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Thermal Desorption of Copper from Iridium Surface.

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Highlights

- **Thermal desorption is an important application of field electron emission microscopy. It can be used to calculate the desorption energy of removing thermally the adsorbate metal atoms from the surface of another metal.**
- **In this study the desorption energy of removing thermally copper atoms from the surface of the iridium tip was measured.**
- **The desorption energy was computed mainly by using desorption curves and Arrhenius plots.**
- **We obtained desorption energy values in the range of 3.30±0.02 eV to 4.00±0.05 eV.**

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ABSTRACT

Desorption of copper from iridium surface has been investigated and the activation energy of this process was evaluated on the whole tip surface of iridium field emitter using a field emission microscope which was designed to permit measurement of electron emission from the emitter surface under ultra-high vacuum (UHV) conditions($< 10^{-10}$ torr) and extreme cleanliness. The level of contamination could be closely monitored by observing the change in field emission current with time at constant applied voltage. In the presence of even small amounts of an active gas, a persistent decay of the field emission current with time was observed and the system was judged to be clean enough to commence the experimental work only when the rate of contamination (RC) is less than 3 volts/minute. The activation energy for desorption was derived from the least square analysis of the Arrhenius plots to be equal to 3.30 ∓ 0.02 eV to 4.00 ∓ 0.05 e.

1. Introduction

Thermal desorption is the removal of adsorbate atoms from a tip surface by heating the tip to a temperature high enough to make the adsorbate atoms depart the substrate surface. The adsorbate can also be removed from the substrate surface without heating the tip by a process called field desorption or field evaporation. In field evaporation, a high positive voltage is applied to the tip. The adsorbate atoms are evaporated in the form of positive ions when the applied field is increased for a sufficiently high value ($\approx 10^8$ volts/cm) (Muller and Tsong, 1969; Brandon, 1968).

The design of the employed microscope in this study did not permit the use of the high voltage required for the field evaporation process. The process of thermal desorption of copper from iridium tip surface takes place at a rate proportional to $e^{\frac{-Q}{kT}}$ (Bradley and D' Asaro, 1959), where Q is the activation energy, K is Boltzmann constant, and T is the absolute temperature. The range of the absolute temperatures used in this study is 1160-1240 K.

2. Experimental

Fig. 1 shows a schematic diagram of a simple field emission microscope which consists of an evacuated glass bulb, the end face of which is covered with a conducting tin oxide layer that acts as an anode, and a layer of phosphor which serves as a screen. The specimen in the form of a sharp point acts as a cathode. To obtain the high field (3-7X10^6 volts / cm) required for electron emission from the point, it is etched electrolytically to about 1000 A^o radius. The electric field (F) at the surface of a free space sphere of radius (r) and a potential (V) is

$$F = \frac{V}{r} \tag{1}$$

At the surface of the tip the electric field is reduced by the presence of the shank and it can be approximated to

$$F = \frac{V}{kr} \tag{2}$$

where (r) is the mean tip radius and (k) is the field reduction factor which has a value of about 5 near the apex (Melmed, 1967). It can be seen from Equ. (2) that electron emission can be obtained by applying a relatively low voltage (1000 to 3000 volts) between the emitter and the anode.

In the presence of even small amounts of an active gas a persistent decay of the field emission current with time was observed and the system was judged to be clean enough to commence the experimental work only when the rate of contamination (RC) is less than 3 volts/minute, i. e.

$$\mathrm{R.\,C.} = \frac{v_2 - v_1}{t} \leq 3 \text{ volts/minute},$$

Where v_1 is the voltage required to draw a chosen field emission current from a clean emitter surface and v_2 is the voltage required to draw the same emitted current after keeping the field on for a period of time (t).

A typical clean field emission pattern from an iridium emitter is shown in Fig. 2. The pattern, as it can be seen in Fig. 2, usually consists of bright and dark areas depending on the flux density of the emitted electrons reaching the screen from different planes of

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the tip surface. The planes of low work functions appear brighter than other higher work function regions.

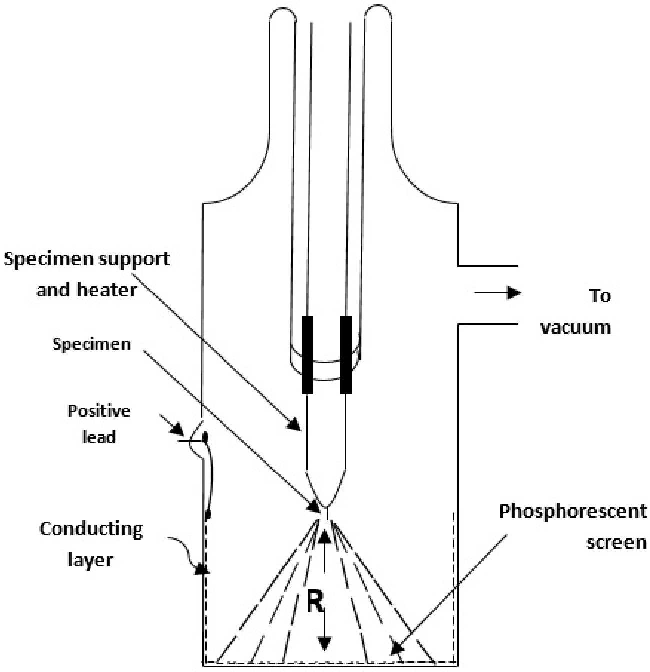

Fig.1. A simple field emission microscope

Fig. 2. Field emission pattern of a clean iridium tip surface.

Ideally, the magnification of the pattern on the screen would be give by Equ. (3), (Gomer, 1978)

$$M = \frac{R}{r} \tag{3}$$

However, due to the presence of the emitter shank, the actual magnification is given by (Dyke and Dolan, 1956; Melmed, 1967)

$$M = \frac{R}{\alpha r} \tag{4}$$

where α lies between 1.5 and 2 (Melmed, 1967; Dyke and Dolan, 1956; Van Oostrom, 1966; Muller 1960; Rose, 1956). In general, an average magnification of the order of 10^5 to 10^6 is obtained (Gomer, 1978).

The large magnification of the microscope could be of little value if the resolution was not proportionally good. The resolution of the field emission microscope is defined as the minimum distance between two objects on the tip surface that will produce separable images on the screen (Muller, 1960; Muller and Tsong, 1969; Gomer, 1952). A resolution of the order of 20 A^o is usually obtained in a field emission microscope (Melmed, 1967; Gomer, 1978; Derochette and Marien, 1977).

2.1 The Tip Assembly

To know how the tip used in this work was assembled see (Hashim, 2000).

i. The Tip Etching

Etching the tip means getting a sharp end with the smallest possible radius. a complete explanation for this process is also mentioned in detail in (Hashim, 2000). (Moran *et al.*, 2015) showed that sharp iridium tips could be obtained by an electrochemical process. Bin and Fritz (Bin and Fritz, 2004) prepared gold sharp tips with a radius of smaller than 30 nm by direct current electro chemical etching . For more information and methods to fabricate sharp tips see (Eisele *et al.*, 2011; Ottaviano *et al.*, 2003; Iwami *et al.*, 1998; Libioulle and Houbion, 1995; Ekvall *et al.*, 1999; and Lindahl *et al.*, 1998).

Iridium has been chosen as a field emitter because of its high melting point (2454 °C) (Zuber and Ciszewski, 2000) and its low vapour pressure (10-8 torr at approximately 1460 °C) allow for suitable cleaning by thermal desorption of impurities.

ii. Cleaning of the tip

A freshly etched tip is usually very sharp, emitting electrons at less than 600 V, and when the field is applied the screen is covered with bright spots having no identifiable pattern. We found that for experimental work the tip had to be cleaned until the pattern was observed on the screen, and the tip is blunted until 1μA of field emission current could be drawn by applying a voltage greater than 2000 Volts**.** Grant (Grant, 1969) in low energy electron diffraction (LEED) study of iridium obtained a clean surface by heating it to 400°C justifying the temperature guide provided by Bettler and Barnes (Bettler and Barnes, 1968) for cleaning field emitters.

In this study, the cleaning procedure started at a flash current of 1.3 amperes (≈ 1080 °C) for 60 seconds. Blunting occurred as expected (Mundschau and Vanselow, 1985; Cranstoun and Pyke, 1974) resulting in gradually increasing voltage required to produce a fixed value of emission current. As the cleaning temperature was increased scattered bright spots were observed on the screen. Since those had occurred by heating alone, they can be attributed to impurities diffused to the surface to form oriented overgrowths as described by Gomer (Gomer, 1961). Then before obtaining the clean pattern, two big bright spots, one on either side of the screen, were always seen.

The clean pattern was finally obtained after the tip had been heated at a temperature of about 1900°C (I - 2 Amperes). The condition for assuming the emitting surface to be clean is that heating at progressively higher temperatures should result in no further changes in the field emission pattern appearance.

During the experimental work, the tip was usually flashed before starting any experiment to remove the adsorbed gases on the surface. The tip was also flash cleaned at the end of every experiment. These falshcleanings were done at temperatures lower than that used initially to get the tip clean in order to keep the blunting to a minimum. In the present study, the temperature used for recleaning was about 1700°C (1.8 amperes).

iii. Vacuum processing

In order to get meaningful observation on surface phenomena using field emission microscopy, the study must be carried out under conditions of ultra high vacuum (UHV), and extreme cleanliness**.**

3. Theory

Thermal desorption is a reaction in which the bonds between the surface atoms and the adsorbate atoms are broken. If n is the concentration of an adsorbate (atoms/ cm^2) over a substrate surface, then its rate of decrease at a particular temperature is given by (Schmidt and Gomer, 1965):

$$-\frac{dn}{dt} = An\exp\left(-\frac{E_{des}}{kT}\right) \tag{5}$$

where A is the pre-exponential factor, E_{des} the activation energy for desorption, and k is a constant. Rearranging equation 5 gives:

$$-\frac{dn}{n} = A\,exp\left(-\frac{E_{des}}{kT}\right)dt \tag{6}$$

by integrating equation 6, we get:

$$-ln(n) = A\,exp\left(-\frac{E_{des}}{kT}\right)t \tag{7}$$

If n_i is the adsorbate density at t_i and n_f is the adsorbate density at t_f, where t is the heating time and $t_f > t_i$ and $n_i > n_f$, then

$$-ln(n_i) = A\,exp\left(-\frac{E_{des}}{kT}\right)t_i \tag{8}$$

$$-\ln(n_f) = A\exp\left(-\frac{E_{des}}{kT}\right)t_f \tag{9}$$

Subtracting equation 8 from Equ. 9 yields:

$$ln\left\{ln\left(\frac{n_i}{n_f}\right)\right\} = ln(A) - \frac{E_{des}}{kT} + ln(\Delta t) \tag{10}$$

Where $\Delta t = t_f - t_i$. Rearranging equation 10 gives:

$$ln(\Delta t) = \frac{E_{des}}{kT} - ln(A) + ln\left\{ln\left(\frac{n_i}{n_f}\right)\right\} \tag{11}$$

A plot of $\ln(\Delta t)$ vs $.\frac{1}{T}$, known as the Arrhenius plot, gives a straight line whose slope is m, and Edes is found by Equ. (12), (Al-Rawi, 1980):

$$E_{des} = mk \tag{12}$$

4. Results

The activation energy for thermal desorption of copper from iridium surface was measured by the following procedure:

The voltage (Vi) required to draw one microampere total emission current from a thermally cleaned tip surface was measured. Then a single dose of approximately four monolayers (θ=4) of copper was condensed onto the clean iridium field emitter surface at a temperature of 78 K. After equilibrating the dose on the tip surface by heating at a temperature of 760 K with no applied field, (Vi) was measured. Removal of copper was accomplished by heating the tip for periods of ten seconds at a predetermined temperature and monitored by measuring (Vi) after each heating, i.e. at 78 K, until the copper had been completely desorbed. The imaging field was applied only as long as necessary to measure (Vi). During the process (Vi) was observed to increase gradually, attaining finally the clean surface value. The tip was then flashcleaned and the whole process was repeated at another desorption temperature, care being taken to establish the same starting conditions for each run. Desorption measurements were made at 1160 K, 1180 K, 1200 K, 1220 K, and 1240 K. Figs. 3 to 7 depict the desorption process, ΔV represents the difference between (Vi) at time t and (Vi) at the starting state (t=0).

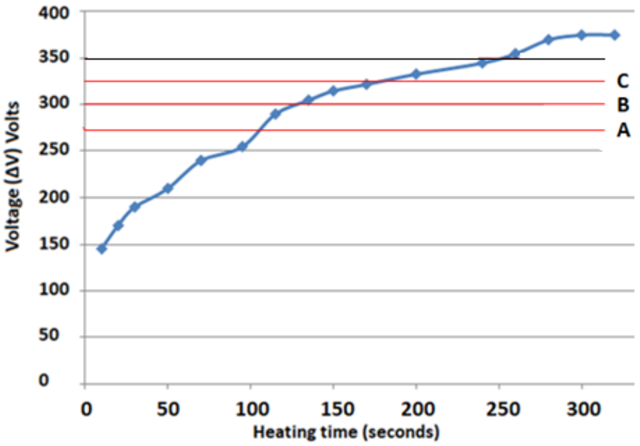

Fig. 3. Desorption curves of copper from iridium at Ts = 1160 K, T is the desorption temperature

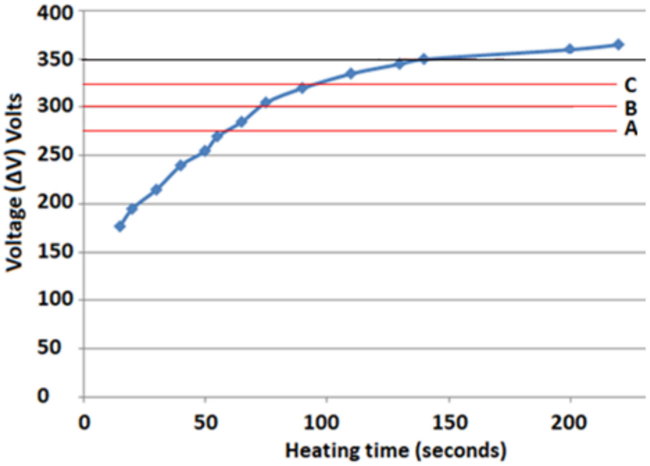

Fig. 4. Desorption curves of copper from iridium at T = 1180 K

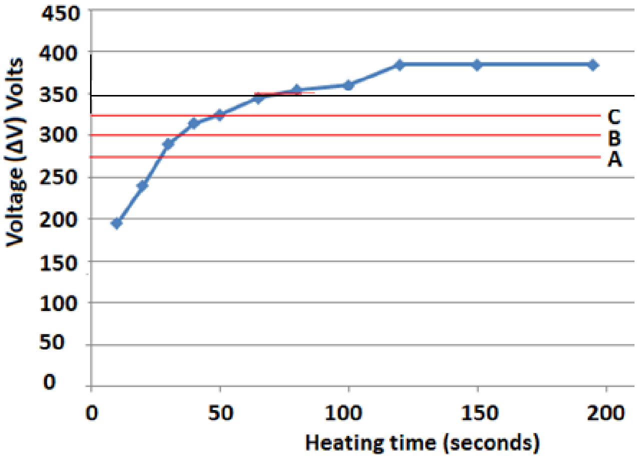

Fig. 5. Desorption curves of copper from iridium at T= 1200 K

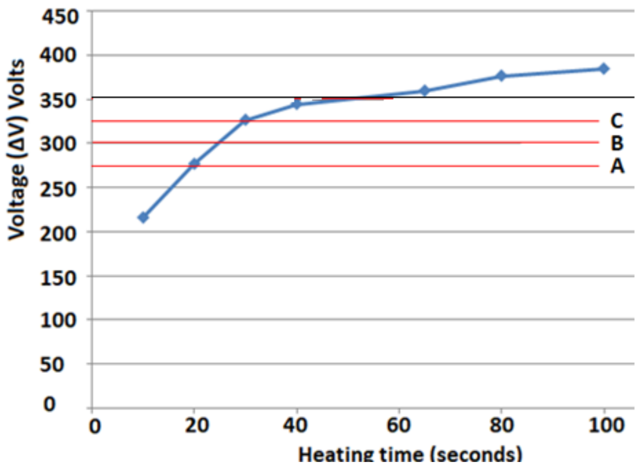

Fig. 6. Desorption curves of copper from iridium at Ts = 1220 K

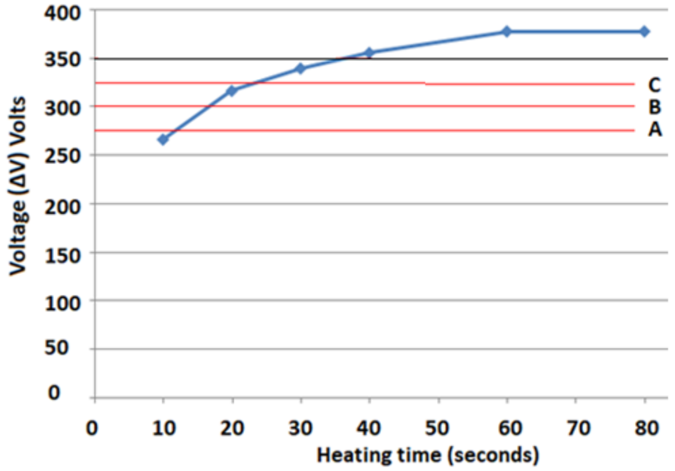

Fig.7. Desorption curves of copper from iridium at Ts = 1240 K

The time required to desorb the same quantity of copper at different temperatures was obtained by drawing from certain points on the voltage axis of Figs. 3 to 7 lines parallel to the time axis to intersect the isotherm curves. This was done at three different intervals of V (275V point A, 300V point B, and 325V point C) and Figs. 8 to 10 show the plots (ln (ΔV) vs. $\frac{1}{T}$) obtained at those three intervals. The activation energies for desorption plots are listed in Table 1.

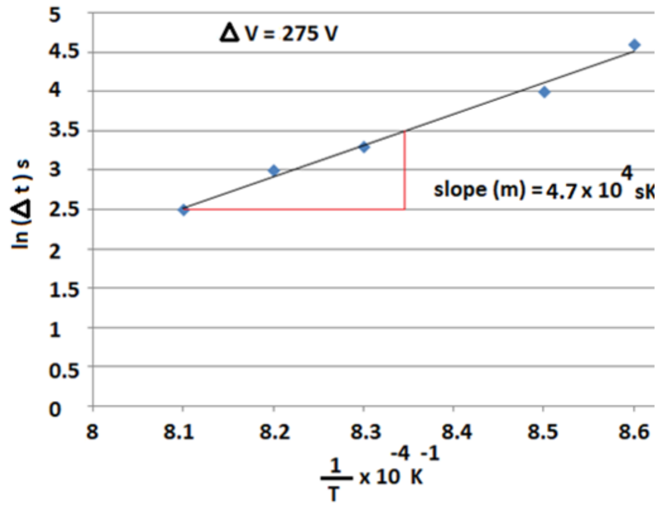

Fig. 8. Arrhenius plot for copper desorption on iridium at ΔV = 275 volts.

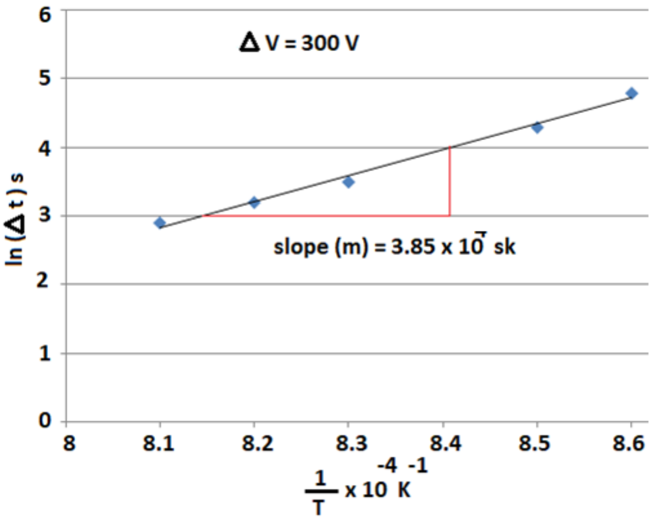

Fig. 9. Arrhenius plot for copper desorption on iridium at ΔV=300 volts.

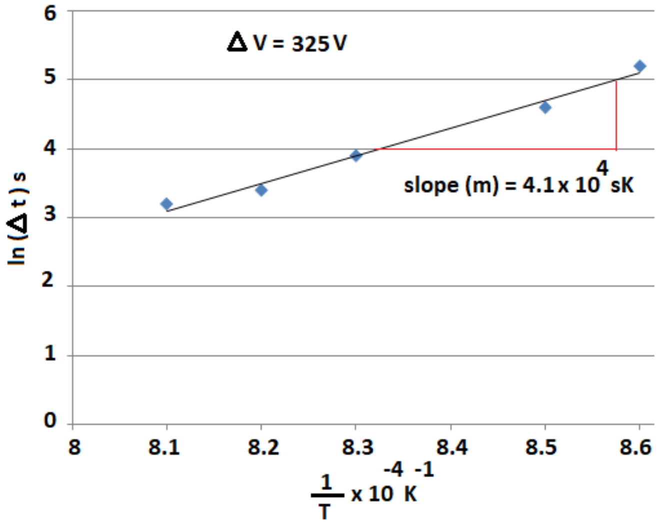

Fig. 10. Arrhenius plot for copper desorption on iridium at ΔV=325 volts.

Table 1

The Activation energies for desorption of the initial loading of copper are equivalent to the coverage of four monolayers (θ=4). The first column on the left depicts the intervals depicted in Figs. 3 to 7.

ΔV (Volts)	E_{des} (eV)
275	4.00 ± 0.05
300	3.30 ± 0.02
325	3.50 ± 0.03

5. Discussion

Figs. 3 to 7 show that at all coverages the desorption curves follow the adsorption curves in reverse (Hashim, 2017), indicating that copper was fully equilibrated at the starting point for desorption. The experimental values of 3.30±0.02eV to 4.00±0.05 eV obtained for the activation energy for thermal desorption(Edes) of copper from iridium may be compared with the theoretical prediction of Levine and Gyftopoulos (Levine and Gyftopoulos, 1964). They write Edes as the sum of the ionic and covalent terms, thus

$$E_{des} = F\varphi_c(1+\sigma) + \sqrt{(\lambda_f \lambda_m)}S_{fm}Q_{fm} \tag{13}$$

Ionc tem *Covalent term*

Where the ionic contribution to E_{des} is assumed to arise from a fraction of charge, F, of the adsorbate, which is transferred to the substrate, σ is a small term ≈ 0.03, $Q_{fm} = \sqrt{(1-\frac{F^2}{V^2})}$ represents the "charge efficiency" ranging from unity for purely covalent bonding to zero for purely ionic bonding. φ_c is the electron work function of the composite surface, λ_f and λ_m are the latent heats of sublimation of the bulk adsorbate and substrate respectively, and

$$S_{fm} = \frac{2}{\frac{S_f}{S_m} + \frac{S_m}{S_f}} \qquad (14)$$

Where S_f and S_m are the orbital strength functions of the adsorbate (copper) and substrate (iridium) atoms. For copper S = 1 (Godwin, 1964) and for iridium S = 2.62 (Levine and Gyftopoulos, 1964) which yields

$$S_{fm} = \frac{2}{\frac{1}{2.62} + \frac{2.62}{1}} = 0.67.$$

Due to the small contribution of the ionic term, it could be neglected (AL-Rawi, 1980; Jones, 1972), then Equ. (9) becomes

$$E_{des} = \sqrt{\lambda_f \lambda_m}\, S_{fm} \qquad (15)$$

Using λf= 3.2 eV for copper (Godwin and Luscher, 1964) and λm = 6.51 eV for iridium (Levine and Gyftopoulos, 1964) yield $\sqrt{\lambda_f \lambda_m}$ = 4.56, hence equation 15 gives Edes = 3.06 eV, which is less than the experimentally measured values of 3.30±0.02 eV to 4.00 ± 0.05 eV. The difference between the experimental and theoretical values may be due to the neglect of the ionic term.

It can be seen from the three experimentally measured values for Edes obtained in the present study that the dependence of Edes on the coverage θ is weak as pointed out by Godwin (Godwin, 1964) because θ appears only in the ionic term which is found to be small and its contribution may be neglected (AL-Rawi, 1980; Jones, 1972). Jones (Jones, 1967; Jones, 1972) in studying silver and gold desorption respectively from tungsten has also found a weak dependence of Edes on θ. However, on the other hand, Al-Rawi (Al-Rawi, 1980) in studying silver desorption from rhenium has found relatively strong dependence of Edes on θ and the same thing was found in the desorption of silver from tungsten (Sugata and Takeda, 1970) and gold from rhenium (Coles, 1976).

6. Conclusion

The activation energy for copper desorption (Edes) is measured to be in the range 3.30±0.02 eV to 4.00±0.05 eV which is a little bit higher than that calculated on the basis of Levine and Gyftopoulos model. The dependence of these values on copper coverage is not detectable.

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