Substrate temperature effects on reactively sputtered Cr$_2$O$_3$/n-Si heterojunctions

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Abstract. To see the effects of substrate temperature on Cr$_2$O$_3$/n-Si heterojunctions, Cr$_2$O$_3$ thin films were formed on n-Si and glass substrates at 40, 150 and 250 °C by radio frequency (RF) reactive sputtering technique. High purity Cr was used as target and oxygen was used as reactive gas. Optical properties of Cr$_2$O$_3$/n-Si thin films were analyzed using UV-vis data. The band gaps of the films were compared. The electrical properties of Cr$_2$O$_3$/n-Si heterojunction were tested by their current voltage ($I-V$) measurements in dark. It was observed that the heterojunction which was fabricated by forming Cr$_2$O$_3$ thin film at 250 °C gave better rectification. The characteristic electrical parameters such as barrier height, ideality factor and series resistance were calculated by using its $I-V$ data. The influence of light intensity on photovoltaic effect behavior of the device was also calculated, finally the barrier height value of the structure obtained from capacitance-voltage ($C-V$) data were compared with the one calculated from $I-V$ measurements.

1. Introduction
Chromium oxide with Cr$_2$O$_3$ formula is a wide band p-type semiconductor. It has been used as protective coating because of its outstanding wear resistance. Kao et al (1989) formed Cr$_2$O$_3$ thin films by sputtering of Cr$_2$O$_3$ thin films for various substrate temperatures. It was showed that the Cr$_2$O$_3$ thin films formed at 150 °C in pure argon annealed at 300 °C had the hardness about 25 GPa [1].

Erdogan and Gullu [2] obtained Cr$_2$O$_3$ nanoparticles by hydrothermal technique. They formed Cr$_2$O$_3$ thin film on p-Si substrate by spinning using nanoparticle solution and annealed at 500 °C for 1 h. They studied optical, morphological and structural properties thin film. They used x-ray diffraction (XRD), non-contact atomic force microscopy (AFM), ultraviolet-visible spectroscopy (uv-vis) and photoluminescence (PL) spectroscopy. They reported that the thickness of the film is about 70 nm and the band gap of the film was 3.08 eV. They also formed Au/Cr$_2$O$_3$/p-Si metal-insulator-semiconductor (MIS) diodes to determine electronic parameters by means of $I-V$ and $C-V$ data. They calculated ideality factor and barrier height of the device as 2.14 and 0.74 eV, respectively. They also calculated interface state density distribution of the diode.

Formation of thin films to fabricate heterojunctions can be performed using many kinds of techniques such as spin coating, ultrasonic spray, thermal evaporation, pulsed laser deposition,
electron beam and magnetron sputtering. It is very difficult to form thin films of refractory metals or ceramics. Magnetron sputtering technique is a unique method to obtain uniform thin films of ceramics refractory metals or ceramics [3].

In this study, Cr$_2$O$_3$ thin films were formed on n-Si semiconductor and substrate by means of reactive sputtering technique at 40, 150 and 250 °C. A chromium metal target used as source and O$_2$ used as reactive gas. Optical properties of the thin films were determined using UV-vis data. Au metal was evaporated on Cr$_2$O$_3$/n-Si structures. Electrical properties of the Cr$_2$O$_3$/n-Si heterojunctions were examined using their I-V measurements in dark at room temperature. It was seen that the device obtained using the Cr$_2$O$_3$ formed at 250 °C gave an excellent rectification property. The characteristic electrical parameters including barrier height, ideality factor and series resistance of the rectifying diode were determined. The effect of the light on photoelectrical parameters such as sensitivity to light, open circuit voltage and short circuit current were determined for various illumination intensities. Furthermore, capacitance-voltage properties of the structure were also analyzed.

2. Experimental Procedures

In the study, an n-Si wafer with (100) orientation and 1-10 Ωcm resistivity is used. The ohmic contact was formed on unpolished side of n-Si wafer as in literature. Cr$_2$O$_3$ thin films were growth on n-Si semiconductor and glasses by reactive sputtering technique using Nanovak NVTS 400 vacuum system. Cr metal was used as target and O$_2$ was used as reactive gas. For all processes, firstly, pressure of the vacuum system was decreased at 10$^{-6}$ Torr. Argon gas was send to system and the pressure was increased to 20 mTorr. The flow of the Argon gas was about 4 ccm. 80 W power was applied to high purity Cr target and 0.4 ccm oxygen was send to vacuum system to make reactive sputtering process. This process continued 10 minutes. The substrate temperatures were 40, 150 and 250 °C during sputtering process. To increase crystallinity, Cr$_2$O$_3$ thin films were annealed at 500 °C for 30 minutes in air ambient. Au metal was evaporated to obtain front contact. The circular diameters of the Au contacts were about 1.5 mm. To make circular front contacts a shadow mask is used. Electrical and photoelectrical characteristics of Au/Cr$_2$O$_3$/n-Si structures were analyzed using its current-voltage (I-V) and capacitance-voltage (C-V) measurements by the help of Keithley 2400 sourcemeter and Agilent 4294 A impedance analyzer at room temperature in dark, respectively. To see the effect of the light on the photoelectrical properties of the device an Oriel 9600 solar simulator was used. Current-voltage (I-V) measurements were repeated under solar simulator between 40-100 mW/cm$^2$ with 20 mW/cm$^2$ intervals. Optical properties of the thin film on quartz were analyzed using Shimadzu 3600 Uv-vis-nir spectrophotometer.

3. Results and Discussion

1.1. Optical properties of Cr$_2$O$_3$ thin films on glasses

Optical properties of the Cr$_2$O$_3$ thin films were analyzed by means of UV-Vis spectra. Figure 1 shows the absorbance vs. wavelength plots of Cr$_2$O$_3$. As seen from the figure, the absorbance of Cr$_2$O$_3$ thin films decreases sharply till 500-600 nm band then decreases.
slightly till 1000 nm. After this value, the absorbance is nearly constant. It means that the Cr$_2$O$_3$ thin film has small absorbance in infrared region. Furthermore, the absorbance value of thin film decreases with increasing the growth temperature. The film deposited at 250 °C had the lowest absorbance values and the thin deposited at 40 °C had the highest absorbance values. The optical band gap ($E_g$) of the Cr$_2$O$_3$ can be calculated through the equation

$$\alpha = B(h\nu - E_g)^m$$ \hspace{1cm} (1)

Where $\alpha$ is the absorption coefficient, $B$ is a constant, $h$ is the Plank constant, $m$ is $1/2$ for direct band gap and $2$ for indirect band gap. Cr$_2$O$_3$ has absorbance constant higher than $10^4$. Therefore, it can be said that Cr$_2$O$_3$ a direct band gap. In this study, the band gap of sputtered Cr$_2$O$_3$ thin films were calculated by the help of $(Ah\nu)^2-h\nu$ plot using equation 1 using. Figure 2 shows the $(Ah\nu)^2-h\nu$ sputtered Cr$_2$O$_3$ thin films on glasses and The $E_g$ of the Cr$_2$O$_3$ thin films were extracted as 2.99, 3.05 and 3.10 eV for the film deposited at 40, 150 and 250 °C, respectively. The results show the strong effect of substrate temperature on optical properties of Cr$_2$O$_3$ thin films.

1.2. Current-voltage properties of Cr$_2$O$_3$/n-Si heterojunctions

The current-voltage measurements of Cr$_2$O$_3$/n-Si heterojunctions are presented in figure 3. As it is seen from the figure, the diodes fabricated using the film deposited at 40 and 150 °C showed nearly ohmic properties and the device fabricated using the film deposited onto n-Si at 250 °C had an excellent rectification. These behaviors presented the substrate temperature effects of electrical properties of Cr$_2$O$_3$/n-Si. The perfect rectification for the heterojunction fabricated by deposition of Cr$_2$O$_3$ onto n-Si substrate at 250 °C may because of the high quality of Cr$_2$O$_3$ thin film. $I$-$V$ relationship of a heterojunction for $qV \gg 3kT$ (where $q$ is the electron charge, $V$ is the applied voltage, $k$ is the Boltzmann constant and $T$ is the absolute temperature) is owing to thermionic current. According to thermionic emission theory, the current-voltage relationship of a diode with a series resistance can be written as [4]

$$I = I_0 \exp \left[ -\frac{q(V - IR_s)}{nkT} \right]$$ \hspace{1cm} (2)

where, $R_s$ is the series resistance, $n$ is dimensionless ideality factor and $I_0$ is the saturation current which can be expressed.
Figure 3. ln-I-V plots of Cr$_2$O$_3$/n-Si heterojunctions at various substrate temperatures

\[ I_0 = S A^* T^2 \exp \left( -\frac{q \Phi_b}{kT} \right) \]  \hspace{1cm} (3)

where \( S \) is the diode area, \( A^* \) Richardson constant, \( \Phi_b \) is the barrier height. The ideality factor of a diode can be calculated from the slope of the linear region of the ln-I-V plot of the diode using the equation

\[ n = \frac{q}{kT} \frac{dV}{d \ln(I)} \]  \hspace{1cm} (4)

The ideality factor of Au/Cr$_2$O$_3$/n-Si heterojunction formed by deposition of Cr$_2$O$_3$ thin film was calculated as 1.29. Table 1 presents some electrical parameters of the Au/Cr$_2$O$_3$/n-Si diode. The ideality factor of an ideal diode 1.01 when image force lowering of the diode is taken into account. The ideality greater than this value shows a non-ideal diode behavior. The non-ideal diode behavior of the Au/Cr$_2$O$_3$/n-Si may be because of the effect on native oxide layer on n-Si semiconductor. It is known that except for special fabrications, a very thin native oxide layer occurs during fabrication process.

Another important electrical parameter of a diode is barrier height. The barrier height of the junction can be calculated using \( I_0 \) value obtained from interception of ln-I-V plot to I axis by the help of the equation

\[ \Phi_b = \frac{kT}{q} \ln \left( \frac{SA^* T^2}{I_0} \right) \]  \hspace{1cm} (5)

The barrier heights of the device were calculated using saturation current value of Au/Cr$_2$O$_3$/n-Si by the help of the equation 5. The room temperature barrier height value of Au/Cr$_2$O$_3$/n-Si device determined as 0.761 eV. Saglam et al fabricated 24 Au/n-Si Schottky barrier dots and reported the barrier height values between 0.789 and 0.819 eV [5]. Therefore, Au/Cr$_2$O$_3$/n-Si diode has smaller barrier height value than conventional Au/n-Si MS diode. This result implies the strong effect of Cr$_2$O$_3$ thin film on the performance of the device.

The curvature in the plot of Au/Cr$_2$O$_3$/n-Si heterojunction fabricated using the film deposited at 250 °C for high voltages is because strong effect of the series resistance on the current-voltage properties. The series resistance results from the contact wires or bulk resistance of the Cr$_2$O$_3$ and n-Si semiconductors. The series resistances of the Au/Cr$_2$O$_3$/n-Si structure were calculated by means of Norde functions given below as [6]
Table 1. Some electrical parameters of Cr$_2$O$_3$/n-Si heterojunction at room temperature

|     | lnI-V | Norde | C-V |
|-----|-------|-------|-----|
| n   |       |       |     |
| φ$_b$ (eV) | φ$_b$ (eV) | $R_S$ (Ω) | $\phi_b$ (eV) | $N_d$ (cm$^{-3}$) |
| 1.29 | 0.761 | 0.758 | 9169 | 0.718 | 7.434 x 10$^{14}$ |

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

where $\gamma$ is the first integer greater than ideality factor and $I(V)$ is the current obtained from $I$–$V$ measurements. The barrier height of device can be calculated using the minimum value of $F$ vs. $V$ plot using the equation

$$\phi_b = F(V_0) + \frac{V_0}{\gamma} - \frac{kT}{q}$$

Figure 4. Norde plot of Cr$_2$O$_3$/n-Si heterojunction

where $F(V_0)$ is the minimum $F(V)$ value and $V_0$ is the corresponding voltage value. $F(V)$–$V$ curve of Au/Cr$_2$O$_3$/n-Si heterojunction structure is depicted in Figure 4. The series resistance of the device is determined through the relation

$$R_S = \frac{kT(\gamma - n)}{qI_{\text{min}}}$$

Where $I_{\text{min}}$ the corresponding current value at $V_0$. The barrier height and the series resistance values of the heterojunction are also depicted in table 1. As it is seen from the table, the series resistance and barrier height of the diode calculated as 9.169 kΩ and 0.758 eV. The barrier height values of the diode obtained from both lnI-V and F(V)-V plots are nearly same.

Furthermore, figure 5 shows the current-voltage plots of Au/Cr$_2$O$_3$/n-Si junction for various light intensities. As seen from the figure, light intensity has a strong
effect on photoelectrical performance of the device. Some photoelectrical parameters including sensitivity to light at -3V (illuminated current/dark current), open circuit voltage and short circuit current values are given in table 2. As seen from the table, all photoelectrical parameters increase with the increase in light intensity. This property showed that the device had photodiode characteristics which are attributable to the formation of electron–hole pairs following optical absorption. Similar results have been reported for various metal oxide/silicon heterojunctions. For instance, Lee et al [7] optimized n-ZnO/p-Si heterojunctions for photodiode applications. They deposited n-ZnO thin films onto p-Si semiconductor at various temperatures in Ar/O\textsubscript{2} ambient. They reported that all structures had typical rectifying properties and maximum amount of photocurrent observed for n-ZnO/p-Si heterojunction when the ZnO film was deposited at 480 °C. The results showed that film growing conditions had strong effects on photoelectrical characteristics. Similarly, Elsayed et al [8] prepared CuNiO\textsubscript{2} thin film by sol gel method onto p-Si substrate. They determined the size of CuNiO\textsubscript{2} nanoparticles as 115 nm and the band gap of the film as 2.4 eV. They showed that the Al/p-Si/CuNiO\textsubscript{2}/Al heterojunction good rectification property in dark and high photosensitivity value of 1.02 \times 10^3 under 100 mW/cm\textsuperscript{2}.

**Figure 5.** In/I plots of Cr\textsubscript{2}O\textsubscript{3}/n-Si heterojunction in dark and various illumination conditions

**Table 2.** Photoelectrical parameters of Cr\textsubscript{2}O\textsubscript{3}/n-Si heterojunction

| Light intensity (mW/cm\textsuperscript{2}) | \(I_{SC}\) (µA) | \(V_{OC}\) (mV) | Sensitivity to light (Times) |
|-----------------|----------------|--------------|-----------------------------|
| 40               | 3.79           | 10           | 83                          |
| 60               | 4.08           | 30           | 130                         |
| 80               | 4.34           | 30           | 190                         |
| 100              | 5.14           | 50           | 263                         |
4. Capacitance-voltage properties of Au/Cr$_2$O$_3$/n-Si heterojunction

Capacitance-voltage measurements Au/Cr$_2$O$_3$/n-Si heterojunction for various frequencies are depicted in figure 6. As it is seen from the figure, capacitance value of the structure decreased for forward bias values with the increase in frequencies. It means that at sufficiently high frequencies, charge carriers at the interface can no longer follow the AC signal. This situation showed the strong effect of interface states to capacitance of the structure. The depletion region capacitance of a diode is given [4]

$$\frac{1}{C^2} = \frac{2(V_{bd} + V)}{q\varepsilon S N_d},$$  \hspace{1cm} (9)$$

![Figure 6. C-V plots of Au/Cr$_2$O$_3$/n-Si heterojunction for various frequencies](image)

![Figure 7. C$^2$-V plot of Au/Cr$_2$O$_3$/n-Si heterojunction at 1 MHz](image)
Where $V_{bi}$ is the built-in potential, $\varepsilon_S$ is the dielectric constant of the semiconductor and $N_d$ is the donor concentration. $N_d$ was determined from the intercept of a plot of $C^{-2}$ as a function of $V$, and $V_{bi}$ was determined from the gradient of this plot, as shown in Fig. 6.7. The built-in potential, the barrier height and the donor concentration of the Au/Cr$_2$O$_3$/n-Si diode were executed as 0.46 V, 0.718 eV and $7.434 \times 10^{14}$ cm$^{-1}$, respectively. The barrier height value of the diode is inconsistent with the value obtained from ln$I$-$V$ and Norde plots. Erdogan and Gullu [2] reported the carrier density, the built-in potential and the barrier height of the Au/Cr$_2$O$_3$/p-Si MIS diode as $5.28 \times 10^{14}$ cm$^{-3}$, 0.73 V and 1.10 eV, respectively. The obtained result for carrier density is very near to the one obtained in this study.

5. Conclusion
In this study, three Cr$_2$O$_3$ thin films deposited on n-Si and glass substrates 40, 150 and 250 °C by reactive sputtering technique. Optical properties of the Cr$_2$O$_3$ thin films were analyzed by means of UV-Vis spectra. It was seen that the absorbance value of thin decreased with increase in deposition temperature. The band gaps of sputtered Cr$_2$O$_3$ thin films were calculated by the help of $(Ahv)^2$-$hv$ plot using UV-Vis data. The results showed the strong effect of substrate temperature on optical properties of Cr$_2$O$_3$ thin films. The electrical properties of Cr$_2$O$_3$/n-Si heterojunctions were examined using current-voltage measurements. The results showed that the diodes fabricated using the film deposited at 40 and 150 °C had nearly ohmic properties and the device fabricated using the film deposited onto n-Si at 250 °C had an excellent rectification. These behaviors presented the substrate temperature effects of electrical properties of Cr$_2$O$_3$/n-Si devices. The perfect rectification for the heterojunction fabricated by deposition of Cr$_2$O$_3$ onto n-Si substrate at 250 °C may be because of the high quality of Cr$_2$O$_3$ thin film. The electrical properties of Cr$_2$O$_3$/n-Si device fabricated by deposition of Cr$_2$O$_3$ onto n-Si substrate at 250 °C analyzed by means of both current and capacitance-voltage measurements. Furthermore, current-voltage measurements of Au/Cr$_2$O$_3$/n-Si junction were taken under a solar simulator with AM1.5 Global filter for various light intensities. It was seen that light intensity had a strong effect on photoelectrical performance of the device. Some photoelectrical parameters including sensitivity to light at -3V (illuminated current/dark current), open circuit voltage and short circuit current values were calculated. It was seen that all photoelectrical parameters increase with the increase in light intensity. This property showed that the device had photodiode characteristics which are attributable to the formation of electron–hole pairs following optical absorption.

6. References
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