Effect of dissolved hydrogen on Schottky barrier height of Fe-Cr alloy heterojunction

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Abstract. The presence of water vapour at high temperature oxidation has certain effects on ferritic alloy in comparison to dry environment. It is hypothesized that at high temperature; water vapour provides hydrogen, which will dissolve into ferritic alloy substrate and altering their electronic state at the metal-oxide interface. This work aimed to clarify the change in electronic state of metal-oxide heterojunction with the presence of hydrogen/water vapour. In this study, the Schottky Barrier (SB) was created by sputtering Cr,O, onto prepared samples by using RF Magnetron sputtering machine. The existence of Fe/Cr,O, junction was characterized by using XRD. The surfaces were observed by using Optical Microscope (OM) and Scanning Electron Microscope (SEM). The samples were then exposed in dry and humid condition at temperature of 473 K and 1073 K. In dry condition, 100% Ar is flown inside the furnace, while in wet condition mixture of 95% Ar and 5% H was used. I-V measurement of the junction was done to determine the Schottky Barrier Height(SBH) of the samples in the corresponding ambient. The results show that in Fe/Cr,O, junction, with presence of hydrogen at temperature 473 K; the SBH was reduced by the scale factor of 1.054 and at 1073 K in wet ambient by factor of 1.068. Meanwhile, in Fe-Cr/Cr,O, junction with presence of hydrogen, the value of SBH was increased by scale factor of 1.068 at temperature 473 K while at 1073 K, the SBH also increased by factor of 1.009.

1. Introduction

Ferritic alloys are the most common material being used to fabricate boiler tubes due to its properties such as low thermal expansion coefficient and high thermal conductivity [1]. Despite the properties mentioned, ferritic alloys also susceptible to corrosion that will cause the material to scale, exfoliate and undergo changes in physical properties. Many studies have shown ferritic alloys resistance towards corrosion is significantly challenged by the presence of water vapour [2–8]. However, the reason behind the phenomena is still unexplainable.

Oxide layer act as a semiconductor at high temperature [9–10]. The region where metal-oxide contacts will cause rectifying effect which causes the presence of potential difference between the metal and semiconductor itself. This area can be modelled as Schottky Barrier Height (SBH). The SBH indicates the mismatch in the energy position of the majority carrier band edge of the semiconductor and the Fermi level of the metal across the metal-oxide junction. At high temperature; in the case of Fe-Cr alloy, Fe remains its characteristics as a metal.
It is well known that hydrogen is highly soluble in iron. However, its solubility is one to three magnitude lower in iron oxide [11]. This difference in solubility will create space charge layer as shown in figure 1, where solute hydrogen in metal will contributes to positive charge and attract negative charge from the side of oxide layer [10]. This layer will alter the mass transport in the oxide layer, hence changing the overall oxidation rate during the presence of water vapour [10, 12].

Figure 1. Schottky barrier of Fe/Cr$_2$O$_3$ heterojunction. Image are taken from reference [9].

Figure 2 shows the schematic diagram of a Schottky Barrier of a metal-oxide interface. The mismatch in the energy position of the majority carrier band edge at the metal semiconductor (MS) interface and the Fermi level across the MS interface and the surface states of the semiconductor will determine the magnitude of the SBH. This paper intent to clarify the effect of hydrogen on SBH by measuring $I-V$ change of metal/oxide samples in dry and humid condition.

2. Experimental procedures
SBH are usually deduced from transport measurements of Schottky Barrier Diodes patterned on non-degenerate semiconductors. Current-voltage ($I-V$) method is one of the most common techniques for SBH determination. One tacit assumption in using these measurement techniques is that the SBH under investigation is homogeneous. In an $I-V$ experiment, the junction current is measured as a
function of the applied bias voltage. From a plot of the logarithmic of the forward-bias current, the saturation current and the ideality factor can be determined. According to the thermionic emission theory, the diode saturation current is related to the SBH by the following equations:

\[ I = A A^* T^2 \exp\left(-\frac{q \Phi_b}{kT}\right) \]  

(1)

\[ \Phi_b = \frac{kT}{q} \ln\left(\frac{A A^* T^2}{I_0}\right) \]  

(2)

Two different samples were prepared; 99.99% Fe and Fe-Cr ferritic alloy (T91). Samples were cut into coupons using automated saw and EDM. The dimension is 10mm x 10mm x 1mm. The sample were then ground with rotating discs of emery paper of grit size P60, P800, P1000, P1500 and P2000. Then the samples were polished with 0.5 μm down to 0.03μm diamond paste. Samples were then sonicated and let dry in autoclave. The polished samples were then sputtered in RF magnetron sputtering machine at room temperature in base pressure less than 5x10^{-8} Torr for 1 hour. RF power is 150 W with gas flow set to be 30sccm. The sputtering target was 99.99% Cr. The concept of sputtering Cr$_2$O$_3$ onto the samples can be seen in figure 3. Characterization after the sputtering were done using XRD (scanning range, 2θ = 20–80°) for each sample.

![Cr$_2$O$_3$ to be sputtered on the samples.](image)

**Figure 3.** Schematic of Cr$_2$O$_3$ to be sputtered on the samples.

After sputtering and XRD were done, samples were exposed separately in different temperature and ambient (dry and humid). Two temperature parameter has been chosen which are 473 K (lower temperature) and 1073 K (higher temperature). The experiment setup is shown in figure 4. The ambient was dry and wet. In dry condition; at lower and higher temperature, 100% Argon was supplied into the isothermal zone in the reaction chamber. For wet condition, 95% Argon was supplied with addition of 5% Hydrogen. Electrical potential was biased into the circuit and the corresponding current were recorded by the data logger. The temperature inside the isothermal zone were monitored using R-type thermocouple.
3. Results and Discussion
The image of microstructure for 99.99% Fe after sputtering can be seen in figure 5. It shows an almost uniform microstructure of Fe grain size. The cross-section of 99.99%Fe specimen, after sputtering can be clearly seen. The chromia layer is clearly shown and its layer was also being measured by SEM. The layer as observed in the figure was approximately 2.50 µm.

The X-Ray Diffraction (XRD) pattern for 99.99% Fe and T91 alloy after Cr₂O₃ sputtering is presented in figure 6. The result confirms the structural formation of Cr₂O₃ on 99.99%Fe. Fe and Cr₂O₃ is characterized by a prominent (110) and (200) peak at 2θ. The pattern of the spectra matches the value in the database for ferritic alloy. It shows a dominant peak at reflection appearing at an angle of 2θ = 44.5°.

Figure 7 and figure 8 shows I-V plot comparison for 99.99% Fe/Cr₂O₃ and Fe-Cr/Cr₂O₃ alloy in 100% Ar; and 95% Ar-5%H₂ environment. There are variations in the value of $I_o$ for each sample in different ambient and temperature. Here, $I_o$ for 99.99% Fe is $3.17 \times 10^{-5}$A for temperature at 1073 K whilst $I_o$ for Fe-Cr at the same temperature is $1.9068 \times 10^{-5}$ A. For sample 99.99% Fe at 473 K, the value of $I_o$ is $3.42 \times 10^{-4}$ A.

The difference between the values of $I$ stated above and the corresponding $I_o$ from linearized curves contributed significantly in the values of SBH for each sample. It can be seen in figure 9 that for 99.99%Fe, the calculated SBH value decreased with the presence of water vapour by scale factor of 1.054 at 473 K, while at 1073 K, the SBH calculated was reduced by the factor of 1.068. For Fe-Cr alloy however; as seen in figure 10 and figure 11, the value of SBH increased in the presence of water vapour. At 473 K, the SBH increased by factor of 1.003 with presence of humidity, and SBH also increased at 1073 K by factor of 1.009 with presence of water vapour. The increase of SBH value for Fe-Cr alloy in humid environment probably due to presence of protective Cr layer in the alloy.
**Figure 5.** Image of SEM for 99.99% Fe cross section after Cr$_2$O$_3$ sputtering. The measurement of Cr$_2$O$_3$ layer were 2.40mm, 2.50mm and 2.40mm respectively.

**Figure 6.** X-RD characteristic of Fe-Cr alloy (top) and 99.99% Fe sputtered with Cr$_2$O$_3$ (bottom).
Figure 7. (a) Plot of $I$-$V$ for samples in dry condition (b) the corresponding close up.

Figure 8. (a) Plot of $I$-$V$ for samples in wet condition (b) the corresponding close up.
Figure 9. Plot of SBH for 99.99%Fe in dry and humid condition at 473 K and 1073 K.

Figure 10. Plot of SBH for Fe-Cr in dry and humid condition at 473 K and 1073 K.
Figure 11. Corresponding close up for values in figure 10. (a) values of SBH at 473 K, (b) values of SBH at 1073 K.

In this work, it is clearly shown that the presence of hydrogen in humid condition may have change the region of space charge layer at the metal oxide junction. Many previous work suggested the presence of dissolved hydrogen have significant effect on high temperature oxidation of Fe-Cr alloy [2, 13–16]. The variation of corresponding $f$ with different temperature and environment (dry and humid) proved the space charge layer was altered and supported by the values of the corresponding SBH in the given condition. Therefore, the results obtain from this work are in agreement with other previous work regarding increased in oxidation rate of Fe-Cr alloy in humid condition at high temperature due to effect of dissolved hydrogen in the metal oxide junction.

Conclusion
In conclusion, we have successfully fabricated Fe/Cr$_2$O$_3$ and Fe-Cr/FeCr$_2$O$_4$ junction. The $I$-$V$ curves obtained from the experiment shown that the presence of water vapour/ hydrogen does affects the electronic state of the metal-oxide junction by altering its Schottky Barrier Height, thus proving the presence of hydrogen altered the electronic state of metal oxide junction. However, the solubility of hydrogen in the metal oxide junction was not measured in this work. Therefore, the relation between hydrogen solubility and alteration of space charge layer will be further investigated in future work.

Acknowledgement
This work was financially supported by International Islamic University Malaysia (IIUM).

References
[1] Viswanathan R, Sarver J, and Tanzosh J M 2005 Journal of Materials Engineering and Performance 15 255–274
[2] Michalik M, Tobing S L, Hänsel M, Shemet V, Quadakkers W J, Young D J 2014 Materials and Corrosion 65 260–266
[3] Othman N K, Othman N, Zhang J and Young D J 2009 Corrosion Science 51 3039–3049
[4] Kaderi A, Ani M H, Herman S H and Othman R 2012 Advanced Materials Research 557-559 100–107
[5] Ani M H 2009 The Effect of Water Vapor on Transition of Internal/External Oxidation in Ferritic Fe-Cr Alloys at 1073 K thesis
[6] Issartel C, Buscail H, Wang Y, Rolland R, Vilasi M and Aranda L 2011 Oxidation of Metals 76 127–147
[7] Othman N K, Zhang J and Young D J 2010 *Oxidation of Metals* **73** 337–352

[8] Lepingle V, Louis G, Petelot D, Lefebvre B and Vaillant J C 2001 *Material Science Forum* **369–372** 239–246

[9] Zaharudin M Z 2016 *The Schottky Barrier Of Ferritic Alloy/ Cr₂O₃ Heterojunction* thesis

[10] Zainal M S 2013 *The effect of dissolved hydrogen on Schottky barrier at Fe/Cr₂O₃ heterojunction* thesis

[11] Mitsutoshi U, Hideto K, Kenichi K and Toshio M 2004 *Joint International Meeting of The Electrochemical Society and Fall Meeting of the Electrochemical Society of Japan* 127

[12] Ku Saad K M S 2014 *The Effect of Dissolved Hydrogen on Schottky Barrier of Fe/Cr₂O₃ Heterojunction at 1073K* thesis

[13] Surman P L 1973 *Corrosion Science* **13** 113-124

[14] Tveten B, Hultquist G and Norby T 1999 *Oxidation of Metal* **52** 221–233

[15] Mu N, Jung K, Yanar N M, Pettit F S, Holcomb G R, Howard B H and Meier G H 2013 *Oxidation of Metal* **79** 461–472

[16] Fukumoto M, Sonobe H, Hara M and Kaneko H 2017 *Oxidation of Metals* 1–8