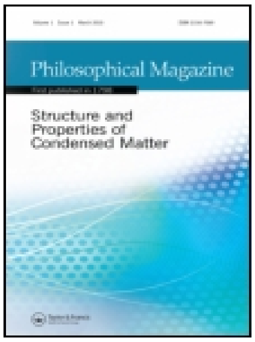


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# Electrical characteristics of p-Si/$TiO_2$/Al and p-Si/$TiO_2$-Zr/Al Schottky devices

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# Electrical characteristics of p-Si/$TiO_2$/Al and p-Si/$TiO_2$-Zr/Al Schottky devices

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**ABSTRACT**

Electrical devices involve different types of diode in prospective electronics is of great importance. In this study, p-type Si surface was covered with thin film of $TiO_2$ dispersion in $H_2O$ to construct p-Si/$TiO_2$/Al Schottky barrier diode (D1) and the other one with $TiO_2$ dispersion doped with zirconium to construct p-Si/$TiO_2$-Zr/Al diode (D2) by drop-casting method in the same conditions. Electrical properties of as-prepared diodes and effect of zirconium as a dopant were investigated. Current–voltage (*I–V*) characteristics of these devices were measured at ambient conditions. Some parameters including ideality factor (*n*), barrier height ($\Phi_{B0}$), series resistance (*Rs*) and interface state density (*Nss*) were calculated from *I–V* behaviours of diodes. Structural comparisons were based on SEM and EDX measurements. Experimental results indicated that electrical parameters of p-Si/$TiO_2$/Al Schottky device were influenced by the zirconium dopant in $TiO_2$.

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p-Si/$TiO_2$-Zr/Al structure; *I–V* characteristic; interface states; series resistance

## 1. Introduction

Layered structures fabricated from metal-semiconductor (MS) and metal-insulator-semiconductor (MIS) are generally called as Schottky barrier diodes [1–5]. Oxide thin film naturally formed on metal surface is not accounted as semiconductor and device including such oxide film is categorised as MS. On the other hand, presence of an unnatural insulating interfacial layer between the metal and the semiconductor converts the MS diode into a MIS diode [6–17]. Electrical circuits involve Schottky barrier diodes in prospective electronics are of great importance because of numerous advantages. Their low forward voltage drop and high switching speeds may be accounted to be the most important parameters and these superiorities make them ideal for output device in switching power supplies, and applications with high frequency [4–12]. Current–voltage characteristics of MS, MIS and similar structures used in solar cells are affected by different parameters including their fabrication methods, formation of insulator layer, device temperature and bias voltage, etc [12–19]. According to recent researches about Schottky barrier diodes, many different inorganic

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[1–15,20–22] or organic [23–37] interfacial layers were fabricated to form MS and MIS diodes and such studies were also aimed to improve the electrical characteristics of diodes. Titanium dioxide ($TiO_2$) with high thermal stability, relatively large band gap (3.05 eV), high refractive index and low leakage current density [37] is an important alternative as an interfacial layer for these devices to improve the efficiency of electrical and optical characteristics of devices [31–37,41]. Its layer on substrate can be fabricated by various approaches including chemical vapour deposition, electron beam evaporation, sol–gel method, sputtering, atomic layer deposition and drop-casting method [34]. Beside its usage in solar cells and Schottky diodes, it is also used in many different areas such as application of catalysis, sensors and antireflection coating [35–37,41,42]. Asar et al. [34] investigated the dielectric properties and ac electrical conductivity of Schottky barrier diodes made up of type AuZn/$TiO_2$/p-GaAs (1 1 0) via impedance spectroscopy. They found that the dielectric parameters of device considerably sensitive to frequency and applied bias voltage, and majority of the charges at interface states/traps between $TiO_2$/p-GaAs can also easily follow external ac signal and it contributes to deviation of dielectric properties of the diode. Sekhar et al. [41] also investigated the effect of sputter power on the electrical and dielectric characteristics of the structure of Al/$TiO_2$/p-Si using DC magnetron sputtering of titanium target onto p-silicon substrates at different sputtering powers and they investigated the effect of sputter power on structural, electrical-dielectric and optical properties of the air-annealed films. In order to determine the effective current-conduction mechanisms in Au/$TiO_2$/n-4H-SiC, Alialy et al. [31] carried out their current–voltage measurements in the temperature range of 200–380 K. The main conclusion that they reached is that the field emission mechanism in Au/$TiO_2$/n-4H-SiC is quite dominant for current-conduction mechanism rather than the thermionic emission (TE), thermionic field emission, and other; however, they explain the high value of ideality factor ($n$) using Gaussian distribution. Tsui et al. [36] investigated the effect of $TiO_2$ thickness as an interfacial layer on different metal/$TiO_2$/SiC structures. They obtain the maximum Schottky barrier height ($\Phi_{B0}$) of 0.3 eV with a 5-nm-thick $TiO_2$ layer between Ti and SiC. It is suggested by this study that the dielectric insertion technique can be used to control the Schottky barrier height of diodes and to form low resistance ohmic contacts. Electrical analysis of Al/p-Si Schottky diode with $TiO_2$ thin film was performed at room temperature by Aydın et al. [37] via TE theory. They also interpreted the diode characteristics by following the two field lowering mechanisms, which are Poole–Frenkel and Schottky mechanism.

During last decades, doped $TiO_2$ as an interfacial layer in Schottky structures has attracted attention and extensive research has been carried out with $TiO_2$. Doped $TiO_2$ has been generally studied by researchers related to chemistry to alternate the optical response of semiconductor photocatalysts. Doping in $TiO_2$ causes a decrease in the band gap or bringing of intra-band gap states, which results in the absorption of more visible light [38,39]. Zirconium, a transition metal, in $TiO_2$ as a dopant can provide additional energy levels within the band gap of a semiconductor [39]. Electron transfer from one of these levels to the conduction band requires lower energy than in the situation of an unmodified semiconductor. Zirconium ions are incorporated into the bulk lattice of $TiO_2$ and therefore it is predicted that there can be the modification of the electronic properties of $TiO_2$ [40]. Such literature knowledge provide valuable inside into the fabrication of a Zr-doped electronic device. Therefore, in the present work, Al/$TiO_2$/p-Si (D1) and Al/$TiO_2$-Zr/p-Si (D2)

Schottky barrier diodes were fabricated and their electrical parameters from the forward bias *I–V* characteristics comparatively analysed to investigate the effect of zirconium as a dopant in $TiO_2$ on the electrical characteristics of Al/$TiO_2$/ p-Si Schottky devices. Zirconium ions were studied as a dopant for $TiO_2$ to investigate the effect of the same group metal with Ti (both Ti and Zr are the member of $ns^2$ $(n - 1)$ $d^2$ system; where n is 4 for Ti and 5 for Zr) in the periodic table.

## 2. Experimental

### 2.1. Preparation of $TiO_2$ and Zr-doped $TiO_2$

The preparation of $TiO_2$ and Zr-doped $TiO_2$ nanopowder was established as described elsewhere [43]. As briefly: Titanium (IV) butoxide [TBT = $Ti(OC_4H_9)_4$, Aldrich] was used as titanium precursor. 10.0 ml ethanol (EtOH, Merck) and 4.0 ml ethyl acetoacetate (EtAceAc) were mixed with $HNO_3$ (pH 3), and then, 4.0 ml TBT was added to the mixture by the flow rate of 1.0 ml/min at the ambient temperature (25 °C). The mixture was continuously stirred for 1 h, followed by slowly addition of deionised water in order to establish the volume ratio of reaction mixture as TBT:$H_2O$:$HNO_3$:EtAceAc:EtOH = 1:8:3:0.05:5. Solution mixture was refluxed for 24 h in order to complete the reaction. On the other hand, to prepare Zr-doped $TiO_2$, appropriate volume of zirconium (IV) oxychloride $ZrOCl_2.8H_2O$; Sigma) solution was added to as-prepared $TiO_2$ sol to get 0.1% (by mass) Zr-doped mixture at ambient temperature. Afterwards, drying processes was followed at 100 °C for 1 h. Finally, samples were calcined at desired temperatures (500, 600, 700, 800, 900, 1000 °C) for 2 h. After annealing process, $TiO_2$ and Zr-doped $TiO_2$ suspension having the concentration of 1.0 mg/ml was prepared by sonication, and surface of Si wafer was modified with the mixture by drop-casting method and thickness of $TiO_2$ and Zr-doped $TiO_2$ modifications was calculated as 0.76 and 0.99 μm.

### 2.2. Fabrication of Diodes D1 and D2 and current–voltage (I–V) measurements

The Al/$TiO_2$/p-Si (D1) and Al/$TiO_2$-Zr/p-Si (D2) Schottky barrier diodes were fabricated on the 2 in. (5.08 cm) diameter flat zone p-type (phosphor-doped) single crystal Si wafer (1 0 0) having thickness of 350 μm with resistivity ≈0.7 Ω-cm. On this step, Si wafer was first cleaned in a mixture of peroxide ammoniac solution and then in aqueous solution of HCl for 10 min. It was thoroughly rinsed in deionised water having resistivity of 18 MΩ-cm using an ultrasonic bath for 15 min, immediately high purity Al metal (99.999%) with a thickness of about 2000 Å was thermally evaporated onto the whole back side of Si wafer in the system having the vacuum value of $10^{-6}$ torr. In order to perform a low resistivity ohmic back contact (1500 Å), Si wafer was sintered at 450 °C for 5 min in $N_2$ atmosphere. $TiO_2$ and Zr-doped $TiO_2$ layer were formed by drop-casting method on p-type Si wafer. After the formation of $TiO_2$ and Zr-doped $TiO_2$ interfacial layer, the rectifier/Schottky contacts were formed in thermal evaporation system using metal shadow mask on the front surface of the p-Si wafer and Al dots having diameter of 1.5 mm. *I–V* measurements were performed by the use of a Keithley 220 programmable constant current source, a Keithley 4200 electrometer at room temperature. Schematic cross section of device and measurement system is shown in Figure 1.

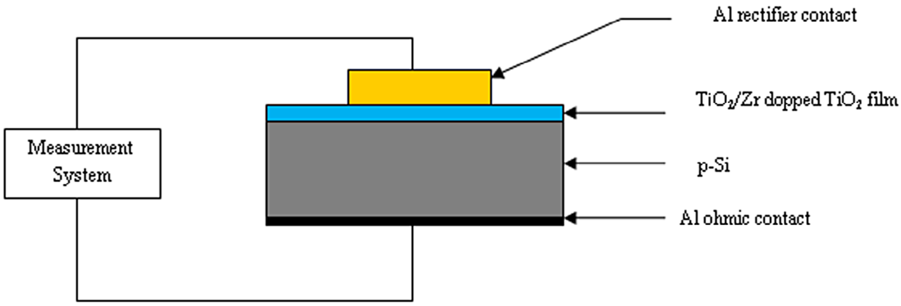


**Figure 1.** (colour online) Schematic cross section of the Al/$TiO_2$-Zr/p-Si Schottky structure.

## 3. Results and discussion

Current–voltage ($I$–$V$) characteristic of D1 and D2 were investigated between the potential range from −4 to +4 V. Figure 2 shows the semi-logarithmic forward and reverse bias $I$–$V$ plots of the D1 and D2. As could be seen from Figure 2, the rectifying ratio (RR) of D1 was calculated to be $3.17 \times 10^4$ and that of D2 was $5.07 \times 10^6$ using the equation RR = $I_F(+4\ \mathrm{V})/I_R(-4\ \mathrm{V})$, where $I_F(+4\ \mathrm{V})$ is forward bias current in +4 V and $I_R(-4\ \mathrm{V})$ is reverse bias current in −4 V. In case of high forward bias voltages, characteristics of both devices deviate from linearity due to the effects of serial resistance ($R_s$), interfacial insulator layer and interface states ($N_{ss}$) [10–17,31]. However, deviation from linearity in forward bias characteristics for D1 is seen more specifically with two small linear regions. Forward bias behaviour for D2 has only one linear region and single linear region of D2 is larger than linear regions of D1. Increase in current with the applied reverse bias was lowered and both devices showed saturation. Ineffectiveness of image force may lower the Schottky barrier height and this behaviour may create the result of such saturation as explained in elsewhere [1]. The presence of an interfacial insulator layer at metal–semiconductor interface may also effect to have saturation [2]. These results can be attributed to the decrease in $N_{ss}$ and $R_s$ with doping with Zr in interfacial layer. Current value for MS and MIS structure is exponentially related to applied forward bias (in case of $V > 3kT/q$) as expressed as follows [1–3,5]:

$$I = I_o\left[\exp \frac{q}{nkT}\left(V - IR_s\right)\right] \tag{1}$$

Here, $I$ is current, $I_o$ is reverse saturation current, $V$ is forward bias voltage, $IR_s$ is voltage drop caused by serial resistance, $n$ is the ideality factor which may be used to confirm whether the diode transport mechanism is pure TE or not, $k$ is the Boltzmann constant and $T$ is temperature in Kelvin. The value of $I_o$ can be obtained from the intercept of the semi-log-forward bias $I$–$V$ plots and expressed as:

$$I_o = A^* A T^2 \exp(-q\Phi_{Bo}/kT) \tag{2}$$

Here, $A^*$ is effective Richardson constant, $A$ is diode area, $\Phi_{B0}$ is zero-bias barrier height and effective Richardson constant for p-Si is 32 Acm$^{-2}$ K$^{-2}$. The values of $\Phi_{B0}$ and $n$ were calculated using Equation 2 and semi-log-forward bias $I$–$V$ plots. Values of $\Phi_{B0}$ and $n$ for D1 with two linear regions were found as 0.74 eV 2.39 for the first linear region and 0.65 eV and 8.29, for the second linear region. They were also calculated as 0.81 eV and 2.43 for D2.

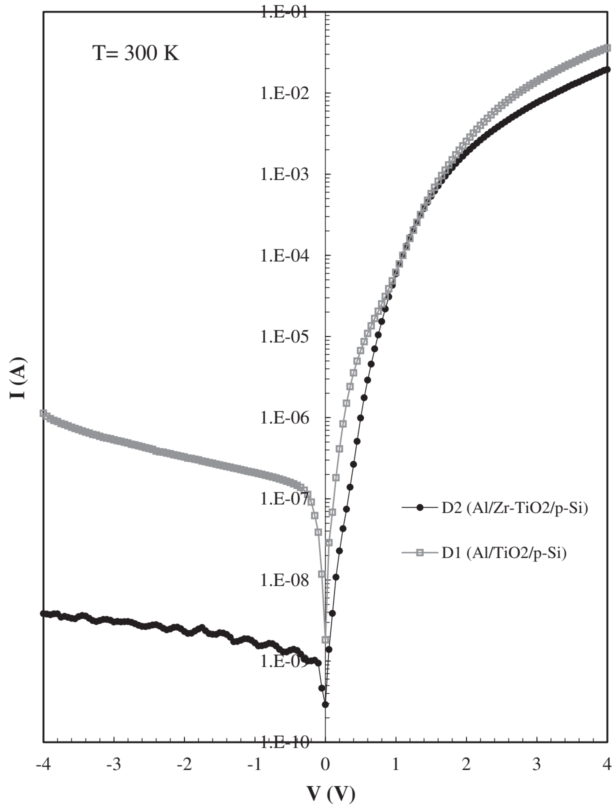


**Figure 2.** (Forward and reverse bias current–voltage (*I–V*) characteristics of the D1 and D2 Schottky barrier diodes at room temperature.

For the first look, ideality factors of both devices are larger than unity and this result is the confirmation of having MIS structure instead of MS structure [11,21,22,31,36]. In case of Zr-doping in $TiO_2$, zero-bias barrier height was increased.

Logarithm of structure resistance was plotted as a function of applied potential (Figure 3) and series resistance ($R_s$) and shunt resistance ($R_{sh}$) were calculated via parameters of this plot. As could be seen from Figure 3, it is clear that at sufficiently high forward bias voltage, the devices resistance decreased and $R_s$ for D1 and D2 were found to be 111 and 205 Ω, respectively. At sufficiently high reverse bias voltage, the devices resistance was levelled off and this limit for resistance was equalled to $R_{sh}$ of device. These behaviours of $R_s$ and $R_{sh}$ are a strong evidence of structural change with the Zr-doping process.

The interface states density ($N_{ss}$) has also important effect on value of ideality factor [11–16,31]. The sufficiently thick interface layer disconnects the interface states from the metal, making them communicate with the semiconductor more readily than with the metal. In spite of the close thickness of $TiO_2$ and Zr-$TiO_2$ interfacial layer, the diversity of diode parameters of D1 and D2 may be accounted as an evidence of having interface states. On the other hand, zirconium dopant in $TiO_2$ on D2 clearly shows the effect of dopant on series resistance and dopant may have an effect on interface states.

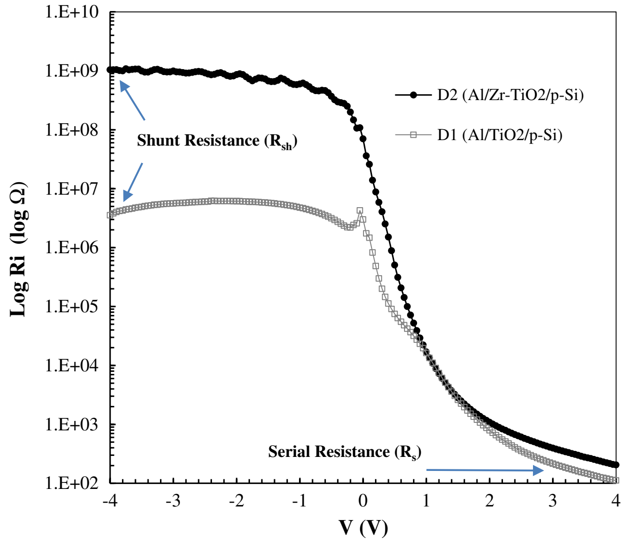


**Figure 3.** (colour online) The diode resistance ($R_i$) vs $V$ plot of D1 and D2.

Energy density distribution profile of interface states were obtained from the forward $I$–$V$ characteristics of D1 and D2. According to literature knowledge, about a Schottky structure with interface states governed by the semiconductor, ideality factor and barrier height are known to be voltage dependent, the expression for the density of interface states as concluded by Card and Rhoderick [1] can be written as following equations:

$$n(V) = \frac{q}{kT}\left[\frac{V}{\ln(I/I_o)}\right] \tag{3}$$

$$\Phi_e = \Phi_{Bo} + \beta(V) = \Phi_{Bo} + \left(1 - \frac{1}{n(V)}\right)V \tag{4}$$

$$N_{ss}(V) = \frac{1}{q}\left[\frac{\varepsilon_i}{\delta}(n(V) - 1) - \frac{\varepsilon_s}{W_D}\right] \tag{5}$$

Here, $\beta(V)$ is the voltage coefficient of the effective barrier height ($\Phi_e$), $\delta$ is the thickness of interfacial layer, $W_D$ is the width of the space charge region, $\varepsilon_i$ and $\varepsilon_s$ are permittivity of the interfacial insulator layer and the semiconductor, respectively, and $N_{ss}$ is the density of the interface states in equilibrium with the semiconductor. Thickness of interfacial layer ($\delta$) was obtained from SEM micrographs as given in Figure 4. According to SEM micrographs, thickness of interfacial layer for D1 is determined by calculating the mean value of thickness of different points in Figure 4. These values for D1 (in μm) 0.800, 0.722, 0.784, 0.760, 0.750

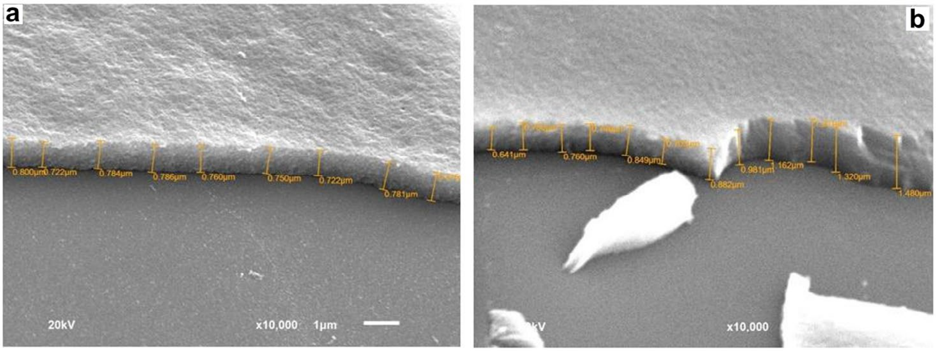


**Figure 4.** (colour online) SEM micrographs of (a) $TiO_2$ and (b) Zr-doped $TiO_2$ thin films on p-Si surface.

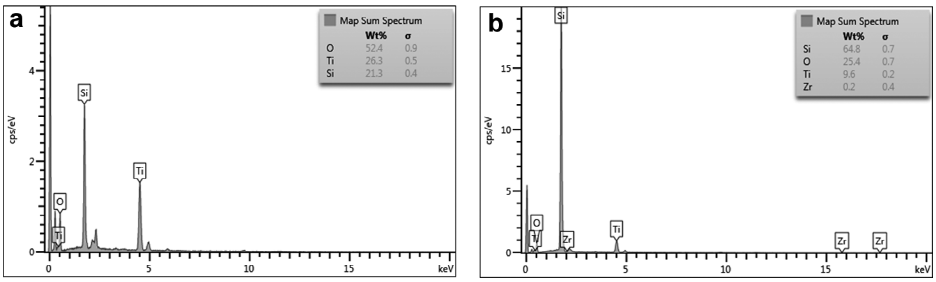


**Figure 5.** EDX data of (a) $TiO_2$ and (b) Zr-doped $TiO_2$ thin films on p-Si surface.

and their mean value was found to be 0.76 µm. Also thickness of interfacial layer for D2 is determined by the similar way and average of 0.641, 0.760, 0.849, 0.882, 0.931, 1.320 and 1.480 µm was calculated to be 0.99 µm.

Elemental composition of D1 and D2 surfaces were investigated via EDX measurement and results were given in Figure 5. The EDX data of $TiO_2$ on p-Si show three peaks around 0.5, 1.5 and 4.5 keV. The intense peak (1.5 keV) is assigned to Si and the less intense one (4.5 keV) to the $TiO_2$. The EDX data of Zr-doped $TiO_2$ show also three peaks around 0.5, 1.5 and 4.5 keV. The peaks of Zr are apparent in Figure 5(b) at 1.56, 15.5 and 16.5 keV. Mass percents of surfaces were given in related figure as an in-set. As could be seen in Figure 5(b), zirconium dopant with 0.1 mass percent is clearly verified.

The energy of the interface states $E_{ss}$ (for *p*-type semiconductors) with respect to the top of the valance band at the surface of semiconductor is given elsewhere [1] and expressed as:

$$E_{ss} - E_v = q(\Phi_e - V) \tag{6}$$

Figure 6 shows the energy distribution profile of the $N_{ss}$ obtained from the forward bias $I$–$V$ characteristics of D1 and D2. The energy values of $N_{ss}$ are in the range of $(E_V + 0.36)$ to $(E_V + 0.67)$ eV for D1 and $(E_V + 0.38)$ to $(E_V + 0.69)$ eV for D2. Values of $N_{ss}$ in given range are calculated to be $3.30 \times 10^{13}$ and $3.53 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$, for D1 and $2.19 \times 10^{13}$ and $3.53 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$, for D2.

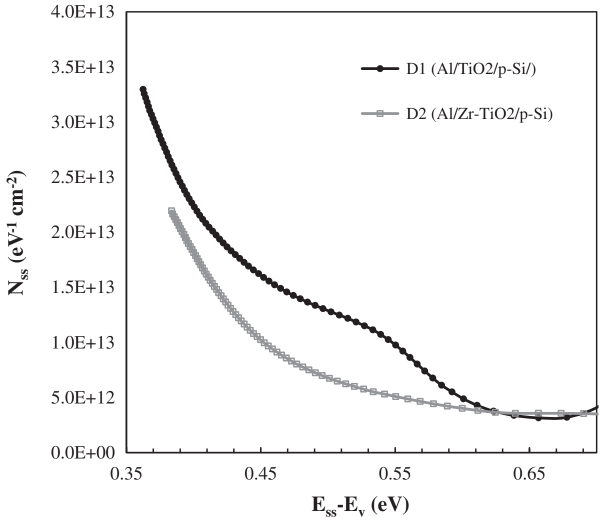


**Figure 6.** The interface states energy distribution curves of D1 and D2 at room temperature.

## 4. Conclusion

Schottky barrier diodes of MIS configuration of Al/$TiO_2$/p-Si and Al/$TiO_2$-Zr/p-Si were constructed and *I–V* characteristics of these devices were measured at room temperature and electrical parameters were calculated via *I–V* characteristics. Zirconium as a dopant by the mass percent of 0.1, enhanced the diode with greater rectifying ratio and larger-single linear region and also increased the barrier height which is supported by literature [44]. Change in electrical parameters related to zirconium doping is very limited and this limitation may be related to its low mass percent and its similar chemical and electrical properties to those of titanium because of being the member of the same periodic group. Al/$TiO_2$/p-Si shows nearly nonlinear forward bias *I–V* characteristics of having two slopes with the two ideality factors of 2.39 and 8.29. Forward bias characteristics with two small linear regions change into single-larger linear region due to the zirconium dopant in $TiO_2$ interfacial layer. However, whether with zirconium dopant or without it, constructed devices did not behave as an ideal Schottky diode which may be concluded as an effect of insulator layer of $TiO_2$ and, also effects of series resistance and interface states density.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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