Silicon MIS diodes with Cr$_2$O$_3$ nanofilm: Optical, morphological/structural and electronic transport properties

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**ABSTRACT**

In this work we report the optical, morphological and structural characterization and diode application of Cr$_2$O$_3$ nanofilms grown on p-Si substrates by spin coating and annealing process. X-ray diffraction (XRD), non-contact mode atomic force microscopy (NC-AFM), ultraviolet–visible (UV–vis) spectroscopy and photoluminescence (PL) spectroscopy were used for characterization of nanofilms. For Cr$_2$O$_3$ nanofilms, the average particle size determined from XRD and NC-AFM measurements was approximately 70 nm. Structure analyses of nanofilms demonstrate that the single phase Cr$_2$O$_3$ on silicon substrate is of high a crystalline structure with a dominant in hexagonal (1 1 0) orientation. The morphologic analysis of the films indicates that the films formed from hexagonal nanoparticles are with low roughness and uniform. UV–vis absorption measurements indicate that the band gap of the Cr$_2$O$_3$ film is 3.08 eV. The PL measurement shows that the Cr$_2$O$_3$ nanofilm has a strong and narrow ultraviolet emission, which facilitates potential applications in future photoelectric nanodevices. Au/Cr$_2$O$_3$/p-Si metal/interlayer/semiconductor (MIS) diodes were fabricated for investigation of the electronic properties such as current–voltage and capacitance–voltage. Ideality factor and barrier height for Au//metal/interlayer/semiconductor (MIS) diodes were calculated as 2.15 eV and 0.74 eV, respectively. Also, interfacial state properties of the MIS diode were determined. The interface-state density of the MIS diode was found to vary from $2.90 \times 10^{13}$ eV$^{-1}$ cm$^{-2}$ to $8.45 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$.

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1. Introduction

In many advanced technological applications such as solar cells, gas detectors, transparent electrodes and other optoelectronic devices, the extensive use of transparent conductive oxides has raised to intense investigation of their chemical/physical/ optoelectronic nature [1]. These materials are crystalline and catalytically active, which change their resistance due to electron transfer between the measured material and the sensing material, as a consequence of surface chemical reactions at operating temperatures [2]. Among these materials, Cr$_2$O$_3$ is used in optical applications as a solar absorber material or in photolithography masks [3]. However, no systematic reports on the optical characteristics, structural and electronic device properties of Cr$_2$O$_3$ have been found in the literature. Hones et al. reported an optical band gap of 4.7–5.0 eV for quasi-amorphous Cr$_2$O$_3$ films deposited by reactive sputtering at 290 K $< T <$ 570 K [3]. For polycrystalline Cr$_2$O$_3$ films of unknown stoichiometry deposited by a chemical vapour deposition (CVD), Hones et al. determined an optical band gap between 3.09 eV and 2.98 eV [3]. Furthermore, Cr$_2$O$_3$ is the hardest material among all oxides [4,5]. It has a high hardness of 29 GPa as compared to 12 GPa for silicon dioxide and 22 GPa for α-alumina [4,5]. Due to its high hardness, Cr$_2$O$_3$ films are used as wear resistant and protective top coatings for magnetic recording media [4,6].

There has been considerable interest in the experimental studies of metal-semiconductor (MS), metal-interlayer-semiconductor (MIS) type Schottky diodes in the past decades [7–9]. The popularity of such studies is rooted in their importance to the interlayer between the metal and the semiconductor. Because the performance and reliability of these devices are especially dependent on the formation of interlayer and can affect the device characteristics as well as the interface-state density, Schottky barrier height (SBH) and ideality factor [8–9]. When any interlayer is inserted between the semiconductor and the metal, the electrical parameters of MS structures could be modified by it. The studies made in literature have shown that the barrier height could be either increased or decreased by the interlayer on the semiconductor substrate [10–18]. In this way, new electrical properties of the MS contacts can be promoted by means of the choice of suitable interlayer [10].

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In this paper, the optical, morphological and structural properties of the \( \text{Cr}_2\text{O}_3 \) films deposited on p-Si substrates by the spin coating method have been investigated by using the ultraviolet-visible (UV-vis) spectroscopy and photoluminescence (PL) spectroscopy, non-contact mode atomic force microscopy (NC-AFM), X-ray diffraction method (XRD). Also, we have studied the electrical properties of the Au/Cr2O3/p-Si MIS structure. To our knowledge, no information is available in the literature on the electronic device properties of the Au/\( \text{Cr}_2\text{O}_3 \)/p-Si MIS diode.

2. Experimental details

2.1. Preparation of \( \text{Cr}_2\text{O}_3 \) nanofilms

The solutions were prepared from reagent grade chemicals and deionized water (resistivity >18 MΩ). Dispersions of \( \text{Cr}_2\text{O}_3 \) nanoparticles prepared by the hydrothermal technique, as described in the Ref. [19] were spin coated on p-Si substrates and then annealed. The p-type Si (100) wafer was chemically cleaned by using the RCA cleaning procedure (i.e., 10 min boil in NH4F + H2O2 + 6H2O followed by a 10 min HCl + H2O2 + 6H2O at 60 °C temperature) before metal contact deposition. The \( \text{Cr}_2\text{O}_3 \) nanoparticles were dispersed in nonpolar organic solvents such as cyclohexane or toluene. The dispersions were added onto the Si substrate with a pipette. The substrates were spin coated at 1000 rpm and then accelerated to the final rotation speed. The final rotation speed was adjusted between 3000 rpm and 4000 rpm for 20–30 s. After coating, the samples were annealed in oxygen atmosphere at 500 °C for 1 h. The thickness of the \( \text{Cr}_2\text{O}_3 \) films was measured as about 70 nm by a gravimetric weight difference method [20].

2.2. Optical and morphological/structural characterization of the \( \text{Cr}_2\text{O}_3 \) nanofilms

The absorbance spectrum of \( \text{Cr}_2\text{O}_3 \) nanofilm on the p-Si substrate was measured by using a PerkinElmer Lambda 35 model UV–vis spectrophotometer in the spectral range of 250–800 nm at room temperature. The PL spectrum was taken at room temperature by using a Shimadzu RF-5301 PC Spectrofluorophotometer. XRD experiments for nanofilms on Si (100) wafer were performed by a Rigaku Advance Powder X-ray Diffractometer instrument. The instrument uses CuKα radiation (λ = 1.5405 Å) and operates at 30 kV and 30 mA over 2θ range of 20–70°. The XRD phases in the deposits were identified with the help of JCPDS-ICDD. The surface morphologies of the films were examined by NC-AFM (PicoSPM, Molecular Imaging Inc.). The images were taken in air. The silicon nitride cantilevers with a spring constant of 48 N/m and a resonant frequency of 190 kHz were used for NC-AFM measurements. AFM images were taken in different zones of the films to check their homogeneity.

2.3. Fabrication and electronic characterization of Au/\( \text{Cr}_2\text{O}_3 \)/p-Si MIS diodes

After the deposition of \( \text{Cr}_2\text{O}_3 \) nanofilms on p-Si substrates with Al ohmic contact, Au metal contact was evaporated on \( \text{Cr}_2\text{O}_3 \) nanofilm by a vacuum coating unit at about 10^-3 mbar. Diameters of Au dots were about 1.0 mm (diode area = \( 7.85 \times 10^{-3} \) cm²). Current-voltage (I-V) and capacitance-voltage (C-V) measurements were performed by using a Keithley 487 Picoammeter/Voltage source and a HP 4192A LF Impedance Analyzer, respectively, at room temperature and in dark conditions (see Fig. 1).

3. Results and discussion

3.1. Optical properties of \( \text{Cr}_2\text{O}_3 \) nanofilms

Optical absorption of the \( \text{Cr}_2\text{O}_3 \) nanofilm on the p-Si substrate was analyzed by the following relationship,

\[
\alpha h\nu = B(h\nu - E_g)^m
\]

where B is a constant, \( E_g \) is the optical band gap of the nanofilm, \( \alpha \) is absorption coefficient of the film, which was calculated from the optical absorbance (A) of the film according to \( A = e^{-\alpha d} \). 

The exponent m depends on the nature of the transition, \( m = 1/2, 2, 3/2, \) or 3 for allowed direct, allowed non-direct, forbidden direct or forbidden non-direct transitions, respectively. The absorption \( (\alpha \geq 10^4 \text{ cm}^{-1}) \) is related to direct band transitions [22–24]. From the absorption spectrum of the \( \text{Cr}_2\text{O}_3 \) thin film on the p-Si substrate, Fig. 2(b) shows the plot of \( (\alpha h\nu)^2 \) vs. \( h\nu \) according to Eq. (1). A satisfactory fit is obtained for \( (\alpha h\nu)^2 \) vs. \( h\nu \) indicating the presence of a direct band gap [23,24]. The optical energy gap of the \( \text{Cr}_2\text{O}_3 \) film was determined as 3.08 eV by extrapolating the linear portion of this plot at \( (\alpha h\nu)^2 = 0 \) which indicates that the direct allowed transition dominates in the \( \text{Cr}_2\text{O}_3 \) film. This band gap energy value is in well agreement with some values previously reported by different workers. For example, Cheng et al. [25] reported that the optical band gap energy was between 2.98 eV and 3.09 eV for chromium oxide films formed at different substrate temperatures. Also, Cheng et al. [26] found that the \( \text{Cr}_2\text{O}_3 \) surface oxide (bulk oxide) had a band gap of about 3.0 eV. Al-Kuhaili and Durrani [27] reported that the band gap of chromium oxide thin films deposited by electron-beam evaporation was between 2.67 eV and 2.86 eV.

The optical properties of the \( \text{Cr}_2\text{O}_3 \) films were also studied by using the PL spectrum under the excitation with a wavelength of 320 nm at room temperature. PL study is a powerful tool to investigate the optical properties of these nanofilms. Fig. 3 presents the room-temperature luminescence spectrum of \( \text{Cr}_2\text{O}_3 \) nanofilms. The PL spectrum of \( \text{Cr}_2\text{O}_3 \) films shows a strong sharp ultraviolet emission peak at 356 nm, which is attributed to the near-band-edge emission. The strong emission peak indicates the high optical quality of the prepared \( \text{Cr}_2\text{O}_3 \) nanofilms [28,29]. This narrow emission peak also proves that the \( \text{Cr}_2\text{O}_3 \) films are of high-crystal quality.

3.2. Morphological and structural characterization of the \( \text{Cr}_2\text{O}_3 \) nanofilms

Fig. 4(a) shows the AFM image of the spin coated and annealed \( \text{Cr}_2\text{O}_3 \) film, and an enlarged image of the \( \text{Cr}_2\text{O}_3 \) deposit is shown in Fig. 4(b). The AFM images of the deposits reveal that the films are uniform, and the substrate is well covered with hexagonal shaped nanoparticles that have homogeneous distribution. The surface roughness of the film was found to be very small (~10 nm). The crystallite sizes observed of the \( \text{Cr}_2\text{O}_3 \) films were about 70 nm in diameter with the standard deviation of 8.7 nm.
The XRD pattern of the hexagonal phase Cr$_2$O$_3$, with lattice constants \(a = 0.496\) nm and \(c = 1.359\) nm prepared with spin coating and annealing technique on the Si substrate is shown in Fig. 5. For peak comparison, the standard cards pertained to Cr$_2$O$_3$ and Si are JCPDS-ICDD 38-1479 and 27-1402, respectively. The XRD diffractogram of spin coated and annealed Cr$_2$O$_3$ film consists of a single strong diffraction peak at 36.2° (2θ scale) arising from (1 1 0) reflections of Cr$_2$O$_3$. The weak peak at 69.1° corresponds to (4 0 0) reflection of Si, which belongs to substrate in this study. The other weak diffractions at 24.5°, 33.6°, 41.5°, 50.2°, 54.8° and 65.1° correspond to (0 1 2), (1 0 4), (1 1 3), (0 2 4), (1 1 6) and (3 0 0) reflections of Cr$_2$O$_3$. This case indicates that the crystallites in the film have a preferred growth in this direction and the all peaks belong to single phase Cr$_2$O$_3$. The (1 1 0) reflection of Cr$_2$O$_3$ gives full width at half maximum value of 0.12°. These results indicate that highly crystalline deposits of Cr$_2$O$_3$ can be grown at kinetically preferred orientation on the Si substrates. The average crystallite sizes of the Cr$_2$O$_3$ nanoparticles were determined from the width of the reflection according to the Debye–Scherrer equation. By applying this equation to the line broadening of the (1 1 0) peak in Fig. 5, the crystalline size was calculated as 69 nm. However, the average particle size analysis of AFM images (Fig. 4(a) and (b)) gives mean diameter of about 70 nm, which is highly harmony with particle sizes obtained from XRD measurements.
3.3. Analysis of current–voltage characteristic of the Au/Cr$_2$O$_3$/p-Si MIS structure

Fig. 6 shows the experimental semi-log $I$–$V$ characteristic of the Au/Cr$_2$O$_3$/p-Si MIS Schottky device at room temperature. As clearly seen from Fig. 6, the Au/Cr$_2$O$_3$/p-Si Schottky structure is rectifying. The weak voltage dependence of the reverse-bias current and the exponential increase of the forward-bias current are the characteristic properties of the rectifying contacts. The curvature at high current in the $I$–$V$ plot for forward-bias region is due to series resistance from contact wires or bulk resistance of the Cr$_2$O$_3$ layer and p-Si semiconductor. By using thermionic emission (TE) theory [7,30], the ideality factor ($n$) and BH ($\phi_b$) can be obtained from the slope and the current axis intercept of the linear region of the forward-bias $I$–$V$ plot, respectively. The values of the BH and the ideality factor for the Au/Cr$_2$O$_3$/p-Si diode have been calculated as 0.74 eV and 2.15, respectively. The ideality factor determined by the image-force effect alone should be close to 1.01 or 1.02 [31–33]. Higher values of ideality factors are attributed to secondary mechanisms which include interface dipoles due to interface doping or specific interface structure as well as fabrication-induced defects at the interface [31–34]. According to Tung [33], the large values of $n$ may also be attributed to the presence of a wide distribution of low-Schottky barrier patches caused by laterally barrier inhomogeneous. Also, the image-force effect, recombination-generation, and tunneling may be possible mechanisms that could lead to an ideality factor value greater than unity [30].

The barrier height value of 0.74 eV that we obtained for the Au/Cr$_2$O$_3$/p-Si MIS device with Cr$_2$O$_3$ interlayer is significantly higher than that achieved with conventional Au/p-Si MS contacts, where $\phi_b$ is about 0.50 eV [7]. In literature, many works have made for the barrier modification of MS diodes by using the interlayer films [35]. Recently, Yakuphanoglu et al. [35] have studied the electrical characteristics of Al/CoPc/p-Si structure. The ideality factor, barrier height and series resistance for the Al/CoPc/p-Si contact from current–voltage characteristics have been reported as 1.33, 0.90 eV and 314.5 kΩ, respectively [35]. Also, Temirci and Çakar [36] have reported a barrier height of 0.78 eV and ideality factor value of 1.54 for Cu/Rhodamine-101/p-Si/Al diode by using forward $I$–$V$ characteristic. The obtained barrier height value of the diode was higher than the conventional Cu/p-Si [7]. In another work, Gupta et al. [37] have fabricated Au/STO/p-Si/Au structure by using pulsed laser deposition technique at room temperature. They [37] have reported that Au/STO/p-Si/Au structure showed non-ideal diode characteristic with the value of ideality factor of 5.1 and barrier height of 0.41 eV. They [37] have concluded that the high ideality factor of the device may be due to large series resistance and amorphous nature of STO film. This value for the barrier height is lower than that of the conventional Au/p-Si diode, whose barrier height is 0.50 eV [7]. In another work, Ozdemir et al. [38] have studied the electrical properties of Al/conducting polymer (P2ClAn)/p-Si/Al contacts. They have reported that the barrier height of 0.787 eV for this structure was higher than that for the conventional metal/p-Si diodes. They [35–38] have evaluated that the barrier heights could be modified by using the thin interfacial layers. This may also be attributed to the interlayer effect modifying the effective barrier height by influencing the space-charge region of the inorganic substrate [39–41]. According to Roberts and Evans [42], the change in the $\phi_b$ in the metal/organic/GaAs device could be attributed to the substrate band bending originated from the organic interlayer. Zahn et al. [43] have recently indicated that the initial increase or decrease in effective barrier height for the organic interlayer was correlated with the energy level alignment of the lowest unoccupied molecular orbital with respect to the conduction band minimum of the inorganic semiconductor at the organic/inorganic semiconductor interface. These studies indicate that the interlayers can be used to modify the effective barrier heights of metal/p-Si MS diodes. In our work, the Cr$_2$O$_3$ interlayer builds up a physical barrier between Au metal and the p-Si semiconductor wafer. This interlayer can lead to substantial shift in the work function of the metal and in the electron affinity of the semiconductor and in turn, it gives an excess barrier of 0.24 eV. In this way, the barrier height of Au/p-Si MS diode increases by the insertion of a dipole layer between p-Si semiconductor and Cr$_2$O$_3$ interlayer. As a result, we have concluded that Au/p-Si MS contact could be designed to show the needed properties by means of the selection of the interlayer [35].

It is well known that the downward concave curvature of the forward-bias current–voltage plots at sufficiently large voltages is caused by the effect of series resistance ($R_s$), apart from the interface states which are in equilibrium with the semiconductor [44]. The $R_s$ values have been obtained by using a technique developed by Cheung and Cheung [45,46]. According to Cheung
and Cheung [46], the forward-bias I–V relation of a MIS diode with the series resistance can be expressed as:

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

(2)

where $IR_s$ term is the voltage drop across series resistance of device. The values of the series resistance can be determined from following functions by using Eq. (2):

$$\frac{dV}{d\ln I} = \frac{nkt}{q} + IR_s$$

(3)

$$H(I) = V - \left( \frac{nkt}{q} \right) \ln \left( \frac{I}{IA^2T^2} \right)$$

(4)

and $H(I)$ is given as follows:

$$H(I) = n\Phi_b + IR_s$$

(5)

A plot of $\frac{dV}{d\ln I}$ vs. $I$ will be linear and the slope will give the $R_s$ value and the y-axis intercept will give the ideality factor. Fig. 7 shows a plot of $\frac{dV}{d\ln I}$ vs. $I$ at room temperature. The values of $n$ and $R_s$ have been calculated as $n = 3.89$ and $R_s = 3.27 \times 10^3 \ \Omega$, respectively. It is observed that there is a large difference between the values of $n$ obtained from the forward-bias ln–V plot and that obtained from the $dV/d\ln I$–$I$ curve (see Fig. 7). This may be attributed to the existence of the series resistance and interface states to the voltage drop across the interfacial layer (native oxide plus Cr$_2$O$_3$ interlayer) [47].

Besides, $H(I)$ vs. $I$ plot have to be linear according to the Ref. [46]. The slope of this plot gives a different determination of $R_s$. By using the value of the $n$ obtained from Eq. (3), the value of $\Phi_b$ is obtained from the y-axis intercept. $H(I)$ vs. $I$ curve is shown in Fig. 7. From $H(I)$ vs. $I$ plot, $\Phi_b$ and $R_s$ have been calculated as 0.71 eV and 3.52 $\times 10^3 \ \Omega$, respectively.

Norde developed an alternative method to determine the series resistance [48]. The following function has been defined in the modified Norde’s method:

$$F(V) = \frac{V}{\gamma} - \frac{1}{\gamma} \ ln \left( \frac{I(V)}{IA^2T^2} \right)$$

(6)

where $\gamma$ is the first integer (dimensionless) greater than value of the ideality factor. $F(V)$ is current obtained from the $I$–$V$ plot and $\beta$ is a temperature-dependent value calculated with $\beta = \frac{q}{nkt}$. Once the minimum of the $F$ vs. $V$ plot is determined, the value of barrier height can be obtained from Eq. (7),

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

(7)

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

Fig. 8 shows the $F(V)$–$V$ plot of the MIS diode. From Norde’s functions, $R_s$ value can be determined as:

$$R_s = \frac{kT(\gamma - n)}{qI}$$

(8)

From the $F$–$V$ plot by using $F(V_0) = 0.71 \ \rm{V}$ and $V_0 = 0.23 \ \rm{V}$ values, the values of $\Phi_b$ and $R_s$ for the Au/Cr$_2$O$_3$/p-Si MIS diode have been determined as 0.76 eV and $4.59 \times 10^4 \ \Omega$, respectively. There is a difference in the $\Phi_b$ values obtained from the forward-bias ln–$V$, Cheung functions and Norde functions. Differences in the barrier height values obtained from three methods for the device may be attributed to the extractions from different regions of the forward-bias current–voltage plot [49]. However, the value of the series resistance obtained from Norde function is higher than that obtained from Cheung functions. Cheung functions are only applied to the nonlinear region in high voltage section of the forward-bias ln–V characteristics, while Norde’s functions are applied to the full forward-bias region of the ln–V characteristics of the junctions [49]. The value of series resistance may also be larger for the higher ideality factor values. Furthermore, the value of series resistance is very high for this device. This indicates that the series resistance is current-limiting factor for this structure. The effect of the series resistance is usually modeled with series combination of a diode and a resistance $R_s$. The voltage drop across a diode is expressed in terms of the total voltage drop across the diode and the resistance $R_s$. The very high series resistance behavior may be ascribed to decrease of the exponentially increasing rate in current due to space-charge injection into the Cr$_2$O$_3$ thin film at higher forward-bias voltage [49]. Furthermore, Norde’s model may not be a suitable method especially for the high ideality factor of the rectifying junctions, which disagree with pure thermionic emission theory. Therefore, the series resistance value from Norde functions can be much higher than one from Cheung model for especially non-ideal rectifying structures [49].
3.4. Analysis of interfacial properties of the Au/Cr$_2$O$_3$/p-Si MIS structure

For a MS diode having interface states in equilibrium with the semiconductor, the ideality factor $n$ becomes greater than unity as proposed by Card and Rhoderick [50] and then interface-state density $N_{SS}$ is given as:

$$N_{SS} = \frac{\varepsilon_s}{q} \left( \frac{n(V)}{w} - \frac{\Phi_b}{w} \right)$$

(9)

where $w$ is the space-charge width, $\varepsilon_s$ is the permittivity of the semiconductor, $\varepsilon_i$ is the permittivity of the interfacial layer, $\delta$ is the thickness of Cr$_2$O$_3$ interlayer, and $n(V) = V/((kT/q)\ln(1/I_b))$ is voltage-dependent ideality factor. In p-type semiconductors, the energy of the interface states $E_{SS}$ with respect to the top of the valence band at the surface of the semiconductor is given by:

$$E_{SS} - E_V = q\Phi_b - qV$$

(10)

where $V$ is the voltage drop across the depletion layer and $\Phi_b$ is the effective barrier height. The energy distribution or density distribution curves of the interface states can be determined from experimental data of this region of the forward-bias $I$–$V$ plot. Substituting the voltage-dependent values of $n$ and the other parameters in Eq. (9), the $N_{SS}$ vs. $E_{SS}$–$E_V$ plot was obtained as shown in Fig. 9. It is seen that $N_{SS}$ values decrease with increasing $E_{SS}$–$E_V$ values. The density distribution of the interface states for the Au/Cr$_2$O$_3$/p-Si MIS diode changes from $2.90 \times 10^{13}$ eV$^{-1}$ cm$^{-2}$ to $8.45 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$. Recently, Çakar et al. [51] have found that the interface-state density values for Au/PYR-B/p-Si contact changed from $4.21 \times 10^{13}$ cm$^{-2}$ eV$^{-1}$ to $3.82 \times 10^{13}$ cm$^{-2}$ eV$^{-1}$. Aydin et al. [52] have reported that the interface-state density properties of the Sn/methyl-red/p-Si/Al diode varied from $1.68 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$ to $1.80 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$. In other work, Yakuphanoglu et al. [53] have reported that the interface-state density values for Au/TDA/n-Si and Au/ODM/p-Si were calculated as $3.36 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$ and $4.15 \times 10^{13}$ cm$^{-2}$ eV$^{-1}$, respectively. In another study, Yakuphanoglu et al. [55] have found that the interface-state densities for the Al-CoPc/p-Si diode varied from $1.23 \times 10^{14}$ cm$^{-2}$ eV$^{-1}$ to $6.90 \times 10^{13}$ cm$^{-2}$ eV$^{-1}$. In this study, the interface-state density calculated for the Au/Cr$_2$O$_3$/p-Si MIS diode agrees with those of mentioned diodes above. The Cr$_2$O$_3$ thin interlayer film enhances the effective barrier height upon the modification of the semiconductor surfaces and the chemical interaction at the interface of the Cr$_2$O$_3$ to the p-Si and native oxide-Cr$_2$O$_3$ interface states will give rise to new ones [35,53–55]. As seen from the interface-state density values given above, the differences among the reported values for various metal/interlayer-semiconductor structures may originate from the same parameters such as interface layer thickness, chemical interactions between the metal and the substrate, film preparation conditions (electrochemical techniques, spin casting, vacuum evaporation).

3.5. Analysis of capacitance–voltage characteristic of the Au/Cr$_2$O$_3$/p-Si MIS diode

For MIS diodes, the measurement of the capacitance–voltage can provide important information about the fixed charge concentration and barrier height. Any variation of the charge within a p–n diode with an applied voltage variation yields a capacitance which must be added to the circuit model of a p–n diode. The junction capacitance dominates for the reverse-biased diodes, while the diffusion capacitance dominates in strongly forward-biased diodes [56]. Fig. 10 illustrates the variation of the junction capacitance by the bias voltage at frequency of 500 kHz for the Au/Cr$_2$O$_3$/p-Si MIS device. At zero bias, the capacitance is around 6.4 pF and is observed to increase with the application of forward voltage. This is due to the decrease of space-charge layer width with the forward voltage [57]. In addition, Fig. 10 shows $C^2$–$V$ characteristic of the Au/Cr$_2$O$_3$/p-Si MIS device. The $C^2$–$V$ characteristic shows three distinct regions (Fig. 10). The flat region in the reverse-bias condition shows that the junction is fully depleted and the value of capacitance in this region measures the depletion region capacitance [57]. The linear region, i.e., near zero voltage, which indicates the formation of Schottky junction [58], is used to estimate the carrier concentration, since the inverse slope in this region is proportional to the carrier density as well as the built-in potential and barrier height. By using standard Mott–Schottky relationship between capacitance–voltage [7,30], the calculated carrier density, the built-in potential and the barrier height of the Au/Cr$_2$O$_3$/p-Si MIS diode are $5.28 \times 10^{14}$ cm$^{-3}$, 0.73 V and 1.10 eV, respectively. A flat part in the MIS device plot at high forward-bias indicates that there is a charge accumulation near the interface. It could also be due to the high series resistance of the MIS diode and was also reported in the literature [57]. The difference between $\Phi_b(I–V)$ and $\Phi_b(C–V)$ values for the Au/Cr$_2$O$_3$/p-Si MIS diode arises from the different nature of the $I$–$V$ and $C$–$V$ measurements. Due to different nature of the $C$–$V$ and $I$–$V$ techniques, the barrier heights extracted from them are not always the same. The capacitance $C$ is insensitive to potential fluctuations on a length scale of less than the space-charge region and $C$–$V$
method averages over the whole surface and measures to describe BH. The DC current $I$ across the interface depends exponentially on barrier height and thus sensitively on the detailed distribution at the interface [30,59]. In addition, the discrepancy between the barrier heights of the MIS structure may also be explained by the existence of an interfacial layer (native oxide and Cr$_2$O$_3$) and trap states in the semiconductor [50,60].

4. Conclusions

In summary, the Cr$_2$O$_3$ nanofilms on p-Si substrate were grown by a spin coating and annealing process. The Cr$_2$O$_3$ nanofilms were characterized by XRD, NC-AFM, UV–vis spectroscopy and PL spectroscopy. The average particle size extracted from XRD and NC-AFM measurements of the nanofilms was about 70 nm. Structure analyses demonstrate that the single phase Cr$_2$O$_3$ on silicon substrate is of high a crystalline structure with a dominant in hexagonal (1 1 0) orientation. The morphologic analysis of the silicon substrate is of high a crystalline structure with a dominant in hexagonal (1 1 0) orientation. The morphologic analysis of the films indicates that the films formed from hexagonal nanoparticles are with low roughness, homogeneity. UV–vis absorption measurements show that the band gap of the Cr$_2$O$_3$ film is 3.08 eV. The PL measurements display that the Cr$_2$O$_3$ nanofilms have a strong and narrow ultraviolet emission, which facilitates potential applications in future photoelectric nanodevices. Also, Au/Cr$_2$O$_3$/p-Si MIS diodes were fabricated. Electronic properties of these structures such as current–voltage and capacitance–voltage were investigated. Also, interfacial state properties of the MIS diode were obtained.

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