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On the work function of metals and the electron affinity of crystal surfaces of semiconductors

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Abstract: *This research study presents a new method of determining the metal work function and the electron affinity ofsemiconductor crystal surface through Metal-Insulator-Semiconductor characterization with amorphous thermal silicon dioxide as the insulator. The method gives precise value for the electron affinity of Si as 4.1 eV which is very close to the reported value of 4.05 eV. The metal work functions obtained by this method for Al and Mg are a bit lower and the reasons are discussed in the discussion section. The Al work function comes out to be 3.9 to 4.02 eV by this method and the reported value is 4.20±0.05 eV in the studies by another research group. The work function of Au obtained by the new method is exactly as reported at 5.3 eV.*
Keywords: *Electron Affinity, Work function, MOS, Metals, Semiconductors, Tunnelling*

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I. Introduction

A Metal-Oxide-Semiconductor-Field-Effect-Transistor (MOSFET) is the workhorse of the Si electronics field, the use of which has evolved into a personal computer of today. Billions of these MOSFETs are now integrated into a thumb size Silicon chip that forms part of the processors in the personal computers. The heart of this transistor is the MOS device that can be easily fabricated and studied in an Electronics laboratory of a University or College or even at an Industry setting. The study of this device reveals the properties of the device that can make the transistor efficient and reliable. Some of the main properties are: Interface states at the oxide/semiconductor interface and in the oxide near the interface, charge densities in the oxide, Electrical breakdown strength of the oxide, leakage current in the oxide, the onset field for electron and hole tunnelling current and many others. An excellent 900 pages book on the MOS Physics and Technology is available from Wiley and Sons publishers, written by E.H. Nicollian and J.R. Brews that can provide detailed knowledge on the MOS device, supplemented with books on Solid-State Physics and Solid-State Device Electronics [1].

The onset field for Fowler-Nordheim(FN) tunnelling electron and hole current relates to the conduction band offset (CBO) in the device by a factor of 2, through the threshold electric field for electron heating in the oxide of 2 MV/cm-eV, and therefore finding this onset field can lead to the determination of the CBO which could be the metal/oxide barrier height in eV or the semiconductor/oxide barrier height in eV. An addition of the oxide electron affinity of 0.9 eV would give the work function of metal or the electron affinity on the semiconductor crystal surface. This forms a viable method for the determination of the above properties and is discussed in this research study with examples of Al, Mg, and Au as metals and Si as the semiconductor.

II. Theory

This research study reports on the determination of the work function of metals and the electron affinity in semiconductors by utilizing the Metal-Insulator-Semiconductor (MIS) characterization method of observing the FN onset electric field across a MOS device having an oxide as an insulator. The minimum field for electron heating in the oxide is 2 MV/cm-eV, where 1 eV is the minimum energy needed for vacuum emission of hot electrons. This has been shown by DiMaria et al. and confirmed by the author in his earlier study on ionization in the thermal SiO_2 [2-3]. The FN onset field in a MOS device divided by this minimum field for electron heating of 2 MV/cm-eV gives the CBO in the MOS device. The CBO can be the metal/oxide interface barrier height for the Al/SiO_2/n-Si MOS device with Al as the negative electrode (cathode), for the current-voltage characteristics at a low voltage ramp-rate of 0.1 to 0.5 V/s. It could also be the semiconductor/oxide interface barrier height for the Al/SiO_2/n-Si MOS device with Si semiconductor as the cathode for the current-voltage characteristics [4]. The CBO becomes the Al-SiO_2 barrier height or the Si/SiO_2 barrier height. If the SiO_2electron affinity of 0.9 eV [5]is added to the either of the two interface barrier heights, then one can get the metal work function or the electron affinity of the crystal surface of the semiconductor.

III. Results and Discussions

The results of three barrier heights of Al-SiO_2, Si-SiO_2, and Mg-SiO_2 are discussed first and finally Au-SiO_2 barrier height is discussed starting from the research study of Lenzlinger and Snow in 1969 [4]. The first row of Table I below, presents the results obtained by Lenzlinger and Snow. The Al-SiO_2 barrier height was taken as 3.2 eV from the photoemission experiments and the calculated electron effective mass in $SiO_2$was 0.39m, calculated from the slope constant B of the Fowler-Nordheim electron tunnelling current through the n-MOS device with Al as cathode and taken at room temperature in air at about 300 Kelvin. The Si-SiO_2 barrier height was taken as 3.25 eV from the photoemission measurements and the calculated electron effective mass in SiO_2 was 0.42m with Si as the cathode for the current-voltage characteristics on the n-MOS device. The slope constant B was 258 MV/cm and the oxide thickness t_{ox} taken was 100nm. Finally, the Mg-SiO_2 barrier height was taken as 2.4 eV and the calculated electron effective mass in the 100 nm thick thermal silicon dioxide was 0.48m. It needs to be mentioned that this n-MOS device has not undergone any annealing such as low temperature 500°C post-metallization anneal in an inert atmosphere of N_2 or Ar gas for good contact, or high temperature 1000°C post-oxidation annealing in an inert atmosphere that can anneal out electron traps in the oxide [6]. Annealing can have an effect on the slope constant B and the FN onset field in the MOS device [7].

Table I. Metal and semiconductor barrier heights with thermal SiO_2 and the electron effective mass in SiO_2 for different measurement methods [4].

Measurement Method	Al-SiO_2 barrier height (eV)/Electron effective mass in SiO_2	Si-SiO_2 barrier height (eV)/Electron effective mass in SiO_2	Mg-SiO_2 barrier height (eV)/Electron effective mass in SiO_2
Photoemission	3.2/0.39m	3.25/0.42m (B=258MV/cm, t_{ox}=100nm)	2.4/0.48m
FN onset field	3.0/0.47m	3.20/0.44m	2.2/0.62m
FN slope constant B, with the electron mass of 0.42m in SiO_2	3.12/0.42m	3.20/0.42m (B=254MV/cm, t_{ox}=8.5nm)	2.5/0.42m

The second row in Table I presents results similar to that in the first row, but utilizes the method of finding the barrier heights outlined in the theory section of this article of observing the FN onset field on the n-MOS device. The FN onset field on the n-MOS device with Al as the cathode is 6 MV/cm which when divided by 2MV/cm-eV gives the Al-SiO_2 barrier height of 3.0 eV. The same FN onset field of 6 MV/cm in the MOS device is also shown by Rai et al even after annealing [7]. Dressendorfer and Barker measured the Al-SiO_2 barrier height on MIS Schottky diodes having 40 nm oxide by internal photoemission. They found the barrier height as 3.0 to 3.1 eV for both thin and thick oxide after barrier lowering corrections [8]. Osburn and Weitzman conducted electrical breakdown measurements on Al/SiO_2/Si MOS devices having thick oxides and 5-minute post metallization anneal at 500°C in N_2 ambient. They found the FN onset field after cycling the high electric field many times to be 6.1 MV/cm with Al as cathode [9]. This gives an Al-SiO_2 barrier height as 3.05 eV. The electron effective mass calculated with this barrier height of 3.0 eV utilizing the equation of the slope constant B for the FN electron tunnelling current comes out to be 0.47m. This is because the change in barrier height does not change the bulk oxide and the equation of the slope constant can be used as follows [10-11]:

$$B = 68.3\, x \left(\frac{m_{ox}}{m}\right)^{1/2} x(\emptyset_0)^{3/2} \ldots\ldots MV/cm \qquad (1).$$

Then for the same B, $(m_{ox}\ x\ \emptyset_0{}^3)$in the first row can be equated to $(m_{ox}\ x\ \emptyset_0{}^3)$ in the second row. This gives the values of barrier heights and the electron effective masses in the oxide in the second row using the m_{ox} and $\emptyset_0$ values of the first row. One can clearly observe that for a lower barrier height obtained from the FN onset field, the electron effective masses in the oxide become larger than 0.42m which is the accepted value [10-11]. Mg-SiO_2 barrier height obtained by the FN onset field method is 2.2 eV and the electron effective mass in the oxide comes out to be 0.62m which is abnormally high. This Mg-SiO_2 barrier height is not unusual as Deal, Snow and Mead have reported a value of 2.25 eV for Mg-SiO_2 in 1966 with the MOS device fabricated on p-(111)-Si substrate [12]. A year later Snow reported a value of 2.3 eV for the Mg-SiO_2 barrier height and an electron mass of 0.47m [13]. In this paper, the FN plot begins to deviate from the straight line at 0.23 cm/MV of reciprocal of the field. This point identifies the field to be the FN onset field in the MOS device on p-Si with Mg as the gate cathode. FN onset field is thus 4.35 MV/cm and the Mg-SiO_2 barrier height becomes 2.17 eV with the method presented in this study. This is nearly the same as 2.2 eV obtained from Lenzlinger and Snow's work from the FN onset field method on n-MOS device [4]. Both the research studies have a no-annealing condition for the MOS device. The type of the substrate does not change the Mg-SiO_2 barrier height by the FN onset field method.

The third row in the Table I presents the barrier heights using the accepted electron effective mass in the thermal silicon dioxide (SiO_2) of 0.42m. Here, the thermal oxide in the second column of the third row is different with a lower slope constant B of 254 MV/cm instead of 258 MV/cm [10-11] with a matching Si-SiO_2 barrier height of 3.20 eV obtained by observing the FN onset field in the n-MOS device. The Al-SiO_2 barrier height has been shown to be 3.15 eV on a MOS device fabricated on the n-Si substrate by Deal, Snow and Mead in their early works of 1966 by photoemission measurements [12]. Similarly, the Mg-SiO_2 barrier height has been reported to be 2.5 eV by photoemission experiments later onin 2002 [14-15]. The photoemission experiments are performed under high vacuum and there is much less chance of water vapour adsorption of the metal surface unlike the MOS device characterization which is performed in the room ambience. The adsorption of water on the metal surface is known to lower the work function of the metal by as much as 1 eV [16]. The Si-SiO_2 barrier height of 3.20 eV by the FN method is exceptional because here the Si is not exposed to the room atmosphere for possible water vapour adsorption.

Extremely careful studies on work function of metals on glass under high vacuum has been performed, giving Al work function as 4.20 ± 0.05 eV [17]. Another study of work function of Al deposited on substrates of Al (100), Al (110) and Al (111) gives the values as 4.20 ± 0.03 eV, 4.06 ± 0.03 eV, and 4.26 ± 0.03 eV respectively, under high vacuum, and polycrystalline Al film gave a work function of 4.28 ± 0.01 eV. If the electron affinity of 0.9 eV is added to the concluded value of 3.12 eV for the Al-SiO_2 barrier height measured in open at room temperature through MOS device characterization, then the work function of Al on thermal SiO_2 comes out to be 4.02 eV. This is close to 4.20 ± 0.05 eV value presented above, with glass being the substrate. It should be remembered that the difference can be due to adsorption of water vapour on the Al from the atmosphere when the MOS device is characterized by the I-V and C-V based method, although Dressendorfer and Barker got the same value for the Al-SiO_2 barrier height of 3.0-3.1 eV by photoemission method which is performed under vacuum. It may just be experimental differences. The author vouches for 3.12 eV as the Al-SiO_2 barrier height based on the electron effective mass of 0.42m in the amorphous thermal silicon dioxide. The work function of Mg can similarly be said to be 2.5 + 0.9 = 3.4 eV. The electron affinity of the Silicon semiconductor crystal surface will be 3.20 + 0.9 = 4.1 eV. A value of 4.05 eV is an accepted reported value. It is to be noted that the electron affinity of a single atom is different than that on the crystal surface.

Au-SiO_2 barrier height is reported by Lenzlinger and Snow as 4.2 eV by photoemission. The current voltage data from the experiments by them shows an FN onset field of at least 8.8 MV/cm. This gives the Au-SiO_2 barrier height as the CBO to be 4.4 eV. Adding the oxide electron affinity of 0.9 eV gives the work function of Au by the FN method of this study to be 5.3 eV. This is exactly the work function of Gold (Au) deposited at 50°C as reported by Sachtler et al. in 1966 [18]. A word about the electron affinity in thermal SiO_2 of 0.9 eV is worth mentioning that it should remain the same at 0.9 eV [5] for the MOS device fabricated on both p- and n-Si substrates because the electron affinity is from the oxide conduction band to the vacuum level, and the oxide traps and interface states at the oxide/Si interface are deep in the oxide below the oxide conduction band. Hatsoff to DiMaria et al. [2-3], for their marvellous discovery of the threshold electric field in SiO_2 for electron heating of 2MV/cm-eV that led to the generation of the idea of this novel method of finding the work function of metals and the electron affinity on the semiconductor crystal surface.

IV. Conclusions

The method of observing the FN onset field in a MOS device to determine the work function of metals and the electron affinity on the semiconductor crystal surface is a viable method. Here, in the present report, the work function of Al and Mg is found to be 4.02 and 3.4 eV. The work function of freshly deposited Au at 50°C is found exactly as reported to be 5.3 eV. The electron affinity on the Silicon semiconductor crystal surface is 4.1 eV, very close to the reported value of 4.05 eV. Many processing, surface, ambient conditions have to be re-examined in the MOS device in conjunction with this method of finding the work function of metals and the electron affinity of the semiconductor crystal surface. MOS characterization under high vacuum may alter the FN onset field.

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