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The Effects of Surface Oxidation and H-Termination Processes Applied to Si Using Electrolytic Hydrogen Peroxide Solution to The Produced Cu/p-Si Schottky Contact Parameters

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Highlights:

- Electrolytic hydrogen peroxide (H_2O_2) solution was applied to the p-Si crystal surface for oxidation and H-termination. As far as we know, the use of electrolytic hydrogen peroxide solution for p-Si crystal surface treatment has not been previously available in the literature.
- Rectification ratios and barrier heights of the Cu/p-Si diodes (MIS and SP) were determined to decrease with surface oxidation and surface passivation.
- It has been determined that the H-Termination process is very effective in the passivation of the surface states, similarly, the surface oxidation process is also effective.

Keywords:

- H-termination
- Hydrogen Peroxide
- Schottky Contact
- Surface improvement
- Surface passivation

ABSTRACT:

By using electrolytic hydrogen peroxide (H_2O_2) solution, oxidation and H-termination processes were applied to the p-Si crystal surface, which will be used for Cu/p-Si Schottky contact production, in a selective and controlled manner. Before the oxidation and H-termination processes, the p-Si(100) wafer used in this study was subjected to conventional chemical cleaning, and ohmic contact was made using pure aluminum (99.99%) metal on its back surface. The p-Si/Al with ohmic back contact was divided into three parts. A rectifying contact was immediately made to the front surface of one of them by using pure copper (99.98%) metal and called the REF (Reference) sample. The front surface of one of the remaining two p-Si/Al parts was oxidized, and the front surface of the other was H-Terminated. Rectifier contacts were made for both using pure copper (99.98%) metal and were named MIS (metal-insulator-semiconductor) and SP (surface passivated), respectively. Current-voltage (I-V) measurements of Schottky diodes of REF, MIS, and SP samples were performed at room temperature and in the dark. From the obtained data, the ideality factor (n), barrier height (Φ_{bo}), and series resistance (R_s) values of the samples were determined. As a result of the investigations, it was observed that the surface oxidation and H-Termination processes caused a decrease in the rectification factor and Φ_{bo} values of MIS and SP samples. These interesting situations were interpreted by the double-layer theory, which Bardeen predicted could exist on the surface of a semiconductor crystal and contribute to its work function.

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INTRODUCTION

The fact that contacts between metal and semiconductor materials can show rectifying properties goes back to 1874 (Braun, 1874). Braun, in a series of experiments he conducted in 1874, determined that the electrical current passing through metal sulfides was antisymmetric, depending on the direction. That the flow of the current in one direction is greater or smaller (unequal) than in the other direction means that different resistances appear in different directions. In particular, if the current flowing in one direction is very large compared to the current in the opposite direction, these contacts can be called rectifier contacts. Schottky et al. explained for the first time that metal-semiconductor (MS) contacts exhibit rectifying properties (Schottky et al.,1931). Schottky and Mott, independently of each other, pointed out that the rectifying property of any contact can be explained by the passing of electrons over a potential barrier at the contact (Schottky, 1938; Mott, 1938). Similar ideas on this subject were also developed by Davydov (Davydov, 1939; Davydov, 1941). An important contribution regarding the passing of electrons over the barrier in metal-semiconductor rectifier contacts came from Bethe. Bethe suggested that the Thermionic Emission Theory could be applied to Schottky contacts (Bethe, 1942). Accordingly, the passing of electrons over the barrier at the contact is determined by the emission process instead of drift and diffusion. However, before the passing of electrons over the barrier to the metal occurs, the electrons are transferred from the inside of the semiconductor to the interface. The movement of electrons within the electric field of the barrier is based on diffusion and drift mechanisms (Rhoderick, 1972; Rhoderick and Williams, 1988).

There are two main theories for the barrier formation of Schottky diodes. These are the Schottky-Mott theory and another is the Bardeen Model. If the metal and semiconductor are electrically neutral and there are no surface states at the interface, then the Fermi level is independent of the influence of the interfacial states, and then barrier formation at the contact can be interpreted based on the Schottky-Mott theory. Otherwise, if there are interface states, the electrical charges arising from the interface states would also be effective on the barrier layer, and in this case, it would be necessary to take into account the surface states in the explanation of the barrier formation mechanism (Rhoderick, 1972; Rhoderick and Williams, 1988). In this context, barrier formation for some structures such as Sn/p-Si (Temirci et al., 2001; Temirci et al., 2011), Au/n-GaAs (Biber et al., 2002), Au/n-Si (Ayyıldız et al., 2001, and Co/n-Si (Koçyiğit et al., 2021) can be explained based on the Schottky-Mott theory, whereas in some Schottky contacts such as Co/p-Si (Koçyiğit et al., 2021), Pt(II) complex/p-Si (Imer et al., 2014), Al/n-Si (Türüt and Sağlam, 1992; Daş et al., 2021), and Zn/n-Si (Ateş et al., 2011) it would be more appropriate to explain the barrier formation with the Bardeen model instead of Schottky-Mott theory. Of course, the most important thing in the above statements is the structure of the contact interface and the situations at the interface. Because interface states have effects on Schottky diode parameters. In this context, semiconductor surface cleaning, improvement or passivation studies are important, so it attracts the attention of researchers related to the subject (Temirci et al., 2001; Kim et al., 2005; Gu et al., 2007; Schifano et al., 2007; Mohanty et al., 2021). For this, dilute aqueous solutions of various chemicals are used. Hydrogen peroxide was tested on the ZnO film to be used for the Schottky diode and it was emphasized that it had effects on the electrical, optical and structural properties of the film (Kim et al., 2005; Gu et al., 2007; Schifano et al., 2007; Mohanty et al., 2021). From the $I - V$ and $C - V$ measurements, Hydrogen Peroxide surface treatment applied to Zn-terminated ZnO (0001) surfaces on Pt/ZnO contacts, contributes significantly to Schottky contact formation was evaluated. In addition, it has been stated that hydrogen peroxide treatment is very effective in reducing deep-level defects (Kim et al., 2005). Conversely, in another

experimental study it has been experimentally evaluated that in Au/n-ZnO contacts, H_2O_2 pre-treatment does not affect the deep levels, but it causes a decrease in OH pollution on the surface and the formation of vacancy-type defects; thus contributed to the formation of rectifier contacts by reducing the conductivity on the surface (Gu et al., 2007). It has been experimentally noted that hydrogen peroxide surface treatment on Pd/n-ZnO contacts is highly effective on the electrical current rectification ratio. In this context, in the evaluation made using $I-V,\ C-V, and\ C-f$ measurements; it was also evaluated that the 1.0-1.2 eV Φ_{bo} value obtained was reasonable and in agreement with the Schottky-Mott model (Schifano et al, 2007). Further, it is demonstrated by XRD, SEM, and PL measurements the H_2O_2 treatment has improved the surface morphology, crystal structure, and optical properties of the ZnO thin film (Mohanty et al, 2021).

The present study aims to use electrolytic H_2O_2 solution both for surface oxidation and surface improvement by H-termination of Si wafer and is to investigate the effects of the processes on the electrical parameters of the Cu/p-Si Schottky contacts.

MATERIALS AND METHODS

In this study, the p-Si (100) wafer with a resistivity of 5-10 Ω-cm was used. The wafer was first subjected to the conventional chemical cleaning procedure. That is ultrasonic washing for 10 minutes each in acetone and methanol, respectively. Washing in deionized water thoroughly between two treatments. Then, wash with RCA1 (H_2O, H_2O_2, NH_3; 6:1:1) at 60 °C. Washing for 30 sec. with dilute HF (H_2O, HF; 10:1). Washing for 10 min. in RCA2 (H_2O, H_2O_2, HCl; 6:1:1) at 60 ^{o}C. Washing in deionized water thoroughly. Washing for 30 sec. with diluted HF (H_2O, HF; 10:1). Again washing in deionized flowing water thoroughly for about 10 minutes and finally drying with Nitrogen (N_2) gas. The deionized water used in the experiment is at 18.2 MΩ-cm resistivity standard. After the conventional chemical cleaning process, 99.999% pure aluminum was evaporated on the back (matt) surface of the p-Si wafer at 10^{-5} Torr pressure using a vacuum coating unit. Immediately after, it was annealed in a nitrogen gas atmosphere for 3 minutes in a quartz tube furnace preheated to 580 ^{o}C and so, ohmic contact was made. The p-Si wafer with ohmic back contact was divided into three parts. One of them was named REF and is to be considered as a reference sample. The second was named MIS (metal-insulator-semiconductor) and is to be produced and evaluated as an interfacial layered sample. The third was named SP (surface passivated) and is to be evaluated by applying surface improvement to this sample.

To remove possible particles and dust from the REF sample surface due to the cutting process, it was washed with deionized water and dried. A 99.98% pure copper (Cu) metal was evaporated to the front surface of it. So, rectifying contact was made to the front surface of the REF sample. For the MIS structure, the p-Si/Cu sample with ohmic back contact was first thoroughly washed with deionized water. Next, a 10% hydrogen peroxide (H_2O_2) solution was prepared. The sample was connected to the positive pole of the constant DC voltage of 3 volts and only the front surface was immersed in the solution. The process was carried out until the current flowing through the circuit reached a certain minimum value (0.001 A/cm^2), and then it was removed, washed with deionized water, and only the front surface was etched by a dilute hydrofluoric acid (HF) solution of 10% (H_2O, HF; 10:1) for 30 s.

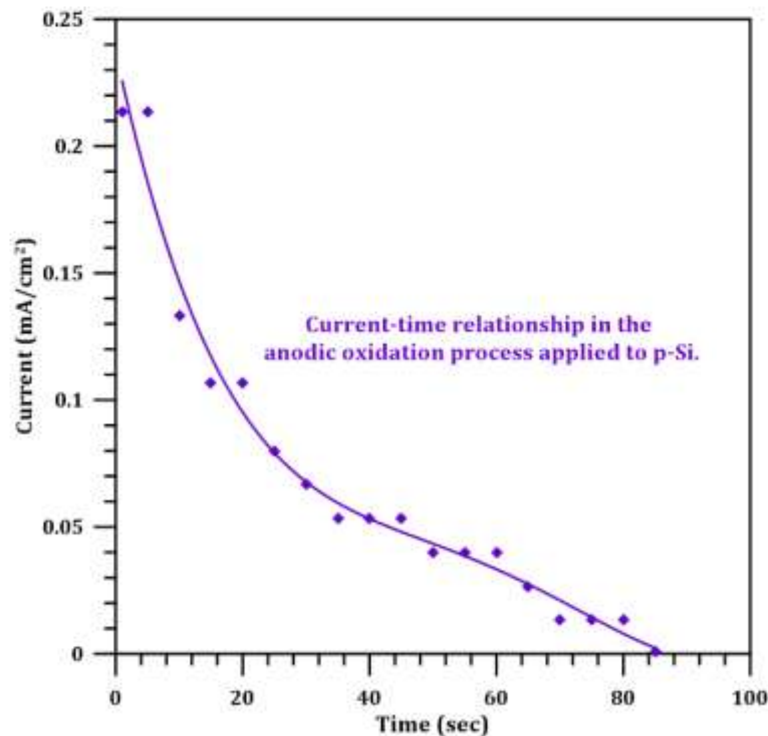

Figure 1. The current-time relationship during the surface oxidation of the $p-Si$ used for MIS sample fabrication

It was then washed again with deionized water. Thus, a transaction cycle is completed. This process cycle was repeated three times. Finally, after the sample was treated with H_2O_2, without etching with HF, a 99.98% high purity copper metal was evaporated to its front surface by taking it to the vacuum coating unit. The graph in Figure 1 shows the electric current passing through the circuit depending on the time in the oxidation process of the surface of the MIS sample. As can be understood from the graph in Fig. 1, the electric current passing through the circuit is initially maximum, but gradually decreases to a minimum level. This is due to the accumulation of negative ions on the surface of the sample held at the positive pole, which shows an increased resistance against the electric current passing through the circuit with time. Surface treatment of SP (surface passivated) sample with electrolytic H_2O_2 solution is the same as that of MIS sample, the only difference is to change the polarity of the DC supply. That is, the SP sample was connected to the negative pole of the DC supply, thus allowing H-Termination to occur on its surface. After surface improvement processes with electrolytic H_2O_2 solution, a rectifier contact was made in the vacuum coating unit using pure copper metal. The changing of the current flowing through the circuit depending on the time during the surface improvement process applied to p-Si with the electrolytic solution in the production of the SP sample is seen in Figure 2. As can be seen from fig. 2, the electric current decreases over time and reaches a certain minimum value (0.082 A/cm^2). The reason for the decrease in this electric current over time is the accumulation of positive ions on the surface of p-Si, which is connected to the negative pole, and therefore it shows increasing resistance to current flow. When the resistance reaches a maximum value, the current decreases to its minimum value. Keithley 6487 Picoammeter/Voltage source was used for forward and reverse current-voltage (I-V) measurements of the samples, and all the measurements were performed at room temperature and in the dark.

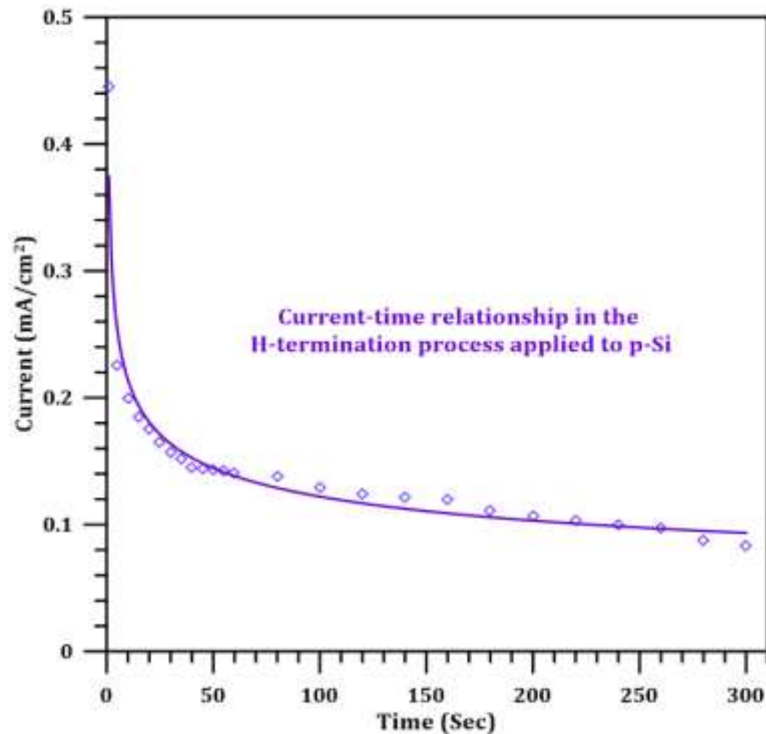

Figure 2. The current-time relationship during the surface improvement of the $p-Si$ used for SP sample fabrication

RESULTS AND DISCUSSION

Reverse and forward bias current-voltage $(I-V)$ measurements of the $Cu/p-Si/Al$ Schottky contacts, belonging to REF, MIS, and SP samples were carried out. From the measurement data, $I-V$ graphs were drawn and the characteristic parameters of the diodes such as n, Φ_{bo}, and R_s were calculated. According to Schottky-Mott theory, the work function of the metal is important in the formation of rectifier contact between the metal and the semiconductor. According to Bardeen, the surface states of the semiconductor should be considered rather than the work function of the metal (Bardeen, 1947; Rhoderick and Williams, 1988). Literature information on the work functions of silicon and copper used in Cu/p-Si Schottky contact fabrication is available so, it can be made a better assessment. (Michaelson, 1977; Rhoderick and Williams, 1988).

Thermionic emission (TE) is known as the release of electrons from a hot surface. Bethe demonstrated that the thermionic emission theory can be applied to metal-semiconductor rectifier contacts (Bethe, 1942). TE theory is the primary mechanism for the forward current of Schottky barrier diodes. Based on the thermionic emission theory, the current equation for a Schottky diode can be written as (Rhoderick and Williams, 1988):

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

For the case of $qV >> 3kT$, Eq. 1 can be rewritten in the following form:

$$I = I_0\left[exp\left(\frac{qV}{nkT}\right)\right] \quad (2)$$

where

$$I_0 = AR^*T^2 exp\left(\frac{q\Phi_{b0}}{kT}\right) \quad (3)$$

is the saturation current. Φ_{b0} is the barrier height at zero bias, R* is the effective Richardson constant, equals 32 Acm^{-2} K^{-2} for p-type Si, q is the electron charge, V is the applied voltage, A is the diode area, k is the Boltzmann's constant, T is the ambient temperature (K), n is the ideality factor, and it is determined from the slope of the linear region of the forward bias $\ln I - V$ graph, through the relation derived from Equation 2:

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

For an ideal diode, n should be equal to 1, or at least very close to 1. However, in applications, the n value is often obtained as greater than 1. This can be attributed to the presence of interfacial states, an interfacial layer, or recombinations at the depletion region. Φ_{bo} can be obtained from the following equation derived from equation 3:

$$\Phi_{bo} = \frac{kT}{q} ln\left(\frac{AR^*T^2}{I_0}\right) \tag{5}$$

Figures 3, 4, and 5 show the reverse and forward bias $I - V$ graphs of the REF, MIS, and SP samples, respectively. It is seen from the three graphs that the electric currents are antisymmetric, so all three samples exhibit rectifying properties, too. The rectification factors for the diodes of REF, MIS, and SP samples are $2.4 \times 10^3 \pm 0.7,\ 3.7 \times 10^2 \pm 0.7\ and\ 4.0 \times 10^1 \pm 0.7$, respectively. When the rectification factors of the Schottky diodes of REF, MIS, and SP samples are examined, it is understood that the largest value of the rectification factor belongs to the REF sample and the smallest value of the rectification factor belongs to the SP sample. Surface oxidation and passivation treatments applied to the diodes of MIS and SP samples caused the rectification factors to decrease.

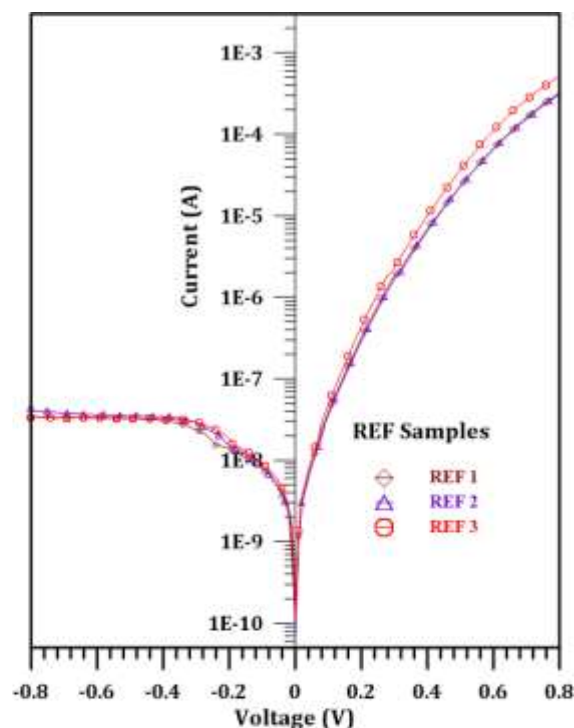

Figure 3. Forward and reverse bias current-voltage $(I - V)$ graph of the $Cu/p - Si/Al$ Schottky contacts of REF sample

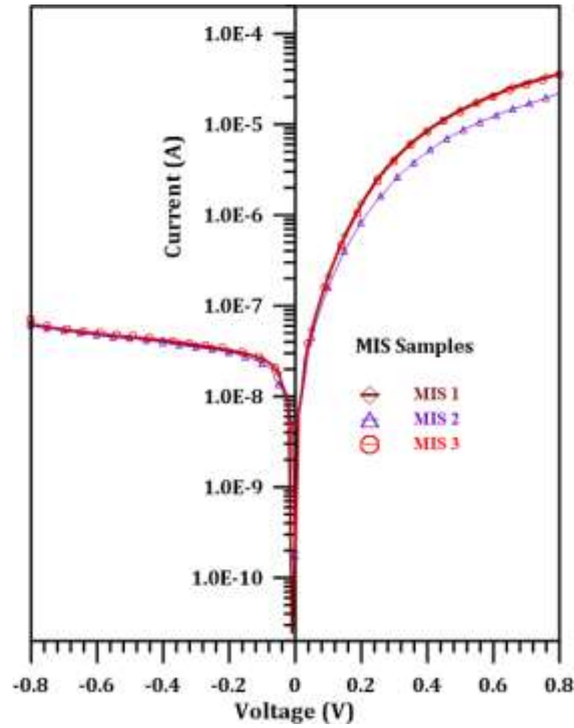

Figure 4. Forward and reverse bias current-voltage $(I - V)$ graph of the $Cu/p - Si/Al$ Schottky contacts of MIS sample

Using equation 4, n values of the Schottky contacts of REF, MIS, and SP samples were obtained and their mean values were calculated to be $n = 1.68 \pm 0.02$, $n = 1.98 \pm 0.04$, $n = 1.50 \pm 0.01$, respectively. Using equation 5, Φ_{bo} values of the Schottky contacts of the REF, MIS, and SP samples were obtained, and their mean values were calculated to be $\Phi_{b0} = 0.764 \pm 0.002\ eV,\ \Phi_{bo} = 0.715 \pm 0.001\ eV, and\ \Phi_{bo} = 0.518 \pm 0.001\ eV$, respectively.

We used the Cheungs' functions to check the n and Φ_{b0} values obtained from the $I - V$ data and to determine the R_s values (Cheung and Cheung, 1986). According to the Cheungs' a part of the voltage applied to the device drops through the R_s and equation 2 can be rewritten as follows:

$$I = AR^*T^2 exp\left(-\frac{q\Phi_{bo}}{kT}\right)\ exp\left[\frac{q(V-IR_s)}{nkT}\right] \quad (6)$$

where the term IR_s is the voltage drop across the R_s of the device. If Eq.6 is solved for V, the following expression can be obtained:

$$V = \frac{nkT}{q} ln\left(\frac{I}{AR^*T^2}\right) + n\Phi_{bo} + IR_s \quad (7)$$

Using Equation 7, the Cheungs' functions can be derived as follows:

$$\frac{dV}{d(lnI)} = \frac{nkT}{q} + IR_s \quad (8)$$

$$H(I) = n\Phi_{bo} + IR_s \quad (9)$$

$$H(I) = V - n\left(\frac{kT}{q}\right) ln\left(\frac{I}{AR^*T^2}\right) \quad (10)$$

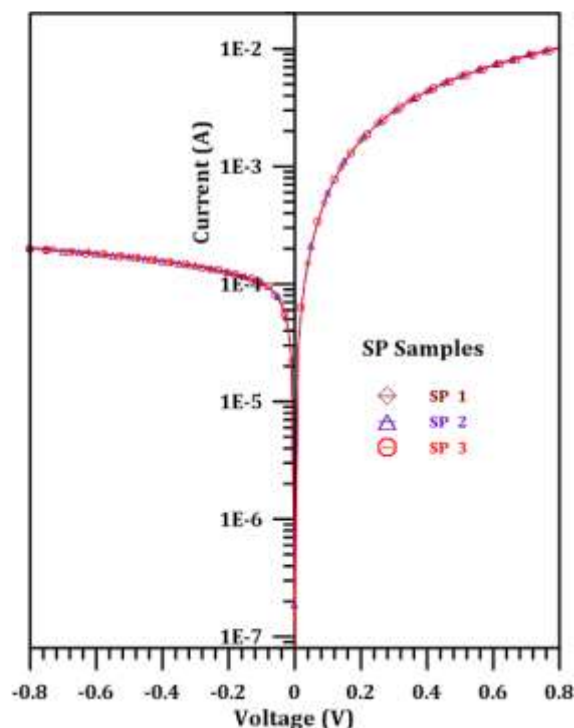

Figure 5. Forward and reverse bias current-voltage $(I - V)$ graph of the $Cu/p - Si/Al$ Schottky contacts of SP sample

Equations 8 and 9 are known as Cheungs' functions. Notice that equations 8 and 9 are linear, and should give straight lines for the data of the downward-curvature region of the forward-bias $I-V$ characteristics. Therefore, the slope and y-axis intercept of a plot of $dV/d(ln\, I)\ vs. I$ will give R_s and nkT/q, respectively. Since the kT/q value is known here, the n can be calculated. Similarly, the slope and y-axis intercept of a plot of $H(I)$ vs. I will give R_s and $n\Phi_{bo}$, respectively. Here, since the value of the n is known, the Φ_{b0} can be calculated. The $dV/d(\ln I) - I\ graphs$ obtained for REF, MIS, and SP diodes by using equation 8 with $I - V$ data are shown in Figures 6, 7, and 8, respectively. Although Eq.8 is in a linear equation form and should give a straight line when $dV/d(\ln I) - I$ graphs (Figures 6 and 7) belonging to the REF and MIS samples are examined carefully, and it is seen that there are deviations from the straight line. This situation may be attributed to the interface states. Using the $dV/d(\ln I) - I$ graphs with equation 8, mean values of the n for the REF, MIS, and SP samples were determined to be 2.89 ± 0.06, 2.28 ± 0.08, and 1.24 ± 0.02, respectively. As can be understood from the values given above, the highest n value belongs to the REF sample, and the smallest value belongs to the SP sample. The R_s values of the REF, MIS, and SP samples were determined from the $dV/d(\ln I) - I$ graphs and their mean values were calculated to be $R_s = (35 \pm 5) \times 10^1\ \Omega$, $R_s = (15 \pm 3) \times 10^3\ \Omega$, and $R_s = 63 \pm 0.2\ \Omega$, respectively. As can be understood from the R_s values given above, the MIS sample has the largest, and the SP sample has the smallest R_s values. The ratio between the largest value of the R_s of the MIS sample and the smallest value of the SP sample is 311.4.

Such a large difference between R_s values can be attributed to the effect of the interface oxide layer in the MIS sample and the effect of the improvement process applied to the SP sample. Figures 9, 10, and 11 show $H(I) - I$ plots for the diodes of the samples of the REF, MIS, and SP, respectively. Using the $H(I) - I$ plots with equation 9, mean Φ_{b0} values for REF, MIS, and SP samples were obtained as $0.705 \pm 0.002\ eV,\ 0.700 \pm 0.003\ eV,\ and\ 0.514 \pm 0.003\ eV$. As can be seen, the REF sample has the highest Φ_{b0} value and the SP sample has the smallest Φ_{b0} value.

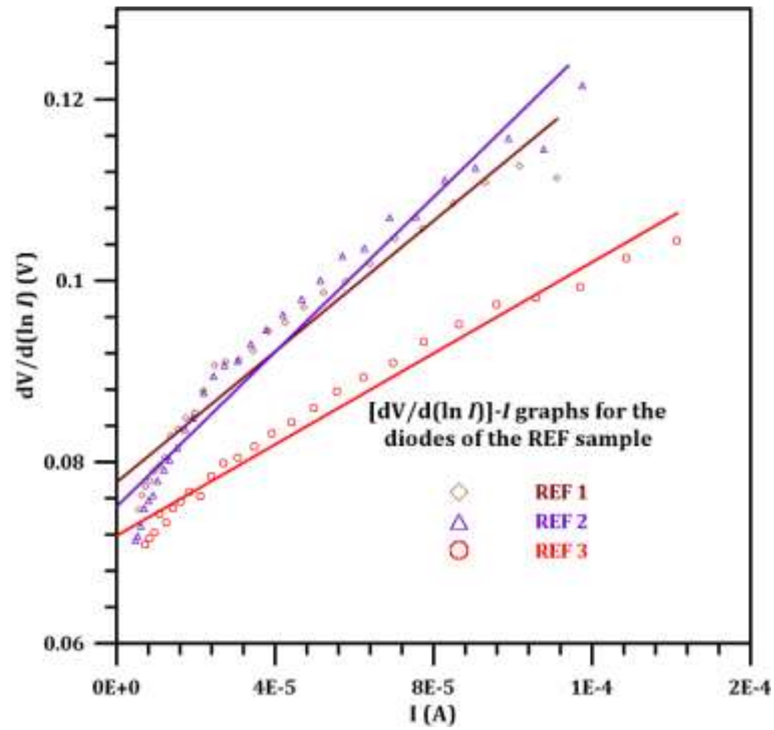

Figure 6. $dV/d(ln\ I) - I$ graphs obtained for the diodes of the REF sample

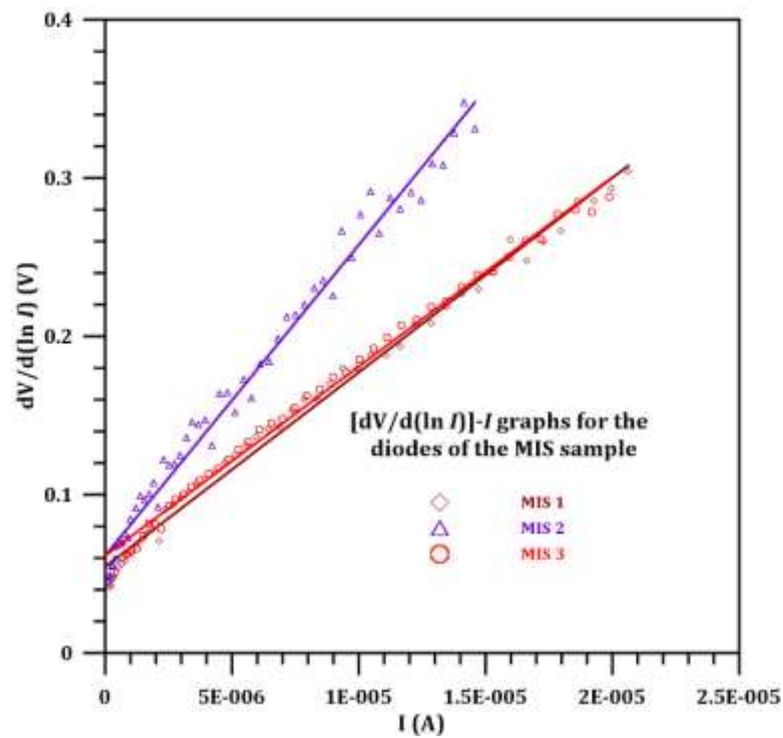

Figure 7. $dV/d(lnI) - I\ graphs$ obtained for the diodes of the MIS sample

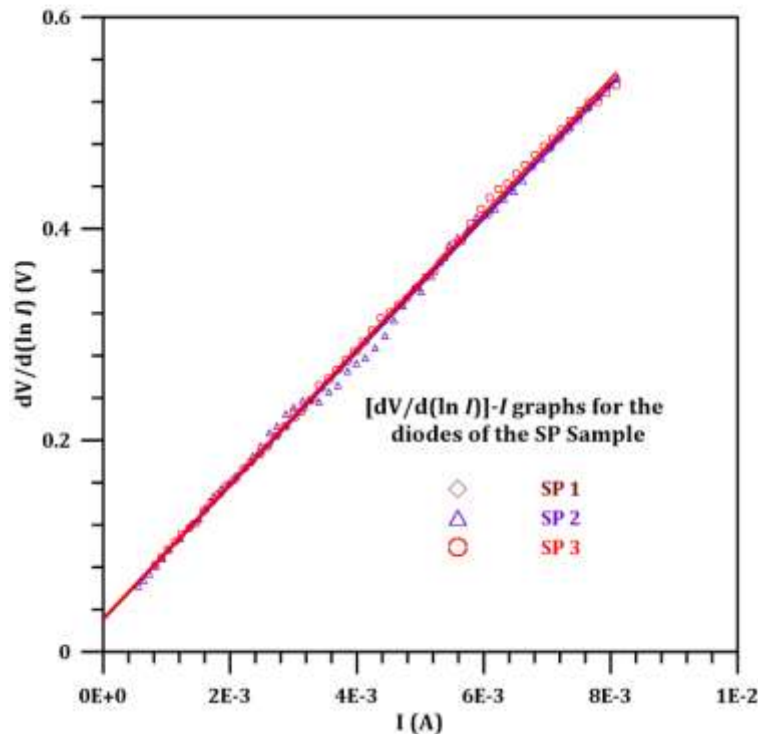

Figure 8. $dV/d(ln\ I) - I\ graphs$ obtained for the diodes of the SP sample

The determined mean R_s values from the $H(I) - I$ graphs and Eq.9 for REF, MIS, and SP samples are $(38 \pm 6) \times 10^1\ \ \Omega$, $(15 \pm 3) \times 10^3\ \Omega$, and $63 \pm 0.3\ \Omega$. As can be understood from the R_s values given in Table 1-3, the MIS sample has the largest R_s value of $20.4 \times 10^3\ \ \Omega$ and the SP sample has the smallest R_s value of 63.0 Ω. The ratio between the largest value of the R_s of the MIS sample and the smallest value of the SP sample is 323.8. Experimentally obtained characteristic parameters of the Schottky diodes of the REF, MIS, and SP samples can be seen in detail in Tables 1, 2, and 3, respectively.

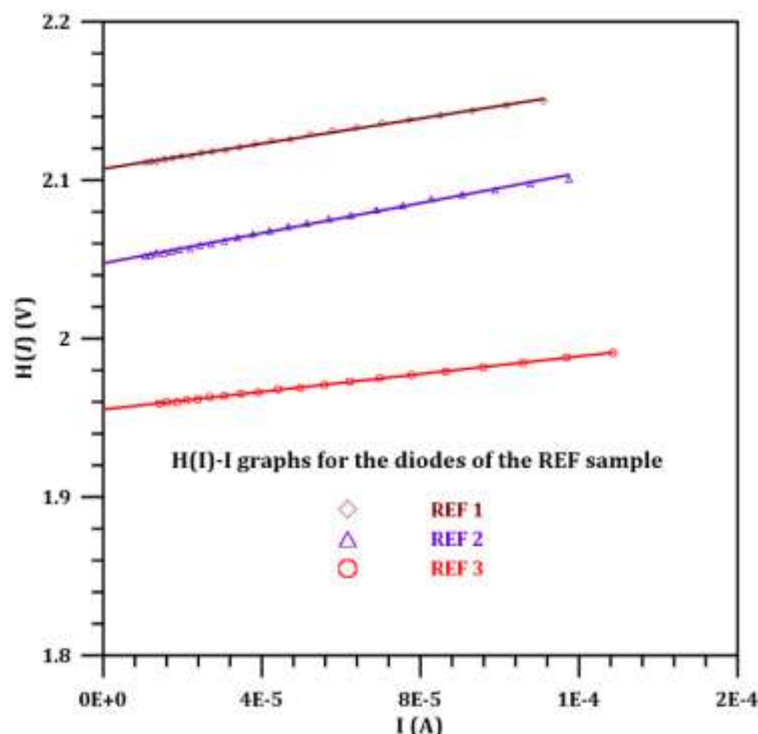

Figure 9. $H(I) - I$ graphs obtained for the diodes of the REF sample

When we examine the current-voltage graphs of the REF, MIS, and SP samples, the current values at -0.6 volt are 3.39x10^{-8} A, 4.93x10^{-8} A, and 1.80x10^{-4} A, respectively. The current values of REF, MIS, and SP samples at 0.6 volt are 8.11x10^{-5} A, 1.78x10^{-5} A, and 7.24x10^{-3} A, respectively. It is understood from the above data that the current value of the MIS sample at -0.6 volts is 1.45 times greater than that of the REF sample, and the current value at 0.6 volts is 4.56 times smaller than that of the REF sample. The fact that the current value of the MIS sample increases by 1.45 times in reverse bias and decreases by 4.56 times at the forward bias can be evaluated as a reflection of the effect of surface oxidation of the Si crystal in the electrolytic H_2O_2 solution. Moreover, the increase of the reverse bias current and decrease Φ_{b0} of the MIS sample can be attributed to the passivation effect of the surface states of the oxidation treatment applied to the Si surface. Furthermore, the fact that the same oxidation process causes very large R_s in the MIS sample, which negatively affects the forward bias current, can also be considered as the presence of the surface oxide layer. It is understood that the current value of the SP sample at -0.6 volts is 5310 times and at 0.6 volts is 89.27 times greater than that of the REF sample.

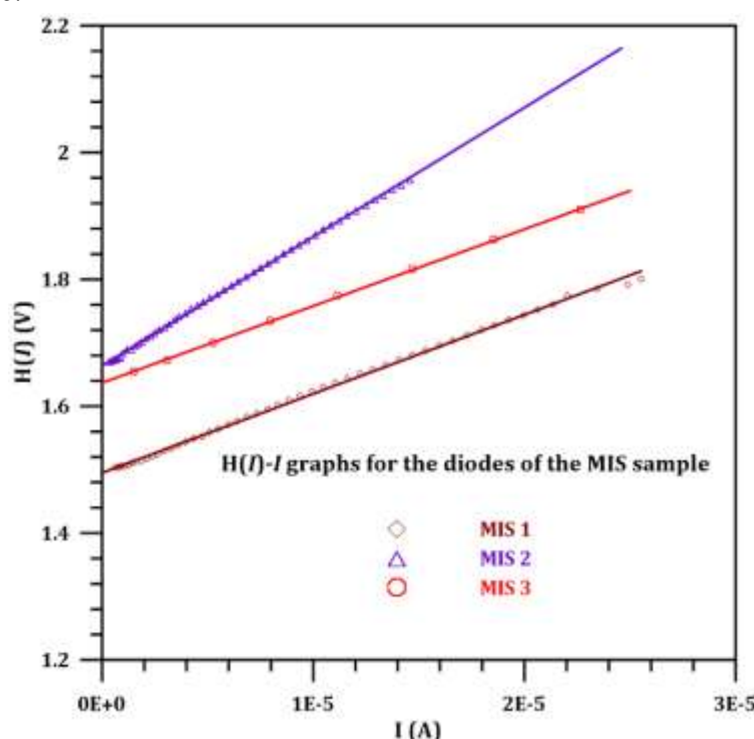

Figure 10. $H(I) - I$ graphs obtained for the diodes of the MIS sample

Table 1. Some experimental characteristic parameters of the diodes of the REF sample

Samples	n $(I-V)$	n $(Cheung)$	$\Phi_{bo}(eV)(I-V)$	$\Phi_{bo}(eV)$ $(Cheung)$	R_S (Ω)x10^1 $(dV/dlnI)$-I	R_S (Ω) x10^1 $(H(I)$-$I)$
REF 1	1.69	3.00	0.765	0.702	36.1	39.7
REF 2	1.71	2.89	0.766	0.708	42.7	47.5
REF 3	1.63	2.78	0.761	0.706	25.1	26.8

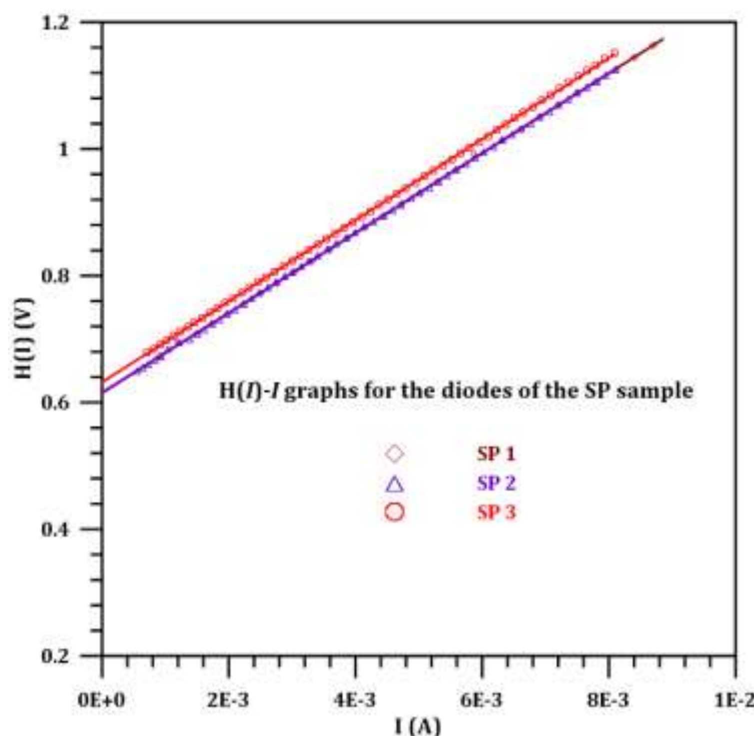

Figure 11. $H(I) - I$ graphs obtained for the diodes of the SP sample

Table 2. Some experimental characteristic parameters of the diodes of the MIS sample

Samples	n $(I-V)$	n $(Cheung)$	$\Phi_{bo}(eV)(I-V)$	$\Phi_{bo}(eV)$ $(Cheung)$	R_S (Ω) x10^3 $(dV/dlnI)$-I	R_S (Ω) x10^3 $(H(I)$-$I)$
MIS 1	1.92	2.13	0.714	0.702	12.3	12.5
MIS 2	2.06	2.36	0.718	0.705	19.6	20.4
MIS 3	1.96	2.36	0.714	0.694	12.0	12.1

Table 3. Some experimental characteristic parameters of the diodes of the SP sample

Samples	n $(I-V)$	n $(Cheung)$	$\Phi_{bo}(eV)(I-V)$	$\Phi_{bo}(eV)$ $(Cheung)$	R_S (Ω) $(dV/dlnI)$-I	R_S (Ω) $(H(I)$-$I)$
SP 1	1.51	1.20	0.517	0.518	63.3	63.0
SP 2	1.48	1.27	0.519	0.515	63.1	63.0
SP 3	1.50	1.24	0.517	0.509	63.8	63.9

That is, the current value of the SP sample increases in both reverse and forward bias conditions, however, the increase in current is much larger in the reverse bias condition than in the forward bias condition.

As can be seen in Figures 1 and 2, during the surface treatment process with electrolytic H_2O_2 solution, the process was operated until the electric current passing through the circuit was minimum depending on time. The surfaces of the p-Si wafers appear to be saturated in the oxidation and H-termination processes for MIS and SP samples, respectively. When Tables 1, 2, and 3 are examined, it is understood that the R_s values of the MIS sample have a tremendous size compared to that of the REF and SP samples. From Figure 4, the negative effect of this R_s on the current can easily be seen. It can be seen from Figures 3 and 5 that the reverse bias current and forward bias current increase in the SP sample compared to the reference sample. It can be considered that this situation is a result of the surface improvement treatment applied to the SP sample. Because, as can be seen from Tables 1-3, the R_s values of the SP sample are much smaller than the other two samples. Therefore, it can be

interpreted that the H-termination process applied to the SP sample is quite effective. When the Φ_{b0} values which are given in Tables 1, 2, and 3 are examined, it is understood that the Φ_{b0} values of the contacts of the REF sample have the highest value, and the Φ_{b0} values of the contacts of the MIS sample are in the second rank, and the Φ_{b0} values of the contacts of the SP sample are smaller than those of the other two samples. Bardeen stated that for semiconductors with sufficiently high surface-state densities, there may be a double layer on the free surface, one consisting of the charge of the surface states and the other of the oppositely charged space charges. He predicts that this double layer can generate a work function that is independent of the Fermi level inside and thus the number of impurities (Bardeen, 1947). The fact that the rectification factor and Φ_{b0} values are the largest in the REF sample and the smallest in the SP sample can be interpreted as experimental confirmation of Bardeen's double layer theory. That is, it seems that with the effect of the H-termination process applied to the surface of the SP sample, the charges in the surface states were passivated and thus weakened the work function resulting from the double layer. In the case where the interface states are largely governed by the semiconductor, the following equation can be written for the ideality factor (Card and Rhoderick, 1971; Singh, 1985):

$$n = 1 + \frac{\delta}{\varepsilon_i} \cdot \left(\frac{\varepsilon_s}{W} + qN_{ss}\right) \tag{11}$$

Where δ is the interfacial layer thickness and is determined by the equation $C_{it} = \varepsilon_i \varepsilon_o A/\delta$ from the upper limit of $C-V$ measurements performed at high-frequency (1 MHz) (Temirci et al., 2001; Biber et al., 2002). ε_i *and* ε_s are the permittivities of the interfacial layer and the Si semiconductor, respectively. $\varepsilon_i = 4\varepsilon_0$ is given for the interface oxide layer (Temirci et al., 2001; Biber et al., 2002) and $\varepsilon_s = 11.8\varepsilon_0$ (Rhoderick and Williams, 1988). Dielectric constant for the interface SiH_2 layer was obtained to be 9.21 using the ABINIT program. Using the capacitance (C_{it}) equation, the δ values for REF, MIS and SP are obtained as about 4 nm, 45 nm, and 50 nm, respectively. N_{ss} is the interface states density, q is the charge of an electron and W is the width of the space charge region and is expressed as:

$$W = \left(\frac{2\varepsilon_s V_{d0}}{qN_A}\right)^{1/2} \tag{12}$$

Where V_{d0} is the diffusion potential at 0 voltage, and it is determined from $C^{-2}-V$ characteristics, N_A is the acceptor concentration and is obtained using the values of $\mu_p = 450\ cm^2/V \cdot s$ (Neamen, 1992), $\rho = 7\ \Omega \cdot$cm, $e = 1.6x10^{-19}\ C$ as $1.98x10^{15}\ cm^{-3}$. If the W value in Equation 12 is substituted in Equation 11 and this equation is solved according to N_{ss}, the following equation can be derived.

$$N_{ss} = \frac{\varepsilon_i}{q\delta}(n(V) - 1) - \left(\frac{qN_A\varepsilon_s}{2V_{d0}}\right)^{1/2} \tag{13}$$

On the other hand, for p-type semiconductors, the energy of the interface states (E_{ss}) is given on the surface of the semiconductor relative to the upper level of the valence band as follows (Barret and Vapaille, 1976; Singh, 1985):

$$E_v - E_{ss} = q\Phi_{bo} - qV \tag{14}$$

Surface state density distribution curves of the REF, MIS, and SP samples obtained using equations 13 and 14 are given in Figures 12, 13, and 14, respectively. Forward bias $I-V$ characteristics of the SBDs were used in the calculation of the interface state densities. When Figures

12, 13, and 14 are examined, it is understood that the interfacial state densities of the diodes of the REF sample are larger than the others. It is seen that the diodes of the MIS sample have lower values than those of the REF sample. This indicates that controlled surface oxidation has an effect on the passivation of the interfacial states. It is seen that the interfacial state densities of the diodes of the SP sample are lower than those of the REF and the MIS sample. This shows us that the controlled H-termination process applied to the Si surface has a tremendous effect on the passivation of the interfacial state charges. It is determined from the obtained experimentally data that the values of the rectification factor, Φ_{b0}, and n are the highest in the REF sample and the lowest in the SP sample.

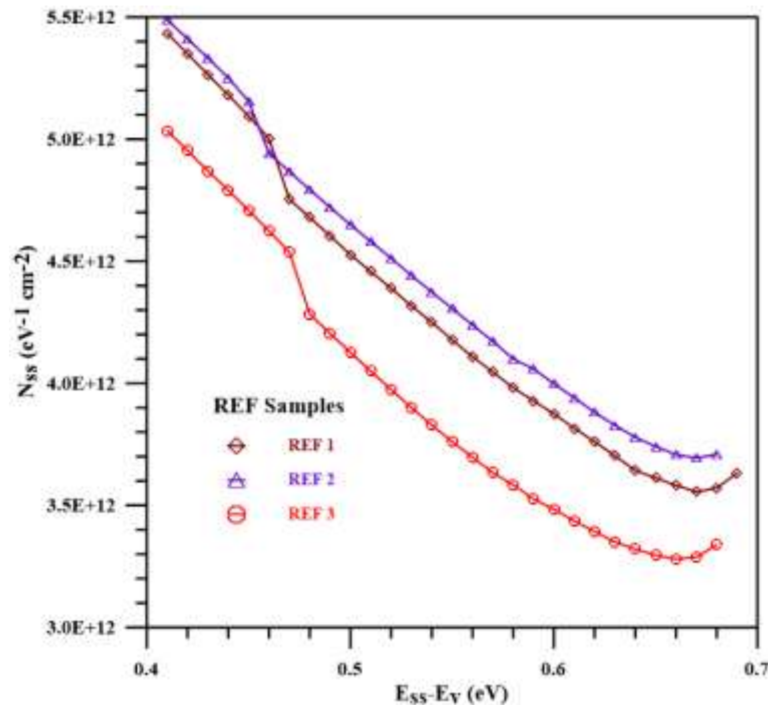

Figure 12. Interface state density distribution curves of the diodes of the REF sample

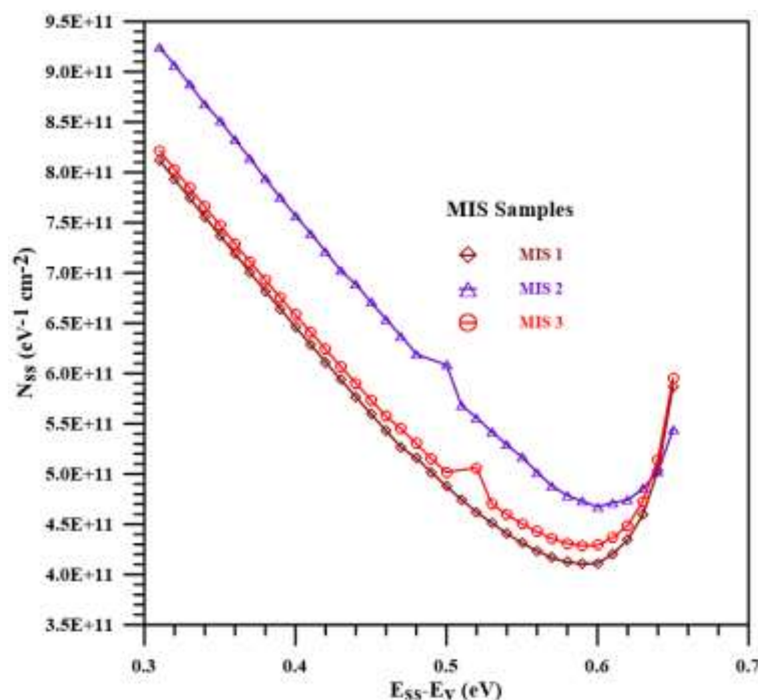

Figure 13. Interface state density distribution curves of the diodes of the MIS sample

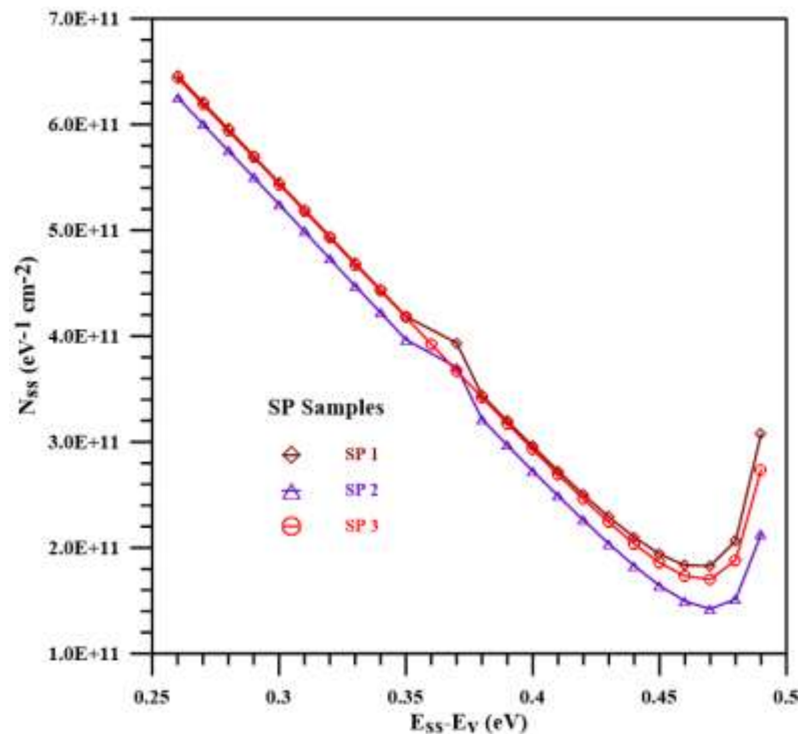

Figure 14. Interface state density distribution curves of the diodes of the SP sample

CONCLUSION

By using only H_2O_2 solution electrolytically, both oxidation and H-Termination processes were carried out on the Si surface in a controlled manner. Surface oxidized and surface H-Terminated p-Si crystals were used in the Cu/p-Si Schottky contact fabrication, and the effects of the surface treatments on the diode characteristic parameters were investigated. From the examination of the characteristic parameters of the MIS sample, it was determined that the surface oxidation of the Si crystal leads to the passivation of the surface states. In addition, it was determined from the examination of the characteristic parameters of the SP sample that the H-Termination process was quite effective in the passivation of the surface states of the Si crystal. It was observed that the surface oxidation and H-Termination processes applied to the Si crystal caused a decrease in the Φ_{b0} and rectification factors values of the MIS sample and especially the SP sample. We interpreted the reason for such a situation with Bardeen's "presence of a double layer on the semiconductor surface that can affect the work function". That is, by passivating the surface states present in the Si crystal by oxidation and H-Termination processes, the power of the double layer to affect the work function may have been reduced. From this perspective, the present study can also be seen as experimental confirmation of the double layer theory, which Bardeen predicts can exist on the semiconductor surface and contribute to the work function.

Conflict of Interest

The article authors declare that there is no conflict of interest between them.

Author's Contributions

The main contribution to this article belongs to Prof.Dr. Cabir Temirci. The other authors have partial contributions.

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