Tuning optical and optoelectronic properties of gold nanoparticle and ZnO thin film hetero-structures

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Abstract
Thin film hetero-structures (TFHSs) involving metal oxide thin films and noble metal nanoparticles are very important for many optoelectronics based device applications. This work reports the growth, characterization, and tuning of photoluminescence and I–V properties of TFHSs involving zinc oxide (ZnO) and gold nanoparticles (GNPs). ZnO thin films and GNPs were respectively deposited by the Pulsed Laser Deposition (PLD) and DC sputtering with subsequent annealing. Three different TFHSs were prepared by varying the relative positions of ZnO and GNPs, namely Si-GNPs-ZnO, Si-ZnO-GNPs, and Si-ZnO-GNPs-ZnO. X-ray diffraction results confirmed the high crystallinity of the films, with single phase nature of the ZnO and GNPs. Scanning electron microscopy micrograph analysis confirmed that the morphology of structures containing both GNPs and ZnO is influenced by the bottom layer. Diffuse reflectance spectroscopy results also indicated that the position of GNPs relative to ZnO affects the plasmon resonance of GNPs as well as the overall optical properties of the TFHSs. Photoluminescence studies revealed that the presence of GNPs relative to ZnO affects the plasmon resonance of GNPs as well as the overall optical properties of the TFHSs. The I–V characteristics showed that the TFHSs where ZnO contains GNPs in embedded form are better suited for photodiode application. This study adds a new dimension to the research on optoelectronics devices.

Introduction
Zinc oxide (ZnO) is an n-type II–VI compound semiconductor with its ionicity lying in between covalent and ionic bonding. ZnO is a well-studied material belonging to the group of metal oxide semiconducting materials known as transparent conducting oxides which preserve high values of the two mutually exclusive properties, namely optical transparency, and electrical conductivity. Owing to the excellent transparent conducting characteristics and due to its wide direct bandgap of 3.4 eV at room temperature, large excitation binding energy (60 meV), ZnO is one of the most sought after functional materials in a wide range of device applications [1–5]. Therefore, ZnO finds its use in gas sensing, optoelectronics, spintronics, dye sensitized solar cell, light emitting diodes, and piezoelectric transducer [6–11]. Quality of ZnO films is very crucial in determining the device performance in most of these applications.

It is well known that the growth conditions strongly affect the properties of ZnO thin films, especially the optical and electrical properties. Some of the frequently used methods for the deposition of ZnO thin film include chemical vapor deposition, spray pyrolysis, Sol-gel, pulsed laser deposition (PLD), electron beam evaporation, thermal evaporation, molecular beam epitaxy, and RF sputtering. The main reason behind the growth dependent change in properties is the variation in the type and concentration of defects. Controlling defects in ZnO thin film in a particular growth technique is as challenging as making it useful for any device application. Some of the applications also need the presence of defects. Visible light photoconductivity in ZnO, for example, is possible only if ZnO contains defects, as the defect free ZnO is useful only in ultra violet photo diode application. Researchers, therefore, attempt to nurture the defects into the required advantages. For this,
different approaches have been followed such as external doping of metals like Mg, Al, Ga [2–4, 12], formation of composites, incorporation of noble metals (Ag, Au) [5–7] and making different structural configurations [8, 9].

In sharp contrast to the transparent nature of ZnO, noble metal nanoparticles absorb light in visible range due to the well-known localized surface plasmon resonance (LSPR). Particularly, gold nanoparticles (GNPs) have been studied intensively for their fascinating LSPR properties that can be tuned easily in the visible region [13]. Apart from the optical contrast, AuNPs also have been shown to be promising in electronics applications like single electron transistor and memory device, when suitably embedded in a matrix [14–16]. Therefore, the combination of ZnO thin film and GNPs can give rise to important optoelectronic properties.

For evaluating the performance of any device involving ZnO thin film, study of Si-ZnO interface becomes inadvertent. Similarly, study of different structures of GNPs-ZnO is very crucial in order to successfully explain the performances of the devices involving ZnO thin films and GNPs. This is because, incorporation of metal layer and dispersion of metal nanoparticles cause dramatic changes in terms of thermal, mechanical, optical and electrical properties of a device [5–7, 17–19]. Although there are some reports on the use of GNPs or silver nanoparticles in ZnO matrix or on ZnO film, the research area focusing the effect of plasmonic particles on the properties of metal oxides is a relatively new one and, a lot of new insights are expected to emerge [20–22]. The present research work reports on the (i) growth and characterization of three types of thin film hetero-structures (TFHSs) formed on Si substrate by varying the relative position of ZnO and GNPs such as Si-GNPs-ZnO, Si-ZnO-GNPs, and Si-ZnO-GNPs-ZnO, and (ii) Comparison of the electrical and optical properties of the fabricated TFHSs. The important aim is to combine the plasmonic resonance of gold nanoparticle and band gap of ZnO and, explore its optical conductivity properties.

Experimental details

ZnO thin films were deposited by using the PLD technique. For this, ZnO target was used in the form of a pellet of 10 mm diameter prepared from 99% pure ceramic ZnO powder (Fisher Scientific). During the pellet formation, the sintering temperature was 700 °C. Silicon substrates were cleaned by piranha solution for 5 min followed by cleaning in acetone for removing organic and inorganic residues. The experimental conditions used during the deposition of ZnO thin film were as given in the table 1.

GNPs were formed by direct current sputtering of Au for 40 s on to Si or Si-ZnO film followed by annealing of the sputtered Au film at 400 °C for 2 h in the atmospheric condition. Three different types of TFHSs involving ZnO thin films and GNPs were formed by changing the sequences of deposition of ZnO thin film and GNPs using the same experimental conditions as mentioned above. The four structures thus formed, including the bare ZnO on Si, are (i) Si–ZnO, (ii) Si–GNPs–ZnO, (iii) Si–ZnO–GNPs and (iv) Si–ZnO–GNPs–ZnO. The last one is a sandwich formed on Si. All the structures contain the same thickness of ZnO layer as 320 nm (640 nm in case of sandwich).

The samples were characterized with respect to the crystal phase purity, morphology, and optical properties using the analytical techniques like X-diffraction (XRD), field emission scanning electron microscopy (FESEM), diffuse reflectance spectroscopy (DRS) and Photoluminescence (PL) spectroscopy respectively. The electrical I–V studies were conducted using a KEITHLEY –2420 source meter. Stainless steel pressure contacts were used for the I–V measurement. A white light source with 18 mW cm$^{-2}$ of optical power was used to study the photoconductivity.

Results and discussion

X-ray diffraction study

The crystal structure was characterized by XRD technique using Rigaku TTRAX III X-ray Diffractometer (Cu-Ko: 1.542 Å, Tube current 100 mA, Voltage 50 kV) with 20 range of 20°–60°. Figure 1 shows the XRD patterns of

| Parameter                  | Value                  |
|----------------------------|------------------------|
| Base pressure              | $5 \times 10^{-6}$ mbar|
| Working Pressure           | $2.7 \times 10^{-2}$ mbar|
| Substrate Temperature      | 300 °C                 |
| Oxygen flow rate           | 14 sccm                |
| No of shots                | 5,000                  |
| Laser energy and wavelength| 1.2 J and 355 nm       |

Table 1. Experimental conditions for deposition of ZnO thin film.
the bare ZnO thin film and of the three TFHSs formed. The insets show the peaks due to Au in the 2θ range of 36°–48° for the films containing GNPs. The XRD patterns indicate the highly crystalline nature of the deposited films. The observed diffraction peaks of ZnO (JCPDS card no. 36-1451) and Au (JCPDS card no. 65-2879) are well matched with the JCPDS data. This confirms the formation of ZnO in hexagonal wurtzite phase and Au with FCC structure. The major peak at 34.3° is due to the preferred orientation (002) of ZnO. This preferred orientation (002) occurs due to lowest surface energy according to Wulff’s theorem [23]. The major peak of (002) orientation in ZnO in the case of the GNPs-ZnO structure was observed to be slightly shifted to higher angles (lower d-spacing) as compared to that of the bare ZnO. This may be due to the structural relaxation [24]. Further, the additional peak due to (002) orientation of Au was also observed in Si-Au-ZnO as seen in the corresponding inset. The average crystallite size (D) was calculated from the XRD plot by using the Scherrer’s formula [25] given in equation 1 and, the results are shown in the table 2.

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

Where \( \theta \) is the Bragg’s angle of the peak, \( \lambda \) is the wavelength of X-ray (Cu Kα radiation, 1.54 Å) and \( \beta \) is the full width at half maximum intensity (FWHM). Based on the calculated results, it is found that the average crystallite size of ZnO and GNPs vary with the relative position of the GNPs and ZnO thin film. Whereas the crystallite size

**Table 2. Structural parameters of the TFHSs.**

| TFHSs            | Crystal size (nm) (±0.5) | FWHM  | Peak position |
|------------------|--------------------------|-------|---------------|
| Si-ZnO           | 42                       | 0.21  | 34.30         |
| Si-gold-ZnO      | 42                       | 0.21  | 0.84          | 34.66 | 38.58 |
| Si-ZnO-gold      | 34                       | 0.24  | 1.51          | 34.32 | 38.15 |
| Si-ZnO-gold-ZnO  | 34                       | 0.25  | 1.44          | 34.31 | 38.35 |

**Figure 1.** XRD patterns of different types of GNPs-ZnO TFHSs.
of ZnO remains same in case of the bare ZnO and Si-GNPs-ZnO, it decreases in the other two structures. Also, it is evident that the crystallite sizes of GNPs decrease when on top of ZnO surface as compared to GNPs on Si surface. It is important to mention here that the annealing of the initially discontinuous Au film was done along with the substrate to form the supported GNPs. In case of the structure Si-GNPs-ZnO, ZnO was deposited after the annealing of Si-Au film. Thus, when on Si alone, smaller Au particles might have got integrated into large particles leading to potential energy difference via solid state diffusion according to Ostwald’s ripening [26]. Also, whereas ZnO films are annealed along with the annealing of Au layer in the last two structures, the first two structures consist of as prepared ZnO. The XRD results indicate that substrate plays major role in formation of crystallites which in turn will reflect on the optical and electrical properties of thin films. Moreover, XRD results confirmed the single phase nature of ZnO and GNPs in the fabricated TFHSs.

Field emission scanning electron microscopy study

The FESEM micrographs, obtained with a scanning electron microscope (Hitachi, S-4800), depicting the surface morphologies of bare ZnO as well as the fabricated TFHSs are given in figure 2. A comparison between figures 2(c) and (e) indicates that Si and ZnO as substrates give rise to different morphology and distribution of GNPs. Whereas relatively better uniformity in distribution of GNPs can be seen in the case of Si substrate, the particle size is bigger in ZnO is used as a substrate. The shapes of GNPs on Si and ZnO are also different. Thus, the substrate surface of Si and ZnO are completely controlling the nucleation and growth of the GNPs under the otherwise same experimental conditions. The morphology of ZnO can also be seen to be varying all the configurations with or without GNPs. Barring the particle size, the morphologies of ZnO in the configurations Si-ZnO and Si-ZnO-GNPs-ZnO are appearing nearly the same (figures 2(a) and (d)). However, ZnO thin film is deposited on to Si in the first case and on top of ZnO-GNPs in the second. Similarly, ZnO grown over the Si-GNPs shows large grain boundaries (figure 2(b)) and exhibits completely dissimilar morphology when compared to other configurations of ZnO. Based on the FESEM analysis, it can be concluded that when the position of the GNPs changes in every configuration of Si-ZnO (either on Si or ZnO surface), the size of GNPs and ZnO as well as the morphology of thin films also vary. Reiterating the results of XRD, the morphological results from the FESEM characterization also suggests that relative position of GNPs and ZnO can strongly influence the optical and electrical properties of the TFHSs.

UV-visible spectroscopy study

Figure 3 shows the diffuse reflectance properties of the fabricated TFHSs, obtained using an integrating sphere in DRS mode of a spectrophotometer (Horiba Scientific, JASCO V-770). As shown in figure 3, the variation in the diffuse reflectance remains almost same (10%–30%) in all the TFHSs. However, the pattern of peaks and valleys are different in different structures. Most of the structure exhibit oscillations of maxima and minima arising due
The oscillations get deformed in the visible region with varying fringe spacing for Si-GNPs-ZnO and Si-ZnO-GNPs. Finally, oscillations with increased number of fringes appear in the visible region for the Si-sandwich structure, where the ZnO thickness has got doubled. Interestingly, additional oscillations can be found to be prominently visible in the UV region of the spectrum for the bare ZnO sample. This observation is usually not anticipated considering that ZnO absorbs the UV rays. There can be different possible reasons such as (I) the exciton spectrum of ZnO which appear as a result of different orientation of ZnO crystallites with respect to the direction of incident light [30], (II) the normal reflectance spectrum of ZnO itself has oscillatory behavior, even in the UV region, due to the space charge effect at the surface of ZnO [29] and (III) the DRS of Si-SiO₂ surface itself has such oscillations [31]. However, when all the spectra are compared, the third possibility appears to be the dominant one. This means that in the case of bare ZnO, the diffuse reflectance spectrum of Si substrate is more dominant compared to the other structures. This explanation is further supported by the increase in number of oscillations only in the visible region (but not in UV region) for sandwich structure indicating the dominance of ZnO thickness over the substrate effect. Additionally, in the structures other than bare ZnO, the presence of discontinuous layer of GNPs possibly contributes to the suppression of the oscillations irrespective of however small the average mass thickness of Au is. All the changes appearing in the DRS pattern in the thin films containing GNPs are a result of the superposition of the thickness driven oscillations and the LSPR due to the GNPs. The LSPR depends a lot on the orientation of the GNPs with respect to the incident light; unless the particles are perfect spheres. Earlier studies [13, 32] on the similar kind of fabrication methods indicate that the prepared nanoparticles are mostly oblates which again vary in different structures as shown in the morphologies in the present study. Since diffuse reflectance spectrum is obtained after integrating the signals from the many randomly oriented particles [33, 34], it is difficult to separate out the individual effects caused by ZnO thickness and LSPR of GNPs. However, the
valleys in the visible region of diffuse reflectance spectra obtained for the thin films containing the GNPs are indicative enough to conclude that GNPs are formed in the TFHSs with LSPR in the visible region. Also, the drastic changes in the reflectance patterns indicate that LSPR of GNPs varies when the supporting/embedding media change. The dielectric function of the substrates or surrounding media plays a key role in deciding the LSPR property of the supported/embedded GNPs [6, 35].

Additionally, the DRS technique is helpful in determining the band gap of the material [36]. The Bandgap energy can be calculated by using the Tauc plot [37] which is obtained by plotting the function \( f(R)hv^2 \) versus \( hv \) for a direct band gap material. Here, \( f(R) \) is the Kubelka-Munk function given by [36]

\[
 f(R) = \frac{(1 - R)^2}{2R} 
\]

Where R is the reflectance obtained from the DRS. Using this calculation followed by obtaining the Tauc plot, shown as an inset to the top panel of figure 3, the band gap of ZnO was found to be 3.24 ± 0.18 eV. The DRS data for the sandwich structure (Si-ZnO-GNPs-ZnO) was used as the raw data for producing the Tauc plot. Here, it was assumed that the presence GNPs does not alter the overall bandgap of ZnO.

**PL-spectroscopy study**

PL studies provide information regarding the effect of GNPs on the emission properties of ZnO. The PL studies were carried out using a photoluminescence spectrophotometer (Horiba Scientific, Fluoromax-4). Figure 4 shows the details of PL studies. Each panel of figure 4 shows the experimental emission spectra recorded with an excitation at 295 nm, along with the cumulative fit obtained after the Gaussian deconvolution of the experimental spectra. The individual de-convoluted peaks and the quality of fit through the \( R^2 \) value are also given. The insets in each panel show the raw data before background subtraction. It is important to observe from figure 4 that 10–12 number of distinct and closely spaced emission peaks can be seen in the fabricated TFHSs in the range of 350 to 500 nm. This is in contrast to the many reports on PL studies where in less number of peaks have been observed in the said range for ZnO thin films or nanostructures [38–44]. The details of the observed emission peaks in the present case have been given in table 3. The relative area under each emission peak in a particular spectrum is also mentioned in table 3. The PL spectra of ZnO usually exhibit emission at UV and visible regions. Whereas the peaks in the UV region correspond to the exciton recombination processes, the peaks in the visible region are believed to be due to the electronic transitions involving at least one defect-associated trap level. There are many defect-associated trap states possible in ZnO structure [38, 39, 45]. These include oxygen vacancies (\( V_O^0, V_O^+ \) and \( V_O^{++} \)), Zn vacancies (\( V_{Zn} \)), oxygen antisite (\( O_{Zn}^\text{a} \)), Zn antisite (\( Zn_{O}^\text{a} \)),

![Figure 4. Room temperature PL spectra of the fabricated TFHSs.](image)

**Figure 4. Room temperature PL spectra of the fabricated TFHSs.**
oxygen interstitial (Oi) and Zn interstitial (Zni). Practically, ZnOi is very less probable because of the high energy of formation. Whereas Zni and VO are donor type defects, VZn, O2-, and Oi are acceptor type. It is a well-known fact that growth conditions as well as excitation energy strongly affect the emission properties of ZnO. For example, Zhang et al. [46] have experimentally demonstrated the PL spectrum of RF sputtered ZnO films on different substrates and with different excitation wavelength. Interestingly, they observed only two emission peaks in most cases (356 nm and 446 nm) related to the near band edge emission (NBE) and deep level emission (DLE). In the present observation, 2–3 emission peaks can be found in the range 350–390 nm alone. The band gap of ZnO as found from the DRS analysis is 3.24 eV (384 nm) can be ascribed to NBE which is the result of recombination of free (intrinsic) excitons in between conduction band (CB) edge and valence band (VB) edge. The other emissions appearing at higher energies (356–374 nm) are due to the recombination of photo generated excitons created as a result of formation of a quasi-Fermi level near the CB edge. This quasi-Fermi level formation is mainly because of two reasons. (i) When the excitation energy is sufficiently higher compared to the band gap [38] and (ii) addition of GNPs lead to transfer of electrons from CB of Au to the CB of ZnO, commonly referred to as Burstein-Moss effect [47, 48]. The latter reason seems to be more effective in the samples containing GNPs as indicated by table 3. Following some of the literature data [38, 39, 45] and based on the present observation of the emission peaks, the possible transitions have been mentioned against the emission peaks in table 3. It is important to mention that several observed peaks have been assigned to a single transition line. This is because of the energy splitting in the mentioned lines or formation of sub bands of energy states. The transition between CB to Oi, for example, involves multiple initial energy states in the CB. Similarly, position of Zni level is reported to have variations from 0.22 to 0.37 eV below CB [38, 39]. Also, the transitions from Zni1 (0.54 eV below CB) and Zni1++ (0.63 eV below CB) to VB have energy difference close to the transitions from CB to Oi and Zni to Oi respectively.

Anderson and Walle [45] have shown from first principle calculations that annealing ZnO matrix can create certain defects that are energetically not favorable at relatively low temperatures. It is important to mention that all the films in the present case have been exposed to at least 300 °C which was the substrate temperature during growth of the films in PLD. Moreover, the film containing GNPs on top of ZnO and sandwich have been additionally annealed at 400 °C. At such temperatures, existence of all the point defects is possible, except for the

| Type of emission | Position of emission (relative area under the emission peak) | Transition details | Type of emission |
|------------------|---------------------------------------------------------------|--------------------|------------------|
| UV               | 356 (9)                                                       |                    | NBE              |
|                  | 363 (17)                                                     |                    |                  |
|                  | 368 (9)                                                       |                    |                  |
|                  | 371 (100)                                                    |                    |                  |
| Violet           | 382 (37)                                                     |                    |                  |
|                  | 383 (100)                                                    |                    |                  |
|                  | 381 (100)                                                    |                    |                  |
|                  | 374 (20)                                                     |                    |                  |
|                  | 384 (46)                                                     |                    |                  |
|                  | 397 (96)                                                     |                    |                  |
|                  | 397 (58)                                                     |                    |                  |
|                  | 405 (100)                                                    |                    |                  |
|                  | 410 (16)                                                     |                    |                  |
|                  | 416 (67)                                                     |                    |                  |
| Indigo           | 420 (29)                                                     |                    |                  |
|                  | 430 (17)                                                     |                    |                  |
|                  | 433 (46)                                                     |                    |                  |
|                  | 430 (75)                                                     |                    |                  |
|                  | 430 (31)                                                     |                    |                  |
|                  | 439 (33)                                                     |                    |                  |
|                  | 440 (4)                                                      |                    |                  |
|                  | 441 (46)                                                     |                    |                  |
|                  | 446 (40)                                                     |                    |                  |
|                  | 446 (60)                                                     |                    |                  |
| Blue             | 450 (17)                                                     |                    |                  |
|                  | 461 (50)                                                     |                    |                  |
|                  | 468 (48)                                                     |                    |                  |
|                  | 463 (91)                                                     |                    |                  |
|                  | 459 (59)                                                     |                    |                  |
|                  | 457 (30)                                                     |                    |                  |
|                  | 474 (25)                                                     |                    |                  |
|                  | 479 (64)                                                     |                    |                  |
|                  | 474 (20)                                                     |                    |                  |
|                  | 482 (9)                                                      |                    |                  |
| Green            | 495 (27)                                                     |                    |                  |
|                  | 499 (69)                                                     |                    |                  |
neutral oxygen vacancy ($V_0^-$) [45]. The area of a particular peak in the PL spectrum is an indication of the concentration of the species responsible for that particular transition, which in turn indicates the defect concentration. Similarly, the broadness in the peak indicates more spread in the corresponding transition energy. As can be seen from the table 3, all the structures show 4–5 major peaks (with relative area $\geq$40%), except for the Si–GNPs–ZnO structure which shows seven major peaks which are also at relatively lower energy as compared to the corresponding emission in bare ZnO. The addition of GNPs seems to have effect in the rearrangement of defects occurring in the TFHSs, when the individual defect concentrations are carefully observed through the relative area of the peaks given. Therefore, it can be concluded that GNPs affect the PL spectrum of ZnO best when covered or embedded.

I–V characterization

The semi-log plots of electrical I–V characteristics with and without light exposure of the prepared thin films have been presented in figure 5. In each panel of figure 5, the corresponding TFHSs have been shown along with the electrical connection scheme. Common to all the measurements, the voltage has been applied across the topmost layer with respect to the p-Si substrate. Some of the common observations from figure 5 with respect to the I–V characteristics include (i) All the structures show diode characteristics of a junction forming at the Si–ZnO interface, (ii) light current is always higher than the dark current in both forward and reverse bias conditions, (iii) reverse bias current is always higher than the forward current, irrespective of the dark/light condition, (iv) the zero bias current is of the order of a few pA which reaches up to the order of a few $\mu$A with a minimal bias voltage ($\sim$0.5 V), and, (v) at the bias voltage of $-10$ V, almost all the samples show dark current values of the order of a few mA. For the ease of understanding, the photocurrent enhancement factor ($\xi$) can be defined as the ratio of light current to dark current in both forward ($\xi_f$) and reverse ($\xi_r$) bias conditions. It can be noted that the vertical gap between the closed and open symbols at a given voltage represents value of $\xi$ at that particular voltage. The values of $\xi$ at $\pm10$ V are mentioned in each panel of figure 5. The electrical I–V characteristics of a diode showing higher reverse current compared to the forward current is suitable for photodiode application. Thus figure 5(a) indicates that the bare ZnO thin film itself can be used as photodiode in the visible region. Since ZnO in ideal condition is not expected to show photoconductivity in the visible region, the observation in present case can be ascribed to the defects formed in the ZnO thin film during the growth [49, 50]. It is clear from figure 5 that although the diode behavior is observed because of the junction formed by n-ZnO and p-Si, the presence of GNPs helps in enhancing the photoconductivity of the n-ZnO through the LSPR phenomenon. The observations from figure 5 also suggest that TFHSs where ZnO contains GNPs in embedded form are better suited for photodiode application. In addition to the diode characteristics described so far, the photoconductivity of the films alone was also studied as given in figure 6. The electrical I–V plots

![Figure 5. Dark and light I–V characteristics of the fabricated TFHSs showing diode behavior. Insets show the connection scheme in each case.](image)

| Voltage (V) | Current (A) |
|------------|-------------|
| 0          | $10^{-10}$  |
| 0.5         | $10^{-9}$   |
| 1.0         | $10^{-8}$   |
| 2.0         | $10^{-7}$   |
| 5.0         | $10^{-6}$   |
| 10.0        | $10^{-5}$   |

The values of $\xi$ at $\pm10$ V are mentioned in each panel of figure 5.
shown in figure 6 were obtained by using both the contacts on the top-most films, as opposed to the contacts used in case of diode measurement. The inverse of the average slopes, which are believed to be proportionally close to the effective resistance of the films, in each case are mentioned against each structure in bracket. As can be seen from figure 6, most of the I–V plots are linear in both dark and light conditions. Only exception of deviation from the linear trend can be observed in the case of Si-ZnO-GNPs at higher voltages. Whereas the effective resistance of the films varies between 2 to 5.5 kΩ, the value decreases below 1 kΩ when the samples are exposed to light. At this point it is important to mention that the effect of contact resistance, if any in this kind of two-probe measurement system, is expected to remain invariant under the exposure to light, as stainless steel pressure contacts were used. Also, the current distribution in such an arrangement can be through the top most film alone or even through the interior bulk state beneath the top most surface of Si substrate, depending on the thicknesses and type of contacts [51]. The depth up to which the current distribution spreads seems to be varying for different structures and with the applied voltage, as per the present observation. The resistance values observed in dark and light conditions in present work can be compared with the earlier report by J Park et al in their resistive switching study [52]. Also, in case of sandwich structure which has ZnO of thickness twice as compared to that in the other structures shows highest resistance in dark condition and lowest in light condition. This observation in the dark condition is against the usually expected behavior of decrease in sheet resistance with the increase in thickness [33]. The reason behind this could be the presence of discontinuous GNPs in between the ZnO layers. The same reason also accounts for the increase in the resistance of the TFHSs when compared to the bare ZnO. Also, for this reason, a bias dependent resistance change is observed in Si-ZnO-GNPs structure. When exposed to light, almost all the structures show linear behavior with decreased resistance and no bias dependent resistance. This indicates a plasmon assisted conduction in the structures containing GNPs, in addition to the photoconductivity of the bare ZnO. The observation of change in resistance in case of the sandwich sample reiterates the conclusion from the diode I–V characteristics that the structures where GNPs are covered by ZnO are better for nurturing plasmonic properties. To further find out the plasmonic effect of the GNPs on the fabricated TFHSs, variation of electrical current at a fixed bias was recorded with time. Figure 7 gives the current versus time (I-t) plots of the TFHSs recorded after switching off the light and at a bias of 0.1 V.

As seen from figure 7, photocurrent in ZnO stabilizes quickly (in only a few seconds, 106 μA to 103 μA, ∼3% and then, it takes 20 min to reach 100 μA). With GNPs beneath ZnO layer, the value of photocurrent is enhanced (dark current by 60% and light current by ∼70%) and takes a little longer time to come down to the dark current value after switching off the light (178 μA to 162 μA, ∼6% in 80 s), as compared the bare ZnO. The current value

![Figure 6. Dark and light I–V characteristics showing the photoconductivity of the fabricated TFHSs. Both the connections were taken from the top-most layer.](image-url)
increases for few minutes and comes down again after about 25 min, all in the dark condition after switching off the light source. In case of the film with GNP on top of ZnO, the I-t curve shows a completely different trend compared to all the other three types of samples. Similarly, decay trend of current value in case of the sandwich structure is similar to the combination of the other three trends. The absolute value of the light current in sandwich structure is ~4 times that of the bare ZnO film, highest among all the structures. Similarly, the light current is lowest in case of GNP on top of ZnO film. The observed trend in the I-t plot for bare ZnO matches well with a recent study by Barnes and Das [54], except for the difference in the absolute values of the change in current from highest value to the stable one. This is due to the huge difference in the applied bias voltage. A close look at all the I-t curves reveals that addition of GNP (i) has increased the intrinsic light current values and (ii) a further increase in the dark current for some time after switching off the light source. This can be explained based on the photo thermal effect of the GNP. In photo thermal effect, the incident radiation absorbed by the GNP during LSPR phenomenon is released in the form of heat energy into the surrounding medium. The maximum increase in temperature ($\Delta T_{\text{max}}$) of the GNP can be written as [55]

$$\Delta T_{\text{max}} = \frac{R^2 I_0}{3 K_0 \lambda} \left[ \frac{3 \varepsilon_0}{2 \varepsilon_0 + \varepsilon_{\text{NP}}} \right]^2 \text{Im}\left( \frac{\varepsilon_{\text{NP}}}{\varepsilon_0} \right)$$

Wherein, $I_0$ is the incident light intensity, $R$ is the radius of GNP, $K_0$ and $\varepsilon_0$ are respectively, the thermal conductivity and dielectric constant of the surrounding medium, $\lambda$ is the excitation wavelength and $\varepsilon_{\text{NP}}$ is the dielectric function of GNP. Even though the value of $\Delta T_{\text{max}}$ depends on several parameters as per equation 3, it mainly varies with the dielectric function and thermal conductivity of the surrounding media in present case, with the other parameters ($I_0$, $R$ and $\varepsilon_{\text{NP}}$) being almost same for all the structures. Whereas the surrounding for GNP is completely ZnO in case of sandwich structure, it is a mixture of ZnO and air in case of the structure with GNP on top of ZnO. Similarly, the surrounding is shared by ZnO, air and Si for the structure with GNP beneath the ZnO layer. The heat energy released by GNP heats up the ZnO film, which further helps in increasing the electrical current, even in the absence of light. This heat is dissipated within the ZnO film which finally cools down with time, thereby bringing the electrical current down to a stable dark current value. Because of difference in surrounding to GNP in different TFHSs, the dominance of photo thermal effect also varies.

Figure 7. Fall time response of TFHSs at $V = 0.1$ V.
Conclusions

ZnO thin films were deposited by using the PLD method. Similarly, GNPs were formed by the DC sputtering of Au and, annealing in optimize condition was followed. Three different GNPs-ZnO TFHSs were formed on Si substrate by varying the relative position of ZnO and GNPs such as Si-GNPs-ZnO, Si-ZnO-GNPs, and Si-ZnO-GNPs-ZnO. The XRD results confirmed high crystallinity of the films, with single phase nature of the individual constituents ZnO and GNPs. The FESEM results confirmed that relative position of GNPs and ZnO can strongly influence the morphology which, in turn, can influence the optical and electrical properties of the TFHSs. The DRS results indicated that position of GNPs relative to ZnOs affects the LSPR of GNPs as well as the overall optical properties of the TFHSs. The PL results revealed that the presence of GNPs affects the defect concentration in the TFHSs. The electrical I–V characteristics showed the photodiode behavior of most of the TFHSs. Similarly, the electrical resistance of the TFHSs was found to increase in presence of GNPs at different positions. The switching in the photoconductivity was found to be affected by the photo thermal effect of GNPs. The combined comparative studies of PL and electrical I–V showed that the plasmonic effect of GNPs is best utilized when these are covered by the dielectric layer.

Conflicts of interest

The authors declare that they have no conflict of interest.

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