CHAPTER - VIII
PHOTOCONDUCTIVITY MEASUREMENT ON STUDY MATERIALS: PHOTO DETECTION

8.1 INTRODUCTION

Photoconductivity is the increase in conductivity of a material resulting from the absorption of optical photons. If the energy of the incident photon is greater than the energy difference between the lowest point of conduction band (CB) and highest point of valance band (VB), then each photon absorbed in the material has a high probability of producing an electron-hole pair (EHP) i.e., a photon is absorbed by ionizing an electron originally in the VB. In this case, the electron in the CB and the hole in the VB contribute to the electrical conductivity of the material under an applied bias. Thus increase in the electrical conductivity of a material caused by irradiation is termed as Photo-conductivity [331]. It has traditionally played a significant role in materials research, most notably in the study of covalently bonded semiconductors and insulators. The photoconductivity study gives substantial information regarding the electronic transition in semiconductors [332, 333]. Photoconductivity is considered to be an important tool for providing information regarding the nature of the photo-excitations.

Since last decade the photoconductive properties of the nano structured inorganic material have become subject of intensive study [334]. Not only because of fundamental interests in the nature of the electronic excitations but also due to their applications in wide range of optical and electronic devices. A good photoconductive device requires not only efficient charge separation but also efficient transport of charge carriers to electrode [335]. The phenomenon of PC vary tremendously with
material, temperature, doping level, presence of donors, acceptors and traps and their concentration, capture cross section, mobility of charge carriers, types of electrical contacts and potential barriers created near them and unintentionally created defect states in the growth process. The measurement of PC helps to identify the steady state Fermi level, the key parameter, needed to understand their complex recombination kinetics. Photo conducting properties of various materials have been investigated by many researchers [336, 337].

In view of the importance of photoconductivity, it has been decided to test the suitability of the study materials as photodetectors and to evaluate their performance parameters. This chapter focuses on the theoretical background of photoconductivity and the photo conducting performance of the study materials in terms of parameters like sensitivity, response time and decay time.

8.2 THEORETICAL BACKGROUND

The basic principle involved in photoconductivity is that when photons of energy greater than that of the band gap of the semiconductors are incident on the material, electrons and holes are created resulting in the enhancement of electrical conductivity. This phenomenon is called intrinsic photoconductivity. It is also possible to observe photoconductivity when the energy of the incident photon is less than that of the band gap. When the energy of the photon matches the ionization energy of the impurity atoms, they are ionized, creating extra carriers and hence an increase in conductivity is observed. This phenomenon is called extrinsic photoconductivity [338]. Usually a slab of material is taken for the purpose of photodetection without internal gain. various types of PN junction can also be used for photodetection with internal gain.
In a semiconductor with free electrons and/or free holes, the electrical conductivity in dark is given by:

\[ \sigma_0 = q \left( n_0 \mu_{n0} + p_0 \mu_{p0} \right) \]  

(8.1)

where, ‘\(n_0\)’, ‘\(p_0\)’ are the equilibrium concentrations of electrons and holes respectively and \(\mu_{n0}, \mu_{p0}\) are the electron and hole mobilities respectively. When the semiconductor is illuminated with light, its conductivity is increased by the generated charge carriers which is represented as ‘\(\Delta \sigma\)’,

\[ \sigma_{\text{ill}} = \sigma_0 + \Delta \sigma \]  

(8.2)

Thus the conductivity under illumination can be given as:

\[ \sigma_0 + \Delta \sigma = (n_0 + \Delta n) q (\mu_{n0} + \Delta \mu_{n}) + (p_0 + \Delta p) q (\mu_{p0} + \Delta \mu_{p}) \]  

(8.3)

Which indicates that photo-excitation can change both the carrier density \((\Delta n/\Delta p)\) and the carrier mobility \((\mu)\). Then considering the case of one-carrier transport for simplicity,

\[ \Delta \sigma = q \mu_{n0} \Delta n + (n_0 + \Delta n) q \Delta \mu_{n} \]  

(8.4)

Since carriers are being generated due to photo-excitation, it is generally true that,

\[ \Delta n = G \tau_{n} \]  

(8.5)

where, ‘\(G\)’ is the photo-excitation rate \((\text{m}^{-3} \text{s}^{-1})\) and ‘\(\tau_{n}\)’ is the electron lifetime, so that:

\[ \Delta \sigma = q \mu_{n0} G \tau_{n} + n q \Delta \mu_{n} \]  

(8.6)
This is the general expression for PC for a material with one-type of charge carrier. Photo-conductivity ‘Δσ’ can be approximated to:

\[ Δσ ≈ qG(μ_n0τ_n + \mu_p0τ_p) \]  \hspace{1cm} (8.7)

so that the "figure of merit" for a single-carrier photoconductor can be defined as:

\[ \Delta σ/qG = \mu \tau \]  \hspace{1cm} (8.8)

Thus the lifetime-mobility product is a measure of the photoconductor's sensitivity to photo-excitation [331].

8.2.1 Photosensitivity

Two major definitions of ‘photosensitivity’ are found in literature. One of these simply describes photosensitivity by the magnitude of ‘Δσ’, whereas the other is in terms of the ratio \( Δσ/Δσ_0 \). Some of the scientific definitions of parameters related to photosensitivity are the following:

(a) Specific Sensitivity

‘Specific Sensitivity’ is a measure of the material's actual sensitivity in terms of the \( \mu \tau \) product [331]. It is cited for large signal PC (\( Δσ >> σ_0 \)) in insulators as:

\[ S^* = \Delta I d^2/\varphi P \]  \hspace{1cm} (8.9)

where, \( \Delta I = \Delta σ A \varphi/d \), ‘d’ is the distance between the two electrodes across which a bias ‘\( \varphi \)’ is applied and ‘A’ is the area of illumination. ‘P’, the input light power is given as:

\[ P = G h \nu d A \]  \hspace{1cm} (8.10)
Using these two definitions, eq. (8.9) can be rewritten as:

\[ S^* = \frac{(q/\hbar)v}{\tau \mu} \]  

(8.11)

**b) Photoconductivity Gain**

The gain of a photo-detector can be defined as the number of charges collected in the external circuit for each photon absorbed. If ‘F’ is the total number of photons absorbed, so that the photo-excitation rate \( G = F/Ad \), then the gain ‘\( G^* \)’ can be expressed as:

\[ G^* = \frac{(\Delta I/q)}{F} = \frac{\tau \mu \phi}{d^2} \]  

(8.12)

where, ‘A’ is area of the detector and ‘d’ the distance between the electrodes. This can be rewritten in the form of \( G^* = \frac{\tau}{(d^2/\mu \phi)} \), which represents the ratio of the carrier lifetime to the carrier transit time. If both electrons and holes contribute to PC, then:

\[ G^* = (\tau_e \mu_e + \tau_h \mu_h) \frac{\phi}{d^2} = \frac{(h\nu/q)}{(\phi/d^2)} S^* \]  

(8.13)

This gain can be physically pictured as following: photo-excitation creates free electrons and holes. If the lifetime of a carrier is greater than its transit time, it will make several effective transits through the material between the contacts, provided contacts are ohmic and are able to replenish carriers drawn off at the opposite contact.

**8.2.2 Model of a Photoconductor**

In the simplest model of a photoconductor, it is assumed that EHPs are produced uniformly throughout the volume of the material by irradiation with an external light source. Recombination of the EHP is postulated to occur by direct recombination. The rate of change of the electron concentration ‘n’ is given by [339]:

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\[ \frac{dn}{dt} = L - Anp = L - An^2 \text{(by using } n = p) \quad (8.14) \]

where, ‘L’ is the number of photons absorbed per unit volume per unit time, ‘A’ is the recombination coefficient; ‘Anp’ gives a recombination rate proportional to the product of hole and electron concentrations. A similar expression for hole concentration can be written as:

\[ \frac{dp}{dt} = L - Anp \quad (8.15) \]

In the steady state, the concentrations are constants and therefore,

\[ n_0 = (L/A)^{1/2} \quad (8.16) \]

The associated PC can be written as:

\[ \sigma = n_0 e\mu = (L/A)^{1/2} e\mu \quad (8.17) \]

This relation predicts that the photocurrent will vary as the light intensity to the power, 1/2. The exponent value is usually between 0.5 and 1.0. If the illumination is cut off suddenly, the decay of carriers is described by:

\[ \frac{dn}{dt} = -An^2 \quad (8.18) \]

which has the solution:

\[ n = n_0 / (1 + Atn_0) \quad (8.19) \]

where, ‘n_0’ is the concentration at time \( t = 0 \), when the illumination is switched off.

The carrier concentration would drop to \((1/2) n_0\) in the time:
\[ t_0 = \frac{1}{An_0} = \frac{n_0}{L} \quad (8.20) \]

The above elementary theory predicts that, for a given illumination level \( L \), the response time is proportional to the photoconductivity (Eq. 8.20). Sensitive photoconductors would have longer response times. Sensitivity or Gain factor \([G]\) can be defined as the ratio of the number of carriers crossing the specimen to the number of photons absorbed in the specimen. If the thickness of the specimen is \( \text{'}d\text{'} \) and the cross section area is unity, then the voltage ‘\( V \)’ produces a particle current \( I = J \), the current density, as the cross sectional area is unity.

\[ J = I = \sigma E = ne\mu E \quad (8.21) \]

or \( \frac{1}{e} = \frac{n_0 \mu V}{d} \), where the steady state value \( n = n_0 \) is considered. Thus,

\[ J = \frac{V\mu Ld}{(d^2(AL)^{1/2})} \quad (8.22) \]

The gain can hence be expressed as:

\[ G = \frac{(V\mu)}{(d^2(AL)^{1/2})} \quad (8.23) \]

The transit time between the electrodes for a carrier is given by \( T_d = \frac{d}{(V\mu/d)} \).

If we take the lifetime of the electron equal to the response time (Eq.8.20) \( t_0 = T_0 \), we have:

\[ G = \frac{T_0}{T_d} \quad (8.24) \]

If ‘\( T_0 \)’ is taken as the observed response time, it is found that the gain thus calculated is very much larger than that observed experimentally. A study of the above phenomenon of direct recombination in terms of extrinsic materials results in
modification of Eq. (8.14) [340]. If ‘\(n_0\)’ and ‘\(p_0\)’ are the equilibrium concentrations of both electrons and holes at \(t = 0\), the excess carrier concentration can be given as \(\delta n_0\) and \(\delta p_0\). For any time ‘\(t\)’, the instantaneous excess carrier concentrations can be given as \(\delta n(t)\) and \(\delta p(t)\). Hence,

\[
\frac{d\delta n}{dt} = Aen_0^2 - Ae (n_0 + \delta n)(p_0 + \delta p) \tag{8.25}
\]

When the excess carrier concentrations \(\delta n_0\), \(\delta p_0\) are both equal and the material to be p-type \(p_0 \gg n_0\) and neglect higher order terms of minority carriers the equation becomes:

\[
\frac{d\delta n}{dt} = -Aep_0 \delta n(t) \tag{8.26}
\]

whose solution is of the form:

\[
\delta n(t) = \delta n_0 \exp (-Aep_0 t) \tag{8.27}
\]

Excess electrons in a p-type semiconductor thus recombine with decay constant \(\tau = 1/Aep_0\). This can also be called as the 'minority carrier lifetime' as it depends on electrons which are minority carriers in p-type materials or as the recombination lifetime. Similar is the case of excess holes in an n-type semiconductor, where the decay time becomes \(\tau = 1/Aep_0\).

**8.3 FACTORS AFFECTING PHOTOCONDUCTIVITY**

**8.3.1 Effect of Traps**

If a crystal with ‘\(N\)’ electron trap levels per unit volume is considered, the effect of traps modifies the Eq. (8.14) as [341]:

\[
\frac{dn}{dt} = L - An^2 - AnN + Bn_t \tag{8.28}
\]
where, ‘n’ is the electron concentration in the conduction band. The last term represents the rate of thermal evaporation of trapped electrons back to the conduction band, which is negligible at low temperatures. In the steady state:

\[ n_0 (n_0 + N) = \frac{L}{A} \quad (8.29) \]

However, it is difficult to grow crystals with trap concentrations ‘N’ less than \(10^{14} \text{ cm}^{-3}\) and at low illumination level, the concentration of carriers ‘\(n_0\)’ is very much less than this. If ‘\(n_0\)’ is very less Eq. (8.29) changes to:

\[ n_0 = \frac{L}{AN} \quad (8.30) \]

So the photocurrent is now proportional to the illumination ‘L’. At high levels of illumination if \(n_0 \gg N\), the equation (8.30) becomes:

\[ n_0 = (\frac{L}{A})^{1/2} \quad (8.31) \]

This equation is similar to Eq. (8.16) in the absence of traps. The three major effects of traps in a semiconductor can be summarized as: (a) decrease in speed of response, (b) decrease in drift mobility and (c) a decrease in the photosensitivity.

**(a) Decrease in speed of response**

The speed of response of a material is inversely proportional to the time constant associated with the increase of PC to its steady state value after turning on the photo-excitation (the rise time) and the time constant associated with the decrease of PC to its dark value after turning off the photo-excitation (the decay time). In the absence of traps in the material, the free carrier lifetime in the material determines the value of these time constants. However in the presence of traps, additional time dependent processes are involved with trap filling [during the rise] and trap emptying [during the decay]. This leads to an increase in the observed decay time of the
photocurrent making it longer than the carrier lifetime. So the 'measured' lifetime is considered as the time for photocurrent to decay to 1/e of initial value, cannot be less than the actual lifetime (without trap effects), but can be much larger. The speed of response is inversely proportional to the experimentally measured lifetime, so that, the speed of response decreases, as lifetime increases. Thus, the presence of traps leads to a decrease in the speed of response [331].

(b) Decrease in mobility

The drift mobility is determined by the time taken by the carriers at one point to travel to a distant point under an electric field. If there are no traps, the injected carriers are free and the drift mobility is same as the conductivity mobility $\mu$. If traps are present, the carriers spent some amount of time in the traps which increases their time of travel and hence a decrease in mobility [331]. On modifying drift mobility as $\mu_d = \gamma \mu$, where ‘$\gamma$’ is the average time spent by the carriers in the traps divided by the average time to escape from a trap and ‘$\mu$’ the mobility in the absence of traps. Now the drift mobility can be written as [331]:

$$\mu_d = [\nu \exp (-E_t/kT)/vS_tN_t]$$  \hspace{1cm} (8.32)

where, ‘$\nu$’ is the attempt-to-escape-frequency, ‘$v$’ the thermal velocity, $E_t$ is the energy difference between the lowest part of conduction band and the trap level, ‘$S$’, is the capture cross section of the trap for electrons and ‘$N_t$’, the density of traps.

c) Decrease in photosensitivity

Eq. (8.5) can now be modified as [331]:

$$G = n/\tau = nS_t\nu N_t$$  \hspace{1cm} (8.33)
where, ‘$N_r$’ is the density of available empty recombination centers with cross section ‘$S_t$’. For every free electron, there is a corresponding hole either in the valence band, $p$ or in $N_r$ so that $n = N_r + p$ and it is reasonable to assume that $N_r \gg p$. Hence from Eq. (8.33), the lifetime without traps can be written as

$$\tau_1 = \frac{1}{n
u S_t}$$ \hspace{1cm} (8.34)

In the presence of traps $N_r = n + N_t \approx N_t$ where, ‘$N_t$’ is the total density of trapped electrons and the lifetime is given by

$$\tau_2 = \frac{1}{N_t \nu S_t}$$ \hspace{1cm} (8.35)

It is evident by comparing the two equations, the lifetime is reduced by the factor $n/N_t$. Thus in the presence of traps the photosensitivity of the materials gets reduced.

**8.3.2 Temperature Dependence of Photoconductivity**

In many photoconductors, the photocurrent is essentially independent of temperature. For an exponential trap distribution, the expected variation of photocurrent is rapid and photocurrent increases with temperature. The change in photocurrent with temperature can be used to predict the activation energy of levels involved in the PC. This is done with the help of the Arrhenius relation [331]:

$$I_{\text{ph}}(T) = I_0 / \{1 + c \exp (-E_a/kT)\}$$ \hspace{1cm} (8.36)

where, ‘$I_{\text{ph}}(T)$’ is the photocurrent at a temperature $T$, ‘$I_0$’ is the photocurrent at temperature 0 K, ‘$c$’ is a constant related to the capture cross section of traps/defect levels and ‘$E_a$’ is the activation energy of the respective traps/defect levels. The plot obtained for variation of photocurrent with temperature can be fitted with the above equation and the activation energy of the trap involved can be predicted.
8.3.3 Effect of excitation intensity on photoconductivity

Variation of the photocurrent with intensity gives the information regarding the recombination process existing in the material. In general, the photocurrent excitation intensity relation is given by:

\[ I_{\text{ph}} \alpha I_{\text{ex}}^\gamma \]  

(8.37)

where, ‘\( I_{\text{ph}} \)’ is generated photocurrent, ‘\( I_{\text{ex}} \)’ is the excitation intensity and ‘\( \gamma \)’ is a dimensionless constant. Evidently, the induced photocurrent depends on the value of \( \gamma \). When \( \gamma = 0.5 \), the emission is due to bimolecular recombination, where the photocurrent varies as the square root of incident light intensity [331]. A model has also been developed stating that when \( \gamma = 0.5 \), the bimolecular recombination is at the surface and when \( \gamma = 1 \) it represents monomolecular reaction in the bulk. In the model that does not deal with traps, \( \gamma = 1 \) for low light intensities and \( \gamma = 0.5 \) for high light intensities, where surface recombination becomes important.

8.3.4 Fermi Level in Photoconductor

The thermal equilibrium Fermi level is useful because knowledge of its location permits the description of the occupancy of all other levels in the semiconductor. Even under illumination, the concept of a Fermi level can be usefully retained. A solution of equations considering the trapping and recombination processes and optical excitation helps in determining the position of Fermi levels in dark and under excitation. The position of Fermi level in the dark and under excitation is shown in the Fig. 8.1. The steady state Fermi level describes the occupancy of those levels that are still in effective thermal equilibrium with the bands i.e. with those imperfections whose occupancy is determined by thermal exchange with the bands rather than by recombination. An alternate way of expressing this is to say that the steady state Fermi level continues to describe the occupancy of traps during illumination, but not of recombination centers.
The position of the electron Fermi level from the CB is given by the equation [339]:

$$E_f = kT \ln \left( \frac{N_c e \mu}{\sigma} \right) \tag{8.38}$$

where, ‘$N_c$’ the effective density of states in the CB, ‘$T$’, the absolute temperature and ‘$\mu$’, the mobility.

Similar definition can be made for the 'Hole Fermi level' too. It is also considered that the defect levels which are lying above the electron Fermi level or below the hole Fermi level can act as a trapping center and the levels in between the Fermi levels can act as a recombination center. So a recombination center can act as a trap at another condition of light level and temperature as the Fermi level varies with light level and temperature. As evident from equation (8.38) as the temperature increases the electron Fermi level shifts down and the hole Fermi level moves up.
8.4 EXPERIMENTAL SECTION
8.4.1 Photoconductivity Measurement

For photoconductivity measurements, the optimized samples of pure and transition metal ions (Ni, Co, Ag) doped samples were used. The optimized samples considered are: CuO (0.2 M), Cu\textsubscript{(1-x)}Ni\textsubscript{x}O (x = 0.005), Cu\textsubscript{(1-x)}Ag\textsubscript{x}O, (x = 0.02), Cu\textsubscript{(1-x)}Co\textsubscript{x}O (x = 0.02). Prior to photoconductivity measurements, these samples were vacuum dried at 80 °C. For the photo response measurements, two silver electrodes (of 150 nm thickness) were coated on the film surface with the separation of 0.5 cm by DC sputtering technique using a shadow mask. The photocurrents were measured by illuminating the sample with white light LED of 100 W/cm\textsuperscript{2} and 3 V biasing condition using the Keithley source meter (Model 2400). All the experiments were done in ambient air at room temperature.

The schematic diagram of the photoconductivity measurement setup is as shown in the Fig. 8.2.

![Fig. 8.2 Photoconductivity measurement setup](image-url)
8.4.2 Dependence of Dark current and Photocurrent on Bias Voltage

The variation of field dependence dark current ($I_d$) and photocurrent ($I_p$) with applied voltage ($V$) for pure and transition metal ion (Ni, Ag, Co) doped CuO films are shown in Fig. 8.3 (a-b). The corresponding variation in ln – ln scale is shown in Fig. 8.3 (c-d).

It is observed that both dark and photo currents of pure and transition metal ion (Ni, Ag, Co) doped CuO films increase linearly with the applied voltage. The measured dark and photo current values are found proportional to the applied voltage in the measured range. The linear increase of current in the dark and visible light
illuminated thin films with an increase in applied field depicting the ohmic nature of the contacts [342, 343]. Moreover, dark current is more in the doped samples than the pure CuO thin film, this may be due to the effect of transition metal ion doping causes the decrease of resistivity, increase of carrier concentration and mobility. Similar findings were observed in CuO thin film and other semiconducting thin films also [13, 344].

The measured current values after illumination (photocurrent) are always higher than dark current. The difference between dark and illuminated photo current clearly showed that undoped and transition metal ion doped (Ni, Ag, Co) doped CuO thin film has good photoconduction response. Hence, it can be said that the material exhibits positive photoconductivity. This is caused by the generation of mobile charge carriers caused by the absorption of photons [345]. The increase in mobile charge carriers during positive photoconductivity can be explained using the Stockman model [346]. The forbidden gap in the material contains two energy levels in which one is located between the Fermi level and the conduction band while the other is located close to the valence band. The second state has high liberate electrons and holes. As it liberate electrons from the conduction band and holes from the valence band, the number of charge carriers in the conduction band gets complete and the current increase in the presence of radiation. Thus the films is said to exhibit positive photo conducting effect. Similar findings were observed for other semiconductor thin films also [342, 347].

From the obtained results, Cu$_{(1-x)}$Ni$_x$O thin film prepared for the doping concentration (x = 0.005) shows the maximum photocurrent among the samples.
considered. This may be due to the effect of Ni doping that causes better in the crystallinity, crystallite size/grain size and/or less grain boundary scattering and large surface-to-volume ratio [348, 349]. Moreover, Ni doping alters the occupancy of the defects by electrons and holes which may reduce the concentration of oxygen adsorption centers and capacity of adsorption on the surface of semiconductor [348, 350]. This may also enhance the photocurrent. The observed linear dependence of photocurrent with applied voltage also supports that, deposited films are free from traps and the change in conductivity may be due to capture of minority carriers rather than capturing majority carriers to bring about recombination [351].

Fig. 8.3 (c) shows variation of dark current ($I_{dc}$) with applied voltage in pure and transition metal ions (Ni, Ag and Co) doped CuO thin films on ln-ln scale. The ln (I) versus ln (V) curves follows the power law, $I_{dc} \propto V^r$, where ‘r’ represents the slope of the line. For all samples, CuO as well as transition metal ions (Ni, Ag and Co) doped CuO are found to exhibit super linear dependence ($r > 1$) of dark current on applied voltage which may be attributed to injection of additional charge carriers from one of the electrodes [352-356].

Fig.8.3 (d) shows the variation of photocurrent ($I_{pc}$) with applied voltage in pure and transition metal ion doped CuO thin films on ln-n scale. From the figure, it is clear that the dependence of photocurrent ($I_{pc}$) with applied voltage also shows super linear ($r > 1$) behavior for all the samples. Super linear behavior dark current as well as photocurrent indicates that the metal-semiconductor contact does not alter under white light illuminations [357].
8.4.3 Rise and Decay of Photocurrent

Fig. 8.4 shows the time resolved rise and decay of photo-current in pure CuO as well as transition metal ions (Ni, Ag, Co) doped CuO samples. The photocurrent growth and decay shown in Fig. 8.4 are measured in ambient air by switching the white light “ON” and “OFF” for 13 min each at 3 V bias. The cell was first kept in dark until the dark current became stable.

![Photocurrent vs Time Graph](image)

**Fig. 8.4 Time-resolved rise and decay of photocurrent in pure and doped CuO thin films**

In all the samples, on illumination, the photocurrent initially increases and reaches a maximum value. This initial increase in the photocurrent is because of absorption of photons which in turn produce additional electron-hole pairs [30]. When the light is switched off, the photocurrent decreases because of the recombination of photo generated carriers, and then stabilizes at a value slightly higher than that of the
initial stable dark current. The difference between the stabilized photocurrent and the
initial stable dark current is known as remnant current [115]. The increase or decrease
of photocurrent may be due to the dominance of adsorption or desorption of oxygen
molecule on the surface of the semiconducting materials [357]. The adsorption and
desorption of Oxygen molecule on the surface of pure CuO can be explained based on
its defect equation.

It is generally accepted that CuO is metal deficient (\(\text{Cu}_{1-x}\text{O}\)) oxide material
with a corresponding defect equation described as:

\[
\frac{1}{2} \text{O}_2 \leftrightarrow V_{\text{Cu}}^{2^-} + 2h^+ + \text{O}_0
\]  

(8.39)

where, ‘\(V_{\text{Cu}}^{2^-}\)’ and ‘\(h^+\)’ represent the concentration of copper vacancies and holes,
respectively. The existence of copper vacancies results in the production of holes and
agrees with the p-type semiconducting behavior of CuO [358].

The surface defects of metal oxides nanostructures are act as \(\text{O}_2\) adsorption
sites in air because of the high availability of the surface area [115]. According to the
defect equation, it may also be suggested that the concentration of holes and thus the
electrical carrier concentrations are highly sensitive to the presence of absorbed \(\text{O}_2\)
molecules. So that the conductivity of nano structured CuO thin film may also
depends on the presence of absorbed \(\text{O}_2\) molecules on its surface.

In the dark, the \(\text{O}_2\) molecules adsorbed on the CuO surfaces capture the
minority charge carriers, i.e., electrons of the p-type CuO
\([\text{O}_2(\text{gas}) + e^- \rightarrow \text{O}_2(\text{adsorbed})]\). This electron transfer lowers of the quasi-Fermi
level and increases the free hole density. As a result, the conductivity of the p-type
CuO increase and a low-conducting depletion layer is formed near the surface. On illumination by the white light, the photo generated and free holes of the p-type CuO drift to the surface along the potential slope produced by band bending and trapped by the adsorbed O$_2$ through the surface electron-hole recombination

\[ h^+ + O_2(\text{adsorbed}) \rightarrow O_2(\text{gas}) \]

and simultaneously the excess holes increase the conductivity of the CuO suddenly. Consequently, the unpaired electrons are either collected by the anode or recombine with holes generated when oxygen molecules are readsorbed and ionized at the surface of CuO. When the light is off, the electrons recombine with the holes and also are captured by the readsorbed O$_2$ molecules causing the increase of depletion width, which gives the faster decay in the current [359]. From the figure it is also found that some remnant current in all the samples, after sudden fall of the current, which may result from the presence of the excess photo generated holes in study materials [115].

The growth and decay process follows the exponential behavior given by the equations [346]:

\[ I_t = I_0(1 - e^{-\zeta_r}) \]

and

\[ I_t = I_0 e^{-\zeta_d} \]

where, ‘$I_t$’ current at the time t, ‘$I_0$’ maximum photocurrent, and ‘$\zeta_r$’ and ‘$\zeta_d$’ are the rise and decay time constants.

The rising and decaying time constant for all the samples were determined by non linear curve fitting function of ORIGIN 7.0 software. The experimental and fitted growth and decay curves of the photocurrent in nano structured CuO, Cu$_{(1-x)}$Ni$_x$O (x = 0.005), Cu$_{(1-x)}$Ag$_x$O (x = 0.02) and Cu$_{(1-x)}$Co$_x$O (x = 0.02) thin films are shown in the Fig 8.5.
Photosensitivity defined as the ratio of maximum photocurrent ($I_{pc}$) to dark current ($I_{dc}$) was calculated. Trap depths are calculated from decay curves. From time-resolved rise and decay of photocurrent curves, the trap depths are calculated by peeling off the decay portion of the curves into the possible number of exponentials governed by exponential law of the current amplitude given by $I = I_0 \exp(-pt)$ [360], where, ‘$I_0$’ is the current at the time when light is switched off, ‘$I$’ is photocurrent at any instant of time, and the ‘$p$’ (= $S \exp(-E/kT)$), is the probability of escape of an electron from trap per second. The trap depth ($E$) can be calculated using following equation:
\[ E = kT \left( \log_e S - \log_e \left( \frac{I_p}{I_d} \right) \right) \]  

(8.42)

where, ‘E’ denotes trap depth, ‘k’ is Boltzman’s constant \((1.381 \times 10^{-23} \text{ J/K})\), ‘T’ is absolute temperature and ‘S’ is attempt to escape frequency of the order of \(10^9\) at room temperature. The photosensitivity, rise time, decay time and trap depth for all the samples are calculated and are listed in Table 8.1

<table>
<thead>
<tr>
<th>Sample details</th>
<th>(I_{dc}) (µA)</th>
<th>(I_{pc}) (µA)</th>
<th>Sensitivity (\eta = \frac{I_{pc}}{I_{dc}})</th>
<th>Rise time (\tau_r) sec</th>
<th>Decay time (\tau_d) sec</th>
<th>Trap depth (E) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>6.7</td>
<td>10.7</td>
<td>1.59</td>
<td>218</td>
<td>58</td>
<td>0.35</td>
</tr>
<tr>
<td>(\text{Cu}(1-x)\text{Ni}_x\text{O}) ((x = 0.005))</td>
<td>7.5</td>
<td>13.4</td>
<td>1.78</td>
<td>328</td>
<td>64</td>
<td>0.36</td>
</tr>
<tr>
<td>(\text{Cu}(1-x)\text{Ag}_x\text{O}) ((x = 0.02))</td>
<td>6.8</td>
<td>12.4</td>
<td>1.82</td>
<td>251</td>
<td>49</td>
<td>0.35</td>
</tr>
<tr>
<td>(\text{Cu}(1-x)\text{Co}_x\text{O}) ((x = 0.02))</td>
<td>6.2</td>
<td>9.27</td>
<td>1.49</td>
<td>230</td>
<td>94</td>
<td>0.32</td>
</tr>
</tbody>
</table>

It is evident from the result that, the transition metal ion (Ni, Ag and Co) doped samples shows higher rise and decay time than the undoped sample. These higher values are due to the defects introduced at the grain-boundary. Hence, doping of transition metal ion onto CuO resulted in the degradation of the photoresponse, due to the doping elements acting as trapping centers and this produce slow response. The role of traps is an important parameter for the photoconductivity process [361]. The slow response may be attributed to presence of trap levels, recombination centers, defect states within the band gap and also surface related process [362, 363]. Similar slow photoconductivity in doped films has been reported earlier [364, 365]. The \(\text{Cu}(1-x)\text{Co}_x\text{O}\) \((x = 0.02)\) sample shows minimum rise time (230 sec) which has the
maximum response among the study material. Generation of photocurrent under white light illumination, and the reversibility and stability of the photoresponse may make these pure and transition metal ion doped CuO semiconductors suitable for devices such as in photo detectors, solar cells and in optical switches.

8.5 CONCLUSION

As metal oxide nanostructures are good for photodetection, spray pyrolitically prepared CuO, and transition metal ions (Ni, Ag and Co) doped CuO thin films have been engaged for photoconductivity study to identify its photosensitivity, photoresponse such as rising time and decay time. From the observed photo response parameter, the undoped CuO thin film shows good photo response behavior, since it has minimum rising time. Also, the Co doped CuO sample shows good photo response among the doped samples.