where there is a change in surface energy) or less surface energy. Also depending on the defect, the size and shape of the clusters formed may vary [23]. Here, we witnessed Ag fractal cluster formations which showed different size and shape at different regions of the thin film as claimed above. Due to the small size of Ag nanoparticles, we expected it to be occurring in between the voids rather than clustering above the thorns. Still in some areas on the surface, they spread inside the voids between the thorns. As we observed from our previous paper, the surface morphology of annealed Sb2O3 thin film is different from that of Sb2O3 thin film. Its surface not only contains thorn structures but also some polygonal structures that formed from the agglomeration of these thorn structures during annealing. Because of this differing surface morphology a different kind of Ag nanoparticle assembling effect is observed on the surface of the annealed Sb2O3 thin film. Figure 3(a) shows the FESEM images of Ag nanoparticles drop cast on annealed Sb2O3 thin film surface. Rather than forming Ag fractal clusters they spread within the voids among the thorn like structures (figure 3(a1) and figure 3(a2)) and at some regions they form agglomerates. To observe the difference in clustering nature of Ag nanoparticle at different surface, a study has been made by drop casting Ag nanoparticles on to a plane microscopic glass slide also. The FESEM images of the Ag/Glass surface is shown in figure 3(b). We can see that Ag nanoparticles are highly agglomerated and form clusters on the glass surface but not fractal like clusters (figure 3(b1) and (b2)). In these clusters Ag nanoparticles still exist in its circular morphology with their edges clearly distinguishable from each other. From this we can say that the surface
nanostructuring of the thin film here acted as a substrate or domain helping in the clustering and arrangement of nanoparticle over the film surface.

3.1.3. TEM analysis
Figures 4(a) and (b) represents the TEM images of Ag decorated Sb$_2$O$_3$ thin film and Ag decorated Sb$_2$O$_3$ (annealed) thin film. As mentioned in our previous paper [21] highly agglomerated form of Sb$_2$O$_3$ is obtained with Ag nanoparticle scattered on its surface are seen in figure 4(a). The circular spots detected on the surface of thorn structure are Ag nanoparticles. From HR-TEM analysis d spacing of 0.23 nm for the (111) plane of Ag are found along with d spacing of 0.27 nm, 0.34 nm and 0.66 nm corresponding to the (400), (220) and (111) planes respectively. The sharp fringes indicate highly crystalline nature of the samples. Due to the agglomeration of Ag nanoparticle on the surface of Sb$_2$O$_3$ thin films, their particle size appeared to be greater than those obtained for Ag nanoparticle in solution form used at the time of drop casting process. Figures 4(e) and (f) are the energy dispersive spectrum of the Ag decorated Sb$_2$O$_3$ thin film and Ag decorated Sb$_2$O$_3$ (annealed) thin film respectively. Both the spectrum contains peaks for the elements Sb, O, Ag and Cu. The peak of Cu arises from the copper grid used for TEM specimen preparation. Ag content seems too small compared to other elements that it is unnoticeable in the XRD analysis and no diffraction peak is seen in the XRD.
3.1.4. AFM analysis

Ag nano particle decorated Sb$_2$O$_3$ thin films are investigated using AFM analysis and the images are shown in figure 5. It reveals the surface structure of the thin films. As discussed in previous paper the thorn like morphology of the Sb$_2$O$_3$ thin film is clearly observable from figure 5(a). With annealing, these thorns combines and new structures arises among the thorn on the surface of annealed Sb$_2$O$_3$ thin film (figure 5(b)). Clustering of Ag nanoparticles on the surface of glass is presented in figure 5(c). The clustering is such that Ag nano particles cover the entire glass surface with small voids among them. When it comes to the case of Ag nanoparticles decorated Sb$_2$O$_3$ thin film surface (figure 5(d)) we can see fractal cluster formation of Ag nanoparticles on the film. But on the surface of annealed Sb$_2$O$_3$ thin film (figure 5(e)) instead of fractal cluster formation Ag nanoparticles spreads over the surface covering the thorns. Surface roughness obtained for each sample is given in table 1. It is found that with Ag nanoparticle decoration roughness of surfaces of Sb$_2$O$_3$ thin film and annealed Sb$_2$O$_3$ thin film surfaces decreases.

![Figure 4](image1.png)

**Figure 4.** (a) TEM, (b) HR-TEM image and (e) EDS spectrum of Ag/Sb$_2$O$_3$ thin film and (c) TEM, (d) HR-TEM image and (f) EDS spectrum of Ag/Sb$_2$O$_3$ (annealed) thin film. Ag nanoparticle lies on the surface of the film.

![Figure 5](image2.png)

**Figure 5.** AFM images of (a) Sb$_2$O$_3$/Glass; (b) Sb$_2$O$_3$ (annealed)/Glass; (c) Ag/Glass; (d) Ag/Sb$_2$O$_3$/Glass and (e) Ag/Sb$_2$O$_3$(annealed)/Glass. Film uniformly covers the substrate surface.
Table 1. Roughness parameters and contact angle values obtained for the synthesized sample.

| Sample                  | Roughness parameters (nm) |           |            | Roughness coefficient (r) | Contact angle (degree) |
|-------------------------|----------------------------|-----------|-----------|---------------------------|------------------------|
|                         | Average roughness ($S_a$) | RMS roughness ($S_q$) | Developed interfacial area ratio ($S_d$) |                         |                        |
| Sb$_2$O$_3$/Glass       | 48.96                      | 61.84     | 18.63     | 1.1863                    | 10.31                  |
| Sb$_2$O$_3$ (annealed)/Glass | 42.69                      | 54.51     | 17.02     | 1.1702                    | 13.03                  |
| Ag/Sb$_2$O$_3$/Glass     | 24.18                      | 31.99     | 8.46      | 1.0846                    | 27.14                  |
| Ag/Sb$_2$O$_3$ (annealed)/Glass | 42.16                      | 53.46     | 22.76     | 1.2276                    | 38.28                  |
| Ag/Glass                | 47.16                      | 68.01     | 5.71      | 1.0571                    | 52.30                  |
3.2. Optical characterization- UV–vis absorption spectroscopy

Figures 6 (a) and (b) shows the absorbance spectrum of the synthesized samples. Ag nanoparticles show a plasmon peak around 466 nm as can be seen in supplementary data. In the absorbance spectrum of Sb2O3 with Ag nanoparticle decoration, the Ag plasmon peak is observed around 430 nm and the absorption band edge of Sb2O3 shows a red shift. Likewise in the absorbance spectrum of annealed Sb2O3 with Ag nanoparticle decoration the Ag plasmon peak is observed around 460 nm and the absorption band edge of Sb2O3 shows a blue shift. This displacement in the position of the plasmonic peak of Ag probably happened due to the difference in dielectric environment of the Ag nanoparticles in the dispersion and that on the Sb2O3 surface [24].

It is to be noted that due to the introduction of Ag nanoparticle, the absorption of Sb2O3 thin film in the visible region increased remarkably compared to the Sb2O3 thin film without Ag decoration. This modification in the absorption properties of the thin film can be assigned to the plasmonic absorption of metal nanoparticle on the surface. More precisely, the surface plasmons confined between the metal nanoparticle and the Sb2O3 thin film surface can trap the light and enhance the absorption. This light trapping effect is more prominent around the plasmon resonance peak which can be tuned by modifying the dielectric environment [25]. At the same time the visible absorption of Sb2O3 (annealed) thin film is slightly reduced. This reduction in absorption can arise due to the scattering of incident photons at the modified film surface. The band edge shift can be associated with the band structure modification in Sb2O3 thin film due to Ag incorporation. As seen from FESEM analysis, Sb2O3 thin film surface and Sb2O3 (annealed) thin film surfaces induces two different type of clustering or agglomeration of Ag nanoparticles. These two different forms of Ag nanoparticles with different size and shape may have two different band structure modifications. Hence when these bands interact with the band structure of Sb2O3 thin film, there is a chance that the band gap may become narrow or wide [26].

The band gap modifications happening to the thin film samples after Ag nanoparticle surface decoration were studied using Tauc plot analysis as expalained in our previous paper. The effect of annealing on the band gap of Sb2O3 thin film is also discussed in this paper and the band gap showed a decrease [21]. As seen from UV absorption spectra in figure 6, the band gap of Sb2O3 thin film reduced with Ag nanoparticle introduction whereas that of and Sb2O3 (annealed) thin films increased. Sb2O3 (annealed) thin film increased (see figure 7). This clearly indicates the occurrence of band gap narrowing in Sb2O3 thin film and band gap widening in Sb2O3 (annealed) thin film with Ag nanoparticle decoration.

3.3. Contact angle measurements

The wetting behaviour of the synthesized thin film surfaces are understood using contact angle measurements and the obtained results are tabulated in table 1. Shape of water droplet on each surface is shown figure 8. Measurements show that the contact angle of Sb2O3 and Sb2O3 (annealed) samples increase due to the introduction of Ag nanoparticles onto its surface. This increase in contact angle can be attributed to the new modifications happened on the surface of Sb2O3 and Sb2O3 (annealed) thin films because of the presence of Ag nanoparticles. As different researchers define superhydrophilicity in different ways it is difficult to tell whether
Figure 7. Tauc plots of the synthesized samples.

Figure 8. Image of water droplets on (a) Sb$_2$O$_3$/Glass (b) Sb$_2$O$_3$ (annealed)/Glass (c) Ag/Sb$_2$O$_3$/Glass (d) Ag/Sb$_2$O$_3$ (annealed)/Glass and (e) Ag/Glass. Hydrophilic nature of thin films revealed.
the synthesized films fall in the superhydrophilicity regime. A hydrophilic surface is that which attracts water and have a water contact angle less than $90^\circ$ [27]. A superhydrophilic surface is that which have water contact angle less than $10^\circ$ [28, 29]. For a surface whose contact angle is nearly $10^\circ$ can be considered as extremely hydrophilic. As we go through the contact angle values of the synthesized film we can see that initially Sb$_2$O$_3$ thin film have extremely hydrophilic nature (contact angle $\approx 10^\circ$) which on Ag nanoparticle introduction (contact angle $< 90^\circ$) become hydrophilic. This extreme hydrophilicity of the films are due to the presence of voids among the thorn like structures as water droplets can penetrate into these voids through 2D capillary effect according to the Wenzel’s model as shown in figure 9 [30, 31]. Due to the introduction of Ag nanoparticles space between the voids may reduce enormously and the water droplet penetration into these voids is much less (see figure 9) and we can assume water spreading on the surface as Cassie–Baxter model and there occurs partial wetting [29]. That is the surface topography can highly affect the wettability of the surface depending on the size and shape contours and protrusions present.

As we know surface roughness has an important role in hydrophilic/phobic nature of a surface. The surface roughness of films from AFM studies are given in table 1. To understand the effect of roughness and wetting behaviour the roughness coefficient ‘r’ is more commonly used. It is defined as, $r = 1 + \frac{S_{dr}}{100}$, where $S_{dr}$ is the interfacial area ratio roughness parameter [32]. $S_{dr}$ describes the ratio between projected area and the rough area of the solid surface on which the liquid drop is deposited for the measurement [33]. For a hydrophilic surface r is greater than 1 [34, 35]. The r values obtained for the samples are given in table 1. From table we can see that all the samples have r value greater than 1, which means they all are hydrophilic in nature.

### 3.4. SERS analysis

RhodamineB (RhB) was selected to be a model analyte as it is usually employed as a Raman probe molecule. For detecting the SERS application of Ag nanoparticles decorated Sb$_2$O$_3$ thin film, we introduced 10 $\mu$l solution of 10$^{-12}$ M RhB in water onto its surface. Then the RhB/Ag/ Sb$_2$O$_3$/Glass structure is air dried to obtain the RhB analyte adsorbed onto Ag/Sb$_2$O$_3$/Glass surface. The same is repeated in the case of Ag/Sb$_2$O$_3$(annealed)/Glass surface, Ag/Glass surface, Sb$_2$O$_3$/Glass surface and on plain glass surface.

It is difficult to obtain the Raman spectrum of RhB on glass substrate as the concentration of RhB is too low to be detected. The observed SERS spectra of RhB on the surface of Ag/Glass, Ag/Sb$_2$O$_3$/Glass and Ag/Sb$_2$O$_3$ (annealed)/Glass are shown in figure 10. Usually the normal SERS spectrum of RhB shows peaks at 1183 cm$^{-1}$, 1193 cm$^{-1}$, 1278 cm$^{-1}$, 1311 cm$^{-1}$, 1355 cm$^{-1}$, 1426/1430 cm$^{-1}$, 1504 cm$^{-1}$, 1512 cm$^{-1}$, 1526 cm$^{-1}$, 1532 cm$^{-1}$, 1561 cm$^{-1}$, 1572 cm$^{-1}$, 1644 cm$^{-1}$ [36, 37]. When we compare the obtained RhB/(Substrate) SERS spectra with these previous results it can be seen that they are not exactly the same for all the samples we studied. We get some abnormal SERS spectrum as described by Sun et al [36]. According to them 1258 cm$^{-1}$, 1343 cm$^{-1}$, 1390 cm$^{-1}$, 1585 cm$^{-1}$ are abnormal SERS peaks of RhB. Raman spectrum of RhB on glass substrate is not exactly resolved into observable peaks. When it comes to the case of RhB on Sb$_2$O$_3$/Glass substrate few of the peaks emerges out with normal and abnormal Raman peaks. In the case of RhB on Ag nanoparticle substrate there is an enhanced Raman peak at 1503 cm$^{-1}$ and all other peaks are not well resolved. For RhB on Ag/Sb$_2$O$_3$(annealed)/Glass substrate there is enhanced Raman peak at 1561 cm$^{-1}$. A highly resolved and enhanced Raman spectrum is obtained for RhB on Ag/Sb$_2$O$_3$/Glass substrate. It contains both normal and abnormal Raman peaks of RhB. We can see an abnormal enhancement of certain Raman peaks of RhB on substrates Ag/Sb$_2$O$_3$/Glass, Ag/Glass and Ag/Sb$_2$O$_3$(annealed)/Glass. This enhancement of peaks is based on selection rule that tells which bonds are Raman and SERS active [38]. This intensity variation can also happen if there is an enhanced charge transfer occuring between RhB molecules and SERS substrate surface. Another reason may be the difference in the spatial orientation of the adsorbed molecules with respect to the substrate surface [39].

We can see that RhB on Ag/Sb$_2$O$_3$/Glass has more enhanced SERS spectrum than Ag/Glass and Ag/Sb$_2$O$_3$ (annealed)/Glass substrates. This may be due to the presence of Ag fractal clusters on the Sb$_2$O$_3$ thin film surface.
SERS enhancement is significantly influenced by the shape, size and band gap modulations of Ag NPs [40]. Here the clusters formed possess numerous amounts of edges and corners, there is chance of accumulation of surface plasmons at these points and thereby helping to enhance the RhB Raman spectrum [41]. The spatial arrangement of Ag nanoparticle on the Sb2O3 thin film surface is also an important factor that affects the SERS enhancement of the dye spectrum [42]. Here, the random arrangements of Ag fractal cluster are in favour of the SERS enhancement thereby have acting as SERS hot spots. In the case of Ag / Glass, as the Ag nanoparticles being circular in shape, the accumulation of surface plasmons at edges and corners are not possible in Ag clusters. The same goes for Ag / Sb2O3 (annealed) / Glass substrate. Here almost all Ag nanoparticles are filled in between the voids of Thorn like structures so that their exposed area is less compared to Ag / Sb2O3 / Glass. Therefore the possibility of accumulation of RhB molecule on the surface of Ag nanoparticles decreased, which drops the hot spot formation, and thus it showed a reduced SERS spectrum than Ag / Sb2O3 / Glass. A better performance can only be attained with the substrate Ag / Sb2O3 / Glass.

To quantify the SERS activity of the better performed substrate Ag / Sb2O3 / Glass we have calculated its efficiency factor (EF) by comparing the intensity of the SERS signal with the intensity of bulk Raman signal of RhodamineB using the formula,

$$\text{Efficiency factor (EF)} = \frac{I_{\text{SERS}}}{I_{R}} \times \frac{N_{R}}{N_{\text{SERS}}}$$

Where $I_{\text{SERS}}$ and $I_{R}$ are the intensities of the SERS and normal Raman signals of RhodamineB respectively. $N_{\text{SERS}}$ and $N_{R}$ are the number of molecules probed for SERS and normal Raman scattering measurements respectively [43]. The EF was determined using the procedure described elsewhere [44]. The EF of one of the strongest peak at 1346 cm$^{-1}$ is obtained as $2.6 \times 10^8$. This result is somewhat comparable to the previously reported results for RhodamineB on other substrates [45].

To check the reproducibility of substrate Ag / Sb2O3 / Glass as a SERS-active substrate, SERS spectra of RhB molecules from two different regions on the substrate are collected under the same experimental conditions as shown in figure 11. It can be noticed that the SERS spectra taken at these different regions are nearly similar, demonstrating that the Ag / Sb2O3 / Glass is an SERS substrate with good reproducibility. The observation of
slight variations in the peak intensity of some peaks can attributed to the nonuniform adsorption of Ag nanoparticle onto the substrate surface.

4. Conclusion

The properties of a thin film which is improved by surface nanostructuring can again be improved by metal nanoparticle decoration. We observed that the properties exhibited by antimony trioxide and its annealed variant, varies drastically when their surface is decorated with Ag nanoparticles. The surface modification highly influenced optical absorption as well as the hydrophilicity of antimony trioxide samples. The modifications happening to Ag nanoparticles through this decoration process is also discussed in here. Here, we observe a fractal like cluster formation of Ag nanoparticle on the surface of nanostructured Sb$_2$O$_3$ thin film. Whereas on the surfaces of Sb$_2$O$_3$(annealed) thin film and glass plate, clustering of Ag nanoparticle is found to be different. On annealed Sb$_2$O$_3$ thin film surface, instead of forming fractal clusters most of the Ag nanoparticles fill inside the voids between the thorns like structures present on the film surface. All the synthesized films have roughness coefficient > 1 and all are hydrophilic in nature. Nano structured Sb$_2$O$_3$ thin film is extremely hydrophilic and they become hydrophilic due to the introduction of Ag nanoparticle. Due to the presence of Ag nanoparticles in the voids between the thorns structures the water droplet penetration into these voids by capillary effect probably not happened and accordingly, a partial wetting occurred. We also studied the use of the prepared thin films for SERS application. The SERS activity of the synthesized substrates in the case of RhodamineB dye reduces in the fashion Glass < Sb$_2$O$_3$ < Ag/Sb$_2$O$_3$(annealed)/Glass < Ag/Glass < Ag/Sb$_2$O$_3$/Glass. Comparable EF and good reproducibility of Ag/Sb$_2$O$_3$/Glass make it a good candidate for SERS application.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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