Long Term Drift Observed in ISFET Due to the Penetration of H$^+$ Ions into the Oxide Layer

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Abstract. Ion Sensitive Field Effect Transistor (ISFET) and related biosensors when undergo prolonged hours of operation, witnesses a temporal change in threshold voltage which is termed as drift. Drift is a secondary effect which leads to instability of the device resulting into inaccuracy in both in vivo and in vitro measurements. Various types of drift have been of great interest for researchers and long term drift is one of its kinds. Long term drift is observed in different sensing layer in ISFET devices of which silicon dioxide (SiO$_2$) gate ISFET witnesses the maximum. This paper presents the modeling and analysis of long term drift observed in ISFET due to diffusion of H$^+$ ions into the oxide layer and the field caused by this penetration. The additional hydrogen ions left after the protonation of dangling bonds penetrate through the sensing layer which results into an electric field that influences the threshold voltage. A physical model has been designed explaining the effect of this penetration of positive ions into sensing layer and simulations of this model has been carried out. This model has been further experimentally validated using a Schottky based ISFET device with SiO$_2$ as the sensing layer. Both the theoretical and experimental data indicates toward the existence of this drift and its prominence can be observed in lower pH values.

Keywords: Biosensors · Diffusion · Ion Sensitive Field Effect Transistor · Long term drift · Threshold voltage

1 Introduction

In 1970, ion sensitive field effect transistor abbreviated as ISFET was introduced to the semiconductor industry by Bergveld [1–3], which had SiO$_2$ as the sensing layer. Around at the same time Matsuo and Wise develop similar device using silicon nitride as the sensing layer [4]. Right from its inception, work progressed mostly along two directions- one regarding its sensitivity to ions other than hydrogen ions and the other was explaining the mechanism involved in the operation of pH ISFET. However, limited work is reported on the secondary issues such as drift, hysteresis etc. Drift is an inherent problem related to ISFETs and related bioFETs as it results into instability of the device and degradation in accuracy of measurement with time. Drift can be defined as slow, monotonic, temporal change in the value of threshold voltage [5]. It is also

defined as shift in the rate of change in the gate to source voltage under constant current. Two types of drift are mentioned by Hein and Egger- storage drift and long term drift [6]. Few probable causes of drift stated in reported works are- Variation of surface state density D_{it} at the Si/SiO$_2$ interface, partially dehydrated surfaces which observe slow surface effect such as rehydration, electric field enhances the ion migration such as sodium ion within the gate insulator, negative space charges inside SiO$_2$ films due to injection of electrons from electrolyte at strong anodic polarization, buried layer beneath the surface [7]. Long term drift is significantly low in silicon nitrite sensing layer when compared with silicon dioxide but its effect cannot be neglected. This takes place in silicon nitride due to slow conversion of the nitride surface to hydrated SiO$_2$ or oxynitride layer and this hydration rate is due to dispersive mechanism [8]. The variation observed in threshold voltage with time for ISFET with different sensing membrane when immersed for a duration of 10^3 min was 3–30 mV for Ta$_2$O$_5$, 30–60 mV for SiO$_2$, 40 mV for silicon nitride, 50 mV for aluminum oxide etc. [9]. In a work by Jamasb et al. it was indicated that the pH dependent threshold voltage change is function of the effective charges induced in the semiconductor by the total charges in the insulator [8]. Further, a technique was presented in a work by Anita Topkar et al. to investigate the penetration of ions into the silicon dioxide when it is exposed in electrolyte [10]. Although works as mentioned above indicates about drift and causes of it; but no proper explanation is provided on the penetration of ions which leads to the creation of the electric field due to diffusion of hydrogen ions which causes long term drift in ISFET and other BioFET. In this work, a mathematical model has been proposed to formulate a relation of the voltage change as the function of time due to the field caused by the diffusion of hydrogen ions which leads to the long term drift in SiO$_2$ gate pH ISFET. This can lead to further refinement of the data acquisition process using ISFET based sensor and can enhance the accuracy.

2   Mathematical Model

Diffusion of protons into the sensing layer is a process by which species moves as a result of concentration gradient. The longer is the duration for which the ISFET is immersed in the electrolyte higher is the number of protons penetrating into the oxide layer. The electric field due to this diffusion is given by [11].

$$E_{diffusion} = \frac{qD_p}{\sigma} \frac{dP}{dx} \tag{1}$$

The electric field developed due to the diffusion itself act as a field which causes movement of the additional protons inside silicon dioxide layer. Therefore the electric field responsible for additional proton drift is the same field that occurs due to the diffusion of hydrogen ion at the edge of the oxide layer i.e. $E_{diffusion} = E_{drift}$. E_{drift} is termed here as the electric field that causes proton drift inside oxide layer as depicted in Fig. 1.
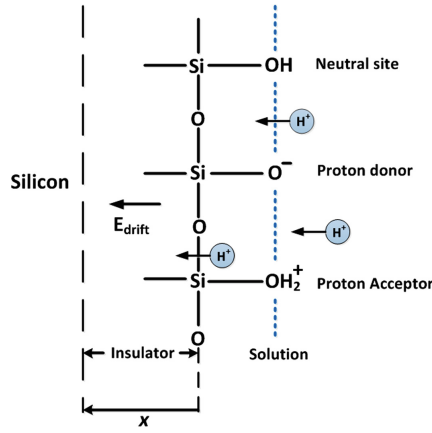
Fig. 1. Figure depicting diffusion of protons and the field caused by it

$$E_{drift} = \frac{qD_p}{\sigma}\frac{dP}{dx} \tag{2}$$

Here, D_p is the co-efficient of hydrogen ion near the oxide-solution interface, q is the electronic charge, σ is the conductivity, P is the concentration of the proton and dP/dx is the concentration gradient. Differentiating both sides of the Eq. (2), the equation obtained is

$$\frac{dE_{drift}}{dx} = \frac{qD_p}{\sigma}\frac{d^2P}{dx^2} \tag{3}$$

Further Fick's law of diffusion is given by

$$\frac{dP}{dt} = -D_p\frac{d^2P}{dx^2} \tag{4}$$

The Eqs. 3 and 4 can be simplified as,

$$\frac{dE_{drift}}{dx} = -\frac{q}{\sigma}\left(\frac{dP}{dt}\right) \tag{5}$$

Further, time variant concentration P is given by

$$P = \frac{Q}{\sqrt{\pi D_p t}}e^{-\frac{x^2}{4D_p t}} \tag{6}$$

Here Q is the surface concentration. Since the temporal variation of threshold voltage happen to be observed for comparatively longer duration of time and the minimum distance x is very small, we can approximate as

$$x^2 << 4D_pt \tag{7}$$

With the above assumption, the exponential term in Eq. (6) tends to unity. Hence Eq. (6) can be written as

$$P = \frac{Q}{\sqrt{\pi D_p t}} \tag{8}$$

Substituting Eq. (8) in (5)

$$\frac{dE_{drift}}{dx} = -\frac{q}{\sigma}\frac{d}{dt}\left(\frac{Q}{\sqrt{\pi D_p t}}\right) \tag{9}$$

Differentiating Eq. (9) can be written as

$$\frac{dE_{drift}}{dx} = \frac{q}{2\sigma}\left(\frac{Q}{\sqrt{\pi D_p}}\right)\left(t^{-1.5}\right) \tag{10}$$

Further integrating Eq. (10), the obtained equation is

$$E_{drift} = \frac{qQ}{2\sigma}\frac{1}{\sqrt{\pi D_p}}t^{-1.5}x \tag{11}$$

The constant of integration has been formulated using a boundary condition as E_{drift} $(x) = 0$, when $x_{minimum} \leq x < 0$. Here we have considered that the field is created only after the protons have moved to a certain distance which is explained in Eq. 14. Integrating Eq. (11) with necessary constraints we get

$$-\int_0^V dV = \frac{qQ}{2\sigma}\frac{1}{\sqrt{\pi D_p}}(t)^{-1.5}\int_{x_j}^{x_{ox}} xdx \tag{12}$$

Equation (12) can be simplified as

$$V = \frac{qQ}{4\sigma}\frac{1}{\sqrt{\pi D_p}}(t)^{-1.5}(x_j^2 - x_{ox}^2) \tag{13}$$

x_{ox} is the oxide thickness. Further, x_j is the distanced travelled by proton in silicon dioxide which is given as follows [11].

$$x_j = 2\sqrt{D_p t}\,erfc^{-1}\left(\frac{C_{sensing}}{C_s}\right) \tag{14}$$

Here $erfc^{-1}$ is the inverse complementary error function, C_S is the surface concentration and $C_{sensing}$ is the trapped charges in the oxide layer. Therefore, substituting Eq. (14) in (13),

$$V_{drift} = \frac{qQ}{4\sigma}\frac{1}{\sqrt{\pi D_p}}(t)^{-1.5}\left(4D_p terfc^{-1}\left(\frac{C_{sensing}}{C_s}\right)^2 - x_{ox}^2\right) \tag{15}$$

Equation (15) is the voltage developed because of the field created due the diffusion of additional protons into the oxide. The voltage developed due to diffusion of protons into the silicon dioxide is found as [12]

$$V_{th} = 2|\phi_f| + \frac{Q_B}{C_{ox}} - \frac{q}{\varepsilon_{ox}}(x_{ox} - 2\sqrt{Dt}erfc^{-1}\frac{C_{sensing}}{C_s}) \tag{16}$$

The later part of the Eq. 16 can be expressed as the voltage developed due to the diffusion of hydrogen ions. This voltage is further addressed here as $V_{diffusion}$ as shown in Eq. 17.

$$V_{diffusion} = \frac{q}{\varepsilon_{ox}}(x_{ox} - 2\sqrt{Dt}erfc^{-1}\frac{C_{sensing}}{C_s}); \tag{17}$$

$$V_{th} = 2|\phi_f| + \frac{Q_B}{C_{ox}} \tag{18}$$

The effect of the diffusion and field due to it on the threshold voltage can be expressed as

$$V_{th(final)} = V_{th} - \left(V_{diffusion} + V_{drift}\right) \tag{19}$$

Substituting the Eqs. 16, 17 and 18 in Eq. 19 the final expression of the threshold voltage can be obtained, as given in Eq. 20

$$V_{th(final)} = 2|\phi_f| + \frac{Q_B}{C_{ox}} - \left(\begin{array}{c}\left(\frac{q}{\varepsilon_{ox}}(x_{ox} - 2\sqrt{Dt}erfc^{-1})\frac{C_{sensing}}{C_s} + \right) \\ \frac{qQ}{4\sigma}\frac{1}{\sqrt{\pi D_p}}(t)^{-1.5}\left(4D_p - terfc^{-1}\left(\frac{C_{sensing}}{C_s}\right)^2 - x_{ox}^2\right)\end{array}\right) \tag{20}$$

Here q is the charge per unit area, ϕ_f is the fermi-potential, Q_B is the bulk depletion charge, C_{ox} is the gate capacitance. The whole analysis has been carried out in isothermal condition and reference electrode voltage is considered zero. It has been observed from Eq. (20) that the temporal change of threshold voltage due to diffusion is proportional to $t^{1/2}$ and due to electric field resulting from diffusion is $t^{-3/2}$. Hence, it can be concluded that temporal change of threshold voltage due to diffusion is more dominant than that of the field created by diffusion with the passage of time.

3   Experimental Details

A Schottky based ISFET fabrication has been discussed in brief in this section, however, the detailed fabrication process flow of the same device has been reported in [2]. Silicon dioxide of thickness 480 nm has been deposited by thermal oxidation technique at a temperature of 1050 °C with a gas flow of 2 slpm (standard liquid per minute) of oxygen on a 3 inch double-sided polished p-type silicon wafer. Then first lithography was done to define the area where the metal has to be directly deposited on silicon substrate to form Schottky contact. The second lithography was done to partially etch out the active area to form the sensing area. Buffer oxide etchant was used for the etching purpose. Thus the sensing region obtained is about 120 nm thick measured using prism coupler (Metricon 2010M). Finally silver was deposited on the region exposed in the first step of lithography thus forming the Schottky contacts. The silicon substrate was then mounted on PCB board with adhesive. For the source and drain connections male connectors were soldered on the PCB board. The connectors were further bonded to the metal (Ag) layers using silver paste. A glass chamber was constructed using cover slip so that the electrolyte can be poured on the sensing layer. Silicone has been used for the sealing and passivation purpose. The schematic of the fabricated device and the picture of the actual device are illustrated in the Fig. 2(a) and (b) respectively.
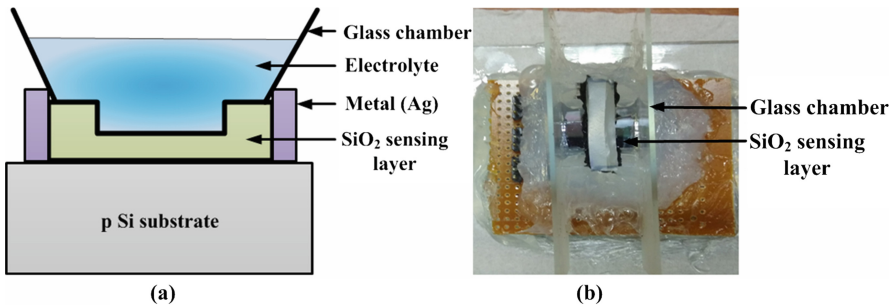

Fig. 2.   (a) The schematic of the fabricated device (b) The picture of the actual device fabricated

3.1   Measurement Procedure

Measurement of the fabricated ISFET device was performed to witness the change in threshold voltage with the passage of time for different pH values. The experiment was carried out by maintaining a constant voltage of 0.27 V across the source and drain using a two electrode Electrometer (Keithley 6517B) as illustrated in the Fig. 3(a). The electrometer also measures the drain current. With passage of every 1200 s, the transfer characteristics of the device are obtained by varying the gate to source voltage and carefully noting the drain current at constant ambient temperature of 25 °C. The threshold voltage can be extracted by extrapolation of the linear region of transfer characteristics. The experiment was carried out for the three pH value (pH 4, 7 and 10). The schematic of the measurement has been illustrated in Fig. 3(b).
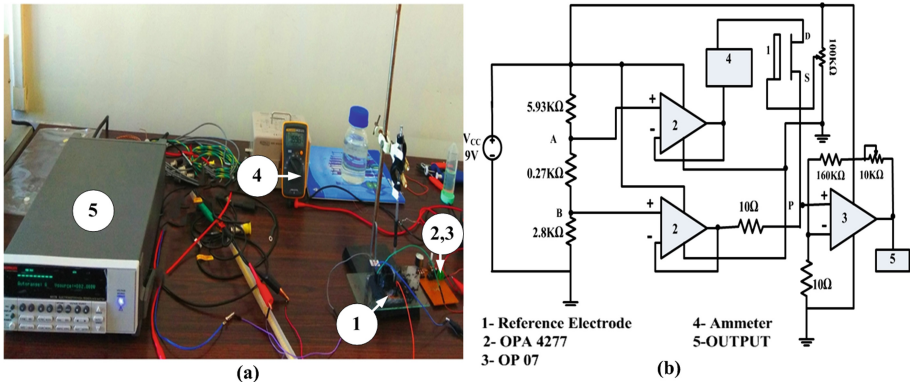
Fig. 3. (a). The measurement set up (b) Schematic of measurement set up

4   Results and Discussion

The above explained analysis has been simulated considering the necessary boundary conditions and feasible values for the constant parameters as reported in [12]. The following parameters have been set prior to simulation of the derived mathematical expressions. The fixed oxide charges ($C_{sensing}$) present in carefully treated Si/SiO$_2$ interface system for <100> surface is found to be 1×10^{10} atoms/cm^3 [13]. Doping concentration N_a is taken as 1×10^{16}/cm^3. Other parameter values for simulation considered are as stated in Table 1.

Table 1. Following Table shows the values of volume concentration, surface concentration and surface charge density for pH values of 4, 7, 10

pH values	Volume concentration C_S (atom/cm^3)	Surface concentration (atom/cm^2)	Surface charge per unit area (C/cm^2)
4	6.022×10^{16}	1.53×10^{11}	2.448×10^{-8}
7	6.022×10^{13}	1.53×10^{9}	2.448×10^{-10}
10	6.022×10^{10}	1.53×10^{7}	2.448×10^{-12}

It is observed from Fig. 4(a) that for pH 4 the temporal variation in threshold voltage due to the electric field caused by diffusion becomes almost steady after 5000 s and the variation seems significantly higher before this point. This occurs because of the higher electric field caused by diffusion due to the higher concentration gradient at the oxide/electrolyte interface. The electric field decreases as it moves from the interface of the electrolyte/oxide into the depth of the oxide layer. When considering only the variation in threshold voltage due to the diffusion of hydrogen ions into the SiO$_2$ layer the change is observed to be 11.75 mV for a period of 10 h. In the first couple of hours significant change in the threshold voltage can be observed and this change gradually decreases in the later hours. Further, when solely the field caused by

diffusion is considered, the contribution of this in the drift of threshold voltage is seen to be 0.969 mV for a period of 10 h. Further Fig. 4(a) depicts the combined effect of the diffusion and field caused by it on the threshold voltage of the device for pH 4. In the later hours the change in threshold voltage is dominated by the diffusion and the overall change in threshold voltage almost traces the plot of resultant threshold voltage due to diffusion. The variation in threshold voltage for pH 7 is found to be 0.12 mV for a period of 10 h as illustrated in Fig. 4(b) This can be explained as the concentration of hydrogen ions in the solution is lower in case of higher pH values. Further for pH 10, the variation in threshold voltage was found to be approximately 1.2 µV as depicted in Fig. 4(c). Therefore, it was observed from the simulated data that the change in threshold voltage for SiO_2 gate ISFET is prominent for lower pH values and for higher pH values these drift effect is quite low.
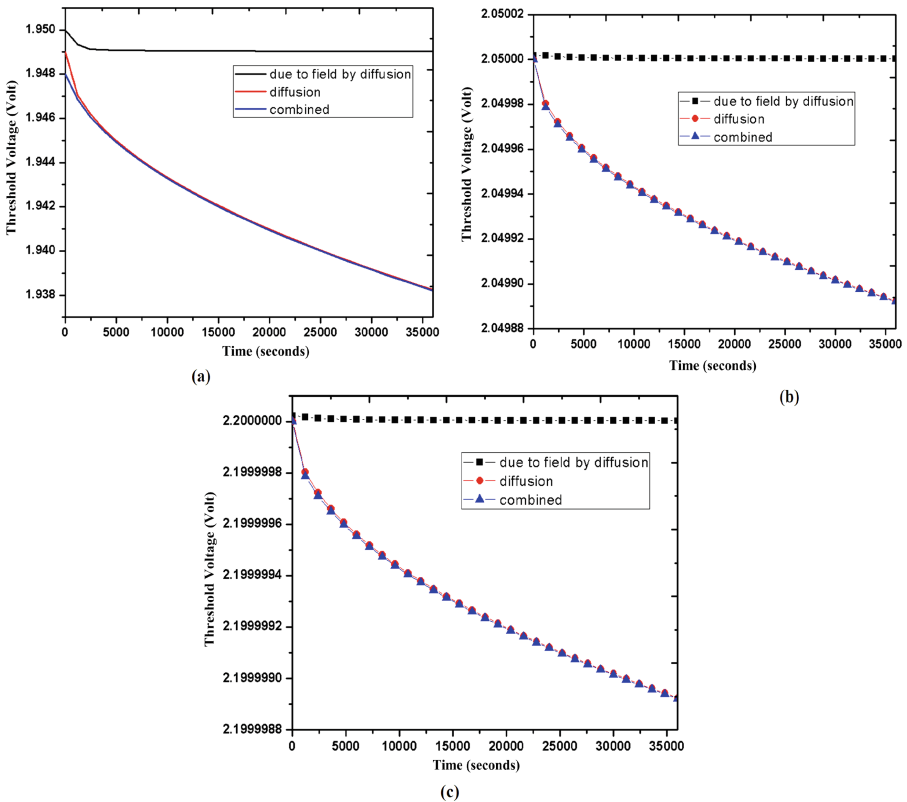

Fig. 4. (a, b & c) variation of threshold voltage with time, considering the diffusion of hydrogen ions into the sensing layer, the field caused by the diffusion and the combined effect of both for pH 4, 7 and 10 respectively.

The simulated data is compared with experimental data obtained from a fabricated SiO$_2$ gate pH ISFET. The experimentally obtained data along with the theoretical data for pH 4 is illustrated in Fig. 5(a). The fabricated ISFET showed a drift of 31.38 mV for a period of 10 h. The variation in the threshold voltage for both experimentally and theoretically obtained data shows a similar trend. However, a noticeable margin in the two values was observed as not all the parameters are considered in the MATLAB simulation environment. Further, in Fig. 5(b), the theoretical and the experimental values for the drift in threshold voltage for pH 7 are plotted. The fabricated ISFET showed a drift of approximately 0.4 mV for a period of 10 h. The variation in the threshold voltage exhibit similar trend for both experimentally and theoretically obtained results. In Fig. 5(c), the theoretical and the experimental plots for drift in threshold voltage for pH 10 are illustrated. Negligible variation between the results is observed as hydrogen ion concentration for pH 10 is significantly low.
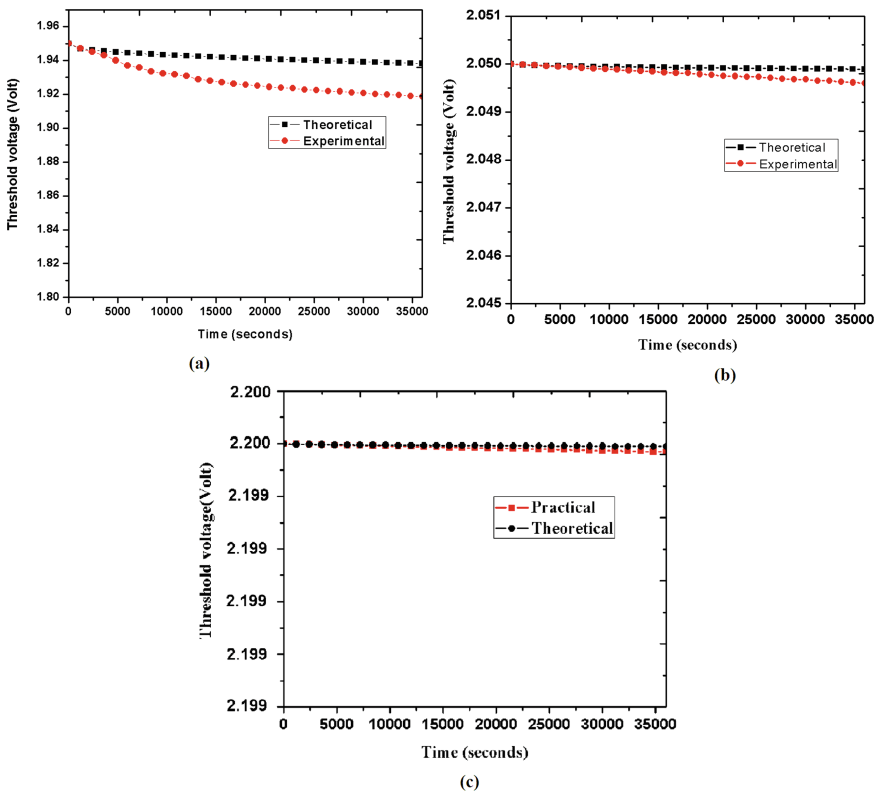

(a)

(b)

(c)

Fig. 5. (a, b, & c). Theoretical estimation of variation in threshold voltage with time for considering both diffusion and field caused by it along with the practical data obtained for SiO$_2$ gate pH ISFET when exposed for 36000 s (10 h) in pH 4, 7 and 10 respectively.

5 Conclusion

Long term drift, that brings instability to ISFET devices when kept immersed in electrolytes for long hours, cannot be overlooked as it results into inaccuracy in measurements. Most of the ISFETs and related BioFETs exhibit this effect. The diffusion of protons into the oxide layer results into this long term drift. The electric field resulting due to the diffusion of protons is more prominent in lower pH values and must be taken into account. The combined effect on the threshold voltage due to diffusion and due to electric field caused by diffusion of ions lowers the threshold voltage of the ISFET devices at lower pH values. The effect of electric field which brings about temporal change of threshold voltage in ISFET becomes less significant with the increase in pH values. The experiments carried out in this work using a fabricated Schottky based ISFET device the drift was observed to be high in the first few hour and attains a constantly decreasing trend after that. The decrease in threshold voltage after the passage of first hour is observed to be significantly low and can be concluded from the experimental and simulation data that the infiltration of H^+ ions occurs majorly during the initial hours. However, a comprehensive study considering all the factors associated with the sensing layer interface may produce better results and effective long term drift model.

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