

Research Article

Dependence of electrical parameters of co/gold-chloride/p-Si diode on frequency and illumination

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ABSTRACT

In this study, metal-semiconductor contact with an organic interlayer was fabricated. Ideality factor (n), barrier height (ϕ_b), and series resistance (R_s) values for Co/Gold-chloride/p-Si structure were calculated for dark and 100–400 mW/cm² light illumination intensities. The current-voltage (I - V) measurements were used to extract the electrical parameters of Co/Gold-chloride/p-Si device such as ideality factor, barrier height and series resistance using different methods like thermionic emission theory and Norde method. The n values were found in the range of 2.00–2.52 and the ϕ_b were calculated in the range of 0.50–0.53 eV and under light power intensities. Additionally, frequency-dependent capacitance-voltage (C - V) measurements were done at room temperature and frequency range from 100 kHz to 1 MHz. The results show that at sufficiently high frequencies, the interface cannot flow A.C signals. Furthermore, barrier height was also calculated from the C^{-2} - V plot for given the frequency range for Co/Gold-chloride/p-Si device. With this study, it has been shown that the rectifier contact of the organic-inorganic structure formed with suitable organic and inorganic semiconductor can be formed and this structure can be used in optoelectronic applications.

1. Introduction

Recently, many organic and inorganic based compounds have been used in the production of electronic circuit elements [1]. Organic semiconductor materials are widely used in the production of new types of circuit elements due to their superior electrical and optical properties. It is seen as an advantage that these compounds are easy to manufacture and low cost [2]. In addition, organic-based semiconductors are used as active components in solar cell applications, light emitting diode (LED), organic light emitting diode (OLED), thin films, schottky diodes and sensors. Recent studies [3,4] by scientists have focused on the sensitivity and photo response properties of metal-semiconductor diodes. The photovoltaic and photo-susceptibility properties of the circuit elements are tried to be improved by making many organic or inorganic based

doping [5].

When the recent studies are examined, the production of organic-inorganic hybrid based circuit elements; especially photodiodes come to the fore. In this way, the electronic parameters are brought to the desired level with atoms that can be added to the structure from the outside. LED, OLED, photodetector, photovoltaic systems, phototransistor and photodiode are the best examples for optoelectronic device applications [6]. Optoelectronic circuit elements are defined as light-emitting or light-sensitive circuit elements that help transmit light from one section to another. Optoelectronic devices have many uses such as power electronics, control and communication. Photodiodes, known as circuit elements operating in reverse bias, produce reverse current by absorbing the light coming on them [7]. Since photodiodes are very sensitive to light, they have a wide range of uses. It is frequently

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used in photometry devices, flashes, computers, photography, and thin-film transistors [8].

The development of organic-based light-sensitive materials; has offered a wide area of use in technology. An interesting reason for the general interest in organic-based photosensitive organic semiconductors is the possibility of using chemical methods to adjust photoelectric properties [9]. Organic dyes have high thermal and chemical stability as well as photoconductive properties [10]. Nowadays, theoretical and experimental studies on photodiodes produced as hybrid structures of organic compounds and inorganic substrates are increasing rapidly. Several reports in the literature have highlighted the importance of organic dyes in the manufacture and development of electrical and optical devices as follows. The photo-response properties of the Au/Coumarin doping Bi₂O₃/p-Si/Al photodiode under different illumination intensities were investigated. It was determined that the circuit element has very good sensitivity to light [11]. Indigo carmine photodiode was fabricated with a wide range of applied voltage and frequencies as a candidate for optoelectronic applications [12]. Al/coumarin/p-Si/Al diode was fabricated via chemical route and was evaluated that the circuit element can be used as a photo device due to its high photo-response [13]. H. Abd El-Khalek et al. fabricated a photodiode with the architecture of Al/n-Si/ α -6T/Au and reported that the circuit element has the sensitivity to the light [14]. PCBM doped Al/PCBM:ZnO/p-Si devices were fabricated by using chemical and physical methods. In that study, the effect of the PCMB layer on the photoresponse capacity of devices was investigated [15]. Methyl Violet as an organic interlayer was fabricated via a chemical process and some electrical properties were studied. It was found that the barrier height of the diodes can be modified using Methyl Violet organic dye [16].

Gold (III) chloride, traditionally called auric chloride, is a chemical compound of gold and chlorine. With the molecular formula Au₂Cl₆, the name gold trichloride is a simplification, referring to the empirical formula, AuCl₃ [17]. Gold (III) chloride is very hygroscopic and highly soluble in water as well as ethanol. It decomposes above 160 °C or in light. In gold (III) chloride, each gold center is square planar, which is typical of a metal complex. The bonding in AuCl₃ is considered somewhat covalent [18].

In this study, Gold-chloride/p-Si film was prepared by the sol-gel spin coating method, which is a simple, low cost and convenient method, and photodiodes of this film with Co/Gold-chloride/p-Si structure was produced. Fig. 1 shows the schematic diagram of the fabricated device. According to our best knowledge, there are no studies conducted to fabricate and analyze the electrical characterization of this diode. The organic interfacial layers on semiconductor structures have gained attention due to their importance on electronic and optoelectronic applications. It is significance to see the suitability and possibility of use of the Gold (III)chloride organic films in barrier modification of Si MS diode. There is also no any contact engineering work on Gold (III) chloride/p-Si structure and Co has been used as a measuring electrode and Co contact is required in the area of the device needed in experimental calculations.

This study aims to investigate the potential use of Gold-chloride for photodiode applications in Co/Gold-chloride/p-Si sandwich structure. To achieve this, current-voltage (I-V) measurements based on light intensity (P) at room temperature and capacitance-voltage (C-V)

measurements in the dark were performed. The obtained photodiodes were characterized and compared in the details according to responsivity, photosensitivity, and various diode parameters.

2. Experimental

In the device design examined within the scope of the study, a p-type silicon semiconductor plate with (100) crystal orientation, 400 μ m thickness and 5–10 Ω cm resistance was used. Following the cleaning of the p-Si wafer using Radio Corporation of America (RCA) [19] cleaning techniques, the Al metal contact layer with 120 nm thick has been developed on its unpolished side using the DC magnetron sputtering technique at 10⁻⁶ torr pressure. Annealing was carried out at 580 °C for 10 min. An interlayer film was grown by using a gold chloride solution commercially purchased from Merck with the code HT1004. After dropping this solution onto the p-Si wafer, the gold chloride thin film layer was obtained by rotating it with Laurell Model WS-400A-6TFM/LITE spin coater at 3000 rpm for 30 s. The resulting gold chloride/p-Si/Al structure was allowed to dry in the glove box for 12 h before the growing procedure of the working electrode. The device architecture was completed by growing the Co point contacts with 7.85 \times 10⁻³ cm² active surface area on the gold chloride film layer at a 10⁻⁵ Torr pressure with a VAKSIS DC magnetron sputtering device. To investigate the device's response to light Scientec solar simulator (AM 1.5 G) was used. Also, the capacitance-voltage (C-V) measurements of the diode were carried out using the Hewlett Packard 4192A LF Impedance Analyzer at frequencies we chose from 100 kHz to 1 MHz with an OSC level of 30 mV and from -2 V to +2 V in 50 mV steps.

3. Results and discussions

The most common method used to calculate the electrical parameters of photodiodes is the classical I-V method. The I-V characteristics are determined by the current-carrying mechanism of the photodiodes at the junction surface [20]. There are two important parameters for a typical photodiode, low dark current and high breakdown voltage. Low dark current in photodiodes indicates high sensitivity. With I-V analysis of a photodiode, it is possible to determine electronic parameters such as ideality factor (n), barrier height (Φ_b), series resistance (R_s), and reverse saturation current (I_0). Reverse saturation current and barrier height can be calculated by fitting the current in forwarding bias at the point where the voltage is zero. The ideality factor can also be found by the slope of the I-V curves in forwarding bias. When the current is not very high in schottky photodiode, it can be obtained from the following equation with the help of Thermionic Emission (TE) theory [21–23]:

$$I = I_0 \left[\exp\left(\frac{qV}{kT}\right) \right] \quad (1)$$

where q is the electron charge, k is the Boltzmann constant, I current, V is the diode voltage, and T is the temperature in Kelvin. I_0 is the reverse saturation current for majority carriers and is given below:

$$I_0 = AA^* T^2 \exp\left[\frac{-q\phi_b}{kT}\right] \quad (2)$$

here ϕ_b , A, and A* are Schottky barrier height, diode area and Richardson constant, respectively. The ideality factor (n) is added to eq. (1) to determine situations other than ideal. In this case, it is expressed as Eq. (1):

$$I = I_0 \left[\exp\left(\frac{qV}{nkT}\right) \right] \quad (3)$$

here, the ideality factor depends on the interface conditions, applied voltage and temperature, and its value is greater than 1. The ideality factors of the structures obtained were calculated from the slope of the semi-logarithmic I-V curve as follows [24–26]:

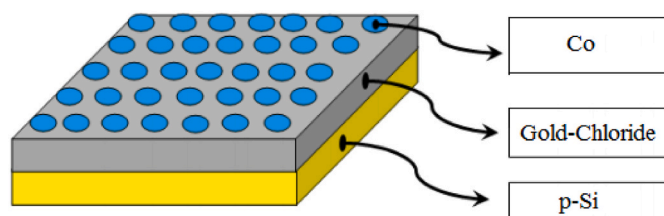


Fig. 1. Schematic representation of the Co/Gold-chloride/p-Si device.

$$n = \frac{q}{kT} \frac{dV}{d(\ln I)} \quad (4)$$

If it is solved according to ϕ_b by taking the logarithm of both sides of Eq. (2):

$$\phi_b = \frac{kT}{q} \ln \left(\frac{AA^* T^2}{I_0} \right) \quad (5)$$

The above equation is obtained. The n and ϕ_b values were determined by using the expressions (4) and (5).

The I–V plots of the Co/Gold-chloride/p-Si photodiode were performed under dark and air mass (AM) 1.5G illumination at room temperature and given in Fig. 2. The Co/Gold-chloride/p-Si device exhibited good rectification properties under dark and all applied light intensity condition. The higher the light power intensity of the photon sent on the photodiode, the more photocurrents are provided to pass. If the light power intensity of the transmitted photon is increased, the resistance at the surface junction decreases and the photocurrents through the photodiode increase. This increase indicates that the diodes are light sensitive and the hole and electrons are formed and contribute to the generated current with the absorption of light [27].

Values of n and ϕ_b for Co/Gold-chloride/p-Si structure under dark and different light illumination intensities were calculated with the help of eqs. (4) and (5) and were given in Table 1. Under dark conditions, the ideality factor and barrier height were obtained as 2.17 and 0.61 eV. The n values were found in the range of 2.00–2.52 under light power intensities and were far from the ideal diode characteristic. These values of the ideality factor depend on the interface states or barrier inhomogeneity caused by the Gold-chloride interface and Gold-chloride and p-Si surface [28]. For the Co/Gold-chloride/p-Si structure, the barrier height was calculated in the range of 0.50–0.53 eV and decreases with increasing light intensity parallel to the general behavior trend. The decrease in barrier height ϕ_b values with the increase of light power intensity is attributed to the charge carriers increasing with the illumination at reverse bias. The tendency of this situation to decrease the barrier height is consistent with the other research in the literature [29]. These results show that the Co/Gold-chloride/p-Si structure reacts as a photosensitive device. K. Koran et al. reported that the photo-response

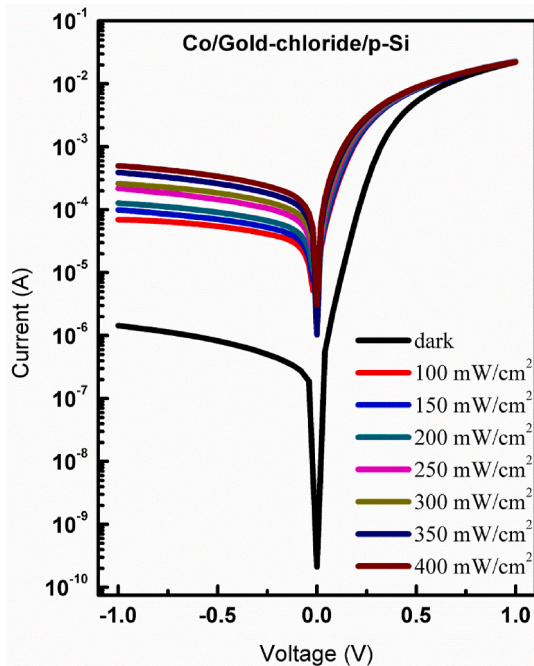


Fig. 2. I–V characteristics of Co/Gold-chloride/p-Si photodiode under dark and different light power intensities at room temperature.

properties of the Al/p-si/phosphazene/Al diode under various power intensities. Photocurrent results showed that the investigated device reacted as a photodiode device [30]. Light voltage-current characteristics under various illumination intensities for [P (EGDMA-VP-CA)-SWCNT]/n-Si were investigated by B. Kirezli et al. [31]. It was shown that the fabricated structure illustrates rectification behavior for the optoelectronic area. A.M. Mansour deposited BCP films and investigated their electrical characteristics using I–V measurements. In illumination mode, the device showed that light-induced charge transfer occurs in the reverse direction, suggesting that BCP-based devices can be used as a photodiode [32].

Fig. 3 demonstrates the n -P and ϕ_b -P plots of the Co/Gold-chloride/p-Si photodiode. According to Fig. 3, the ideality factor values increased with increasing of the light intensity while the barrier height decreased. The increase of the n can be attributed to the decrease of rectification ratio and barrier height or increase of the I_0 and maximum reverse currents. H.H. Gullu et al. investigated the electrical properties of spin-coated Al/PCBM: ZnO/Si diode investigated for photodiode application. The leakage current profile tends to increase with the increase in illumination, and as a result, ϕ_b increases, while n values decrease with the contribution of photo-formed carriers to the current flow [33].

The rectification ratio (RR) is proportional to the forward current (I_F) and the reverse current (I_R) at the specific voltage in dark condition, given in the below equation [34]:

$$RR = \frac{I_F}{I_R} \quad (6)$$

The RR of the dark I–V curve is 1.54×10^4 at ± 1 V bias. The RR (at ± 1 V) versus light power intensity curve has been shown in Fig. 4 and this ratio decreased with increasing light intensity. RR values of Co/Chitosan/p-Si/Al heterojunction were found as a function of power intensities in the range of 100–400 mW/cm², and the dark RR of the photodiode is higher than the lighting conditions. It was reported by Kacus et al. [35] that the device has a good photo-response and can be used in several electronic and optical applications.

In such cases, one of the methods that can be used to calculate series resistance and barrier height sizes was Norde function $F(V)$ [36]:

$$F(V) = \frac{V}{\gamma} - \frac{kT}{q} \ln \left(\frac{I(V)}{AA^* T^2} \right) \quad (7)$$

where γ shows dimensionless integer and greater than n . The $I(V)$ indicates voltage dependent current. The ϕ_b and R_s values are obtained from Norde function and addressed by the following formulas:

$$\phi_b = F(V_0) + \left[\frac{V_0}{\gamma} - \frac{kT}{q} \right] \quad (8)$$

$$R_s = \frac{\gamma - n}{I} \frac{kT}{q} \quad (9)$$

where $F(V_0)$ is the minimum point of $F(V)$ and V_0 is the corresponding voltage.

Fig. 5 illustrates the $F(V)$ – V curves of the fabricated photodiode under dark condition and various light power intensities. The values of the barrier height and series resistance were determined from these plots (using Eqs. (8) and (9)) and summarized in Table 1. The decrease of the barrier height with increasing light power is consistent with the values obtained from the TE model due to the decrease in rectification ratio.

Photodiodes start working when they get enough light and are a current source. Light coming into the photodiode causes a weak current to occur. When a voltage is applied to the photodiode, a photocurrent occurs due to the charge resistance. This charge constitutes the sum of the external circuit resistance. Most of the efficiency of photocurrent occurs on the external circuit and a small part on the internal resistance. The photoconductive behavior of the diodes is analyzed by the following relationship [37]:

Table 1
Electrical parameter values for prepared photodiode under different light power intensities.

Light power intensity (mW/cm ²)	I ₀ Saturation Current (A)	n (TE)	φ _b (TE) (eV)	φ _b (Norde) (eV)	R _s (Norde) (F(V)-V) (Ω)	Rectification ratio (RR)
100	2.23 × 10 ⁻⁵	2.00	0.5361	0.5396	20.85	328
150	2.46 × 10 ⁻⁵	2.02	0.5336	0.5316	25.03	230
200	2.92 × 10 ⁻⁵	2.12	0.5291	0.5289	20.22	180
250	3.56 × 10 ⁻⁵	2.22	0.5240	0.5183	19.75	104
300	3.61 × 10 ⁻⁵	2.26	0.5236	0.5159	17.06	86
350	4.35 × 10 ⁻⁵	2.32	0.5188	0.5058	17.82	57
400	6.38 × 10 ⁻⁵	2.52	0.5089	0.5027	11.05	44

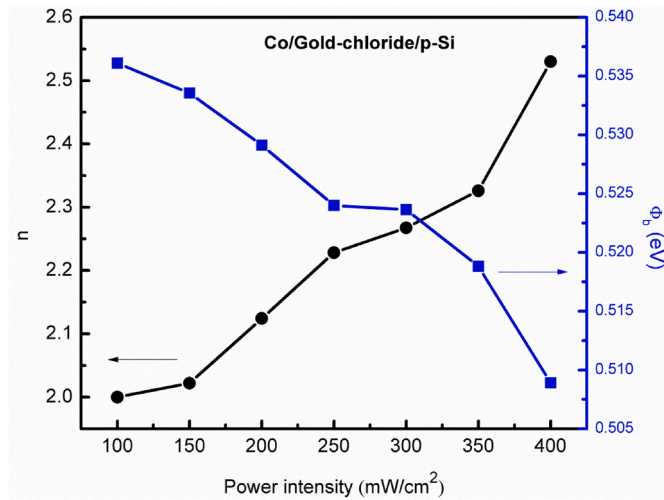


Fig. 3. Variation of *n* and ϕ_b values with power intensities from I–V graph of Co/Gold-chloride/p-Si diode.

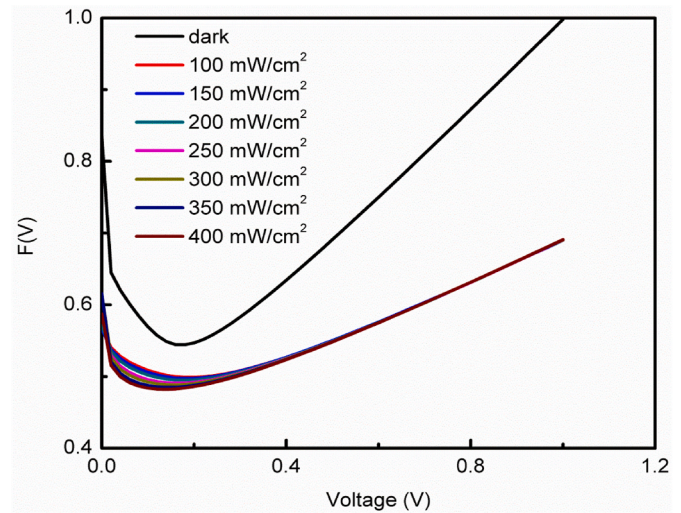


Fig. 5. Norde's function plots for Co/Gold-chloride/p-Si diode under light power intensities.

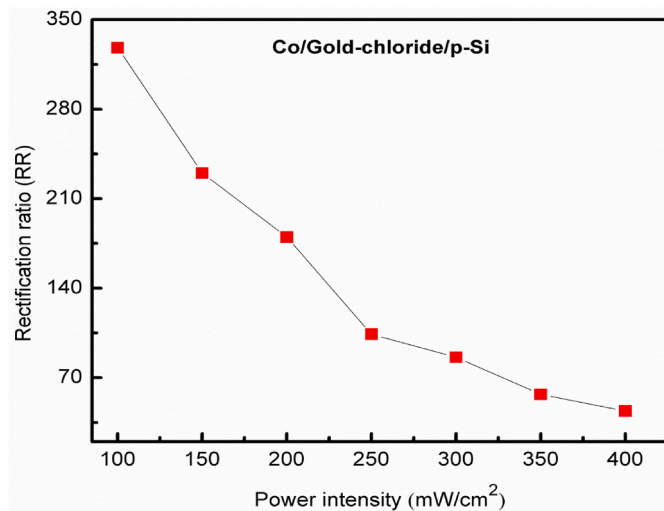


Fig. 4. The rectification ratio of Co/Gold-chloride/p-Si diode under light power intensities.

$$I_{ph} = BP^m \tag{10}$$

where I_{ph} is the photocurrent, *B* is constant, *P* is the illumination intensity, and *m* is the illumination coefficient. The value of the *m* for diodes determines the type of photoconductor mechanism. When the illumination coefficient values are 0.5 and 1, the photoconductivity mechanism of the diodes is related to a bimolecular recombination process and a monomolecular recombination process, respectively. When the value of *m* is between 0.5 and 1, the photoconductivity

mechanism is explained by a continuous distribution of trapping centers in the band. However, values higher than 1 suggest that the photoconductivity mechanism is due to the empty trap levels. The photocurrent-dependent profile of the fabricated photodiode depending on the illumination intensity has been shown in Fig. 6. The slope between log (I_{ph}) and log (*P*) is used in the graph and the illumination coefficient value determined as 1.44. This value shows that the Co/Gold-chloride/p-Si diode exhibits a linear photoconductor mechanism. A similar observation was observed by Yilmaz et al. [38] determining the *m* value as 1.67 for the MG n-Si bio-hybrid photodiode. G. Ersoz Demir [39] obtained the

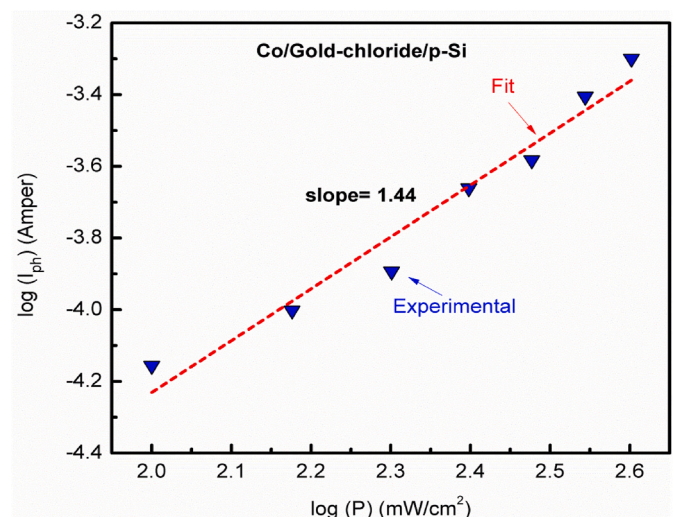


Fig. 6. Log (I_{ph}) – log (*P*) plot for the Co/Gold-chloride/p-Si structure.

m value as 1.74 and this value stemmed from the formation of electron-hole pairs in the space charge zone and the recombination of charge carriers.

It is seen that reverse bias I-V characteristics exhibit an unsatisfactory behavior in the dark, but reach saturation with illumination. Under illumination, photons with energies higher than the band gap energy of the semiconductor can lead to the generation of electron-hole pairs in the depletion region of the semiconductor. Next, the electron-hole pairs are separated at the grain boundaries by the strong local internal electric field. While the electrons are swept out of the organic layer by the electric field, the holes are swept slowly so that they can be trapped by the defects. As a result, there will be an additional conductivity in the diode here [40].

Photodiode responsivity (R), which is an important diode parameter, defined as a measure of light sensitivity, The photodiode responsivity is defined as the ratio of the photocurrent to the power of light falling on the photodiode surface at given wavelengths. In other words, this value is a measure of converting light energy into electrical energy. The photodiode responsivity varies with the wavelength of the light falling on the photodiode as well as the temperature and the applied reverse bias voltage. Photodiode responsivity can be considered based on the following formula [41]:

$$R = \frac{I_{ph}}{P} \quad (11)$$

The responsivity of the Co/Gold-chloride/p-Si photodiode depending on reverse bias has been displayed in Fig. 7. It is clear that as the reverse bias voltage increases, the photodiode responsivity increases importantly and reaches saturation at higher voltages. H. Abdel-Khalek et al. [42] fabricated copper (II) acetylacetonate Cu (acac) 2 thin film to investigate electrical properties for light detection. The fabricated device showed a great response to the variation of illumination intensity. To increase the photodiode responsivity, the ratio between light hitting the photodiode surface and reflected light is reduced. A similar observation was made by Kacus et al. [43]. They found that R values of fabricated diode showed remarkable sensitivity to variation in illumination intensity. Therefore, R values present different variations towards higher densities and can be used in several power applications.

To further explore the Co/Gold-chloride/p-Si photodiode under variable illumination we have analyzed and interpreted the photosensitivity (S), which is calculated by the following equation [44]:

$$S = \frac{I_{ph}}{I_{dark}} \quad (12)$$

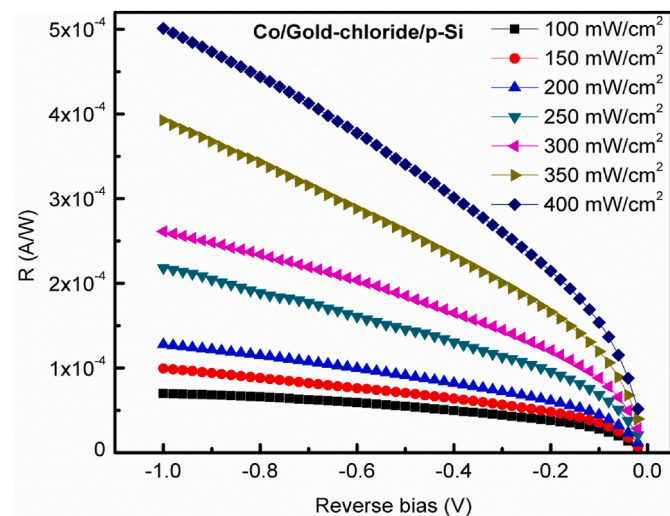


Fig. 7. The responsivity (R) versus reverse bias of the Co/Gold-chloride/p-Si photodiode depending on the light intensities.

where I_{ph} and I_{dark} are indicating is the photocurrent and dark condition current, respectively. The S vs. V plot of the device has been obtained and given in Fig. 8. According to Fig. 8, it is obvious that the device is sensitive to light at all light power intensities. A similar observation was done by Z. Orhan et al. [45] fabricated Cu/HSA/n-Si device to search the behavior of the device in optoelectronic applications. They concluded that the device can be used more efficiently as a photodetector. M. Aslam Manthrammel et al. [46] fabricated Au/Indigo/n-Si photodiode and investigated its diode characteristics. They reported that the diode shows high sensitivity in the reverse bias region where the sensitivity increases very rapidly with the bias voltage. H. Alzahrani et al. [47] investigated the effect of illumination intensity on the performance parameters photodiode based on solution-processed NPD:Alq3 composite film. They concluded that the photodiode sensitivity increased linearly and the photodiode responsivity decreased exponentially with the intensity of illumination.

The Capacitance-Voltage (C-V) characteristic of Schottky diodes is one of the most important features. The C-V characteristic of Schottky diodes has a significant influence on the electrical properties of the devices in which they are found, and they are extremely sensitive to interface states. The C-V graph of the Co/Gold-chloride/p-Si diode is shown in Fig. 9.

Barrier height values can also be calculated from the C-V measurements using reverse bias $1/C^2$ -V plots. $1/C^2$ -V plot has been illustrated in Fig. 10 as the function of applied frequency. According to $1/C^2$ -V plots, good linearity was obtained for all frequencies.

As seen in Fig.10, C^{-2} -V curves show a linear behavior in the negative voltage range for all frequency values. In this linear region; for interfacial layer Schottky diodes, the relationship between C^{-2} and V can be expressed as follows [48]:

$$C^{-2} = \frac{2}{q\epsilon_s\epsilon_0A^2N_A}(V_0 + V_R) \quad (13)$$

where A is the rectifier contact area, ϵ_s is the dielectric constant of the semiconductor. N_A is the density of the acceptor contribution atoms, V_R is the applied inverse bias voltage and V_0 is the built-in voltage obtained by extrapolating the C^{-2} -V curve to the voltage axis. The relationship between V_0 and V_D diffusion potential is given by the following equality:

$$V_0 = V_D - \frac{kT}{q} \quad (14)$$

Here kT/q term is thermal energy in eV. So the potential barrier height values for frequency intensities are obtained using the following

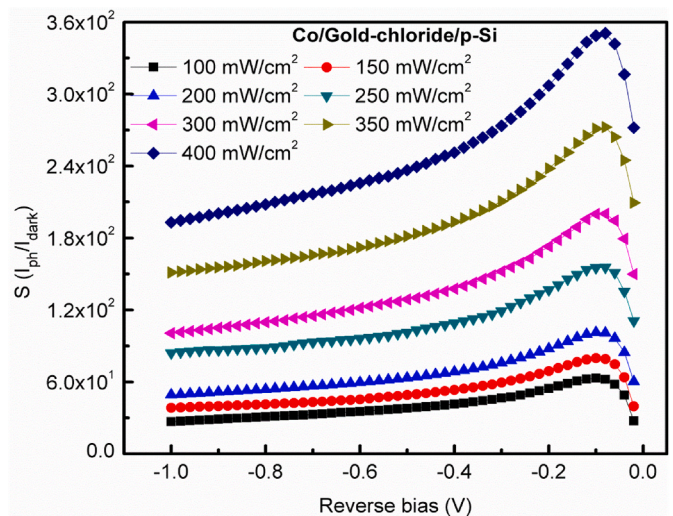


Fig. 8. The photosensitivity (S) versus reverse bias plot of the Co/Gold-chloride/p-Si.

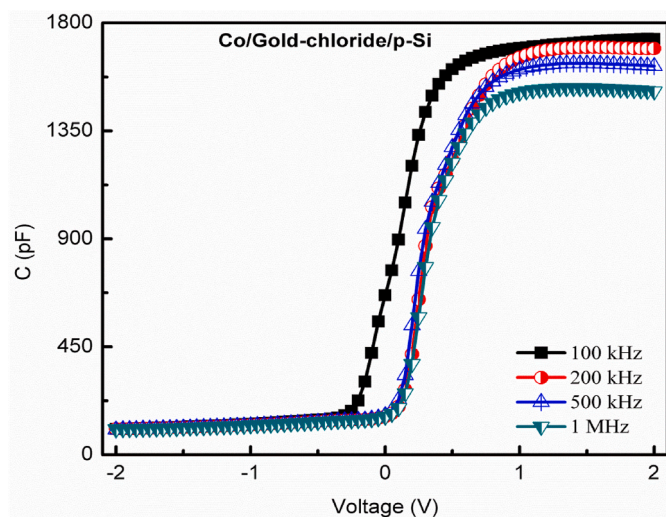
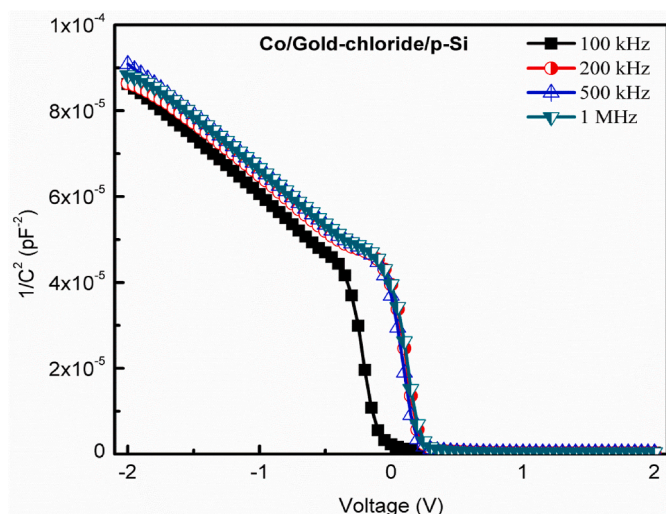


Fig. 9. Capacitance-voltage graph of Co/Gold-chloride/p-Si diode with different AC signal frequencies.



Figs. 10. C^{-2} -V curves for Co/Gold-chloride/p-Si diode.

equation [49]:

$$\Phi_b(C - V) = V_D + E_F \quad (15)$$

Here E_F is the Fermi energy level of the semiconductor. The barrier height values were found to be 0.74, 0.92, 0.94, and 0.97 eV for 100 kHz, 200 kHz, 500 kHz and 1 MHz frequency values, respectively. Kacus et al. [50] fabricated Co/pentacene/n-Si/Al device and investigated its capacitance behavior. They found that one of the electrical parameters Φ_b values are affected by frequency and voltage changes and these values were determined between 0.54 and 1.06 eV under the same frequency values carried out by us. The values determined from capacitance-voltage measurements are higher than the values determined from current-voltage measurements. This may be as a result of the present organic and oxide layer at the interface, inhomogeneities in interface states as well as the effect of image force barrier lowering [51].

4. Conclusion

Current-voltage measurements under different illuminations range from 100 to 400 mW/cm² by 50 mW/cm² interval were taken. The determined results indicate that the fabricated photodiode has a good

photocurrent response to the incident light intensity concerning reverse biasing voltage. Also, the fabricated photodiode has high photo responsivity for incident power of illumination, and good photo sensitivity to detect small signals of incident light at low reverse voltages. It has been observed that the capacitance characteristic diode depends on the frequency, the voltage, and that the capacitance value decreases with the increase of the frequency value. The main reasons for this situation, which are observed depending on the frequency, are that the series resistance between the metal contacts and the interlayer material affects the capacitance, the forbidden energy range and the frequency values of the charges at the interfaces follow the applied ac signal and contribute to the capacitance. With the increase of the applied frequency value, charges in the interface and forbidden energy range and affect the material capacitance lose their ability to follow the ac signal. For this reason, the contribution of these charges to capacitance is reduced. Due to the mentioned factors, the sample diverges from the ideal capacitance-voltage character. As a result, the fabricated device is a good candidate to be used in electrical and optoelectrical applications such as a photodiode.

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CRediT authorship contribution statement

E. Erdogan: Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **M. Yilmaz:** Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **S. Aydoğan:** Conceptualization, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **U. Incekara:** Conceptualization, Methodology. **Y. Sahin:** Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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